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Analytical Methods

Study of solvent sublation for concentration of trace phthalate esters in plastic beverage packaging and analysis by gas chromatography–mass spectrometry

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ABSTRACT

A novel trace analytical method based on solvent sublation (SS) and gas chromatography–mass spectrometry (GC–MS) was developed for the trace determination of twenty-two phthalate esters (PAEs) from plastic beverage packaging. In the solvent sublation section, the effects of solution pH, NaCl concentration, nitrogen flow rate, and sublation time on the sublation efficiency were investigated in detail, and the optimal conditions were obtained. The trace PAEs migrated from plastic beverage packaging to food simulants were separated and concentrated by solvent sublation, and then the trace target compounds in the concentrated solution were analyzed by GC–MS. According to the European Union Regulation, the food simulants including distilled water for the normal beverages and acetic acid solution (3%) for the acetic beverage of yogurt were prepared for migration tests. The trace analysis method showed good linearity, low limits of detection (LODs) of 1.6–183.5 ng/L, and satisfied recoveries (67.3–113.7%).

1. Introduction

Phthalate esters (PAEs) were first introduced in the 1920s (Antian, 1973), and they were widely applied for over 50 years in the plastics industry as plasticizers (such as plastics, rubber, and cellulose) (He, Lv, Zhu, & Lu, 2010; Heudorf, Mersch-Sundermann, & Angerer, 2007). Some PAEs have been identified as endocrine disruptors (LaFleur & Schug, 2011), and the recent studies indicate that some phthalates could cause irritation of the eyes, nose, and throat, some could damage liver, kidneys, and reproductive organs; and others might interfere with growth by acting as a mimic of the sex hormone (Harrison, Holmes, & Humfrey, 1997; Paganetto et al., 2000; Petrovic, Eljarrat, López de Alda, & Barceló, 2001). So these PAEs are not allowed to be used as food additives. However, plastic is a commonly used material for food storage and protection, which is usually in contact with food and drink (Fuji et al., 2003). As PAEs are not chemically bound in the plastics but remain present as a freely mobile and leachable phase, they can be potentially leached into food and beverages from the packaging materials and contaminate it during production or storage (Gómez-Hens & Aguilar-Caballos, 2003). Recently, Chinese Taiwan plasticizer event (http://news.sina.com.cn, 2011) and JiuGui Wine plasticizer event (http://finance.sina.com.cn, 2012) caused a serial food crisis, and much attention of Chinese society focused on the food security about PAEs. Unfortunately, there is not any system regulation has been established for the special migration limits (SMLs) of PAEs from plastic packaging to food.

It is well known that the migration process of PAEs from plastic packaging to food is very slow, and the concentration of PAEs is at trace (or ultra-trace) level. Therefore, an effective pretreatment technique is required by the trace analysis for the investigation of migration mechanism. Until now, different pretreatment techniques such as liquid–liquid extraction (LLE) (Cai, Shi, Liu, Mou, & Lu, 2007; Zhu, Phillips, Feng, & Yang, 2006), solid-phase extraction (SPE) (Blair, Ikonomou, Kelly, Surridge, & Gobas, 2009; Casajuana & Lacorte, 2004; Cinelli, Avino, Notardonato, Centola, & Russo, 2014; Del et al., 2008; Liu, Wang, & Wang, 2013; Sun, Yang, Li, Zhang, & Sun, 2012; Yan, Cheng, & Yang, 2012), solid-phase microextraction (SPME) (Alpendurada, 2000; Carrillo, Salazar, Moreta, & Tena, 2007; He, Lv, et al., 2010; Holadova, Prokupkova, Hajslova, & Poustk, 2007; Li, Su, Li, Sun, & Zhang, 2013; Luks-Betlej, Popp, Janoszka, & Paschke, 2001; Polo, Llompart, Garcia-Jares, & Cela, 2005), liquid-phase microextraction (LPME) (Psillakis & Kalogerakis, 2003; Rasmussen & Pedersen-Bjergaard, 2004), dispersive liquid–liquid microextraction (DLLME) (Cinelli, Avino,

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Notardonato, Centola, & Russo, 2013; Zhang, Chen, & Jiang, 2011), and cloud point extraction (CPE) (Wang et al., 2007) followed by high-performance liquid chromatography (HPLC), gas chromatography (GC), or gas chromatography mass spectrometry (GC–MS) analysis have been developed for the determination of PAEs in different matrices.

Solvent sublation (SS) is a kind of adsorptive bubble separation technique in which the surface active (or hydrophobic) compounds in aqueous phase are adsorbed on the bubble surfaces of an ascending gas stream and then collected in an organic layer placed on top of the aqueous phase (Lv & Zhu, 2001). With many advantages of high separation efficiency, high concentration coefficient, low dosage of organic solvent, soft separation process and simple operation (Bi, Dong, & Dong, 2010), SS is very suitable to separate and concentrate trace hydrophobic compounds from aqueous sample (large volume) to organic solution (tiny volume). As a simple and effective pretreatment technique, SS has been applied for environmental analysis (Han et al., 2011; Kim, Shin, Choi, Lee, & Lee, 2001; Wang, Xu, Han, & Yan, 2011) and food analysis (Chang et al., 2013; Dong, Bi, & Xi, 2008; Xi & Dong, 2007). It is well known that PAEs are of good hydrophobic (Guo & Dong, 2009), and they can be easily adsorbed on the bubble surface, therefore, PAEs are very suitable for SS.

The aim of the present study is to develop a simple, highly efficient and environmental-friendly analytical method for trace analysis of twenty-two PAEs in plastic beverage packaging. Scheme 1 is the trace analysis procedure of 22 PAEs in beverage simulant SS–GC–MS. In the pretreatment process, PAEs were concentrated from 300 ml aqueous phase to 2.00 ml *n*-hexane solution, and the LODs of 22 PAEs were effectively reduced. Moreover, the new method showed good precision and accuracy, and it was applied to the real samples with good results.

2. Experimental

2.1. Instrumentation

The GC–MS analysis was performed with a Shimadzu GC 2010-QP2010 gas chromatography–mass spectrometer, using a 30 m × 0.32 mm i.d. DB-5MS quartz capillary column (0.25 μm film thickness) (Agilent, USA). A PHS-3C pH meter (Shanghai, China) was used to determine the pH of the solution. A GP225D electron balance (Sartorius, Germany) was used. The solvent sublation apparatus was the same as the one mentioned in our earlier reports (Chang et al., 2013).

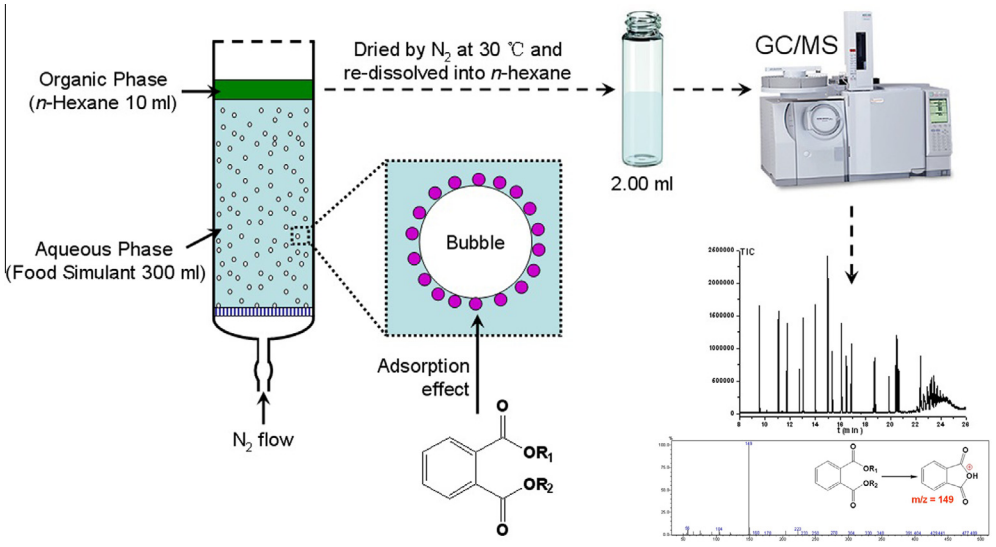
2.2. Chemicals and solutions

The standard mixture solution of 22 PAEs was purchased from Shanghai Anpel Scientific Instrument Co., Ltd (Shanghai, China). In the standard mixture solution, 1000 μg of 20 PAEs (Nos. 1–20) and 10,000 μg of 2 PAEs (DINP and DIDP) were dissolved in 1.00 ml *n*-hexane. After drying with nitrogen, 22 PAEs standards were diluted to 100 ml of acetonitrile (10 μg/ml for PAEs Nos. 1–20, 100 μg/ml for DINP and DIDP), and the standard stock solution was used for the condition optimization of solvent sublation. Sodium chloride, acetic acid, hydrochloric acid and sodium hydroxide (Beijing Chemical Reagent Factory, China) were all of analytical reagent grade. Acetonitrile, *n*-hexane of GC–MS were all of HPLC grade (J&K, China), and water was supplied by Wahaha Pure Water (Zhejiang, China).

The selected plastic beverage packages were acquired in the local supermarket (see Table S1). According to the European Union Regulation (European Union, 2011), the analyzed sample should be prepared by a migration test. In the migration test, the plastic sample (approximately 12 dm^2) was put in 2 L of beverage simulant, and the condition were 10 days at 40 °C (Chang et al., 2013). As shown in Table S1, distilled water was used to be the simulant for the normal beverages, and acetic acid solution (3%) for the acetic beverage of yogurt. After extraction of beverage simulant, an amount of 300 ml of the simulant was applied to the separation and concentration of SS.

2.3. SS procedure

In the optimization of solvent sublation parameters, 1.00 ml of standard stock solution was diluted by 300 ml of pure water, and the pH and NaCl concentration of aqueous solution was adjusted for the SS procedure. After adjusting the N_2 flow rate, 300 ml of the aqueous solution was floated by 10.00 ml of *n*-hexane. Then, the flotation product (approximately 8–9 ml) was transferred into a sample vial, dried by nitrogen at 30 °C, and re-dissolved by 2.00 ml of *n*-hexane. The *n*-hexane solution was determined by GC–MS. In this section, the influence of solution pH (1, 2, 3, 4, 5, 6, 7 and 8), NaCl addition (0.5 g, 2 g, 4 g, 6 g, 8 g, 10 g and 20 g)



Scheme 1. Trace analysis procedure of 22 PAEs in beverage simulant by SS–GC–MS.

in aqueous solution, nitrogen flow rate (20 ml/min, 30 ml/min, 40 ml/min, 50 ml/min, 60 ml/min, 70 ml/min, and 80 ml/min), flotation time (10 min, 20 min, 30 min, 40 min, 50 min, 60 min, 80 min, and 90 min) were studied respectively to yield the maximum separation efficiency.

In the separation and concentration step, the recovery of PAEs was used to optimize the SS parameters. The recovery (R) can be calculated by using the following equation:

$$R = \frac{C_t V_t}{C_0 V_0} \times 100\% = \frac{2C_t}{C_0} \times 100\% = \frac{2A_t}{A_0} \times 100\%$$

where C_t is the concentration of the re-dissolved n-hexane solution, V_t is the volume of PAEs in the re-dissolved n-hexane solution (2.00 ml), C_0 is the concentration of PAEs in the standard stock solution, and the V_0 is the volume of the standard stock solution (1.00 ml). In order to simplify the calculation, the integral areas of GC–MS are used: A_t is the GC–MS integral area of PAEs in the re-dissolved n-hexane solution, A_0 is the GC–MS integral area of PAEs in the standard stock solution.

Regard to the analysis of real samples, the optimal conditions of SS were applied: sodium chloride 4 g was added in 300 ml of the beverage simulant and the solution pH was adjusted to 7 with hydrochloric acid solution, the aqueous solution was transferred to the flotation column, the nitrogen gas flow rate was fixed at 60 ml/min, and then 10.00 ml of n-hexane were added on the top of aqueous column. After 50 min, the flotation product (n-hexane phase) was transferred to a 10-ml sample vial, dried with nitrogen and re-dissolved in 2.00 ml of n-hexane. Finally, the flotation product was determined by GC–MS.

2.4. GC–MS analysis

Analytes were separated on a DB-5MS (30 m × 0.32 mm, 2.5 μm) gas chromatographic column. The carrier gas was nitrogen (purity: no less than 99.99%) at a flow rate of 2.8 ml/min with a split ratio of 10. The GC conditions were as follows: injection volume 1.0 μl; injector temperature 250 °C; initial oven temperature 50 °C for 1 min, increased to 150 °C at a rate of 15 °C/min, the second ramp to 250 °C at a rate of 10 °C/min, and the third ramp to 320 °C at a rate of 7 °C/min with 2 min hold time. Using the mentioned GC–MS conditions, the total ion chromatogram (TIC) of 22 standard PAEs were shown in Fig. 1.

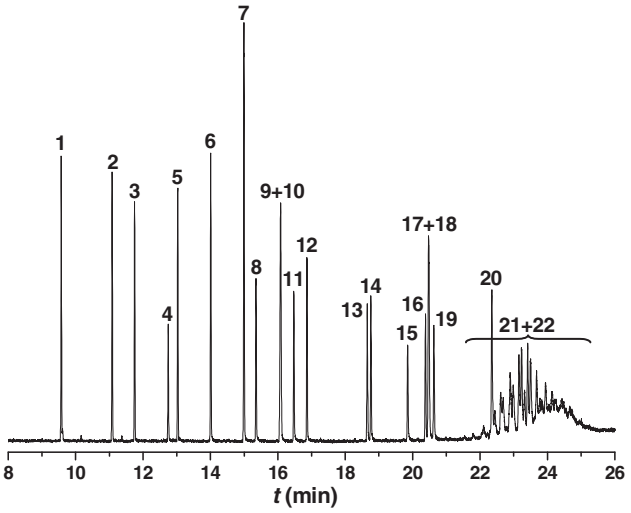


Fig. 1. Total ion chromatogram (TIC) of 22 standard PAEs in n-hexane solution (10 μg/ml for PAEs Nos. 1–20, 100 μg/ml for DINP and DIDP). 1, DMP; 2, DEP; 3, DIPrP; 4, DAP; 5, DPrP; 6, DIBP; 7, DBP; 8, DMEP; 9, DIPeP; 10, DMPP; 11, DEEP; 12, DPP; 13, DHP-1; 14, BBzP; 15, DBEP; 16, DCHP; 17, DEHP; 18, DHP-2; 19, DPhP; 20, DNOP; 21, DINP; and 22, DIDP.

Qualitative analysis and quantitative analysis of PAEs was performed by GC/MS working in the EI positive ion mode, using the electron energy of 70 eV. The ion source temperature and the detector temperature were maintained at 200 °C and 275 °C, respectively. Moreover, the solvent delay time of 3 min was set. Optimized parameters for analysis of 22 PAEs using MS with Selected Ion Monitoring (SIM) Mode are listed in Table 1.

3. Results and discussion

3.1. Selection of characteristic ion pairs for MS detection

In quantitative analysis of GC–MS, the characteristic ion pairs for 22 PAEs were confirmed for signal collection under SIM mode (shown in Table 1). The PAEs are based on the 1,2-benzenedicarboxylic acid structure, and there are number of possible alkyl side chains and the other side groups (R_1 and R_2). Since PAEs with saturated alkyl side chains, the most abundant ion in EI ionization mass spectrum at 70 eV is always m/z 149 (shown in Fig. S1), and m/z 149 is usually selected for many PAEs (Liu et al., 2013; Sun et al., 2012). As shown in Fig. S2, the side groups of DMP are both CH_3 and then the H on the oxygen is replaced by CH_3, consequently, m/z 163 becomes the base peak. Because ethers are more easily ionized for DMEP, the peak m/z 59 gives high signal (shown in Fig. S3).

Though the good resolution of 22 PAEs was given in Fig. 1, three pair PAEs (Nos. 9 and 10, DIPeP and DMPP; Nos. 17 and 18, DEHP and DHP; Nos. 21 and 22, DINP and DIDP) cannot be separated by the optimal GC conditions. Therefore, the different SIM modes for different analysts were applied to qualitative analysis and quantitative analysis. Compared with the characteristic fragment ions of DIPeP and DMPP (shown in Fig. S4), the peaks of m/z 237 and m/z 85 appeared in the MS spectra, respectively. As shown in Fig. S5, the TICs of DIPeP and DMPP were completely overlapped, but the two target compounds could be distinguished in the MICs. Using the mentioned method, some characteristic fragment ions (m/z 279 for DEHP, m/z 265 for DHP-2, m/z 293 for DINP and m/z 307 for DIDP) were selected as monitoring ions for distinguishing the overlapped peaks in TIC (Seen from Figs. S6–S9).

3.2. Optimization of SS procedure

Based on the selection restriction of sublation solvent and the requirement of GC–MS, n-hexane was the suitable organic solvent for the flotation procedure and the after-treatment (dried by N_2 and re-dissolved by n-hexane). Moreover, in comparison to other common sublation solvent (n-octanol, iso-amyl alcohol, and n-butanol), n-hexane also showed the best results with better recovery and lower background interference. Therefore, n-hexane was selected as the sublation solvent.

The solution pH is a very important parameter, since it will determine the molecule state and the adsorption ability of the target compound, and the solubility in the sublation solvent will be greatly influenced (Lv & Zhu, 2001). According to the EU legislation (European Union, 2011) and the China legislation (China, 2009), the beverage simulants were only at neutral condition and acidic condition, therefore, the effect experiments of solution pH (1–8) were followed the legislations. As shown in Fig. 2A, the recoveries were not significantly influenced for most of PAEs at neutral condition and acidic condition. However, some PAEs (DEHP, DHP-2, DINP, and DIDP) showed different results: the maximum values were observed at pH 7–8. Under very low pH condition, the ester carbonyl structure of these PAEs can be easily combined with free

Table 1
Information of 22 phthalate esters and the optimized Parameters of GC–MS analysis with SIM Mode.

No.	Compound	CAS No.	Molecular weight	Purity (%)	t_R (min)	Ion pair (m/z)	
						Qualitative	Quantitative
1	Dimethyl phthalate (DMP)	131-11-3	194	99.0	9.57	163	163
2	Diethyl phthalate (DEP)	84-66-2	222	99.0	11.08	149	149
3	Phthalic acid diisopropyl ester (DIPrP)	605-45-8	250	99.7	11.75	149	149
4	Diallyl phthalate (DAP)	131-17-9	246	98.8	12.75	149	149
5	Dipropyl phthalate (DPrP)	131-16-8	250	98.0	13.03	149	149
6	Diisobutyl phthalate (DIBP)	84-69-5	278	99.0	14.01	149	149
7	Di-*n*-butyl phthalate (DBP)	84-74-2	278	99.0	15.00	149	149
8	Bis(2-methoxyethyl) phthalate (DMEP)	117-82-8	282	98.2	15.35	149	59
9	Diisopentyl phthalate (DIPeP)	605-50-5	306	99.5	16.08	149/237	237
10	Bis(4-methyl-2-pentyl) phthalate (DMPP) (mixture of 2 isomers)	146-50-9	334	99.0	16.06, 16.09	149/85	85
11	Bis(2-ethoxyethyl) phthalate (DEEP)	605-54-9	310	99.3	16.47	149	149
12	Diamyl phthalate (DPP)	131-18-0	306	98.0	16.86	149	149
13	Di-*n*-hexyl phthalate (DHP-1)	84-75-3	334	99.0	18.65	149	149
14	Butyl benzyl phthalate (BBzP)	85-68-7	312	98.0	18.76	149	149
15	Bis(2-butoxyethyl) phthalate (DBEP)	117-83-9	366	99.5	19.85	149	149
16	Dicyclohexyl phthalate (DCHP)	84-61-7	330	99.0	20.38	149	149
17	Dioctyl phthalate (DEHP)	117-81-7	390	99.0	20.47	149/279	279
18	Di-*n*-heptyl phthalate (DHP-2)	3648-21-3	363	98.0	20.49	149/265	265
19	Diphenyl phthalate (DPhP)	84-62-8	318	99.0	20.63	225	225
20	Di-*n*-octyl phthalate (DNOP)	117-84-0	391	98.0	22.35	149	149
21	Diisononyl phthalate (DINP) (mixture of 19 isomers)	68515-48-0	419	99.5	21.69–24.38	149/293	293
22	diisodecyl phthalate (DIDP) (mixture of 20 isomers)	26761-40-0	447	99.0	23.39–25.43	149/307	307

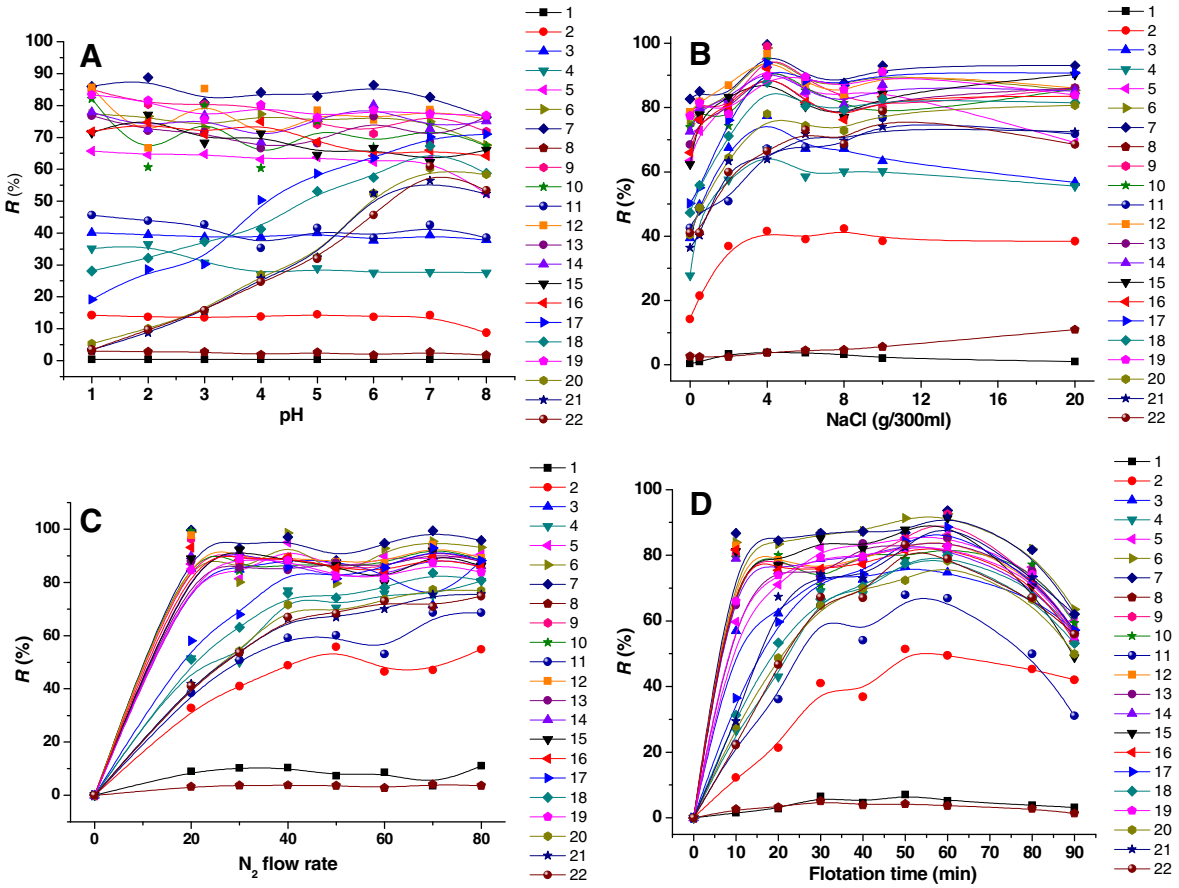


Fig. 2. Effects of separation parameters on SS: (A) solution pH (ublation solvent, *n*-hexane; m_{NaCl}, 0 g; N_2 flow rate, 60 ml/min; and flotation time, 40 min); (B) NaCl concentration (sublation solvent, *n*-hexane; solution pH, 7; N_2 flow rate, 60 ml/min; and flotation time, 40 min); (C) N_2 flow rate (sublation solvent, *n*-hexane; solution pH, 7; m_{NaCl}, 4 g; and flotation time, 40 min); (D) Flotation time (sublation solvent, *n*-hexane; solution pH, 7; m_{NaCl}, 4 g; and N_2 flow rate, 60 ml/min). (1, DMP; 2, DEP; 3, DIPrP; 4, DAP; 5, DPrP; 6, DIBP; 7, DBP; 8, DMEP; 9, DIPeP; 10, DMPP; 11, DEEP; 12, DPP; 13, DHP-1; 14, BBzP; 15, DBEP; 16, DCHP; 17, DEHP; 18, DHP-2; 19, DPhP; 20, DNOP; 21, DINP; and 22, DIDP).

Table 2
Regression data, LOQs, LODs for 22 phthalate esters analyzed by SS–GC–MS.

No.	Compound	Regression equation ($y = ax + b$)	Correlation coefficient (R^2)	Linear range (ng/L)	LOD (ng/L)	LOQ (ng/L)
1	DMP	$y = 1.43x - 24.80$	0.9981	167–33,460	14.2	34.6
2	DEP	$y = 6.96x - 184.30$	0.9952	34–16,670	4.3	10.8
3	DIPrP	$y = 11.37x - 158.21$	0.9964	17–10,000	3.8	9.9
4	DAP	$y = 1.65x + 149.18$	0.9978	60–10,000	23.2	60.0
5	DPrP	$y = 14.21x - 1453.50$	0.9978	10–10,000	2.1	5.4
6	DIBP	$y = 15.75x + 5118.01$	0.9989	334–33,460	2.1	5.3
7	DBP	$y = 17.59x - 642.22$	0.9982	167–33,460	1.6	3.6
8	DMEP	$y = 0.15x + 85.66$	0.9981	315–33,460	127.0	315.3
9	DIPeP	$y = 1.33x - 10.27$	0.9958	34–33,460	10.5	27.8
10	BMPP	$y = 2.93x + 197.72$	0.9955	30–16,670	11.9	29.3
11	DEEP	$y = 0.86x - 102.19$	0.9963	126–16,670	47.8	126.1
12	DPP	$y = 8.36x - 107.09$	0.9997	13–3350	5.0	13.3
13	DHP-1	$y = 4.93x + 90.84$	0.9996	27–3350	9.9	27.0
14	BBzP	$y = 2.78x - 41.87$	0.9999	41–3350	14.8	41.0
15	DBEP	$y = 1.27x - 247.88$	0.9950	334–16,670	18.6	45.8
16	DCHP	$y = 14.39x + 5342.36$	0.9960	34–10,000	2.5	6.2
17	DEHP	$y = 0.97x - 90.50$	0.9979	100–6670	22.3	56.9
18	DHP-2	$y = 0.70x + 107.71$	0.9971	224–16,670	86.1	224.0
19	DPhP	$y = 6.34x - 58.97$	0.9998	8–3350	3.1	8.0
20	DNOP	$y = 1.33x + 637.25$	0.9960	100–10,000	26.8	66.9
21	DINP	$y = 0.71x + 575.23$	0.9995	334–33,460	19.1	46.2
22	DIDP	$y = 0.14x + 343.16$	0.9977	669–33,460	183.5	511.2

Table 3
Contents (ng/kg) of 22 phthalate esters in 11 commercial plastic beverage packages ($n = 3$).

No.	Comp.	Commercial beverage packages										
		1#	2#	3#	4#	5#	6#	7#	8#	9#	10#	11#
1	DMP	nd[a]	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
2	DEP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3	DIPrP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4	DAP	nd	nd	nd	55.5	nd	nd	nd	nd	<LOQ	nd	nd
5	DPrP	nd	<LOQ[b]	nd	10.2	<LOQ	nd	nd	1.0	nd	nd	nd
6	DIBP	nd	nd	48.5	nd	nd	16.8	nd	nd	<LOQ	nd	27.5
7	DBP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
8	DMEP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
9	DIPeP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
10	BMPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
11	DEEP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12	DPP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
13	DHP-1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
14	BBzP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
15	DBEP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16	DCHP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17	DEHP	nd	nd	nd	nd	nd	nd	nd	4.0	nd	nd	nd
18	DHP-2	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
19	DPhP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
20	DNOP	nd	18.1	nd	nd	nd	nd	nd	nd	nd	nd	nd
21	DINP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
22	DIDP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

[a] Not detected.
[b] LOD < concentration < LOQ.

proton (H^+), and the solubility of these PAEs will be increased in aqueous phase. Moreover, because of the 1,2-benzenedicarboxylic structure and the alkyl side chains, it is well known that PAEs are mostly middle polar and strongly lipophilic compounds, and they are of the lower solubility in aqueous solution with neutral condition. In this section, pH 7 was applied for the next experiments.

In SS process, the ionic strength do influences not only the solubility of target compound in aqueous solution, but also the mass transfer process from aqueous system to organic system. In the present work, NaCl was added into the aqueous solution for adjusting the ionic strength, and the experimental results were shown in Fig. 2B. With the increase of NaCl addition, the recoveries of 22 PAEs were significantly increased, and the maximum values were observed at 4 g in 300 ml of aqueous solution. Usually an increase of the ionic strength will decrease the solubility of organic compound, however, the further increase can also reduce the recovery in SS. Because of adsorption competition between the colligend and other ions for the gas–water interface of bubbles, the separation efficiency decreases with increasing NaCl concentration, when the NaCl concentration is more than 4 g in 300 ml of aqueous solution. Therefore, 4 g of NaCl was added into 300 ml of aqueous solution before the SS procedure.

The N_2 flow rate is another important parameter in the SS process: as the bubbles rise through the gas diffuser, the hydrophobic analytes are adsorbed on the gas–liquid interface and then extracted into the organic phase on the surface of the sample solution. As shown in Fig. 2C, the recoveries were increased with the rise of flow rate. When the N_2 flow rate was larger than 50 ml/min, the separation efficiency could not been improved. Moreover, it is recommended that too high gas flow rate should be avoided

because of a turbulent mixing at the solvent-aqueous solution interface (Bi, Dong, Yu, & Chang, 2008; Bi, Dong, & Yuan, 2010). According to the experimental results, the N_2 flow rate could be fixed at 60 ml/min in all the subsequent experiments.

As shown in Fig. 2D, the recoveries of PAEs increased with increasing the flotation time. When the flotation time was fixed at 50 min, the recoveries reached their highest values. However, the longer operation time led to the excessive evaporation of *n*-hexane, and parts of analysts came back to the aqueous phase. So the flotation time should be fixed at 50 min for the best recoveries.

On the basis of the above experiments, the optimal conditions of SS are summarized as follows: *n*-hexane as the sublation solvent, pH 7, 4 g of NaCl in 300 ml of aqueous solution, N_2 flow rate of 60 ml/min, and flotation time of 50 min.

3.3. Performance of the SS–GC–MS method

In order to obtain the calibration curves, a series of blanks spiked with different concentrations of PAE standards (3.5 ng/L, 6.8 ng/L, 10.2 ng/L, 17.1 ng/L, 33.9 ng/L, 100 ng/L, 167 ng/L, 334 ng/L, 669 ng/L, 3350 ng/L, 6670 ng/L, 10,000 ng/L, 16,670 ng/L, and 33,460 ng/L) were analyzed by SS–GC–MS, and the linear ranges were selected for the calibration of real samples. The regression equations of the SS–GC–MS method were shown in Table 2 with good linearity in the range from 8 ng/L to 33,460 ng/L, and the correlation coefficients (R^2) were greater than 0.99. The LODs and LOQs were calculated according to the directives of IUPAC (Long & Winefordner, 1983), taken LOD = $3S_B/a$ and LOQ = $10S_B/a$, where S_B and a are the signal of the blank measurement and the slope of the calibration curve, respectively. The LOD of the SS–GC–MS method was in the range from 1.6 ng/L to 183.5 ng/L, and the LOQ was in the range of 3.6–511.2 ng/L. The LOD values were better than many previous report (Blair et al., 2009; Liu et al., 2013; Sun et al., 2012; Yan et al., 2012), and the SS–GC–MS method was also satisfied for the requirement of China legislation (China, 2008).

The precision of the SS–GC–MS method was determined beverage simulants spiked with 22 PAEs at three different concentration levels of standard mixture (1000, 2000, and 3000 ng/ml). The precision for the 22 analytes was described as relative standard deviation (RSD), and the test results are given in Table S2. The overall precision in stimulants was ranged from 1.13% to 9.47%. The accuracy experiment was carried out by determining the recoveries of 22 PAEs in the beverage simulants spiked at different concentration levels. Table S3 shows that the recovery of the 22 analytes was in the range from 67.3% to 113.7% with RSDs of 3.61–12.13%.

3.4. Application to real sample

The developed analytical method was applied to analyze 11 samples of commercial plastic beverage packages, and the results were listed in Table 3. Of all eleven real samples, DPrP and DIBP were detected in four different samples with the ranges of LOD ~10.2 ng/kg and LOD ~48.5 ng/kg, respectively; DAP was found in milk package (55.5 ng/kg) and pure water-3 package (lower than LOQ); DEHP and DNOP were observed in pure water-2 package (4.0 ng/kg) and disposable drink cup (18.1 ng/kg), respectively. Moreover, there were not any PAEs in three samples (disposable drink porringer, pure water-1 package, and distilled water package) according to the analysis results. To confirm the accuracy of the analysis data for the real samples, a series of recovery experiments were performed for each sample ($n = 3$), and the results were satisfied with the recovery range from 70% to 110%.

Based on the above results, the established SS–GC–MS method can effectively and simultaneously analyze 22 PAEs at low concentration level (ng/L) for the studied plastic beverage packages.

4. Conclusion

In the present work, solvent sublation was applied to concentrate from the simulants of plastic beverage packaging to the extraction solvent. Using the adsorptive bubble separation technique, a new analytical method, SS–GC–MS, was developed and applied to determine 22 PAEs in simulants of plastic beverage packaging with trace levels. The method was proven to be of good linearity, precision, and accuracy. The established method will be a good method for researching the migration behavior of PAEs from plastic packaging to food, and can be used to control the food safety and provide basic data for the development of new legislation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2015.01.013.

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