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# Graphene nanoplatelets as a highly efficient solid-phase extraction sorbent for determination of phthalate esters in aqueous solution

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## ABSTRACT

Graphene nanoplatelet (GN) as a solid-phase extraction (SPE) sorbent in combination with high performance liquid chromatography has been used for the determination of five phthalate esters (PAEs) in aqueous solution. The operation parameters affecting the extraction efficiency were optimized. Comparative studies showed that GN was superior to other common SPE sorbents in terms of recovery and adsorption capacity. Under optimization conditions, detection limits of 0.09–0.33 ng mL$^{-1}$ were achieved for five PAEs and enrichment factors of 402–711 for the analytes were obtained. The proposed method was successfully applied for the determination of PAEs in tap water and drink samples with recoveries ranging from 87.7% to 100.9%.

## 1. Introduction

Phthalate esters (PAEs) are widely used as polymer additives in the manufacture of plastics to improve their flexibility and durability [1]. These plastics have been commonly used in the field of food, pharmacy, cosmetics, etc. PAEs themselves are generally stable in the plastics but they can be released from products with time and migrate into environment water, soil, and plants since they are not chemically but only physically bound to the plastics [2]. Due to massive use and persistent character, PAEs have become ubiquitous pollutants in the environment and several PAEs are suspected to be human cancer causing agents and endocrine disruptors. The intensive use of PAEs and their pollutions have become a major public health concern. Several countries have listed PAEs as the priority contaminants [3–5], including U.S. Environmental Protection Agency (EPA) and China [6]. Therefore, it is necessary to develop a simple, sensitive and reliable analytical method for the determination of PAEs.

Very low concentration of PAEs existing in the complicated environmental samples makes sample pretreatment necessary for establishing a reliable determination method for the determination of PAEs prior to chromatographic separation, e.g. the maximum residue level in drinking water for dibutyl phthalate (DBP) is 3 ng mL$^{-1}$, which is beyond the detection limit of analytical instruments. To effectively determine such PAEs residue, some sample pretreatment methods were employed for PAEs samples such as liquid–liquid extraction (LLE) [4,7], solid-phase extraction (SPE) [1,8,9], solid-phase microextraction (SPME) [10,11], microwave-assisted extraction (MAE) [12] and so on. Among them, SPE is the most widely used one for environmental samples due to some of its desirable features. The choice of sorbent is a key step to perform SPE successfully. High adsorption capacity and high selectivity are favorable features for a good sorbent. Several kinds of sorbents for SPE have been reported for extraction of PAEs, such as $C_{18}$ [4], polymer [9], bamboo charcoal [6], and multi-walled carbon nanotubes (MWCNTs) [1].

Graphene (G), a novel carbon material with monolayer of carbon atoms densely packed into a two-dimensional honeycomb crystal lattice, has aroused much interests in recent years [13,14]. G has advantages of ultrahigh surface area and high chemical stability. In addition, the large delocalized π-electron structure also endows G a strong affinity for benzene ring-based compounds [15]. These features make it a good candidate for adsorption of benzenoid form compounds. So far, G-related sorbents have been used for extraction of polycyclic aromatic hydrocarbons [16] or chlorophenols [17] or carbamate pesticides [18]. Satisfactory results have been achieved for extraction of above analytes. However, there has been no report that uses G sorbent for extraction of PAEs operated in SPE mode except one report that uses homemade G–$Fe_3O_4$ magnetic particles for PAEs [19]. Graphene nanoplate (GN) consisting of multilayers graphene has

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been commercially available, which has excellent electrical and thermal performance. Herein we have made attempts to explore the potential of pure GN sorbent-based SPE for the extraction of PAES in aqueous solution. Five widely used PAEs (their structure and other information are provided in Supplementary material, SI-Table 1), including dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPrP), DBP and dicyclohexyl phthalate (DCHP), have been chosen to be the model analytes. The operation parameters affecting the extraction efficiency were optimized. The results showed that GN sorbent was highly effective for extraction of target analytes and was superior to other sorbents.

## 2. Experimental

### 2.1. Apparatus and reagents

The chromatographic separation was performed on a Waters 2998 Separations module equipped with a photodiode array detector. A ZORBAX SB-$C_{18}$ column (4.6 mm i.d. × 150 mm length, 5 μm diameter) was used for separation at room temperature. The mobile phase consisting of water ($A$) and methanol ($B$) was operated under gradient mode starting from $A/B=50/50$ (v/v) for 10.0 min to $A/B=10/90$ (v/v) for 5 min. The flow rate of the mobile phase was 1 mL/min and the detection wavelength was set at 226 nm. Peak area was used for the measurement of signal intensity.

DMP, DEP, DPrP, DBP and DCHP of analytical grade were supplied by Aladdin (Shanghai, China). HPLC-grade acetonitrile and methanol were purchased from J&K Scientific Ltd. (Beijing, China) and Yuwang Group (Shandong, China), respectively. Four kinds of SPE cartridges containing different sorbents were used for comparison, which included HLB Oasis (5 μm diameter, Waters Corp., USA), $C_{18}$ Silica (5 μm diameter, ~300 $m^2$/g), Active carbon (http://www.sipore.com/e_cpzs.asp, Sipore Corp., Dalian, China), and MWCNTs (90–120 $m^2$/g, Shenzhen Nanotech Port Corp., Shenzhen, China). GN with 6–8 nm average thickness and 15 μm average width was purchased from Strem Chemicals Inc. (http://www.strem.com/catalog/v/06–0215/12/carbon_7782-42-5, Massachusetts, USA). The effective specific surface area of GN was measured to be 126 $m^2$/g, which was close to the value provided by the vendor (120–150 $m^2$/g). Unless otherwise stated, ultrapure water from Milli-Q system (Millipore, MA, USA) was used for solution preparation.

### 2.2. SPE operation procedures

30 mg GN was packed in a 1 mL cartridge (6.4 mm i.d., 150 mm height bed, Agilent Corp., USA) and pressed by a glass rod. Two polytetrafluoroethylene (PTFE) frits were set at each end of the cartridge to hold GN in place. The outlet tip of the cartridge was connected to a vacuum pump (Yukang Instrument Corp., Shanghai, China) and the inlet end of the cartridge was connected to the sample solution through a polytetrafluoroethylene (PTFE) suction tube. The operation level of vacuum is controlled to be ~0.06 MPa by a valve. To reduce the possible interference from organic and inorganic contaminants, the entire SPE assembly was carefully washed with sufficient methanol and ultrapure water before its first use.

The SPE operation procedures were as follows. The cartridge was preconditioned with 5 mL methanol and 5 mL ultrapure water prior to each SPE operation. A known volume of ultrapure water spiked with five PAEs was passed through the above preconditioned cartridge at the flow rate of 4 mL/min. The cartridge was then rinsed with 10 mL ultrapure water to remove the residuals. Subsequently the SPE cartridge was eluted with acetonitrile and the resulting effluent was blown with a gentle $N_2$ flow at room temperature to obtain the residue and then reconstituted to be 1.0 mL. Finally, the extract was analyzed by HPLC with injection volume of 10 μL.

## 3. Results and discussion

### 3.1. Evaluation of GN as SPE sorbent

To evaluate the enrichment effect of GN sorbent, five PAEs mentioned above were selected as model analytes. The operation parameters affecting the extraction efficiency, including eluent solvent and its volume, and the sample volume were optimized. For SPE operation, the flow rate of sample loading solution determines the recovery of analytes and the total analysis time. In our experiment, no observable change of the recoveries for five analytes was found when the flow rate of sample loading on the cartridge was up to 4 mL/min. To save analytical time, 4 mL/min of the flow rate of sample loading was chosen in the further experiment.

The eluent solvent for SPE operation has important influence on sample recovery. The choice of eluent solvent is mainly based on the chemical property of the target samples and the chromatographic mode used downstream. Since the separation of five PAEs was performed by reverse phase HPLC (RP-HPLC), the eluent solvent should be compatible with common mobile phase used in RP-HPLC, that is, the eluent solvent should be miscible with the mobile phase. Here five common solvents including acetone, acetonitrile, methanol, ethanol, and methanol/acetonitrile mixture at 50/50 (v/v) were tested. The effect of eluent solvent on the recovery is shown in Fig. 1. It can be seen that acetonitrile is the most effective eluent for five PAEs, probably resulting from strong interaction between acetonitrile and GN due to its property of aprotic solvent. Thus acetonitrile was selected as eluent in the following studies. In addition, the pH effect on the extraction was also explored and it was found that the pH of sample solutions in the range 5.0–8.0 had no significant influence on the recoveries.

To ensure that the model analytes are eluted from the SPE cartridge completely and no carryover occurs, it is necessary to optimize the volume of acetonitrile. The eluent volume in the range of 4–20 mL was tested with 200 mL standard sample solution spiked at 100 ng $mL^{-1}$. The results are shown in Fig. 2. The recoveries of all PAEs increased with the increase of

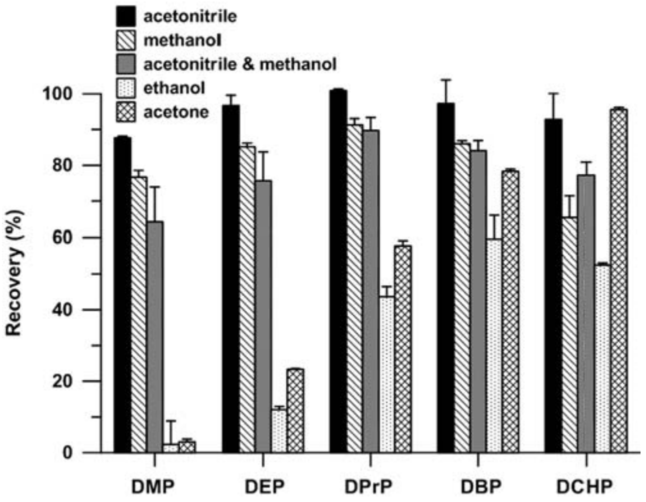

**Fig. 1.** Effect of eluent solvents on SPE efficiency. Conditions: sample loading volume, 200 mL; concentration of five analytes: 100 ng $mL^{-1}$; eluent volume, 16 mL. Three replicate measurements for each analyte.

acetonitrile volume in the range of 4–16 mL, and then remained almost constant over 16 mL. To get a high enrichment factor, 16 mL of acetonitrile was used in the further study. Under such conditions, the recoveries for DMP, DEP, DPrP, DBP, and DCHP were 87.7%, 96.7%, 100.9%, 97.3% and 92.8%, respectively. Though no observable carryover was found, another 5 mL acetonitrile and 5 mL water were employed to elute the cartridge before next extraction in order to get rid of any possible residue of PAEs.

### 3.2. Effect of sample volume

To ensure reliable analytical results and high enrichment factor, the maximal sample loading volume of GN-based SPE cartridge needs to be explored and nonoccurrence of sample breakthrough should be ensured. The experiment was performed by measuring the response of sample by loading different volumes of sample solution. The effect of sample loading volume on the recovery is shown in Fig. 3. It can be seen that the peak area of each analyte increased with increase of loading sample volume up to 1000 mL, indicating rich adsorbed sites on the surface of GN sorbent. 80–101% of recoveries were achieved for the analytes (except DMP) when the sample loading volume was less than 500 mL. Partial sample loss or breakthrough occurred when the loading volume was >500 mL, as indicated by the decrease of recoveries of several analytes. This is especially true for the less-retained species. For the loading volume less than 400 mL, e.g. 200 mL, 87.7–100.9% of the recoveries could be achieved for the PAEs tested, indicating good precision of the developed method. In the further experiment, 200 mL of loading sample volume was used.

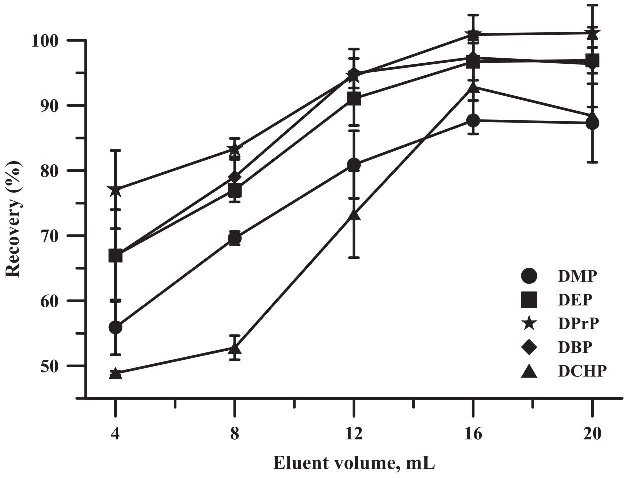

**Fig. 2.** Effect of eluent solvent volume on SPE efficiency. Conditions: sample loading volume, 200 mL; elution solvent, acetonitrile; analyte concentration, 100 ng mL$^{-1}$; three replicate measurements for each analyte.

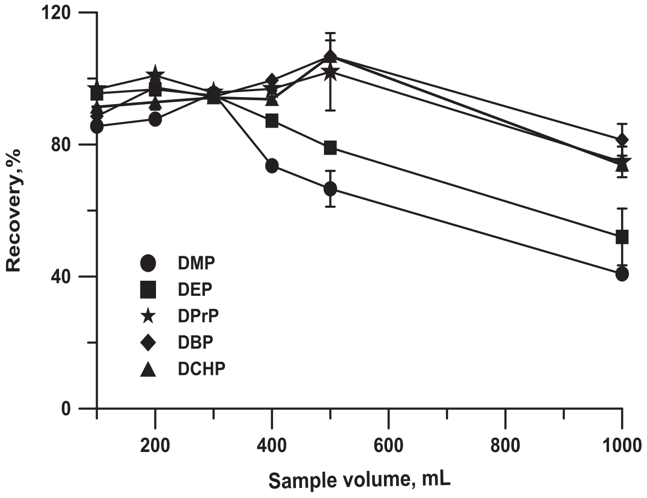

**Fig. 3.** Effect of sample loading volume on SPE efficiency. Conditions: elution solvent, acetonitrile; analyte concentration, 100 ng mL$^{-1}$; eluent volume, 16 mL. Three replicate measurements for each analyte.

### 3.3. Comparison with other extraction sorbents

Comparison of GN sorbent with other commonly used sorbents, including $C_{18}$ silica, HLB Oasis, Active carbon, and MWCNTs, has been made. To ensure the same level of packing sorbent in the cartridge, different amounts of sorbents were used due to their different densities. (Note: if the same amount of sorbents is used, too low level of sorbent in the cartridge will occur for high density of sorbent, causing bad operation reproducibility). $C_{18}$ silica (100 mg), HLB Oasis (100 mg), Active carbon (50 mg), MWCNTs (50 mg) and GN (30 mg) were packed in 1 mL SPE cartridge. These cartridges were loaded with 200 mL of sample solutions spiked at 100 ng mL$^{-1}$ five PAEs above. To determine the possible breakthrough of sample, the effluent at different stages of loading, washing, and elution was collected and determined by HPLC. Methanol as the eluent solvent was used for $C_{18}$ silica and HLB Oasis. Active carbon and MWCNTs were eluted by acetonitrile. The results are provided in Table 1. Clearly, GN sorbent yielded the highest recoveries (85.6–100.9%) among these tested sorbents, although its amount was the smallest (only 30 mg). $C_{18}$ sorbent demonstrated acceptable recoveries (76.2–104.4%) at lower level of spiked analytes (10 μg), while the recoveries decreased significantly when the spiked level was up to 20 μg, especially for DCHP (from 104.4% to 72.2%), indicating limited capacity of $C_{18}$ sorbent relative to GN. This was true if considering that the amount of $C_{18}$ was 3.3-fold of GN amount (100 mg and 30 mg). The recoveries of the analytes on Active carbon sorbent were even much poorer than those of $C_{18}$ silica, which probably resulted from its irreversible adsorption. MWCNTs sorbent demonstrated good recoveries for DEP, DPrP, and DCHP at low spiked level (10 μg) while much lower recoveries were observed for the analytes spiked at high level (20 μg). A direct comparison with related articles is provided in SI-Table 2. By comparison, GN sorbent demonstrated the best performance in terms of recoveries and adsorption capacity among several sorbents. This is probably due to its unique structure, which results in strong π-stacking interaction with the benzene ring in the molecule of PAEs [15]. In addition, GNs have some hydrophilic groups such as hydroxyl and carboxyl groups, which can improve the water-wettability of GN and enhance the retention of polar compounds. These features make GN an attractive sorbent for PAEs.

### 3.4. Analytical performance

A standard chromatogram of PAE is shown in SI-Fig. 1 Five PAEs could be well separated under simple gradient mode. Under the optimal extraction conditions, the proposed GN-based SPE method was first evaluated with the standard samples. The results achieved are given in Table 2. The plots between the peak area and the concentration of five PAEs in the range of 5–500 ng mL$^{-1}$ showed excellent linear relationship with correlation coefficients of ~0.9998. The limits of detection (LODs), based on a signal-to-noise ratio ($S/N$) of 3, were in the range of 0.09–0.33 ng mL$^{-1}$. By comparison, the LODs achieved here were better that those of previous SPE method for PAEs [1,6], e.g. 0.18–0.86 ng mL$^{-1}$ of the LODs @ 500 mg of MWCNTs [1] or 0.35–0.43 ng mL$^{-1}$ of the LODs @1000 mg bamboo carbon sorbent [6]. This was especially attractive if only 30 mg amount of GN used was considered.

**Table 1**
Comparison of several sorbents for extraction of five PAEs.

| Sorbents[a] | Spiked amount (μg) | Recovery (%) | | | | |
|---|---|---|---|---|---|---|
| | | DMP | DEP | DPrP | DBP | DCHP |
| GN | 10.0 | 85.6 ± 0.7 | 95.5 ± 0.5 | 96.7 ± 2.3 | 88.6 ± 1.0 | 91.4 ± 0.7 |
| | 20.0 | 87.7 ± 0.3 | 96.7 ± 1.7 | 100.9 ± 0.3 | 97.3 ± 4.0 | 92.8 ± 4.6 |
| $C_{18}$ | 10.0 | 76.2 ± 0.0 | 87.8 ± 0.3 | 86.7 ± 1.3 | 103.0 ± 0.6 | 104.4 ± 1.3 |
| | 20.0 | 81.4 ± 0.2 | 85.7 ± 0.7 | 82.0 ± 1.5 | 96.1 ± 1.6 | 72.2 ± 0.1 |
| HLB | 10.0 | 100.2 ± 1.7 | 90.4 ± 3.0 | 88.1 ± 1.2 | 104.6 ± 0.7 | 66.2 ± 1.2 |
| | 20.0 | 77.5 ± 0.9 | 83.0 ± 0.8 | 71.7 ± 1.0 | 87.0 ± 1.4 | 53.2 ± 4.2 |
| Active carbon | 10.0 | 39.7 ± 0.8 | 65.5 ± 0.6 | 34.2 ± 1.6 | 65.7 ± 1.0 | 68.1 ± 0.4 |
| | 20.0 | 51.2 ± 0.4 | 74.6 ± 1.4 | 17.1 ± 1.6 | 42.0 ± 5.6 | 41.4 ± 0.5 |
| MWCNTs | 10.0 | 69.2 ± 0.8 | 96.3 ± 3.4 | 55.2 ± 4.3 | 94.3 ± 1.1 | 83.6 ± 2.6 |
| | 20.0 | 49.7 ± 3.2 | 69.1 ± 4.0 | 45.8 ± 2.8 | 71.2 ± 1.8 | 54.7 ± 1.1 |

[a] The SPE cartridges fabricated by 30 mg of GN, 100 mg of $C_{18}$ and HLB Oasis, 50 mg of Active carbon and MWCNTs. The eluent solvent for GN and MWCNTs was acetonitrile while for HLB, Oasis, $C_{18}$ and Active carbon, the eluent solvent was methanol.

**Table 2**
Linear ranges, correlation coefficients and detection limits of GN-based SPE method ($n=3$).

| Compound | Linear ranges (ng mL$^{-1}$) | Regression equation | $R^2$ | LOD (ng mL$^{-1}$)[a] | LOQ (ng mL$^{-1}$)[a] |
|---|---|---|---|---|---|
| DMP | 5–500 | $y=(24279 \pm 5320)x+(4252 \pm 122)$ | 0.9999 | 0.09 | 0.30 |
| DEP | 5–500 | $y=(21405 \pm 4686)x+(3793 \pm 108)$ | 0.9999 | 0.16 | 0.53 |
| DPrP | 5–500 | $y=(18897 \pm 4316)x+(7031 \pm 99)$ | 0.9999 | 0.20 | 0.68 |
| DBP | 5–500 | $y=(17585 \pm 4323)x+(29772 \pm 99)$ | 0.9998 | 0.19 | 0.63 |
| DCHP | 5–500 | $y=(15745 \pm 3544)x+(7288 \pm 81)$ | 0.9999 | 0.33 | 1.09 |

[a] Limit of detection (LOD) and limit of quantity (LOQ) calculated based on $S/N=3$ and 10, respectively.

The enrichment factor (EF) is defined as follows:

$$EF=\left(\frac{C_0}{C_1}\right)\left(\frac{A_1}{A_0}\right)$$

where $C_1$ and $C_0$ are the sample concentration with enrichment by SPE (calculated by calibration curve) and without enrichment (direct injection), respectively. $A_1$ and $A_2$ stand for the peak area corresponding to $C_1$ and $C_0$, respectively. The maximal EFs calculated for DMP, DEP, DPrP, DBP and DCHP were 402, 512, 711, 630, and 688, respectively, if 1000 mL sample loading volume was used. Another good feature of GN sorbent is that it can be recycled. The repeatability was evaluated by performing three replicate runs using a GN-based SPE cartridge (note that no carry-over was observed at each run). The RSD was $<4.6\%$ for all five tested analytes. Large recyclable numbers have not been explored but they will depend to a great extent on the complexity of the samples.

The proposed method has been used for the analysis of tap water, commercial bottled water, and market drinks; the preconcentration effect is demonstrated in Fig. 4 and the detailed results are shown in Table 3 and SI-Table 3. Recoveries were examined by two concentration levels of standard PAEs. From Table 3, it can be seen that the recoveries ranging from 84.3% to 105.6% are satisfactory for real samples in most cases. Good recoveries indicated that little interference was observed to be neglected. For the drink samples tested in SI-Table 3, no DMP, DEP and DPrP were found while trace level of DBP (2.94–13.62 ng mL$^{-1}$) existed in all tested samples, and 3.85–8.64 ng mL$^{-1}$ level of DCHP was found in four tested samples.

In addition, an interesting experiment was carried out to explore the effect of temperature of filled water on the dissolution of PAEs from bottle material. The basic background is that some people around use plastic bottle to fill hot water for drinking and such behavior is supposed to be harmful to health. Such conclusion is made based on the possible leaking of PAEs from bottle when the temperature is increased. Here the bottle made of polyethylene (PE) was used to fill hot water with temperature ranging from 25 to 100 °C. The hot water at each temperature was filled in PE bottle for 2 h, then treated and detected by the above GN-based SPE method. The effect of temperature on the dissolution of PAEs is provided in the Supplementary material of SI-Fig. 2. For water with temperature less than 40 °C, the dissolution amount of PAEs can be neglected and no PAEs were detected. When the water temperature was > 40 °C, the dissolution amount of DBP and DCHP was significant and also increased with the increase of water temperature. While for DMP, DEP and DPrP, no observable amount was found. Thus the dissolution of PAEs can be

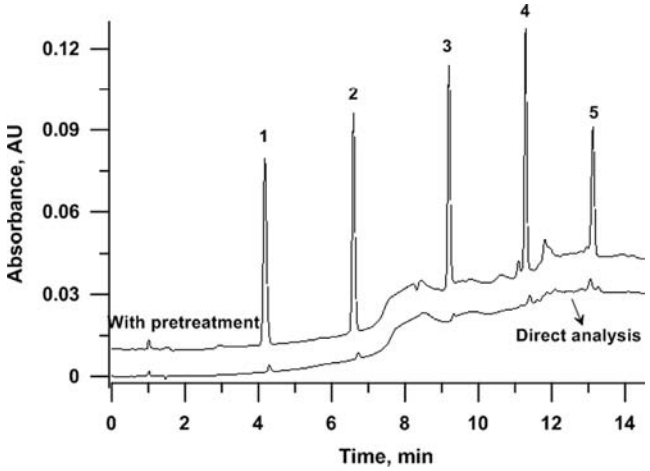

**Fig. 4.** Chromatograms of tap water samples. Conditions: mobile phase consisting of $H_2O$ (A) and $CH_3OH$ (B) operated under gradient mode starting from $A/B=50/50$ (v/v) for 10.0 min to $A/B=10/90$ (v/v) for 5 min; flow rate, 1 mL/min; detection wavelength, 226 nm; tap water spiked at 100 ng mL$^{-1}$ with and without pretreatment; peak identification, 1—DEP, 2—DMP, 3—DPrP, 4—DBP, and 5—DCHP; other conditions are similar to those of Fig. 1.

**Table 3**
Determination and recoveries of five analytes spiked water samples ($n=3$).

| Sample | Analytes | Added (ng mL$^{-1}$) | Found[a] (ng mL$^{-1}$) | Recovery[b] (%) |
|---|---|---|---|---|
| Tap water | DMP | 50.0 | 43.3 | 86.5 ± 3.7 |
| | | 100.0 | 84.4 | 84.3 ± 4.4 |
| | DEP | 50.0 | 46.5 | 92.9 ± 2.7 |
| | | 100.0 | 89.9 | 89.7 ± 6.5 |
| | DPrP | 50.0 | 49.5 | 98.9 ± 1.0 |
| | | 100.0 | 92.6 | 92.6 ± 7.6 |
| | DBP | 50.0 | 45.4 | 90.7 ± 2.3 |
| | | 100.0 | 92.6 | 92.6 ± 0.9 |
| | DCHP | 50.0 | 46.0 | 91.9 ± 0.3 |
| | | 100.0 | 94.3 | 94.3 ± 1.6 |
| Bottled water | DMP | 50.0 | 44.4 | 88.7 ± 2.7 |
| | | 100.0 | 90.4 | 90.4 ± 0.3 |
| | DEP | 50.0 | 48.4 | 96.8 ± 2.4 |
| | | 100.0 | 91.5 | 91.5 ± 5.8 |
| | DPrP | 50.0 | 50.6 | 101.1 ± 1.3 |
| | | 100.0 | 95.6 | 95.6 ± 2.9 |
| | DBP | 50.0 | 52.8 | 105.6 ± 0.3 |
| | | 100.0 | 100.6 | 100.6 ± 4.4 |
| | DCHP | 50.0 | 52.7 | 105.3 ± 1.1 |
| | | 100.0 | 91.6 | 91.6 ± 1.0 |

[a] Based on three replicates; [b] ± RSD; nd, not detected.

regarded as the dissolution of DBP and DCHP other than DMP, DEP and DPrP for PE material.

## 4. Conclusions

A simple and reliable method has been developed for the enrichment and determination of five PAEs in aqueous solution using GN as SPE sorbents. In comparison with several common SPE sorbents, including $C_{18}$ silica, HLB Oasis, Active carbon, and MWCNTs, GN appeared to be more effective in terms of recovery and adsorption capacity. Under the optimized conditions, higher enrichment factors and good recoveries were obtained for five tested PAEs via GN sorbent. It is believed that GN as SPE sorbents has huge potential for the determination of trace PAEs in environmental samples.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.11.079.

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