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Determination of Phthalate Esters in Drinking Water using Solid-phase Extraction and Gas Chromatography

P. Prapatpong and W. Kanchanamayoon
Department of Chemistry and Center of Excellence for Innovation in Chemistry (PERCH-CIC),
Faculty of Science, Mahasarakham University, MahaSarakham, 44150 Thailand

Abstract: Phthalate esters are widely used as plasticizer. They can migrate from plastic materials to the environment. Some of these compounds may have risk to get cancer. Phthalate esters; dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and bis(2-ethylhexyl) phthalate (DEHP) were extracted simultaneously using solid-phase and analyzed by gas chromatograph. The percentage recoveries were carried out on LC-18 and Florisil cartridge using various eluting solvent. The 6 mL Florisil (1 g) with 5 mL of ethyl acetate as eluting solvent showed good recoveries in the range of 98.2-110.0% and the limit of determination in the range of 0.025-00.05 mg L^{-1}. This proposed method was successfully applied to analysis of phthalates in drinking water. The contamination of DMP, DEP and DBP in drinking water samples were in the safe levels, except DEHP concentration in three samples were found out of regulated maximum admissible concentration.

Key words: Phthalate esters, drinking water, slid-phase extraction, gas chromtoagraphy

INTRODUCTION

Phthalate esters are widely use as additives in the manufacture of plastic, paint and cosmetics (Penalver *et al*., 2000; Cai *et al*., 2003) to increase their flexibility, transparency, durability and longevity. Most of phthalate esters are used in the manufacturing of Polyvinyl Chloride (PVC). Dibutyl Phthalate (DBP) is used in epoxy resins, dimethyl (DMP) and Diethyl Phthalate Esters (DEP) are typically used in cellulose ester-based plastics (Stales *et al*., 1997). Phthalate esters can migrate from plastic materials to the environment. They are often found in water, soil, air, food products and the human body (Castillo *et al*., 1998). The finding of some phthalates; DEP, DBP and bis (2-ethylhexyl phthalate (DEHP) show the ability to interfere in environmental samples. Some of these compounds are carcinogen and estrogenic (Holadova *et al*., 2007). The US environmental Protection Agency (EPA) has set the Maximum Admissible Concentration (MAC) or maximum contamination level (MCL) of DEHP at 6 μg L^{-1} (USEPA, 1991), the threshold limit value (TLV) of DEP, DBP, DMP and DEHP were 0.55, 0.45, 5.0 and 5.0 mg L^{-1}, respectively. In order to detect phthalate esters at sub mg L^{-1} levels, preconcentration step is necessary before analysis. Various liquid-liquid extraction have been used for extraction of phthalate esters (Yasuhara *et al*., 1997). However, the conventional pretreatment method need large quantities of sample and organic solvents (Farahani *et al.,* 2007). Solid-phase extraction (Carlo *et al*., 2008), solid-phase microextraction (Luks-Betlej *et al*., 2001; Penalver *et al*., 2001; Prokupkova *et al*., 2002; Feng *et al*., 2005; Holadova *et al*., 2007; Xu *et al*., 2007) and dispersive liquid-liquid microextraction (Liang *et al*., 2008; Farahani *et al.,* 2007) have gained importance for determination of phthalate esters in water samples. Solid-Phase Extraction (SPE) is the most common technique for water sample pretreatment (Zhao *et al*., 2008). It has many advantages such as high recovery, solvent consumption, simplicity and easy operation. The aim of this study was to optimize the condition of solid-phase extraction and applied to determine phthalates esters in bottled drinking water.

MATERIALS AND METHODS

Instrumentation: Gas chromatograph model GC17 (Shimadzu, Japan) with a DB-5 fused silica capillary column (30 m, 0.25 mm id., 0.25 μm film thickness) was used. The injector and detector temperature were 270°C with flame ionization detector and nitrogen gas was used as carrier gas. The temperature program was started from 60°C held for 5 min then ramp to 270°C with the rate of 15°C min^{-1} and held for 11 min.

Corresponding Author: Wanna Kanchanamayoon, Department of Chemistry, Faculty of Science, Mahasakham University, Khamriang, Kantharawichai, MahaSarakham Province, 44150, Thailand
Tel: 66-81-9542187 Fax: 66-43-754246

Chemicals: Dimethyl Phthalate (DMP), Diethyl Phthalate (DEP), Dibutyl Phthalate (DBP) and bis (2-ethylhexyl) phthalate (DEHP) were analytical reagent grade and obtained from Fluka (Switzerland). The individual standard stock solutions were prepared in methanol and stored at 4°C. All organic solvent were HPLC grade from Labscan (USA).

Solid-phase extraction (SPE): The 3.0 mL of LC-18 (500 mg) and 6.0 mL Florisil (1 g) column were obtained from Supelco (USA).

Optimization of solid-phase extraction: Prior to extraction, the SPE columns were conditioned with 5.0 mL methanol under vacuum, following by 5.0 mL with deionized water. The 100 mL deionized water was spiked with the standard solution of phthalate esters (20 mg L^{-1} of each) and subsequently passed through the column with the flow rate of 1.0 mL min^{-1}. The phthalate esters were eluted with various kind of organic solvent. The percentage recovery was carried out by gas chromatography. The limit of detection of solid-phase extraction were taken as the lowest concentration of phthalate esters that could be extracted and yielding good recoveries.

Application to real water samples: Phthalate esters in drinking water which contained in Polyethylene Terephthalate (PET) bottled were analyzed by using the optimum conditions.

RESULTS AND DISCUSSION

Figure 1 showed the chromatogram of DMP, DEP, DBP and DEHP with the retention times of 14.48, 15.76, 18.72 and 24.41 min, respectively. The linearity ranges were 0-100 mg L^{-1} with the correlation coefficient in the range of 0.9935-0.9972, as summarized in Table 1. The percentage recoveries were achieved by spiked sample (20 mg L^{-1} of each) using LC-18 and Florisil cartridge with various eluting solvent. Florisil showed suitable for extraction of phthalate esters, since Florisil form is a powdered magnesium-silica gel and used as normal phase.

Table 1: Linearity range, calibration data of phthalate ester using DB-5 fused silica capillary column (30 m×0.25 mm id., 0.25 μm film thickness)

Phthalate ester	Linearity (mg L^{-1})	Linear equation	R^2	LOD (mg L^{-1})
DMP	0-100	Y = 16X+184	0.9935	0.50
DEP	0-100	Y = 29X+200	0.9937	0.50
DBP	0-100	Y = 39X+96	0.9961	0.25
DEHP	0-100	Y = 58-181	0.9972	0.25

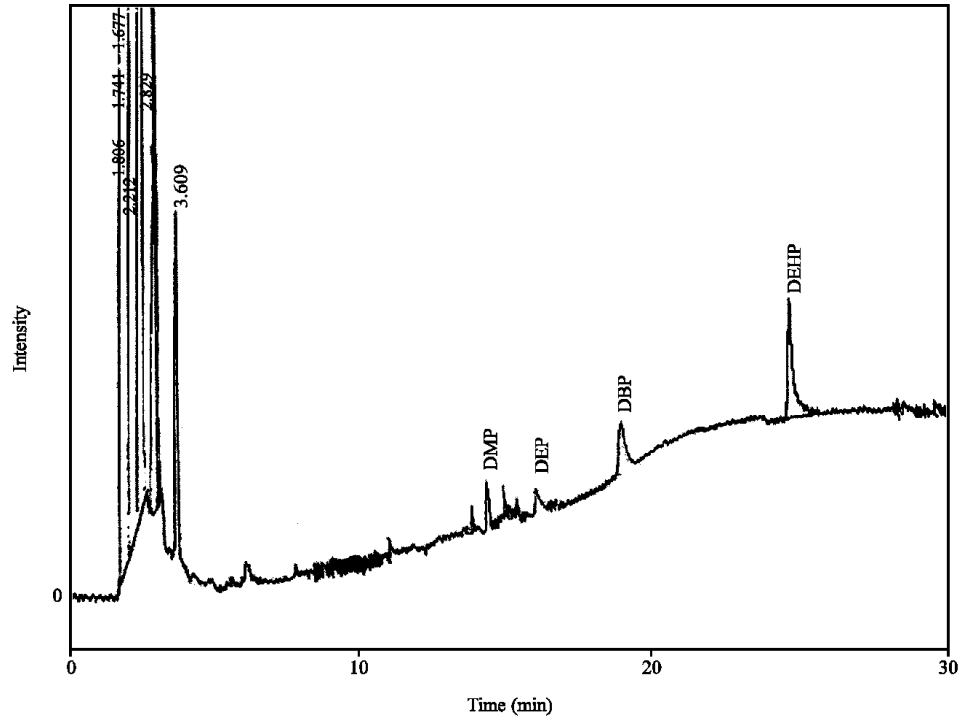

Fig. 1: Chromatogram of DMP, DEP, DBP and DEHP with the retention times of 14.48, 15.76, 18.72 and 24.41 min, respectively, by gas chromatograph using DB-5 fused silica capillary column (30 m×0.25 mm id., 0.25 μm film thickness)

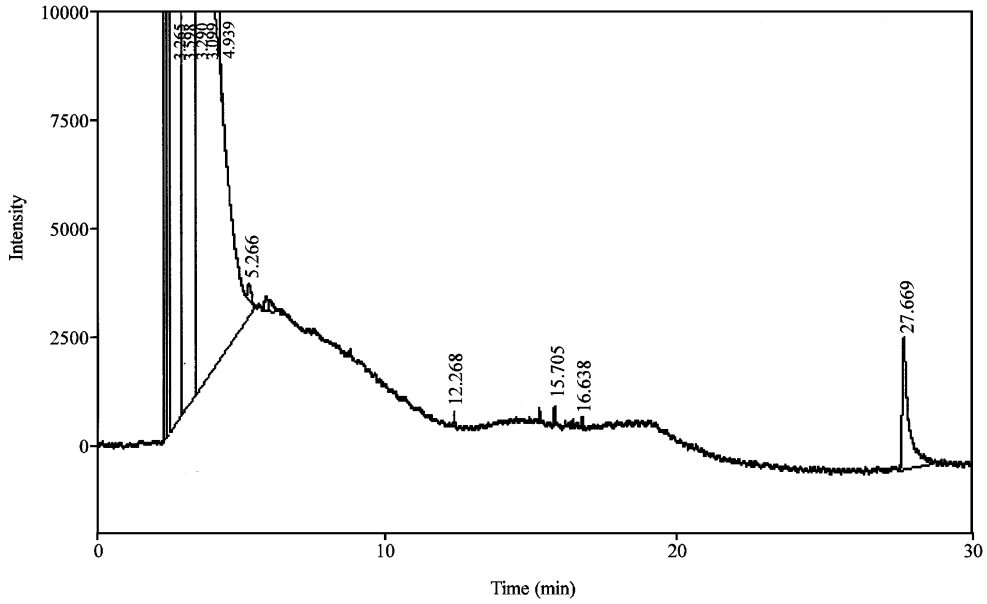

Fig. 2: Chromatogram of mineral water no 1 by solid-phase extraction and gas chromatograph using DB-5 fused silica capillary column (30 m×0.25 mm id., 0.25 μm film thickness)

The interaction is adsorption, elution step is usually carried out with a polar solvent. The 5 mL of ethyl acetate showed good recoveries in the range of 98.2-110.0%, as shown in Table 2. The limit of determination (LOD) and Limit of Quantitation (LOQ) for extraction of phthalate esters by solid-phase were in the range of 0.025-0.050, 0.08-0.17 mg L^{-1}, respectively. The repeatabilities were in the range of 1.20-2.20% RSD, as shown in Table 3.

To achieve the optimum SPE procedure, the technique was applied to determination of phthalate esters in drinking water samples, purchase from supermarket in Maha-Sarakham Province, Thailand. Figure 2 showed the chromatogram of mineral water samples No. 1, the results found DMP, DBP and DEHP. Table 4 showed the phthalate esters concentration in drinking waters and mineral waters from different brands (PET bottle), phthalate esters content were found depend on the sample brand. The DMP was found in drinking water sample No. 2, mineral water sample No. 1, 2 and 4 in the ranges of 0.16-0.53 mg L^{-1}, DEP found only in sample No. 5 with the value of 0.54 mg L^{-1} (TLV 0.55 mg L^{-1}), DBP in sample no. 1, mineral water sample No. 1 and 3 in the range of 0.13-0.33 mg L^{-1} (TLV 0.45 mg L^{-1}). The DEHP content in drinking water sample No. 1, 4 and mineral water sample No. 1 were found in the ranges of 0.28-0.49 mg L^{-1}, the results showed out of regulating maximum admissible concentration at 6 μg L^{-1}. The results are agreed with the previous studies, DEP, DBP and DEHP were found in the water samples from PET bottles (Penalver *et al*., 2000). Prokupkova *et al.* (2002) reported that DBP and DEHP were found in mineral water higher

Table 2: The percentage recoveries of phthalate ester by solid-phase extraction with various eluting solvent (Mean±RD, n = 3)

	LC-18			Florisil	
Phthalate ester	5 mL methanol	5 mL acetonitrile	5mL (1:1) Methanol+ acetonitrile	5 mL ethyl acetate	(1:1) ethyl acetate+ methanol
DMP	58.1±5.6	60.1±0.7	60.2±1.4	110.0±1.4	109.0±1.7
DEP	96.2±0.7	96.5±0.7	118.4±2.1	108.1±1.3	57.7±1.4
DBP	96.3±0.7	89.2±0.7	88.5±0.7	95.2±2.5	97.5±0.7
DEHP	55.6±7.0	47.3±0.7	74.0±1.4	98.2±2.1	90.0±1.4

Table 3: The detection limits of Florisil solid-phase extraction using 5 mL ethyl acetate eluting solvent and reproducibility

Phthalate ester	LOD (mg L^{-1})	LOQ (mg L^{-1})	Reproducibility (%RSD)
DMP	0.050	0.17	1.27
DEP	0.050	0.17	1.20
DBP	0.025	0.08	2.60
DEHP	0.025	0.08	2.20

Table 4: Phthalate esters concentration (mg L^{-1}) in drinking water sample (Mean±SD, n = 3)

Water sample		DMP	DEP	DBP	DEHP
Drinking water	1	Nd	Nd	0.17±0.14	0.50±0.02
	2	0.38±0.01	Nd	Nd	Nd
	3	Nd	Nd	Nd	Nd
	4	Nd	Nd	Nd	0.28±0.07
	5	Nd	0.54±0.03	Nd	Nd
Mineral water	1	0.16±0.01	Nd	0.33±0.01	0.49±0.07
	2	0.53±0.04	Nd	Nd	Nd
	3	Nd	Nd	0.13±0.08	Nd
	4	0.46±0.05	Nd	Nd	Nd
	5	Nd	Nd	Nd	Nd

*Nd: Not detected, lower than LOD

than in the other water samples. Phthalate esters may migration from the plastic bottle and the cap into the content of bottle. People who drink water containing DEHP in excess of the maximum contamination level for many years may have problems with liver and may have an increased risk to getting cancer (Holadova *et al*., 2007).

CONCLUSION

The DMP, DEP, DBP and DEHP can be extracted simultaneously by solid-phase Florisil using 5 mL ethyl acetate as eluting solvent. The results showed good recoveries in the range of 98.2-110%. Application of this proposed method was successful to determination of phthalate esters in PET bottled drinking water samples. The DMP, DEP and DBP contents in drinking water samples were found in the safe levels, while DEHP concentration in three samples were found higher than the regulated maximum admissible concentration.

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