

Dummy Molecularly Imprinted Solid-Phase Extraction for Selective Determination of Five Phthalate Esters in Plastic Bottled Functional Beverages

Hongyuan Yan,* Xiaoling Cheng, and Gengliang Yang

Key Laboratory of Pharmaceutical Quality Control of Hebei Province & College of Pharmacy, Hebei University, Baoding, 071002, China

ABSTRACT: In this paper, a highly selective sample cleanup procedure combining dummy molecular imprinting and solid-phase extraction (DMI-SPE) was developed for the simultaneous isolation and determination of five phthalate esters in plastic bottled beverages. The new imprinted microspheres were synthesized via precipitation polymerization using diisononyl phthalate as a dummy template that showed high selectivity and affinity to the five kinds of phthalate esters and were successfully applied as selective sorbents of DMI-SPE for the simultaneous determination of the phthalate esters from plastic bottled beverages. Good linearity was obtained in a range of 5.0–750.0 $\mu\text{g/L}$, and the average recoveries of the five phthalate esters at three spiked levels ranged from 84.3 to 96.2% with the relative standard deviations less than 5.49%. The developed extraction protocol eliminated the effect of template leakage on quantitative analysis and could be applied for the determination of phthalate esters in complicated functional beverages products.

KEYWORDS: *dummy imprinted solid-phase extraction, molecularly imprinted microspheres, phthalate esters, gas chromatography, bottled beverages*

INTRODUCTION

Recently, phthalates esters (PAEs) have become a major public health concern due to their wide use as plasticizers of common packaging materials such as plastics, rubber, and cellulose.^{1,2} 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.³ Some recent studies show that they may cause hormone-disrupting activities.^{4,5} The toxicological evaluation of PAEs has revealed that low molecular weight phthalates, such as diethyl phthalate (DEP), can cause irritation of the eyes, nose, and throat. However, several larger phthalate molecules, such as butyl benzyl phthalate (BBP), dioctyl phthalate (DNOP), and diisooctyl phthalate (DIOP), are suspected as human cancer-causing agents; could damage liver, kidneys, and reproductive organs; and might interfere with growth by acting as a mimic of the sex hormone.^{6–8} Therefore, a simple, rapid, and selective analytical method for determination of PAEs in the plastic bottled food and beverages is desired.

Until now, different methods such as solid-phase extraction (SPE),⁹ solid-phase microextraction (SPME),^{10,11} and liquid–liquid microextraction¹² followed by high-performance liquid chromatography (HPLC),¹³ gas chromatography (GC),^{3,14} or mass spectrometry (GC-MS) detection had been developed for the determination of PAEs in different matrices. As a traditional pretreatment method, SPE is usually used to clean up a sample before using a chromatographic or other analytical method to quantitate the amount of analyte(s) in the samples. However, one of the main disadvantages of the classical SPE sorbents is the low selectivity. Thus, new sorbents such as molecularly imprinted polymers (MIPs) were increasingly developed to meet the need of selective extraction of target analytes from the complicated sample matrix.

The molecular imprinting technique is a relatively new development in the area of SPE for the sample clean up.^{15–18} MIPs are synthetic polymers possessing specific cavities designed for a target molecule, which exhibit many outstanding advantages such as high selectivity and physiochemical stability and afford specific recognition against the imprinted molecules and structurally related compounds. Therefore, the application of MIPs as SPE sorbents was desired to eliminate the interferences of sample matrix and get cleaner extracts than the traditional SPE, which resulted in a more selective and reliable analytical protocol.^{19–22} Recently, MIPs have become increasingly attractive as class- or compound-specific sorbents, and a number of applications have shown the effectiveness of MIP-SPE for the isolation and preconcentration of traces analytes such as zearalenone,²³ dichlorvos,²⁴ triazines,²⁵ antibiotics,²⁶ methimazole,²⁷ betulin,²⁸ and water-soluble acid dyes²⁹ in environmental or biological samples.³⁰ However, in recent years, most MIPs are synthesized by using the target analyte as a template to show high selectivity, but serious template leaking happens in the SPE procedure, which would affect the results of quantitative analysis in sample application.³¹

In this paper, the new dummy imprinted microspheres (DIMs) were synthesized by using diisononyl phthalate (DINP) as a dummy template with precipitation polymerization and successfully were applied as a special sorbent of DMI-SPE for the selective extraction of five PAEs from plastic bottled beverage products. The developed DMI-SPE protocol significantly improved the sensitivity by loading a large volume

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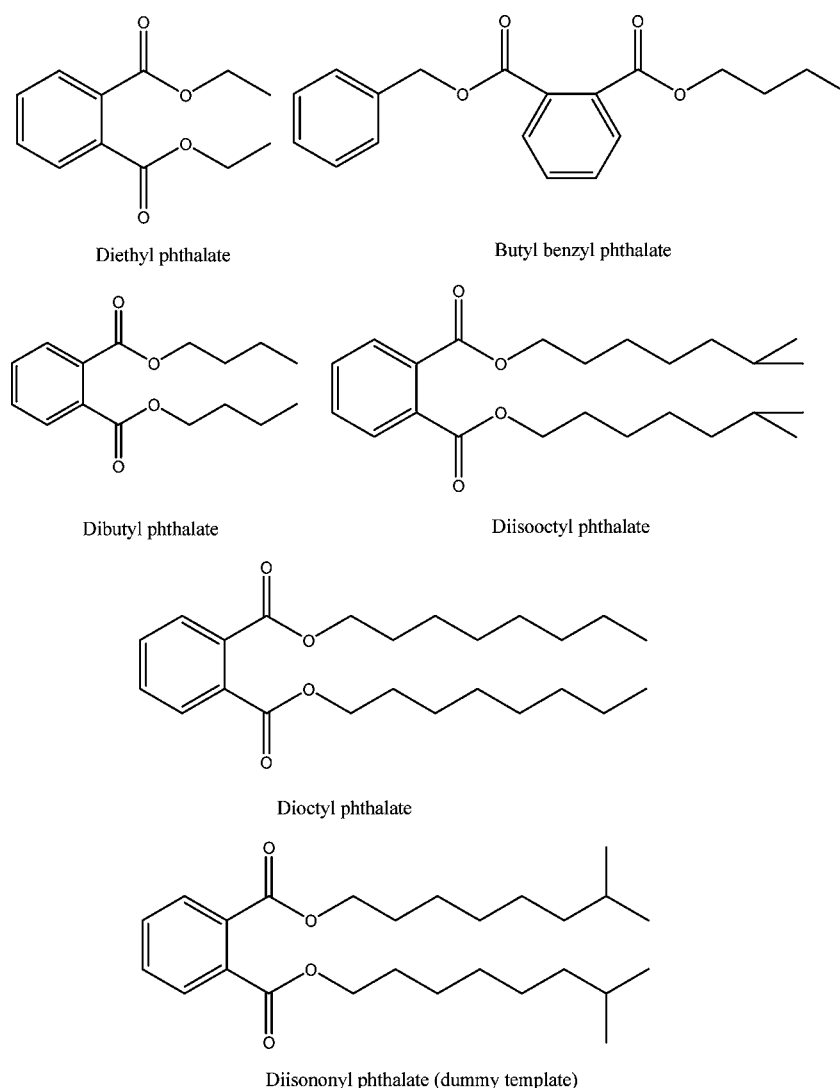


Figure 1. Molecular structures of the related compounds.

of sample and eliminated the effect of template leakage on quantitative analysis.

EXPERIMENTAL PROCEDURES

Chemicals and Reagents. DEP, BBP, DIOP, dibutyl phthalate (DBP), DNOP, and DINP were obtained from Crystal Pure Industrial Co. Ltd. (Shanghai, China) (Figure 1). Chloroform (CHCl_3) was purchased from Tianyi Chemical Co. Ltd. (Tianjin, China). Methanol (MeOH), acetonitrile (ACN), dichloromethane (DM), acetone (AT), ethylacetate (EA), acetic acid (AA), acrylamide (AM), divinylbenzene, and 2,2-azobisisobutyronitrile (AIBN) were purchased Huaxin Chemical Reagent Co. (Baoding, China). All of the reagents used in the experiment were of the highest grade available and were predetermined by GC and GC-MS to avoid phthalates interference. Plastic bottled functional beverage samples (soft drink whose main ingredients included water, sugar, fructose syrup, dietary fiber, food additives, and so on) were purchased from the local supermarkets of Baoding. The stock solution of 1.0 mg/mL was prepared in AT and placed in $-4\text{ }^\circ\text{C}$.

Instrumentation and Conditions. The chromatographic analysis was carried out on a Shimadzu GC-2014 system equipped with a split/splitless injector and an FID detector (Shimadzu, Japan). High-purity nitrogen (99.999%) was used as a carrier gas. A GH-300 high-purity hydrogen generator and GA-2000A air pump (Beijing ZXHL Co. Ltd., China) were used to supply hydrogen and oxygen at the rate of 40 and

400 mL/min, respectively. The capillary column was KB-1 (100% dimethyl polysiloxane as stationary phase, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ mm}$, Kromat, Delran, NJ), and its flow rate was set at 1.7 mL/min with a split ratio of 10. An N-2000 chromatography workstation (Zheda Zhineng, Hangzhou, China) was used as the data acquisition system. The temperature-programmed mode was as follows: the initial oven temperature was $150\text{ }^\circ\text{C}$ for 2.0 min, and then increased to $285\text{ }^\circ\text{C}$ at the rate of $25\text{ }^\circ\text{C}/\text{min}$, and held for 10.0 min. The injection port and detection temperatures were set at 290 and $300\text{ }^\circ\text{C}$, respectively.

DIM and Nonimprinted Microspheres (NIMs) Polymerization. The DIMs were prepared by precipitation polymerization as follows: DINP (1.0 mmol) and AM (4.0 mmol) were dissolved in toluene (4.0 mL) and ACN (26.0 mL) in a glass conical flask, and divinylbenzene (25.0 mmol) and AIBN (1.5 mmol) were added into the solution and then sonicated for 2.0 min to fully dissolve. The polymerization was performed at $60\text{ }^\circ\text{C}$ for 24 h in a water bath. Postsynthesis, the polymeric particulates were freed from template and residual monomers via Soxhlet extraction by using MeOH-AA (9:1, v/v), and then, the products were dried to constant mass under vacuum. To verify that the affinity to analytes was due to molecular recognition and not to nonspecific binding, NIMs were prepared as the same procedure with the omission of the target molecule, DINP.

DMI-SPE Procedure. A 100 mg amount of the dry microspheres was packed into 3.0 mL empty SPE cartridges between two polyethylene frits. Prior to each extraction, the cartridges were conditioned with 3.0 mL of MeOH and water, respectively. A 20.0 mL

amount of sample solution was loaded on the DIM or NIM cartridge and then washed with 3.0 mL of MeOH–H₂O (1:9, v/v), and finally, the analytes were eluted with 3.0 mL of EA. The elution fraction was collected and concentrated to 0.5 mL for further GC analysis.

RESULTS AND DISCUSSION

Synthesis of the DIMs. Precipitation polymerization is one of the most attractive and reliable methods available that allows the preparation of MIP particles. Apart from the inherent advantage of avoiding crushing and sieving steps, this technique leads to a more homogeneous binding site distribution and higher performance in comparison to bulk polymerization.^{32,33} Until now, the most MIPs are synthesized by using the target analyte as a template and to provide excellent molecular recognition and rebinding ability.^{34–36} However, because of the fact that the residual template molecules embedded in the polymer are hard to be rinsed away completely; therefore, the obtained MIPs always exhibit serious template leakage during the procedure of sample extraction, which would affect the results of quantitative analysis in real sample application. Therefore, DINP as a structural analogue of the target analytes was chosen as the dummy template in the present work to prepare the molecularly imprinted microspheres, which provided the special ability to recognize the five kinds of PAEs and eliminate the effect of template leakage on quantitative analysis by the followed chromatographic separation. Besides, the molar ratios of template/monomer/cross-linker were investigated, and 1:4:25 showed the satisfactory mechanical strength and special affinity to the five PAEs. The morphology of the DIM evaluated by scanning electron microscope showed that the DIMs were monodispersed and isolated microspheres in the form of discrete polymer beads with narrow particle size distributions from 1.0 to 5.0 μm (Figure 2).

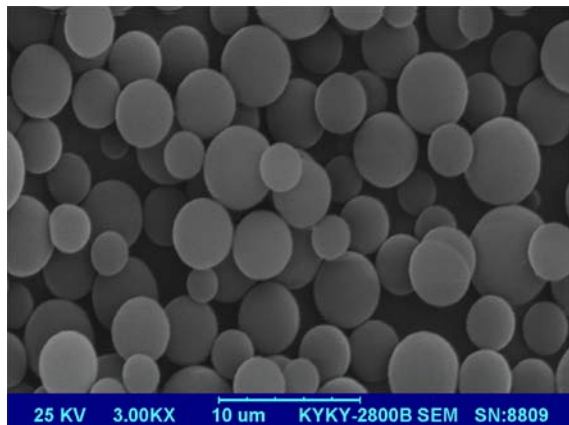


Figure 2. Scanning electron microscope (SEM) image of the DIM.

Optimization of the DMI-SPE Procedure. The DMI-SPE requires the same steps used in a common SPE procedure: conditioning, sample loading, washing, and elution. The loading solvent needs to be carefully selected to promote the rebinding of the substrate to the specific sites. Because the beverages were loaded directly, so the amount of the loading samples was considered. According to the principles of SPE, different loading amounts of spiked samples in a range of 3.0–80.0 mL were evaluated, and none of the PAEs was observed in the effluent liquids of the DIM-SPE cartridges, which revealed the good affinity of DIM to the PAEs. Considering the loading time

and sensitivity, 20.0 mL was selected as the loading amount of beverages samples.

The washing step was a crucial procedure to maximize the specific interactions between the analytes and the binding sites and to simultaneously decrease nonspecific interactions to discard matrix components of the sample.^{27,37} Thereby, after loading 20.0 mL of spiked beverage samples into the cartridge, 2.0 mL of MeOH, H₂O, MeOH–H₂O (1:9, v/v), ACN, ACN–H₂O (1:9, v/v), DM, MeOH–H₂O (2:8, v/v), MeOH–H₂O (1:1, v/v), and CHCl₃ as washing solvent was investigated, respectively (Figure 3). The results showed that ACN and CHCl₃ were sufficient to remove the impurities from the sample matrix, but most of analytes were also eluted out simultaneously. H₂O and ACN–H₂O (1:9, v/v) created little loss of analyte, but the purification effect of the washing step was inapparent. Although the similar purification efficiency for MeOH–H₂O (2:8, v/v) and MeOH–H₂O (1:9, v/v) was obtained, the recoveries of five PAEs by MeOH–H₂O (1:9, v/v) were slightly higher than that of MeOH–H₂O (2:8, v/v). For the purpose of finding a suitable volume of washing solution able to efficiently remove the interferences from sample matrix, recoveries of all analytes were studied in applying different volumes of MeOH–H₂O (1:9, v/v) in a range of 1.0–7.0 mL (Figure 4). The results showed that the recoveries of PAEs reduced slightly from 86.6–96.8% to 84.3–94.5% with the increase of volume of MeOH–H₂O (1:9, v/v) from 1.0 to 3.0 mL and then reduced sharply to 63.3–79.2% with a further increase to 7.0 mL. Comprehensive consideration of the recoveries, purification effects, and economic factors, 3.0 mL of MeOH–H₂O (1:9, v/v) was chosen as the optimum washing solution.

It is necessary to find that a suitable solvent elutes the PAEs from the DIM cartridge before GC analysis, so 3.0 mL of different types of solutions including ACN–AA (95:5, v/v), AT–AA (95:5, v/v), EA–AA (95:5, v/v), CHCl₃–AA (95:5, v/v), DM–AA (95:5, v/v), MeOH–AA (95:5, v/v), EA, MeOH–AA (90:10, v/v), and DM were applied and compared their elution efficiencies. The results of Figure 5 indicated that both EA and MeOH–AA (90:10, v/v) had relatively higher eluting ability for all PAEs than the other elution solvent, and EA provided the highest efficiency, which is possibly due to the interactions between the PAEs and the MIPs disrupted under this condition.² The results in Figure 6 showed that the recoveries of five PAEs were increased with the increasing volume of EA from 1.0 to 3.0 mL and then an almost constant even further increase in the volume of elution solvents to 7.0 mL. Thus, on the basis of the elution efficiency and solvent consumption, 3.0 mL of EA was adopted to elution of the PAEs from the DIM cartridges.

Validation of the DMI-SPE-GC Method. The presented method was validated for linearity, precision, repeatability, recovery, detection limits, and interassay and intra-assay deviation under the optimum condition. The calibration curve was constructed using the areas of the chromatographic peaks measured at nine increasing spiked levels ranging from 5.0 to 750.0 $\mu\text{g/L}$. Good linearity was observed for all analytes throughout the concentration range, and the regression equations were also shown in Table 1. The limit of detection (LOD) and limit of quantification (LOQ) based on the signal-to-noise ratio of 3.0 and 10.0 were 0.85–1.38 and 2.86–4.60 $\mu\text{g/L}$. The accuracy and precision of the method were assessed by performing analyses of spiked samples in five replicates in the same day and consecutive 3 days. The relative standard

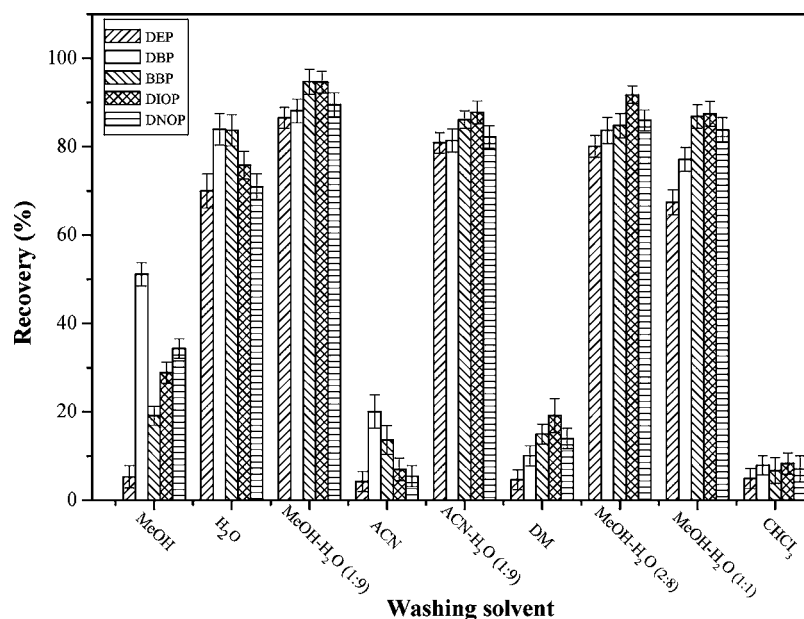


Figure 3. Effect of different washing solvents on recoveries of PAEs.

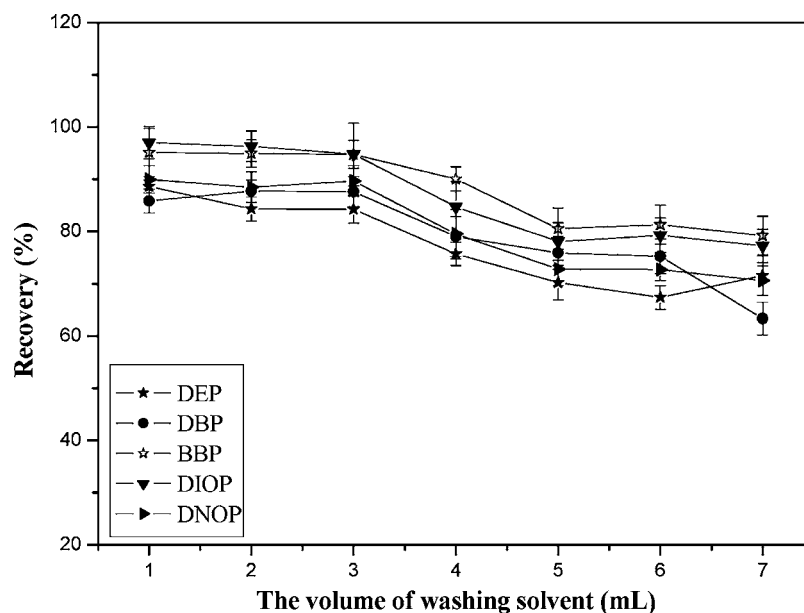


Figure 4. Effect of volume of washing solvent on recoveries of PAEs.

deviations (RSDs) were in a range of 2.06–5.49% for intraday precision and 2.54–6.33% for interday precision. The negative control test revealed that there are no peaks of interferences from sample matrix observed at the retention time of analytes in the chromatogram of blank function beverages (predetermined without analytes by GC-MS), which further demonstrated the practicality and purification effect of the proposed DMI-SPE-GC method.

To further demonstrate the selectivity and extraction efficiency, the DIM was compared with NIM and conventional sorbent such as C_{18} in the SPE procedures according to the previous reports.³⁸ The recoveries of the five PAEs for the sorbents under their respective optimized conditions are shown in Figure 7. The highest recoveries (88.0–95.6%) and clear chromatogram of DMI-SPE demonstrated that DIM can be used as the group-recognition sorbents in SPE for trace

isolation of the PAEs in beverage samples, which overcome the drawbacks of template leakage of MIP in real analysis. Under the same experimental conditions, 29.7–39.0% of analytes were flowed out in the washing step when using NIM as the sorbent, which demonstrated that the higher affinity of DIMs toward the PAEs was due to the specific recognition sites formed by the imprinting effect.³⁹ Moreover, C_{18} sorbent provided lower recoveries for PAEs (67.3–72.6%), which was due to its lower affinities and nonspecific identification to the analytes. Besides, DIM showed a better purifying effect than C_{18} sorbent, and all of the interferences in sample matrix could be effectively eliminated. All of the above indicated that the DMI-SPE-GC method has the advantages of simplicity, rapidity, and sensitivity and could be potentially applied for the monitoring of PAEs residues in beverage products.

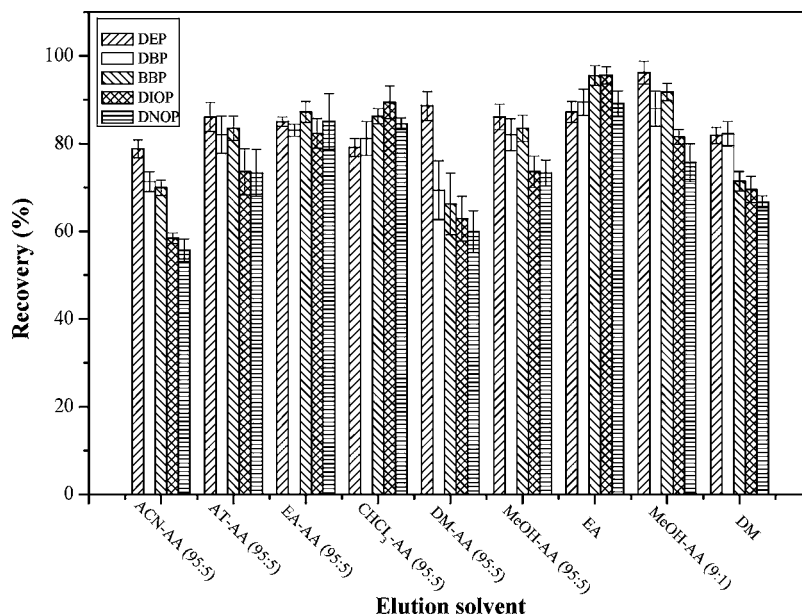


Figure 5. Effect of different elution solvents on recoveries of PAEs.

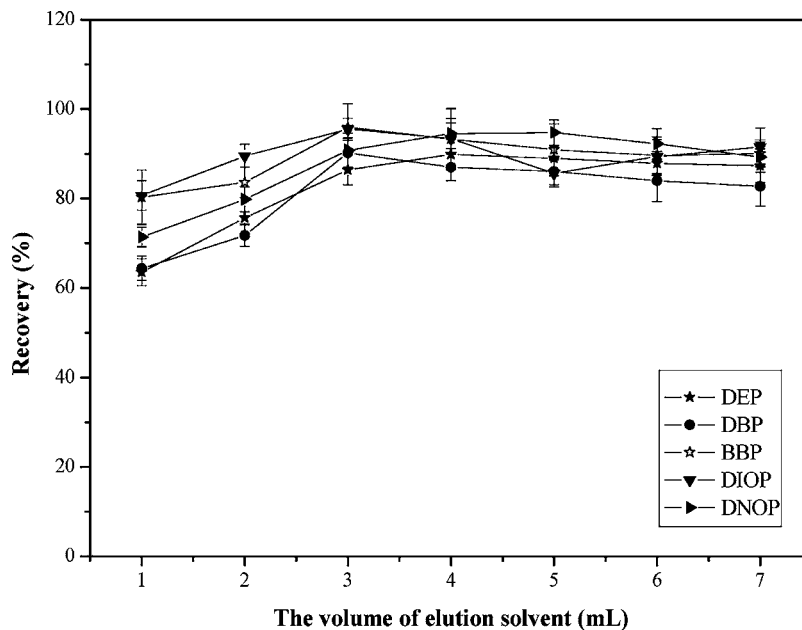


Figure 6. Effect of volume of elution solvent on recoveries of PAEs.

Table 1. Parameters of the MISPE-GC Method

compds	regression equation	r^2	RSD (%)	$\mu\text{g/L}$	
				LOD	LOQ
DEP	$y = 1.07 \times 10^2 x + 7.74 \times 10^2$	0.9994	2.54	1.11	3.69
DBP	$y = 1.28 \times 10^2 x + 4.92 \times 10^3$	0.9996	3.72	1.01	3.37
BBP	$y = 1.49 \times 10^2 x + 7.89 \times 10^1$	0.9993	6.33	0.85	2.86
DIOP	$y = 1.66 \times 10^2 x + 1.87 \times 10^2$	0.9995	5.78	1.04	3.46
DNOP	$y = 1.39 \times 10^2 x - 8.99 \times 10^2$	0.9994	4.35	1.38	4.60

Sample Analysis of Plastic Bottled Beverage Products. To demonstrate the suitability and potential application of the DMI-SPE-GC method, seven plastic bottled beverage products

purchased from the local market of Baoding were processed. It was found that one of the beverage products contains DBP with a concentration of 11.35 $\mu\text{g/L}$. As compared with injection of

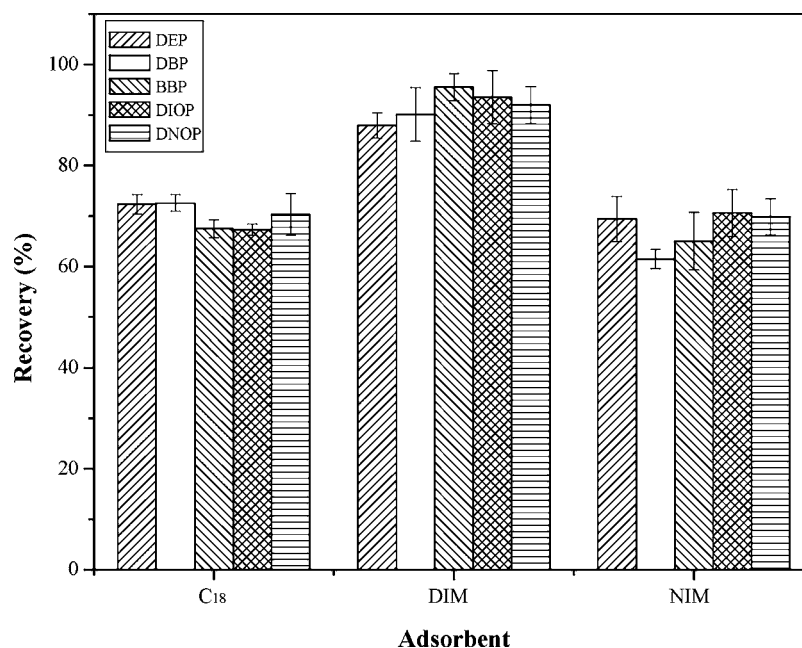


Figure 7. Comparison of different SPE sorbent on extraction of PAEs.

the samples directly for GC analysis, the interferences were significantly reduced after DMI-SPE (Figure 8), which revealed

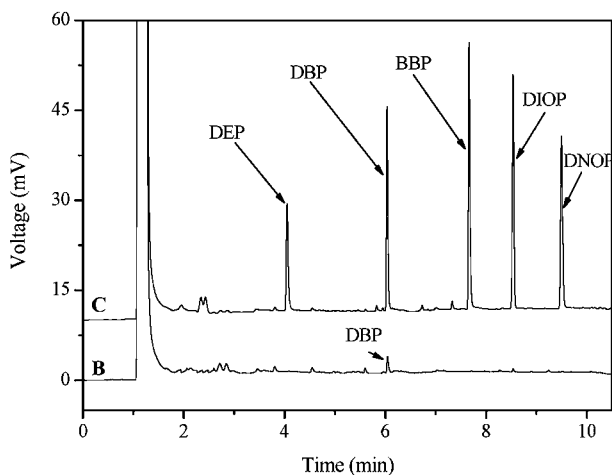
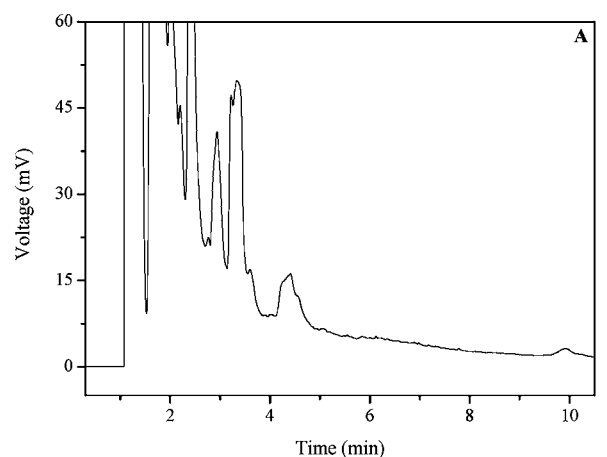


Figure 8. Chromatograms of the beverages samples. (A) Before DMI-SPE, (B) after DMI-SPE, and (C) spiked sample after DMI-SPE.

that the DIM had high affinity and selectivity for PAEs in aqueous solution. To investigate the effect of sample matrix on the accuracy of the DMI-SPE-GC method for real analysis, the recovery experiment was carried out by spiking three different levels of PAEs into the beverage samples, and the results are shown in Table 2. The recoveries ranged from 84.3 to 96.2%

Table 2. Recoveries of PAEs in Spiked Beverages by DMI-SPE ($n = 3$)

analytes	45 $\mu\text{g/L}$		450 $\mu\text{g/L}$		750 $\mu\text{g/L}$	
	recovery (%)	RSD (%)	recovery (%)	RSD (%)	recovery (%)	RSD (%)
DEP	84.3	1.44	85.2	4.07	86.6	1.42
DBP	89.8	2.07	90.5	3.41	91.2	2.15
BBP	92.9	2.33	95.3	3.05	96.2	5.49
DIOP	90.2	1.47	93.6	2.71	95.4	4.27
DNOP	88.9	1.90	92.2	2.19	91.8	4.47

with the RSD less than 5.49%, which demonstrates the feasibility of the DMI-SPE-GC method for determination of the PAEs in bottled beverages products.

■ AUTHOR INFORMATION

Corresponding Author

*Tel/Fax: +86-312-5971107. E-mail: yanhy@hbu.edu.cn.

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Notes

The authors declare no competing financial interest.

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