Talanta 90 (2012) 123–131

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Fast microextraction of phthalate acid esters from beverage, environmental water and perfume samples by magnetic multi-walled carbon nanotubes

Yan-Bo Luo, Qiong-Wei Yu, Bi-Feng Yuan, Yu-Qi Feng*

Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, China

ARTICLE INFO

Article history:
Received 1 November 2011
Received in revised form 3 January 2012
Accepted 6 January 2012
Available online 11 January 2012

Keywords:
Magnetic solid-phase extraction (MSPE)
Magnetic carbon nanotubes (CNTs)
Phthalate acid esters (PAEs)
Beverages
Water
Perfume
Gas chromatography/mass spectrometry (GC/MS)

ABSTRACT

In this work, magnetic carbon nanotubes (CNTs) were prepared by mixing the magnetic particles and multi-walled carbon nanotubes dispersed solutions. Due to their excellent adsorption capability towards hydrophobic compounds, the magnetic CNTs were used as adsorbent of magnetic solid-phase extraction (MSPE) to extract phthalate acid esters (PAEs), which are widely used in many consumable products with potential carcinogenic properties. By coupling MSPE with gas chromatography/mass spectrometry (GC/MS), a rapid, sensitive and cost-effective method for the analysis of PAEs was established. Our results showed that the limits of detection (LODs) of 16 PAEs ranged from 4.9 to 38 ng L^{-1}, which are much lower compared to the previously reported methods. And good linearities of the detection method were obtained with correlation coefficients (R^2) between 0.9821 and 0.9993. In addition, a satisfying reproducibility was achieved by evaluating the intra- and inter-day precisions with relative standard deviations (RSDs) less than 11.7% and 14.6%, respectively. Finally, the established MSPE-GC/MS method was successfully applied to the determination of PAEs from bottled beverages, tap water and perfume samples. The recoveries of the 16 PAEs from the real samples ranged from 64.6% to 125.6% with the RSDs less than 16.5%. Taken together, the MSPE-GC/MS method developed in current study provides a new option for the detection of PAEs from real samples with complex matrices.

1. Introduction

Phthalate acid esters (PAEs), commonly known as phthalates, are widely used in many consumable and household products, such as industrial plastics, polyvinyl chloride (PVC) products and personal care products. PAEs with high molecular weight such as bis(2-ethylhexyl) phthalate (DEHP), are primarily used as plasticizers to soften PVC products; while PAEs with low molecular weight such as diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), are widely used as solvents to hold color and scent in various consumable and personal care products [1]. Due to the extensive use and possible migration, PAEs can be released from these PAEs-containing products. In recent years, the widespread presence of PAEs has attracted considerable public attention because of their suspected carcinogenic properties. The US Environmental Protection Agency (EPA) and several other agencies classified the PAEs as priority pollutants [2,3]. Therefore, a reliable and highly sensitive method for the identification and quantification of PAEs from food, environmental water and other matrices is particularly important.

Gas chromatography (GC) and liquid chromatography (LC) coupled with various detectors were frequently employed for the determination of PAEs [4–10]. Most PAEs are semi-volatile, thermostable, and nonpolar compounds. Therefore, GC with capillary column is the commonly used separation platform for PAEs and mass spectrometry (MS) now becomes the routine detection technique for PAEs. Due to the low concentration of PAEs in real samples and complex matrix interference, it is often essential to perform the enrichment of the analytes before GC/MS analysis [1]. The most widely used approaches in sample preparation include liquid–liquid extraction (LLE) [11], solid phase extraction (SPE) [12,13], and solid phase micro-extraction (SPME) [5,14]. However, SPME has the disadvantages of high cost, memory effects and large batch to batch variation [15]. In addition, the small amount of extraction phase is not favorable for extraction. LLE is time-consuming and large volumes of organic solvents may be toxic. SPE is tedious and relatively expensive. Ideally, sample preparation technique should be simple, rapid and cost-effective. As a new alternative mode of SPE, magnetic solid-phase extraction (MSPE) shows many advantages in sample preparation [16–19], such as easy operation and short extraction time. Moreover, for environmental or biological samples, the MSPE mode can avoid the possible problem of blocking. These merits render MSPE a promising technique for sample preparation. In previous reports, several materials

---

* Corresponding author. Tel.: +86 27 68755595; fax: +86 27 68755595.
E-mail address: yqfeng@whu.edu.cn (Y.-Q. Feng).

0039-9140/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2012.01.015

have been prepared as MSPE adsorbent to extract PAEs from water samples [20–22].

Carbon nanotubes (CNTs), first observed by Iijima [23], have strong adsorption capability towards hydrophobic organic compounds [3,24]. CNTs have been proven to possess great potential to serve as SPE adsorbent for the analysis of various organic compounds [12,25], however, the major drawback of CNTs when used as SPE adsorbent is that the CNTs may hamper the flow of liquid samples, especially if the liquid samples contain suspended particles. Thus the advantage of strong adsorption capacity of CNTs is not utilized in conventional SPE. To solve the problem and simplify the sample preparation process, CNTs have been functionalized with magnetic particles by chemical modifications, which were further used as adsorbents of MSPE to extract various analytes from water, honey, and plasma samples [26–29]. However, these methods were always involved in chemical modifications of CNTs and/or magnetic particles, which were complicated. Besides, the chemical modifications may alter the surface chemistries of CNTs, and eventually affect their adsorption capability towards hydrophobic organic compounds [24].

Recently, Feng's group established a simple method to immobilize graphene sheets onto magnetic particles by simple adsorption [30]. Inspired by this, magnetic CNTs, fabricated without chemical modification were employed as MSPE adsorbent to successfully extract estrogens and benzo[a]pyrene from milk and water samples [31,32]. In the current work, using the similar procedure, we prepared magnetic CNTs and used it as MSPE adsorbent for the enrichment of PAEs from beverage, environmental water and perfume samples. Under optimized conditions, a rapid, sensitive and cost-effective method for the determination of PAEs was established by coupling the MSPE technique with GC/MS (MSPE-GC/MS). The results showed that the established method possesses good performance in terms of limits of detection, linearity, accuracy, and reproducibility for the determination of the 16 PAEs in real samples (beverage, water, and perfume).

2. Experimental

2.1. Chemicals and materials

Ferric chloride hexahydrate ($FeCl_3·6H_2O$), ferrous chloride tetrahydrate ($FeCl_2·4H_2O$), hydrochloric acid, and ammonium hydroxide were purchased from Sinopharm Chemical Reagent (Shanghai, China). Acetone, methanol (MeOH) and *N*,*N*-dimethylformamide (DMF) of HPLC reagent grade were obtained from Tedia (Fairfield, OH, USA). *n*-Hexane (95%, HPLC grade) and ethyl acetate (99.8%, HPLC grade) were supplied by CNW Technologies GmbH (Dusseldorf, Germany). Deionized water was purified with a Milli-Q system (Milford, MA, USA) and used for all experiments.

A mixture standard solution containing 16 PAEs: dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(2-methoxyethyl) phthalate (DMEP), bis(4-methyl-2-pentyl) phthalate (BMPP), bis(2-ethoxyethyl) phthalate (DEEP), dipentyl phthalate (DPP), dihexyl phthalate (DHXP), butyl benzyl phthalate (BBP), bis(2-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), bis(2-ethylhexyl) phthalate (DEHP), diphenyl phthalate (DiPP), di-N-octyl phthalate (DNOP), dinonyl phthalate (DNP) at 1.0 mg mL^{-1} in *n*-hexane was purchased from ChemService Inc. (West Chester, PA, USA). All working solutions of 16 PAEs were prepared in methanol and stored at 4 °C in dark.

Multi-walled carbon nanotubes (MWCNTs, length 5.0–15 μm, diameter 10–20 nm), modified with carboxyl (carboxyl ratio 2.31 wt%) were obtained from Nanotech Port (Shenzhen, China). CNTs were washed with acetone to remove the impurities by wrapping with filter paper in reflux in Soxhlet extractor at 80 °C for 48 h. The resultant CNTs were dried under reduced pressure at 60 °C for 6.0 h before use.

2.2. Preparation of magnetic CNTs

The magnetic particles were synthesized by a solvothermal method [33]. As shown in Fig. 1, $FeCl_3·6H_2O$ (5.4 g) and $FeCl_2·4H_2O$ (2.0 g) were dissolved in a 6.0 M hydrochloric acid solution (25 mL), which was then sufficiently degassed with a nitrogen stream. After that, a 25.0% (v/v) ammonium hydroxide solution (30 mL) was added to the solution with vigorous stirring at 60 °C for 30 min under nitrogen atmosphere. After cooling to ambient temperature, the resultant magnetic particles were attracted to the bottom by a magnet. The black products were washed several times sequentially with sufficient volume of water and ethanol and then dried at 60 °C for 6.0 h under reduced pressure.

The fabrication process of magnetic CNTs was similar to our previously described procedure [16,30]. Briefly, CNTs (100 mg) and magnetic particles (100 mg) were dispersed in DMF (5.0 mL), respectively. After combining the two solutions, the CNTs and magnetic particles were dispersed homogeneously by ultrasonic agitation (5.0 min). During the mixing, the CNTs and magnetic particles can assemble spontaneously to form magnetic CNTs. The resulting magnetic CNTs were washed with sufficient water, and then resuspended in 5.0 mL water. The final concentration of suspension solution was 40 mg mL^{-1}.

2.3. Procedure for the determination of PAEs

Due to the presence of PAEs in many laboratory products including chemicals and glassware, high background may occur for the analysis of PAEs in real samples. To minimize PAEs contamination, all laboratory glassware used in the study was soaked in acetone for at least 30 min, rinsed with *n*-hexane, and then dried at 120 °C for at least 4.0 h before use. The organic solvents were treated with aluminum oxide according to the previous report [34]: 300 mg aluminum oxide was added to 10 mL solvents and shaken for 10 s.

The procedure for the extraction of PAEs from water samples was similar to our previous report for extraction of other analytes [16,17,19,30]. As shown in Fig. 1, an aliquot of magnetic CNTs suspension (0.1 mL) was added into the sample solution (10 mL in a 15-mL vial with PTFE-silicone septum), and the mixture was vortexed vigorously to extract the analytes for 3.0 min. Then an external magnet was applied to the outside of the vial and the magnetic adsorbent was gathered to the side of the vial (within ~60 s, insert in Fig. 2a). The supernatant was then discarded followed by addition of 1.0 mL acetone to elute PAEs from the adsorbent with vigorous vortex for 1.0 min. Afterwards, the magnetic adsorbent gathered to the side of the vial (within ~10 s) using an external magnet. The desorption solvent was collected and evaporated to dryness at 35 °C under gentle stream of nitrogen gas followed by reconstituting in 0.1 mL acetone for the subsequent GC/MS analysis.

To develop a rapid, sensitive and cost-effective method for the determination of PAEs in complex matrix, magnetic CNTs were employed as the adsorbent due to the hydrophobic and π–π electron donor–acceptor interactions between PAEs and CNTs [3]. In order to achieve the best extraction efficiency towards PAEs, several parameters, including desorption solvent, organic phase content and salt concentration in loading solvent, desorption and extraction time, and the amount of adsorbent were investigated.

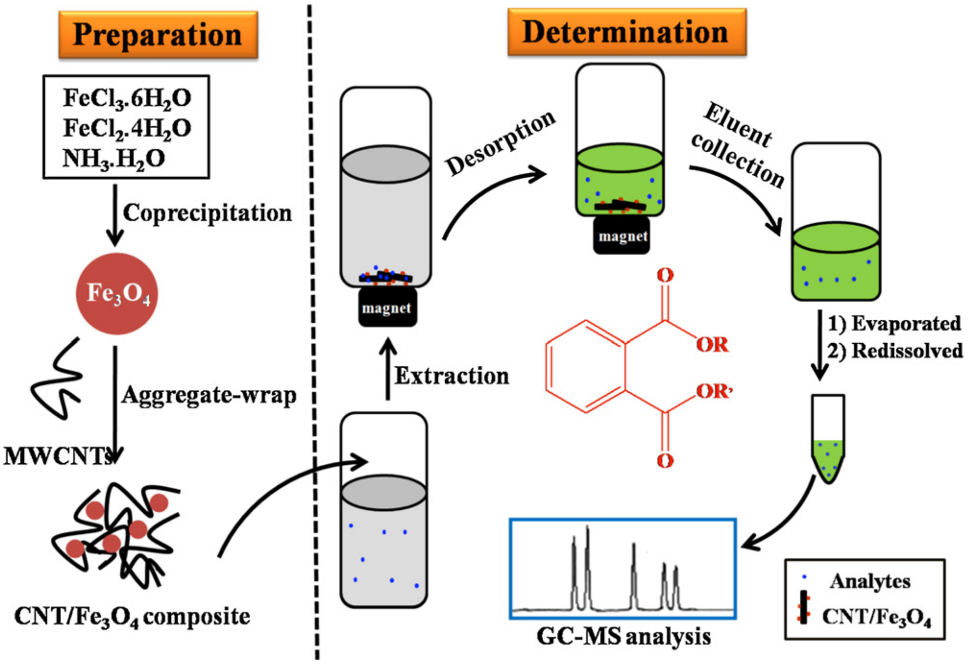

Fig. 1. Schematic illustration of the preparation strategy for magnetic CNTs and the MSPE procedure for the determination of PAEs.

2.4. *Instrumental and analytical conditions*

Transmission electron microscopy image was obtained by using JEM-2100F transmission electron microscope (TEM, JEOL, Japan). The powder X-ray diffraction (XRD) measurements were recorded on a D/MAX-RB X-ray powder diffractometer (RIGAKU, Japan) using Cu Kα radiation (λ = 1.5406 Å) with scattering angles (2θ) of 10–80°.

GC/MS analysis was performed using a Shimadzu GCMS-QP2010 plus equipped with an AOC-20i+s autosampler (Kyoto, Japan). Data acquisition and analysis were performed using the software of GCMS Real Time Analysis and GCMS Postrun Analysis, respectively (Shimadzu, Kyoto, Japan). The separation was achieved on a fused silica capillary column (Rxi® –5 ms, 30 m × 0.25 mm i.d., film thickness 0.25 μm) (Restek, Pennsylvania, USA). The oven temperature was programmed at 60 °C for 1.0 min initially, and increased to 220 °C at a rate of 20 °C min^{-1} and held for 1.0 min, and then increased to 280 °C at a rate of 5.0 °C min^{-1} and held for 4.0 min. The solvent cut time was 5.0 min. The splitless injection mode was used and the injection volume was 1.0 μL. The splitless time was 1.0 min. Helium (purity ≥ 99.999%) was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. The injection port, ion source and interface temperatures were 250 °C, 230 °C and 280 °C, respectively. Selective ion monitoring mode was used for the quantitative determination of the analytes. The retention times, qualitative ions and quantitative ions for the GC/MS analysis of 16 PAEs were shown in Table 1.

2.5. *Sample preparation*

Standard solution was prepared by spiking the analytes into PAEs-free Milli-Q water at a concentration of 50<!– /no-mfc –>ng mL^{-1}<!– /no-mfc –>. Six beverage samples, including juice drinks, carbonated drinks and mineral water, and one perfume sample, were purchased randomly from supermarkets in Wuhan and stored at 4 °C before sample preparation. The carbonated drinks samples were degassed in ultrasonic bath for 5.0 min and then diluted 20 times with loading solvent (water containing 2%

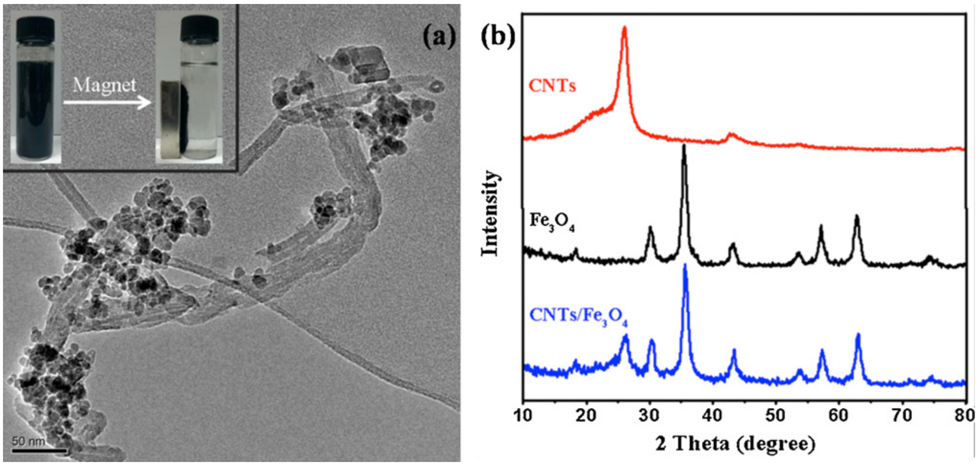

Fig. 2. (a) The TEM image of magnetic CNTs. The inset showed the photos of the aqueous dispersion of the magnetic CNTs before and after separation with a magnet. (b) The wide angle XRD pattern of the magnetic CNTs.

Table 1
The retention times, qualitative ions and quantitative ions for the GC/MS analysis of 16 PAEs.

Compound	Abbreviation	Retention time (min)	Qualitative ion	Quantitative ion
Dimethyl phthalate	DMP	7.51	77, 135, 163, 194	163
Diethyl phthalate	DEP	8.39	121, 149, 177, 222	149
Diisobutyl phthalate	DIBP	10.09	149, 167, 205, 223	149
Dibutyl phthalate	DBP	10.82	121, 149, 205, 223	149
Bis(2-methoxyethyl) phthalate	DMEP	11.14	59, 149, 193, 251	59
Bis(4-methyl-2-pentyl) phthalate	BMPP	11.83	121, 149, 167, 251	149
Bis(2-ethoxyethyl) phthalate	DEEP	12.19	45, 72, 121, 149	45
Dipentyl phthalate	DPP	12.55	149,167, 219, 237	149
Dihexyl phthalate	DHXP	14.66	76, 104, 149, 251	149
Butyl benzyl phthalate	BBP	14.82	91, 149, 206, 238	149
Bis(2-butoxyethyl) phthalate	DBEP	16.25	57, 149, 193, 249	149
Dicyclohexyl phthalate	DCHP	16.91	83, 149, 167, 269	149
Bis(2-ethylhexyl) phthalate	DEHP	17.15	113, 149, 167, 279	149
Diphenyl phthalate	DiPP	17.29	77, 153, 197, 225	225
Di-N-octyl phthalate	DNOP	19.55	149, 179, 261, 279	149
Dinonyl phthalate	DNP	22.07	57, 71, 149, 293	149

methanol, v/v) followed by filtering with 0.45 μm micropore membranes before use. The juice drinks and perfume samples were prepared in the same way but omitting the ultrasonication step. For mineral water samples, 9.8 mL mineral water was directly added to 0.2 mL methanol. As for tap water sample, 9.8 mL tap water was filtered through 0.45 μm micropore membranes and then added to 0.2 mL methanol. All samples were stored in brown glass bottles at 4 °C in refrigerator before MSPE extraction.

3. Results and discussions

3.1. Characterization of magnetic CNTs

In this work, TEM was used to examine the morphology of magnetic CNTs. As shown in Fig. 2a, magnetic particles and CNTs coexisted in proximity of each other. The spherical magnetic particles had a mean diameter of about 10 nm and attached onto the around of CNTs. The combination of magnetic particles and CNTs endows the latter the magnetic merit. Therefore, the CNTs could be separated from matrix solution conveniently by an external magnet. In addition, the prepared magnetic CNTs and its two major components (Fe_3O_4 and CNTs) were characterized by powder XRD (Fig. 2b). The well-resolved diffraction peaks, locating at 2θ of 30.14°, 35.42°, 43.32°, 53.64°, 57.14°, 62.80° and 74.56°, respectively, revealed the good crystallinity of the Fe_3O_4. This data was consistent with previous report [35]. The diffraction peak of CNTs at 2θ of 26.1° was the typical Bragg peak of pristine MWCNTs and can be indexed to the (0 0 2) reflection of graphite [36]. The wide angle XRD pattern of Fe_3O_4/CNTs indicated that the crystal structure of magnetic CNTs comprised two phases of cubic Fe_3O_4 and MWCNTs, which suggested that the preparation strategy of the magnetic CNTs based on ‘aggregation-wrap’ mechanism was successful.

3.2. Optimization of the extraction parameters

3.2.1. Desorption solvent

In this study, some representative PAEs (DIBP, DBP, BBP, DCHP, and DEHP) with different length of alkyl chains were selected as model analytes to investigate the extraction efficiency. Four solvents including acetone, methanol, ethyl acetate and *n*-hexane were studied as desorption solvent to examine their effects on the extraction efficiency. And our results showed that the best extraction efficiency can be obtained while using acetone as desorption solvent. So 1.0 mL of acetone was used as desorption solvent in the following experiments.

3.2.2. Organic phase content and salt concentration

In order to evaluate the effect of organic phase on the extraction efficiency, methanol was added to the water with a volume ratio of 0–10%. Fig. 3a shows the effect of methanol content on the extraction efficiency. The results indicated that with the increase of methanol content, the extraction efficiencies of PAEs with relatively weaker hydrophobicity (DIBP, DBP, BBP, and DCHP) decreased. In this respect, the hydrophobic interaction played the dominant role on the extraction of PAEs, therefore, the addition of methanol was detrimental for the capture of analytes. On the other hand, for PAEs with stronger hydrophobicity (DEHP), the organic modifier reduced its affinity for the glass vessel. Therefore, the result showed that organic phase content has little influence on the extraction efficiency of DEHP, which may be due to the two different effects of methanol towards DEHP. To obtain stable extraction efficiencies, moderate methanol content (2%) was used as loading solvent for the following experiments.

Next, the effect of salt on the extraction efficiencies of PAEs was evaluated. NaCl was added into the loading solvent within the range of 0–200 mM. As shown in Fig. 3b, the extraction efficiencies for PAEs first decreased and then slightly increased. For the initial decrease of extraction efficiencies, it could be explained by oil effect [37,38], which promoted PAEs to move to the water surface and therefore reduced the interaction with adsorbent. The subsequent slight increase of extraction efficiencies may be due to the salting-out effect since addition of salt can decrease the solubility of the target analytes in solution, which will benefit the adsorption of PAEs to the magnetic CNTs. Considering the extraction efficiency and simplification of the method, further experiments were performed without addition of salt.

3.2.3. Desorption and extraction time

The desorption time was investigated by increasing the vortex time from 0.5 to 8.0 min. It can be found that the targeted analytes reach to their desorption plateaus within 1.0 min and the recoveries did not increase with longer desorption time (Fig. 3c). Due to the large interfacial area between solid adsorbent and desorption solvent, the desorption can reach to the equilibrium rapidly. Therefore, the desorption time was fixed at 1.0 min. The extraction time was also investigated from 1.0 to 12 min. The results showed that as the extraction time increased from 1.0 to 3.0 min, the extraction efficiencies for some analytes (DEHP, DCHP, BBP) increased and further prolongation of the extraction time did not significantly increase the extraction efficiencies of these analytes. No obvious change for the extraction efficiencies of DBP and DIBP was

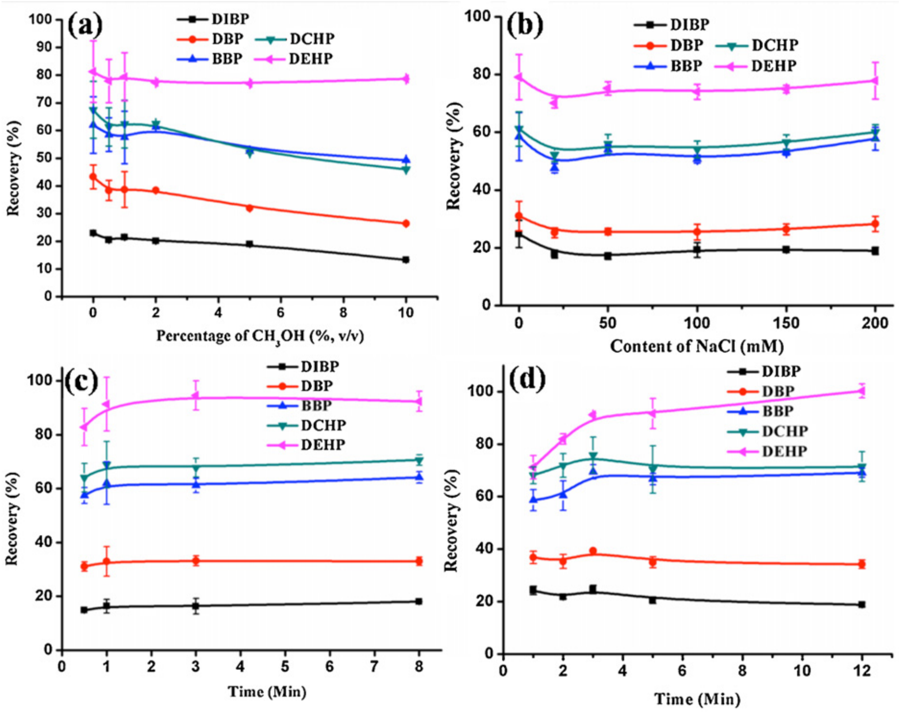

Fig. 3. Optimization of the MSPE parameters. (a) Effect of content of organic phase in the loading solvent on extraction efficiency. (b) Effect of inorganic salt concentration in the sample solution on extraction efficiency. (c) Optimization of the desorption time. (d) Investigation of the extraction time.

observed (Fig. 3d). Therefore, 3.0 min was used for the extraction time. In the MSPE mode, the adsorbent was completely dispersed in the sample/desorption solution, which dramatically increased the interfacial area between the adsorbent and sample/desorption solution and facilitated mass transfer of analytes during the extraction/desorption steps. So the extraction and desorption can be accomplished in a relative short time with MSPE mode.

3.2.4. The amount of adsorbent

To assure sufficient detection sensitivity towards the target analytes, the adsorbent amount was examined from 1.0 to 15 mg. The results showed that the extraction efficiencies of DMP, DEP, DMEP, and DEEP (they were defined as short alkyl chains PAEs with the carbon number of aliphatic chain substitution no more than 2) increased with the increase of adsorbent amount (Fig. 4a), for

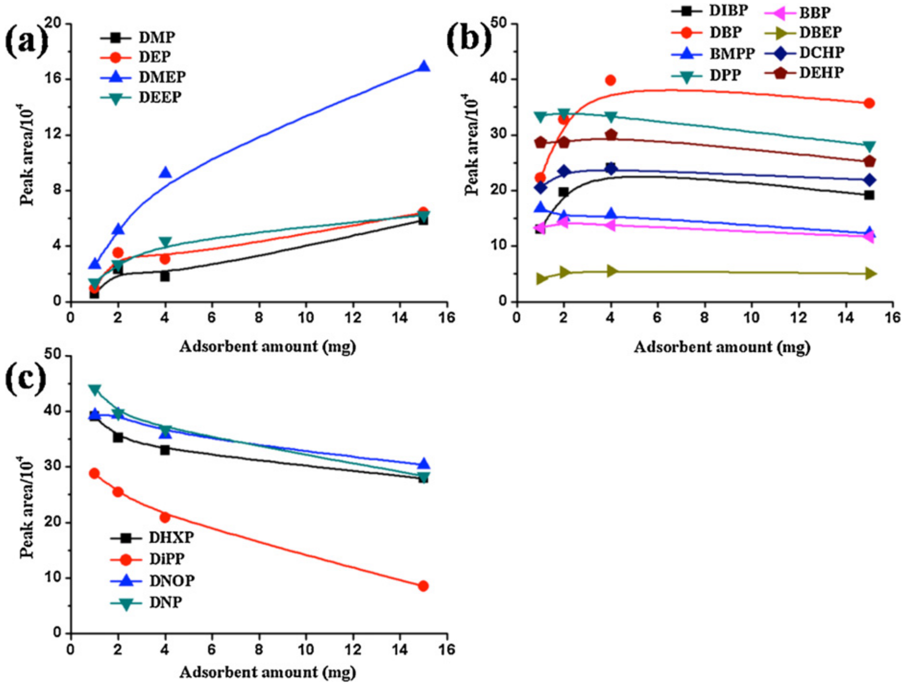

Fig. 4. Effect of the amount of adsorbent on extraction efficiencies of the PAEs. (a) Effect of the amount of adsorbent on extraction efficiencies of DMP, DEP, DMEP and DEEP. (b) Effect of the amount of adsorbent on extraction efficiencies of DIBP, DBP, BMPP, DPP, BBP, DBEP, DCHP and DEHP. (c) Effect of the amount of adsorbent on extraction efficiencies of DHXP, DiPP, DNOP and DNP.

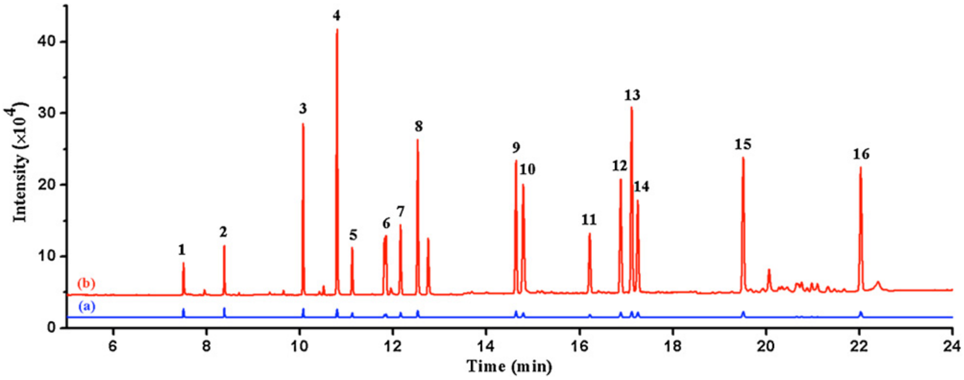

Fig. 5. The total ion chromatograms of 16 PAEs obtained by direct GC/MS analysis (a) or with the MSPE enrichment (b). The concentrations of the spiked PAEs were 10 ng/mL for each PAEs. Peaks identification: (1) DMP, (2) DEP, (3) DIBP, (4) DBP, (5) DMEP, (6) BMPP, (7) DEEP, (8) DPP, (9) DHXP, (10) BBP, (11) DBEP, (12) DCHP, (13) DEHP, (14) DiPP, (15) DNOP), and (16) DNP.

PAEs with moderate alkyl chain (DIBP, DBP, BMPP, DPP, DEHP, BBP, DBEP, and DCHP, the carbon number of aliphatic chain substitution of these PAEs was between 2 and 8), satisfactory extraction efficiencies can be obtained when 4.0 mg of the adsorbent was used (Fig. 4b). However, the extraction efficiencies of DNOP, DNP (they were defined as long alkyl chains PAEs with the carbon number of aliphatic chain substitution no less than 8), DHXP and DiPP decreased with the increase of the adsorbent amount (Fig. 4c). This same phenomenon was also observed by our previous study [39]. The extraction and desorption process should be considered comprehensively to explain this phenomenon. In our work, the extraction of all the PAEs was carried out under the same solution. Thus, the distribution coefficient (K) of PAEs was constant, and increase of the adsorbent amount would be favorable for the extraction. However, in the desorption stage, the adsorptive affinity correlated well with hydrophobicity of PAEs [3]. Due to the hydrophobic interaction between PAEs and magnetic CNTs, PAEs with longer alkyl chains have relatively stronger affinity to magnetic CNTs than PAEs with short alkyl chains. Therefore, the extraction efficiencies of PAEs with longer alkyl chains decreased with the increase of adsorbent amount. Considering the overall extraction efficiencies of all target analytes, 4.0 mg adsorbent was employed for the following experiments.

Taken together, the optimized conditions for MSPE are summarized as follows: water containing 2.0% (v/v) methanol without addition of salt was used as the loading solvent; 4.0 mg of adsorbent was used for the enrichment; the extraction and desorption time were 3.0 min and 1.0 min, respectively; 1.0 mL acetone was used as the desorption solution. Under the optimized conditions, 16 PAEs were analyzed. The total ion chromatograms obtained by direct GC/MS analysis without MSPE (Fig. 5, blue line) or with the MSPE (Fig. 5, red line) demonstrated the significant enhancement of each peak height upon MSPE extraction. The results revealed the remarkable enrichment capability of the adsorbent to the target analytes.

3.3. Validation of the MSPE-GC/MS method

Under the optimized conditions, the linearity, limits of detection (LODs), limits of quantification (LOQs) and reproducibility of the method were determined. The calibration curves of each PAEs was constructed by plotting the peak areas (y) of PAEs versus corresponding concentration of the analytes (x). The LODs and LOQs were calculated as the concentration of the analytes at a signal-to-noise ratios of 3 and 10, respectively. The results showed that the LODs and LOQs for the PAEs ranged from 4.9–38 ng L^{-1} and 16–130 ng L^{-1}, respectively (Table 2). Satisfactory correlation coefficients (between 0.9821 and 0.9993) for 16 PAEs were obtained within the linearity range of 0.2–50 ng/mL (Table 2). The intra- and inter-day relative standard deviations (RSDs) were measured with the PAEs spiked at 5 ng/mL in water. Six parallel extractions of sample solution over a day gave the intra-day RSDs, and the inter-day RSDs were determined by extracting sample solutions that had been independently prepared from three

Table 2
Linear range, correlation coefficients (R^2), limits of detection (LODs), limits of quantitation (LOQs) and precisions of 16 PAEs by MSPE-GC/MS.

Compound	Linear range (ng/mL)	R^2	LOD (ng/mL)	LOD (ng/mL)	Precision[a] (RSD, %)	
					Intra-day (n = 6)	Inter-day (n = 3)
DMP	0.2–50	0.9821	0.035	0.12	9.4	14.1
DEP	0.2–50	0.9922	0.011	0.038	9.0	13.2
DIBP	0.2–50	0.9993	0.0058	0.020	5.6	11.1
DBP	0.2–50	0.9980	0.0031	0.010	9.3	14.6
DMEP	0.2–50	0.9889	0.018	0.059	1.3	6.8
BMPP	0.2–50	0.9928	0.037	0.12	3.4	5.0
DEEP	0.2–50	0.9903	0.022	0.072	2.8	7.9
DPP	0.2–50	0.9957	0.0096	0.032	3.8	5.5
DHXP	0.2–50	0.9940	0.0087	0.029	3.6	5.5
BBP	0.2–50	0.9989	0.017	0.056	5.2	7.2
DBEP	0.2–50	0.9988	0.038	0.13	5.4	8.7
DCHP	0.2–50	0.9983	0.012	0.040	4.3	6.7
DEHP	0.2–50	0.9974	0.0078	0.026	11.7	13.8
DiPP	0.2–50	0.9948	0.014	0.046	7.3	9.3
DNOP	0.2–50	0.9973	0.0049	0.016	5.1	6.6
DNP	0.2–50	0.9970	0.0052	0.018	6.4	8.5

[a] The concentrations of the spiked analytes were 5 ng/mL.

Table 3
Comparison of different analytical methods for the determination of PAEs.

Methods	Matrix	Adsorbent	Time (min)	LOD (μg/L)	Ref.
SPE-HPLC/UV	Water samples	100 mg barium alginate caged Fe_3O_4@C18 magnetic nanoparticles	>70	DBP: 0.059; DCHP: 0.019; DNOP: 0.036	[20]
Micro SPE-GC/MS	Water samples	10 mg C18-functionalized Fe_3O_4@mSiO_2 microspheres	>20	DMP: 25; DEP: 21; DIBP: 60; DBP: 77; BBP: 46; DEHP: 31; DNOP: 37	[6]
SPME-GC/MS^2	Oil samples	DVB/CAR/PDMS fiber	30	DMP: 0.04[a]; DEP: 0.04; DIBP: 0.03; DBP: 0.03; DMEP: 0.03; BMPP: 0.03; DEEP: 0.03; DPP: 0.04; DHXP: 0.04; BBP: 0.03; DBEP: 0.02; DCHP: 0.02; DEHP: 0.03; DNOP: 0.04; DNP: 0.05	[2]
LPME-HPLC/UV	Landfill leachates	20 μL carbon tetrachloride	>40	DMP: 1.2; DEP: 1.4; DBP: 2.2	[4]
SPME-GC/FID	Mineral water samples	Homemade SPME fiber coated with oxidized MWCNTs-polypyrrole	>85	DBP: 0.08; DIBP: 0.10; DPP: 0.09; BBP: 0.05	[42]
SPME-GC/FID	Beer	30 mg benzoxy-C[6]-contained fiber (65 μm)	>110	DMP: 0.126; DEP: 3.429; DBP: 0.064; DPP: 0.003; DEHP: 0.008; DNOP: 0.021; DNP: 0.062	[43]
SPE-HPLC/UV	Water samples	500 mg MWNTs	>130	DEP: 0.18; DIBP: 0.48; DCHP: 0.86	[12]
MSPE-GC/MS	Water samples	40 mg magnetic MWCNTs	>15	DIBP: 11; DBP: 8; DEEP: 24; DPP: 18; DHXP: 21; BBP: 31; DBEP: 47; DCHP: 15; DEHP: 26; DiPP: 34; DNOP: 22	[28]
MSPE-GC/MS	Beverage, water, perfume samples	4 mg magnetic MWCNTs	<30	DMP: 0.04; DEP: 0.01; DIBP: 0.006; DBP: 0.003; DMEP: 0.06; BMPP: 0.04; DEEP: 0.02; DPP: 0.01; DHXP: 0.009; BBP: 0.02; DBEP: 0.04; DCHP: 0.01; DEHP: 0.008; DiPP: 0.01; DNOP: 0.005; DNP: 0.005	This work

[a] The unit of the concentration was μg/g.

contiguous days. The results showed that the intra- and inter-day RSDs were less than 11.7% and 14.6%, respectively (Table 2), which demonstrated that good reproducibility can be achieved by the method.

3.4. Comparison of different analytical methods

Listed in Table 3 is the comparison of different analytical methods for the determination of PAEs. For most of the PAEs, the method developed in our current study gave the lowest LODs, indicating the highly sensitive detection of PAEs with MSPE-GC/MS method. The analysis time with our method is comparable to other methods with rapid detection of PAEs. In addition, the analytical time of our method can be further reduced by handling several samples (usually 6) simultaneously. Compared to previous report which also employed magnetic CNTs for the PAEs extraction [28], our method suggests the advantages of simpler adsorbent preparation processing and smaller required adsorbent amount (Table 3).

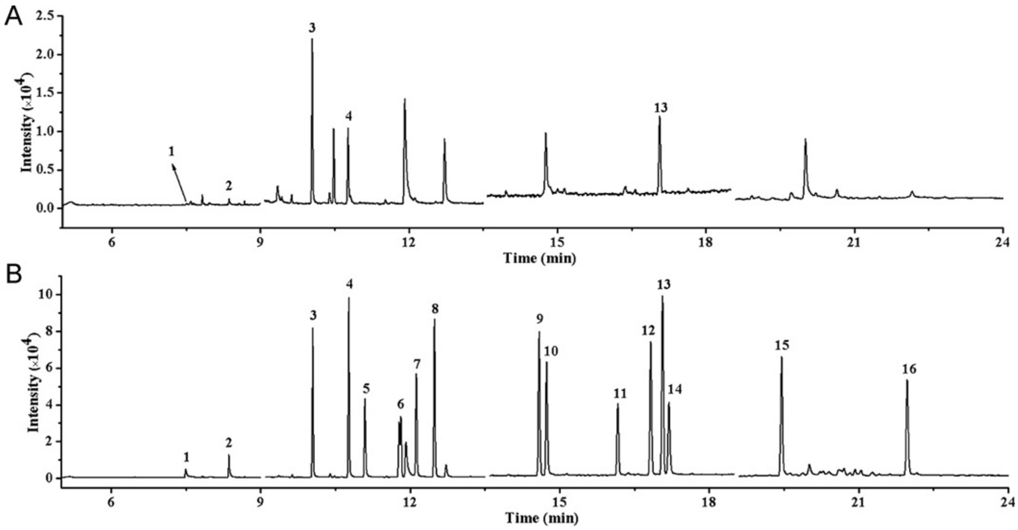

Fig. 6. (a) The total ion chromatogram of beverage sample (sample D) extracted directly by magnetic CNTs. (b) The total ion chromatogram of beverage sample (sample D) spiked with 5 ng/mL of each PAEs and extracted by magnetic CNTs. Peaks identification: (1) DMP, (2) DEP, (3) DIBP, (4) DBP, (5) DMEP, (6) BMPP, (7) DEEP, (8) DPP, (9) DHXP, (10) BBP, (11) DBEP, (12) DCHP, (13) DEHP, (14) DiPP, (15) DNOP, and (16) DNP.

Table 4
Recoveries (%), precision (RSDs, $n = 3$) and concentrations (con., ng/mL) of 16 PAEs in beverage, tap water and perfume samples by MSPE-GC/MS.[a]

Compound	Juice drink A		Juice drink B		Mineral water C		Mineral water D	
	Con.	Recovery (%, RSD%)	Con.	Recovery (%, RSD%)	Con.	Recovery (%, RSD%)	Con.	Recovery (%, RSD%)
DMP	11.1	77.3 (2.3)	22.1	77.5 (0.5)	0.41	84.6 (12.0)	0.36	85.0 (12.7)
DEP	25.6	87.8 (3.7)	nd	77.5 (10.9)	nq	87.5 (5.6)	1.1	85.8 (8.7)
DIBP	20.8	74.4 (8.0)	2.1	79.7 (13.0)	0.36	80.9 (11.0)	1.0	83.1 (9.9)
DBP	5.7	74.2 (4.0)	5.1	74.0 (8.2)	0.42	82.7 (11.4)	0.40	83.4 (12.4)
DMEP	nd	96.4 (5.9)	nd	86.9 (6.4)	nd	125.6 (7.2)	nd	118.9 (8.7)
BMPP	nd	83.3 (0.6)	nd	80.4 (10.4)	nd	83.9 (9.6)	nd	88.1 (11.2)
DEEP	nd	89.8 (9.4)	nd	83.8 (3.6)	nd	102.9 (8.9)	nd	98.2 (8.2)
DPP	nd	81.6 (0.5)	nd	84.9 (9.4)	nd	90.2 (8.6)	nd	85.0 (8.5)
DHXP	nd	88.9 (7.7)	nd	87.8 (2.9)	nd	88.9 (5.7)	nd	91.1 (2.7)
BBP	nd	74.9 (7.8)	nd	71.1 (0.7)	nd	82.1 (6.2)	nd	81.9 (3.3)
DBEP	nd	100.8 (6.2)	nd	84.7 (7.4)	nd	84.3 (6.4)	nd	86.0 (2.2)
DCHP	nd	73.1 (5.8)	nd	74.4 (0.7)	nd	92.1 (6.3)	nd	93.2 (2.4)
DEHP	9.6	89.9 (7.3)	8.4	85.7 (8.7)	0.72	90.7 (4.4)	0.38	92.4 (1.4)
DiPP	nd	107.2 (7.1)	nd	107.4 (3.2)	nd	83.6 (2.9)	nd	88.6 (4.0)
DNOP	nd	99.5 (5.0)	nd	91.7 (8.9)	nd	83.8 (1.7)	nd	88.0 (2.0)
DNP	nd	89.3 (8.5)	nd	87.3 (7.2)	nd	82.0 (2.9)	nd	87.7 (1.1)

Compound	Carbonated drink E		Carbonated drink F		Tap water G		Perfume H	
	Con.	Recovery (%, RSD%)	Con.	Recovery (%, RSD%)	Con.	Recovery (%, RSD%)	Con.	Recovery (%, RSD%)
DMP	nd	87.6 (16.5)	8.3	74.1 (7.2)	nd	103.6 (7.1)	nd	81.6 (9.0)
DEP	nd	89.0 (10.7)	19.8	83.0 (8.1)	nq	97.6 (3.1)	6114	78.3 (3.8)
DIBP	31.0	82.8 (11.8)	38.0	81.4 (4.3)	0.41	103.6 (16.2)	nd	74.3 (5.0)
DBP	32.7	80.3 (5.5)	10.9	76.8 (13.2)	1.4	91.8 (9.6)	nq	77.6 (9.4)
DMEP	nd	81.4 (7.1)	nd	77.4 (5.6)	nd	79.6 (6.2)	3.3	64.6 (4.7)
BMPP	nd	94.1 (9.2)	nd	87.3 (10.6)	nd	101.4 (7.2)	nd	83.9 (4.9)
DEEP	nd	88.4 (10.1)	nd	85.9 (5.3)	nd	112.4 (8.1)	nd	79.8 (6.8)
DPP	nd	90.1 (7.2)	nd	83.6 (6.5)	nd	98.9 (6.7)	nd	76.8 (5.3)
DHXP	nd	92.4 (5.2)	nd	88.0 (4.1)	nd	98.6 (6.4)	nd	83.0 (4.2)
BBP	nd	80.6 (3.8)	nd	70.2 (5.1)	nd	85.6 (8.0)	10.4	74.3 (3.1)
DBEP	nd	77.0 (6.0)	nd	62.9 (6.2)	nd	87.6 (7.7)	nd	75.4 (2.0)
DCHP	nd	85.1 (6.2)	nd	76.1 (4.9)	nd	91.2 (7.2)	nd	69.0 (3.4)
DEHP	16.3	89.2 (6.6)	3.4	76.2 (5.4)	3.3	94.5 (12.5)	nq	75.1 (4.1)
DiPP	nd	93.1 (5.6)	nd	80.1 (5.2)	nd	92.0 (6.6)	nd	81.2 (7.9)
DNOP	nd	80.2 (3.9)	nd	75.8 (4.8)	nd	89.4 (7.3)	nd	70.3 (5.5)
DNP	nd	74.9 (4.3)	nd	71.6 (4.1)	nd	83.3 (9.8)	nd	72.3 (7.1)

nd, not detected; nq, not quantified.

[a] The concentrations of the spiked PAEs were 5 ng/mL.

3.5. *Application to real samples*

Under optimized conditions, the MSPE-GC/MS method was successfully applied to the analysis of PAEs in real samples including bottled beverages, tap water and perfume. Compared to other real sample, the highest variety of PAEs was detected for sample D, and the total ion chromatograms of blank and spiked sample D extracted by magnetic CNTs were shown in Fig. 6. Interferences from the matrix can be separated from the targeted analytes. The recoveries were determined by comparing the measured amounts of spiked PAEs in real samples with the total amounts of spiked PAEs. As listed in Table 4, the recoveries of the 16 PAEs from various real samples were in the range from 64.6% to 125.6% with the RSDs less than 16.5%. Compared to other samples, the matrix of perfume resulted in relatively lower recoveries for PAEs (64.6–83.9%). The PAEs with low molecular weight (DMP, DEP, DIBP, and DBP) have larger water solubility [40] and they are not chemically bonded to the polymer, so these kinds of PAEs can easily migrate from the PVC bottle into beverage [1]. DEHP was found in all bottled beverages, which may be attributed to that DEHP was primarily used as plasticizers and therefore can migrate from bottles into beverages [1]. DEP, DBP, and BBP, which are widely used as solvents to hold color and scent in various consumable and personal care products [1], were detected in perfume product with a high concentration and previous studies also reported their existence in cosmetic products [5,41].

4. Conclusions

In this study, magnetic CNTs were successfully prepared via a simple method based on 'aggregation-wrap' mechanism and the materials were characterized by powder XRD. The strong adsorption property makes magnetic CNTs an excellent candidate for serving as adsorbent of MSPE. The performance of magnetic CNTs for MSPE was evaluated by enriching PAEs. Under optimized conditions, a rapid, sensitive and cost-effective method for the determination of PAEs from beverage, environmental water, and perfume samples was established by the coupling of MSPE with GC/MS. Our results showed that the LODs of most of the 16 PAEs detected by MSPE-GC/MS method were much lower compared to the previously reported methods, which suggested that magnetic CNTs can be used as adsorbent of MSPE for the highly sensitive determination of PAEs in environmental samples.

Acknowledgments

This work was partly supported by grants from the Fundamental Research Funds for the Central Universities, the National Natural Science Foundation of China (91017013, 31070327, 21005057) and the Science Fund for Creative Research Groups (No. 20921062), NSFC.

References

[1] X.L. Cao, Compr. Rev. Food Sci. Food Saf. 9 (2010) 21.
[2] J.J. Rios, A. Morales, G. Marquez-Ruiz, Talanta 80 (2010) 2076.
[3] F. Wang, J. Yao, K. Sun, B.S. Xing, Environ. Sci. Technol. 44 (2010) 6985.
[4] J.R. Yao, H. Xu, L.L. Lv, D.D. Song, Y.F. Cui, T.Z. Zhang, Y.Q. Feng, Anal. Chim. Acta 616 (2008) 42.
[5] R.Y. Su, X.W. Zhao, Z.Y. Li, Q. Jia, P. Liu, J.B. Jia, Anal. Chim. Acta 676 (2010) 103.
[6] Z.B. Li, D.N. Huang, C.F. Fu, B.W. Wei, W.J. Yu, C.H. Deng, X.M. Zhang, J. Chromatogr. A 1218 (2011) 6232.
[7] C. Perez Feas, M.C. Barciela Alonso, E. Pena-Vazquez, P. Herbello Hermelo, P. Bermejo-Barrera, Talanta 75 (2008) 1184.
[8] E.T. Ozer, S. Gucer, Talanta 84 (2011) 362.
[9] L. Sanchez-Prado, M. Llompart, J. Pablo Lamas, C. Garcia-Jares, M. Lores, Talanta 85 (2011) 370.
[10] H.Y. Shen, Talanta 66 (2005) 734.
[11] M. Sharman, W.A. Read, L. Castle, J. Gilbert, Food Addit. Contam. 11 (1994) 375.
[12] Y.Q. Cai, G.B. Jiang, J.F. Liu, Q.X. Zhou, Anal. Chim. Acta 494 (2003) 149.
[13] J.D. Li, Y.Q. Cai, Y.L. Shi, S.F. Mou, G.B. Jiang, Talanta 74 (2008) 498.
[14] X.J. Li, Z.R. Zeng, Y. Chen, Y. Xu, Talanta 63 (2004) 1013.
[15] K. Ridgway, S.P.D. Lalljie, R.M. Smith, J. Chromatogr. A 1153 (2007) 36.
[16] Q. Gao, D. Luo, J. Ding, Y.Q. Feng, J. Chromatogr. A 1217 (2010) 5602.
[17] J. Ding, Q. Gao, D. Luo, Z.G. Shi, Y.Q. Feng, J. Chromatogr. A 1217 (2010) 7351.
[18] M.L. Chen, L.L. Suo, Q. Gao, Y.Q. Feng, Electrophoresis 32 (2011) 2099.
[19] Q. Gao, D. Luo, M. Bai, Z.W. Chen, Y.Q. Feng, J. Agr. Food Chem. 59 (2011) 8543.
[20] S.X. Zhang, H.Y. Niu, Y.Q. Cai, Y.L. Shi, Anal. Chim. Acta 665 (2010) 167.
[21] X.L. Zhang, H.Y. Niu, S.X. Zhang, Y.Q. Cai, Anal. Bioanal. Chem. 397 (2010) 791.
[22] J.R. Meng, J. Bu, C.H. Deng, X.M. Zhang, J. Chromatogr. A 1218 (2011) 1585.
[23] S. Iijima, Nature 354 (1991) 56.
[24] K. Yang, B.S. Xing, Chem. Rev. 110 (2010) 5989.
[25] Q.X. Zhou, J.P. Xiao, W.D. Wang, J. Chromatogr. A 1125 (2006) 152.
[26] Y. Guan, C. Jiang, C.F. Hu, L. Jia, Talanta 83 (2010) 337.
[27] G. Morales-Cid, A. Fekete, B.M. Simonet, R. Lehmann, S. Cardenas, X.M. Zhang, M. Valcarcel, P. Schmitt-Kopplin, Anal. Chem. 82 (2010) 2743.
[28] S.L. Fu, L. Ding, S.H. Zhu, Y.N. Jiao, Q. Gong, J.T. Chen, X.H. Wu, L.B. Wang, Chin. J. Chromatogr. 29 (2011) 737.
[29] Y.H. Deng, C.H. Deng, D. Yang, C.C. Wang, S.K. Fu, X.M. Zhang, Chem. Commun. 41 (2005) 5548.
[30] Y.B. Luo, Z.G. Shi, Q. Gao, Y.Q. Feng, J. Chromatogr. A 1218 (2011) 1353.
[31] J. Ding, Q. Gao, X.S. Li, W. Huang, Z.G. Shi, Y.Q. Feng, J. Sep. Sci. 34 (2011) 2498.
[32] X.S. Li, J.H. Wu, L.D. Xu, Q. Zhao, Y.B. Luo, B.F. Yuan, Y.Q. Feng, Chem. Commun. 47 (2011) 9816.
[33] L. Zhao, R.A. Wu, G.H. Han, H.J. Zhou, L.B. Ren, R.J. Tian, H.F. Zou, J. Am. Soc. Mass Spectrom. 19 (2008) 1176.
[34] A. Fankhauser-Noti, K. Grob, Anal. Chim. Acta 582 (2007) 353.
[35] Q. Lan, C. Liu, F. Yang, S.Y. Liu, J. Xu, D.J. Sun, J. Colloid Interface Sci. 310 (2007) 260.
[36] T.T. Baby, S. Ramaprabhu, Talanta 80 (2010) 2016.
[37] M.S. Garcia-Falcon, B. Cancho-Grande, J. Simal-Gandara, Water Res. 38 (2004) 1679.
[38] Y.B. Luo, J.S. Cheng, Q. Ma, Y.Q. Feng, J.H. Li, Anal. Methods 3 (2011) 92.
[39] Q. Gao, C.Y. Lin, D. Luo, L.L. Suo, J.L. Chen, Y.Q. Feng, J. Sep. Sci. 34 (2011) 3083.
[40] R. Alzaga, A. Pena, J.M. Bayona, J. Sep. Sci. 26 (2003) 87.
[41] H.Y. Shen, H.L. Jiang, H.L. Mao, G. Pan, L. Zhou, Y.F. Cao, J. Sep. Sci. 30 (2007) 48.
[42] H. Asadollahzadeh, E. Noroozian, Sh. Maghsoudi, Anal. Chim. Acta 669 (2010) 32.
[43] C.W. Ye, J. Gao, C. Yang, X.J. Liu, X.J. Li, S.Y. Pan, Anal. Chim. Acta 641 (2009) 64.