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## Research Article

# Graphene-based solid-phase extraction disk for fast separation and preconcentration of trace polycyclic aromatic hydrocarbons from environmental water samples

Graphene has great potentials for the use in sample preparation due to its ultra high specific surface area, superior chemical stability, and excellent thermal stability. In our work, a novel graphene-based SPE disk was developed for separation and preconcentration of trace polycyclic aromatic hydrocarbons from environmental water samples. Based on the strong  $\pi$ - $\pi$  stacking interaction between the analytes and graphene, the analytes extracted by graphene were eluted by cyclohexane and then determined by GC-MS. Under the optimized conditions, high flow rate (30 mL/min) and sensitivity (0.84–13 ng/L) were achieved. The proposed method was successfully applied to the analysis of real environmental water samples with recoveries ranging from 72.8 to 106.2%. Furthermore, the property of anticlogging and reusability was also improved. This work reveals great potentials of graphene-based SPE disk in environmental analytical.

**Keywords:** Gas chromatography mass spectrometry / Graphene / Polycyclic aromatic hydrocarbons / Solid-phase extraction disk  
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## 1 Introduction

Environment pollution has become one of the most significant issues all over the world. The problem caused by environmental contaminants led to unpredictable influences to human life because of their toxicity and widespread use. Therefore, it is crucial to develop simple, rapid, and efficient methods for monitoring the contaminants. However, the problems exist for direct determination, such as (1) the sample matrices are complex, (2) the contaminants are in the extremely low concentration in environmental samples, and (3) the sensitivity and selectivity of the conventional analytical methods are usually insufficient. Therefore, a sample preparation procedure is required.

Sample preparation is the most important procedure to remove the matrix interferences and enrich the analytes, especially for environmental water analysis. Liquid-liquid extraction is the traditional method for sample preparation and has been widely used in environmental analysis. But it suffers from the disadvantages of time-consuming and requiring large amount of toxic organic solvents. SPE [1] is a widely used

technique for the pretreatment of environmental sample in recent years due to its high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation. The most important component of the SPE technique is the adsorbent material, which dominates the selectivity and sensitivity of the method. Many types of sorbents have currently been developed for SPE, such as C18 silica, resin [2, 3], polymer materials [4–6], etc. Recently, carbon nanomaterials are of considerable interests in sample preparation, including fullerenes [7] and carbon nanotubes [8, 9]. Considerable researches have been published focusing on development of carbon nanomaterials-based SPE methods for a great variety of analytes, including endocrine disruptors [10], pesticide residues [11–13], metal ion [14–16], etc.

The novel format of SPE is SPE disk [17], it was first introduced by 3M as an advanced technique in comparison with a SPE cartridge. They possess large cross-sectional area, enable faster flow rates and shorten loading time. They can also reduce the risk of plugging and pollution. Therefore, they were always used when treating large volume environmental water samples. The commercial SPE disk includes many species, such as Empore (3M), Speedisk (J. T. Baker), Universal (UCT), etc. However, the new adsorbents developed for SPE disk are limited. Niu et al. [18, 19] prepared a new SPE disk based on a sheet of single-walled carbon nanotubes and obtained satisfactory results for preconcentration four groups of compounds with different polarities (including phthalate esters, endocrine disruptors, chlorophenols, and sulfonylurea

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**Abbreviations:** GO, graphene oxide; PAH, polycyclic aromatic hydrocarbon; TEM, transmission electron microscopy; XPS, X-ray photoelectron spectroscopy

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herbicides). Katsumata et al. [20] used multiwalled carbon nanotubes SPE disk to the preconcentration of atrazine and simazine in environmental water samples and obtained high precision and accuracy.

Graphene has also been used as the sorbent in the sample preparation because of its ultra high specific surface area, superior chemical stability, and excellent thermal stability. Liu et al. [21] reported the first application of graphene as adsorbent for SPE and revealed the superior performance than carbon nanotubes as adsorbent for SPE. Large specific surface area, simple preparation methods, both the surfaces of graphene sheets for adsorption, easy to functionalize and facilitate retention and elution for polar compounds, all of the merits lead to the numerous applications in SPE [22–28]. Up to the present, there are many applications in other forms of sample preparation, such as solid-phase microextraction [29–37] and magnetic SPE [38–42].

In this study, a novel graphene-based SPE disk was developed for the pretreatment of environmental water samples. Nine polycyclic aromatic hydrocarbons (PAHs) were selected as model analytes for their high toxicity and widespread environmental occurrence. Excellent extraction effect based on  $\pi$ - $\pi$  stacking interaction plays an important role in the adsorption of PAHs onto graphene. The analytes extracted by graphene were eluted by cyclohexane and analyzed by GC-MS. Under the optimal conditions, a rapid, simple, and convenient SPE-GC-MS method for the determination of PAHs in environmental water samples was established.

## 2 Experimental

### 2.1 Reagents and materials

All of the organic reagents used in the experiment were of HPLC grade and purchased from Amethyst Chemicals (J&K Scientific, Beijing). Polycyclic aromatic hydrocarbons, including naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), and benzo[a]pyrene (BaP) were obtained from TCI Chemicals (Shanghai, China). Expanded graphite powder (100 mesh) was purchased from Xinghe Graphite (Qingdao, China). Other reagents were of analytical grade and used without further purification.

The individual standard stock solutions of PAHs (1000  $\mu\text{g/mL}$ ) were prepared in methanol and stored at 4°C. The working standard solution was prepared by combining aliquots of each individual stock solution and diluting to obtain a desired concentration. Fresh working solutions were prepared daily by appropriate dilution of the stock solutions.

### 2.2 Instrumental and analytical conditions

Transmission electron micrographs were taken out on an H-7650B (Hitachi, Japan) transmission electron microscope.

SEM measurement was performed on a FEI Quanta 200 (FEI, Holland) field-emission scanning electron microscope. X-ray photoelectron spectroscopy (XPS) data were collected using a PHI-5300 ESCA X-ray photoelectron spectrometer (PHI, America). Raman spectra were recorded using the Horiba HR800 (Horiba, France) with excitation at 514 nm laser.

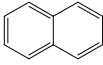
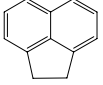
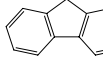
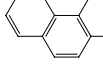
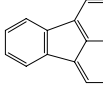
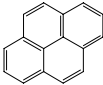
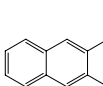
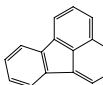
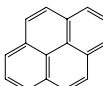
The SPE experiments were performed on an Extrapid solid-phase extraction (LabTech, China) with a VP30 vacuum pump (LabTech, China). The empty SPE disk and its adjuncts were kindly supplied by LabTech.

All the analyses were carried out on a Shimadzu (Kyoto, Japan) GC-MS QP2010 ultra system equipped with a Shimadzu AOC-20i auto injector and a Rxi-5Sil MS fused silica capillary column (30 m  $\times$  0.25 mm id, film thickness 0.25  $\mu\text{m}$ , 5% phenyl/95% dimethylpolysiloxane, Restek, USA). Helium was employed as the carrier gas at a flow rate of 1.0 mL/min. The injector port temperature was set at 280°C in a splitless mode. The GC oven temperature was initially held at 70°C for 3 min, increased to 180°C at the rate of 25°C/min for 2 min, then increased to 280°C at the rate of 15°C/min for 2 min, finally increased to 300°C at the rate of 10°C/min for 5 min. The mass spectrometer was operated in the electron impact ionization mode with an ion source temperature of 200°C. The GC-MS interface temperature was kept at 260°C and the energy of electrons was kept at 70 eV. Selective ion monitoring mode was adopted for quantitative determination of the analytes. The data, retention times, as well as the target ions of all analytes are shown in Table 1.

### 2.3 Preparation of graphene

Graphite oxide was prepared from expanded graphite according to a modified Hummers method. The procedure is briefly described as follows. Sodium nitrate (0.5 g) and potassium permanganate (3 g) were added to 23 mL of 98% sulfuric acid in an ice bath. Expanded graphite powder (0.5 g) was slowly added with vigorous agitation. The reaction mixture was maintained in an ice bath for 24 h in a refrigerator. Afterward, the reaction was transferred to a 35°C oil bath for 30 min. Subsequently, 46 mL of deionized water was gradually added to the reaction mixture and the temperature was increased to 98°C and kept for 15 min. Then, 30%  $\text{H}_2\text{O}_2$  (20 mL) was added dropwise until visible bubbles were generated. Remove the supernatant after laying aside, followed by washing with sufficient hydrochloric acid (5%) and deionized water to remove excess acid. Finally, the material, graphite oxide, was air-dried under ambient conditions. The as-synthesized graphite oxide was ultrasonicated in water to give a brown dispersion, and then subjected to 30 min of centrifugation at 3000 rpm. to remove any unexfoliated graphite oxide, and the graphene oxide (GO) dispersion was obtained. Graphene was synthesized by hydrazine reduction of GO. Then, hydrazine hydrate (10 mL) and ammonia (20 mL) was added to the dispersion. This dispersion was heated at 95°C for 24 h, collected by filtration, washed with water, and then freeze-dried under vacuum to obtain graphene.

**Table 1.** The data, retention times, and target ions for the GC-MS analysis of the target compounds

Compound	Abbreviation	Structure	Molecular weight	Retention time (min)	Qualitative ion	Quantitative ion
Naphthalene	Nap		128	7.06	128, 129, 127, 102	128
Acenaphthene	Ace		154	9.67	154, 153, 152, 76	154
Fluorene	Fle		166	10.68	166, 165, 163, 82	166
Phenanthrene	Phe		178	12.64	178, 176, 152, 76	178
Fluoranthene	Flu		202	15.00	202, 201, 200, 101	202
Pyrene	Pyr		202	15.43	202, 201, 200, 101	202
Benzo[a]anthracene	BaA		228	17.91	228, 226, 229, 114	228
Benzo[b]fluoranthene	BbF		252	20.60	252, 250, 253, 126	252
Benzo[a]pyrene	BaP		252	21.49	252, 250, 253, 126	252

#### 2.4 Preparation of graphene-based SPE disk and experimental procedures

The graphene-based SPE disk was prepared in our work according to the method of J. T. Baker Speedisk with a little modification. The conformation of the disk is shown in Fig. 1A. The manufacture method was as follows: 200 mg graphene was dispersed in water under ultrasound for 30 min and loaded in the cartridge housing when the first glass-fiber filter was placed under vacuum. Immediately stop the vacuum when the water was just near to empty. Then the second glass-fiber filter was placed subsequently and so on. In this design, the glass-fiber filter was used to fix the graphene and make the sorbent uniform between the filter layers. The nylon microporous membrane was to prevent the loss of graphene and the pollutants. The screen was added to keep the water flow-through vertical and harmonious. The diameter of the disk was 47 mm and the obtained sorbent layer was about 2 mm in thickness.

The compendious SPE procedure is displayed in Fig. 1B. Prior to extraction, the disks were preconditioned with 20 mL cyclohexane, 20 mL methanol, and 20 mL water, respectively. Then 1 L water samples were passed through the preconditioned disks. After loading, the disks were kept on vacuum for

30 min to remove residual water. Finally, the analytes were eluted with 20 mL cyclohexane. One microliter of the elution was injected into the GC-MS system for analysis. The disks were renewed by washing with 20 mL cyclohexane, 20 mL methanol, and 20 mL water, respectively, for next extraction.

#### 2.5 Sample preparation

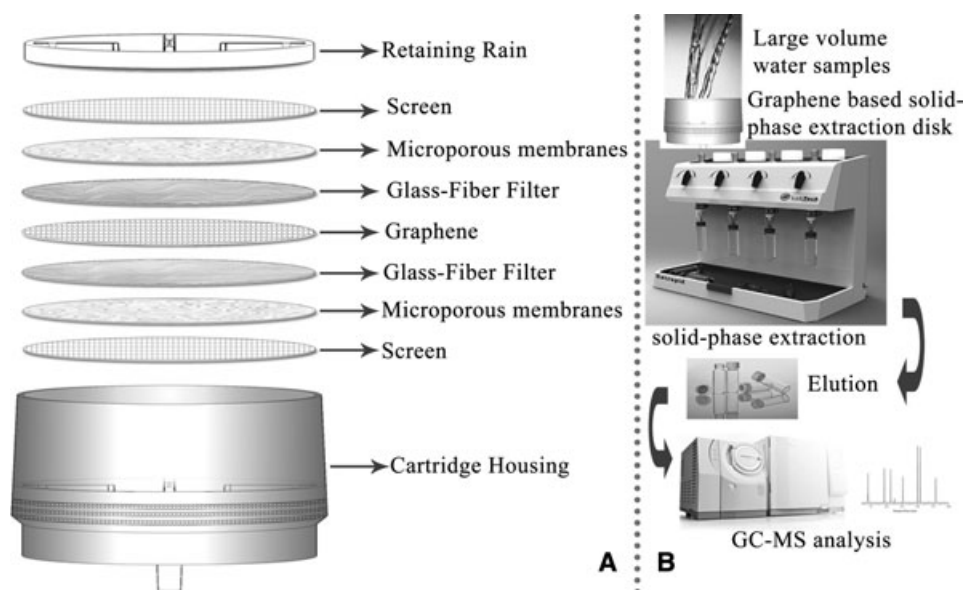
Tap water samples were collected from a water tap in our lab (Beijing, China). River water samples were collected from the Wanquan River in Tsinghua University (Beijing, China). All of the environmental water samples were filtered through 0.45  $\mu\text{m}$  microporous membranes immediately after sampling and stored in a volumetric flask at 4°C in a refrigerator.

### 3 Results and discussion

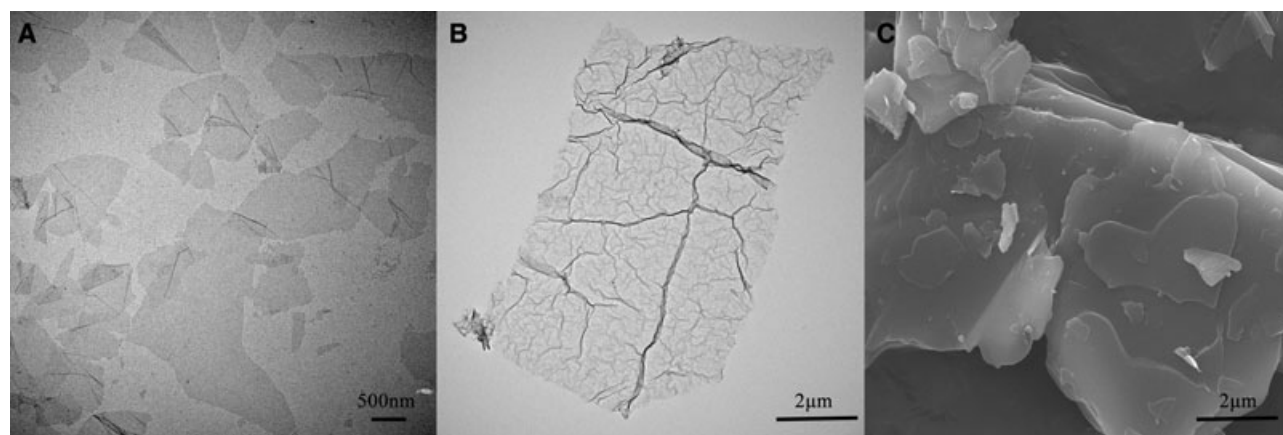
#### 3.1 Characterization of graphene

##### 3.1.1 The morphological structure of graphene

The morphology of the prepared GO and graphene were characterized by transmission electron microscopy (TEM)



**Figure 1.** The method for preparation of graphene-based SPE disk and SPE procedures.



**Figure 2.** The morphological structure of graphene: TEM images of (A) GO and (B) graphene, SEM images of (C) graphene.

and SEM, as shown in Fig. 2. From Fig. 2A, the copper grid substrates were covered with many thin films without bulk aggregates, indicating that the GO nanosheets had been fully exfoliated. The lateral dimensions of the obtained sheets ranged from a few hundred nanometers to many several micrometers. After reduction to graphene, the TEM and SEM images are shown in Fig. 2B and C. The prepared graphene was also micrometer level in size. The transparent films containing lots of wrinkles can be seen. It indicated that the graphene sheet was few layers and maintained high surface area.

### 3.1.2 X-ray photoelectron spectroscopy

XPS was used to determine the chemical composition of GO and graphene. The wide scan XPS spectra (Fig. 3A) of the substances exhibited the same photoelectron lines at binding energies of approximately 280 and 520 eV, which were attributed to C1s and O1s, respectively. Compared with GO, the

intensity for O1s peak of graphene was significantly decreased and the intensity for C1s peak was increased, revealing that GO was reduced to graphene successfully. To understand the electronic states of the elements, higher resolution spectra were also recorded. Figure 3B illustrates the C1s deconvolution spectrum of GO, and four different carbon-containing functional groups were observed: (1) the nonoxygenated carbon ( $\text{C}=\text{C}$ ) at 284.8 eV, (2) the epoxy and alkoxy carbon ( $\text{C}-\text{O}$ ) at 286.9 eV, (3) the carbonyl carbon ( $\text{C}=\text{O}$ ) at 288.2 eV, and (4) the carboxylate carbon ( $\text{O}-\text{C}=\text{O}$ ) at 289.0 eV. After the reduction to graphene, the intensities of all C1s peaks (Fig. 3C) of the carbons binding to oxygen, especially the peak of  $\text{C}-\text{O}$ , decreased dramatically, indicating that most oxygen-containing functional groups were removed after the reduction. A new peak appears at 285.8 eV, probably corresponding to  $\text{C}-\text{N}$  bonds because of the hydrazine reduction. It was also verified by the wide scan spectra, the intensity for N1s peak was increased after the reduction.

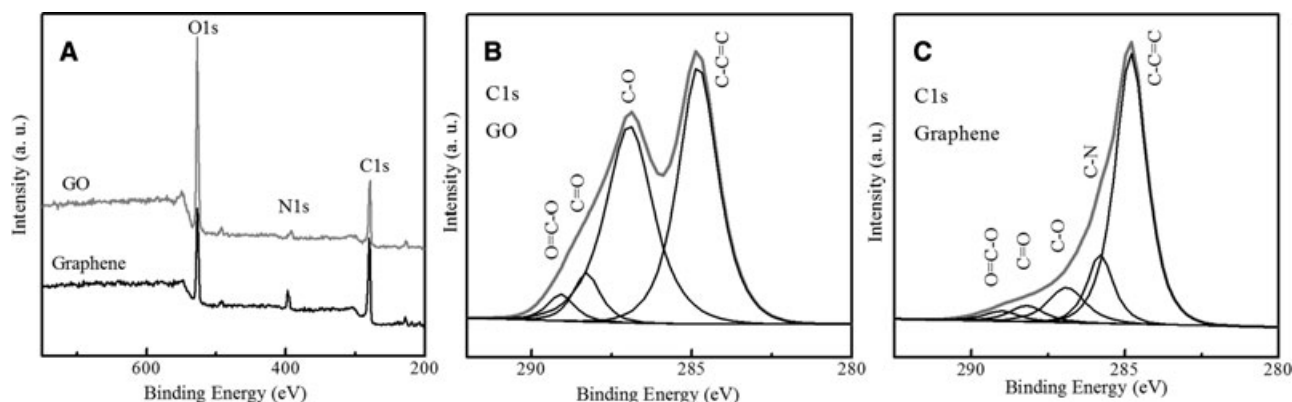


Figure 3. XPS spectra of (A) wide scan of GO and graphene, C1s spectrum of (B) GO and (C) graphene.

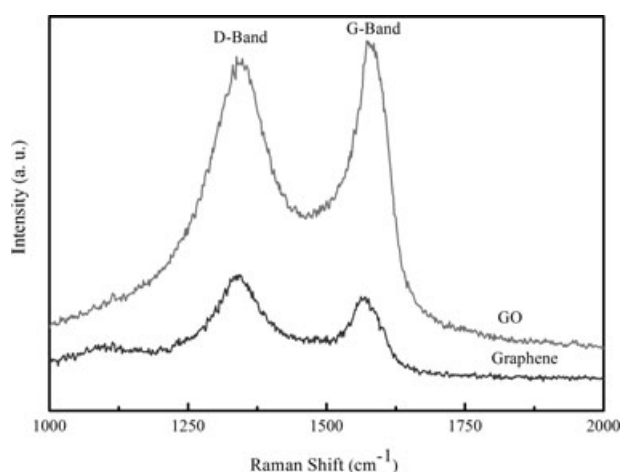


Figure 4. Raman spectroscopy of GO and graphene.

### 3.1.3 Raman spectroscopy

Raman spectroscopy is a useful nondestructive tool to characterize carbonaceous materials, particularly for distinguishing ordered and disordered carbon structures. The change of the electronic conjugation state can also be revealed by the variation of the relative intensities of G (the  $E_{2g}$  mode of  $sp^2$  carbon atoms) and D (the symmetry  $A_{1g}$  mode) bands in the Raman spectra. In Fig. 4, the Raman spectrum of GO and graphene exhibits the presence of D band ( $1337\text{ cm}^{-1}$ ) and G band ( $1572\text{ cm}^{-1}$ ). The intensity of G band and D band is further decreased after the GO was reduced to graphene. Probably the phenomena can be explained either by the fact that the disorder of graphene layer was increased or more defects were produced during the reduction. The relative intensity ratio of the D and G lines ( $I_D/I_G$  ratio) is increased significantly, indicating the reduction did occur.

## 3.2 Optimization of SPE procedures

To select the optimal SPE conditions for extracting the PAHs, deionized water spiked with certain amount of PAHs was used to examine the extraction performance of the SPE

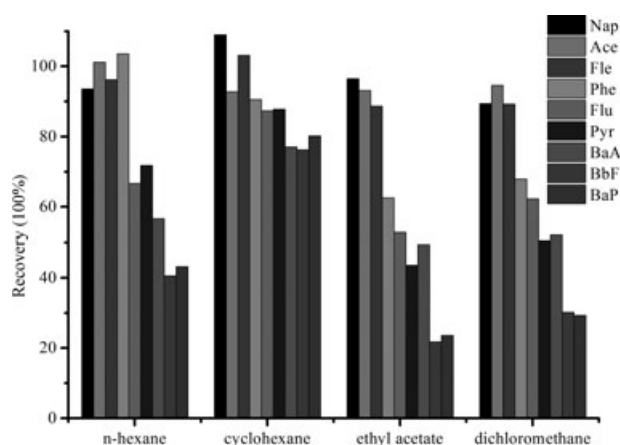


Figure 5. The effect of desorption solvents on the recoveries of PAHs.

under different experimental conditions. In our experiments, several parameters, including the desorption condition, loading rate, sample pH, ionic strength as well as the reusability of the disk were investigated to achieve the best performance for PAHs.

### 3.2.1 Effect of the elution for the desorption of PAHs

It is necessary to choose an effective elution to achieve complete desorption of the analytes and avoid the crossover contamination in subsequent experiments. Therefore, the choice of elution solvent should be carefully considered. In our work, the disks were loaded with  $2\text{ }\mu\text{g}$  each analyte in aqueous solution and several organic solvents (20 mL) with different polarity were compared for the selection of the final eluent. For highly polar solution such as methanol and acetonitrile, the recoveries of the analytes were all  $<30\%$ , in comparison, weakly polar solution including *n*-hexane, cyclohexane, ethyl acetate, and dichloromethane were tested as the elution. The results are shown in Fig. 5. The four solutions can reach satisfactory recoveries for the lower number of condensed ring PAHs. However, the recoveries for higher number of condensed ring PAHs are scant when *n*-hexane, ethyl acetate,

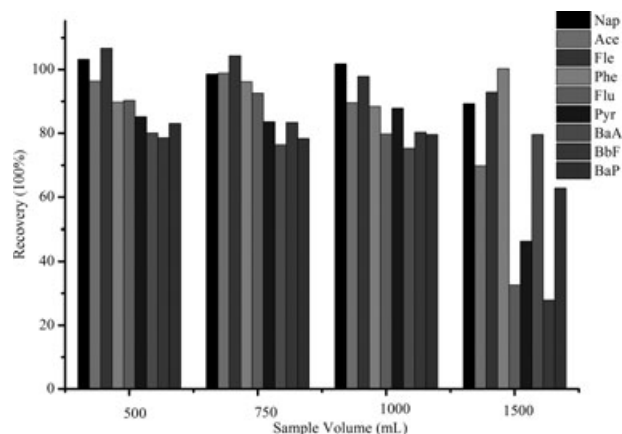


Figure 6. The effect of sample volume on the recoveries of PAHs.

and dichloromethane were used as the elutions. The recoveries can reach >78% for 4–5 ring PAHs (like Flu, Pyr, BaA, BbF, BaP) when using cyclohexane as the elution. The results above can provide a clear proof that the  $\pi$ - $\pi$  stacking interaction mainly possesses the adsorption of PAHs on graphene and the interaction is increasing with the ring number of PAHs. In our study, 20 mL cyclohexane was chosen as the elution for the subsequent experiments.

### 3.2.2 Effect of loading rate

The sample loading rate is one of the most prominent of all the advantages for SPE disk. Fast loading rate cuts down the analysis time and makes it possible for large volume loading. The effect of loading rate on the extraction of PAHs was investigated by pretreating 500 mL of solution spiked with 2  $\mu$ g each analyte. The recoveries were >80% when the loading rate reached about 30 mL/min and the loading time was <20 min for treating 500 mL water sample. As we all know, the conventional loading rate for commercial SPE column is <5 mL/min, which results in a longer time for one treating run. That is a most important reason to choose SPE disk when treating large volume water sample.

### 3.2.3 Effect of sample volume

In order to obtain a high concentration factor as possible, it was very important to get satisfactory recoveries for all analytes in a large volume of sample solutions. Therefore, it is necessary to obtain the breakthrough volumes in the SPE procedure. In this work, four different aqueous solutions (500, 750, 1000, and 1500 mL) spiked with 2  $\mu$ g analytes, the results of recoveries are presented in Fig. 6. The recoveries are >75.3% for all of analytes when the loading volume was under 1000 mL. It was found that the recoveries were extremely unstable when the volume was 1500 mL. It was probably due to the different solubility of the analytes in water. A sample volume of 1000 mL was selected in the subsequent analysis of several environmental water samples.

### 3.2.4 Effect of the pH and ionic strength

In our experiment, the influence of the sample pH on the extraction efficiency was investigated by adjusting the pH in the range of 3–10 by adding appropriate volumes of 1 M NaOH or 1 M HCl. No obvious variations in the recoveries of PAHs were observed. PAHs exist as neutral molecules under common conditions, and their form was maintained invariably when the pH changed. Therefore, there is no need to adjust the sample pH. To investigate the effect of ionic strength on the recoveries of PAHs, NaCl was added to adjust the ionic strength of the solution. No significant variation in the recoveries was observed with the NaCl concentration between 0 and 100 mM. This result indicated that the ionic strength was negligible for the next analytical procedure.

### 3.2.5 Reusability of graphene-based SPE disk

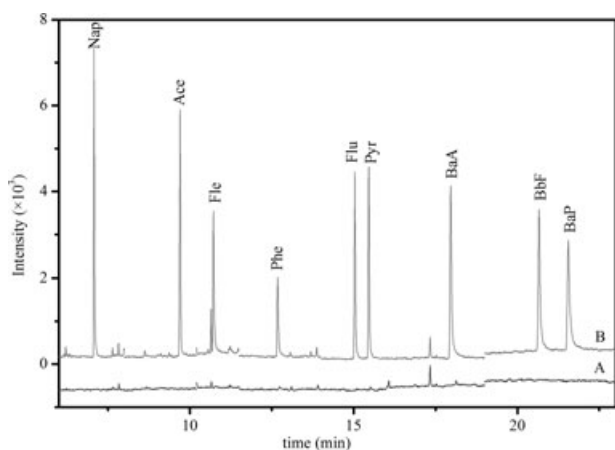
The reusability of the commercial SPE column is a drawback because of the plugging and pollution. However, the SPE disk possesses multichannel and thin sorbent layer, and it can reduce the risk of plugging and pollution. Furthermore, the microporous membranes added in the disks can further enhance the antipollution effect. In order to investigate the reusability of prepared disks, different river water samples spiked with the analytes were tested. The results showed that

Table 2. Parameters of the proposed method for quantitative analysis ( $n = 5$ )

Analyte	Linear range (ng/mL)	Regression equation	$R^2$	RSD (%)	LOD (ng/mL)	LOQ (ng/mL)
Nap	0.05–10	$y = 5065x + 447$	0.9928	10.9	0.00084	0.0028
Ace	0.05–10	$y = 3246x - 212$	0.9895	3.2	0.0046	0.015
Fle	0.05–10	$y = 3480x - 379$	0.9956	5.3	0.0016	0.0053
Phe	0.05–10	$y = 4572x - 820$	0.9930	5.8	0.0021	0.0069
Flu	0.05–10	$y = 12022x - 2645$	0.9906	2.8	0.0024	0.0079
Pyr	0.05–10	$y = 12078x - 2826$	0.9968	6.5	0.0015	0.0051
BaA	0.05–10	$y = 10271x - 3706$	0.9954	6.9	0.0065	0.022
BbF	0.05–10	$y = 9739x - 4048$	0.9780	3.7	0.010	0.033
BaP	0.05–10	$y = 10333x - 4610$	0.9899	5.1	0.013	0.042

**Table 3.** Comparison of different methods for PAHs extraction

Method	Detection	Sample volume (mL)	SPE time	LOD (ng/mL)	Ref.
Multiwalled carbon nanotubes-based SPE	GC-MS	500	115	2–8	[43]
Octadecyl functionalization of monodisperse magnetic ferrite microspheres-based magnetic SPE	GC-MS	50	–	800–36 000	[44]
Zn/Al layered double hydroxide based SPE	GC-MS	250	>50	1.2–3.2	[45]
Multiwalled carbon nanotubes-based flow injection SPE	GC-MS	50	>50	1–150	[46]
Molecularly imprinted SPE	GC-MS	30	–	5.2–12.6	[47]
Metal-organic framework MIL-53(Al)-based solid-phase microextraction	GC-MS/MS	10	35	0.10–0.73	[48]
Sulfur microparticles-based SPE	HPLC-UV	100	>100	7–48	[49]
Multiwalled carbon nanotubes-based SPE	HPLC-UV	500	>125	5–58	[50]
Metal-organic framework MIL-101-based magnetic SPE	HPLC-PDA	20	>25	2.8–27.2	[51]
Porous metal membranes-based SPE	HPLC-UV	1000	>60	30–82	[52]
Graphene-based SPE disk	GC-MS	1000	40	0.84–13	This work

**Figure 7.** The total ion chromatograms obtained from (A) unspiked river water sample and (B) the sample spiked with 2 ng/mL of each analyte.

the plugging was not presented and the recoveries had no significant variation for ten times. Therefore, the disk can be used at least ten times when treating real water samples.

### 3.3 Analytical figures of merit

The figures of merit for the developed SPE disk with graphene as sorbent for GC-MS determination of PAHs are summarized in Table 2. Under the optimized conditions, a series of quantitative parameters with regard to the linear range, correlation coefficient, LOD, LOQ, and reproducibility were examined. The calibration curves of each PAHs was constructed by plotting the peak areas ( $y$ ) of quantitative ions versus corresponding concentration of the analytes ( $x$ ). The LODs and LOQs were calculated as the concentration of the analytes at a  $S/N$  of 3 and 10, respectively. We can see that the LODs and LOQs for the PAHs ranged from 0.84 to 13 and 2.8 to 42 ng/L, respectively. The precision of the SPE-GC-MS method was assessed by five parallel extractions of

the analytes (0.5 ng/mL). The results showed that the RSDs were <10.9%, which demonstrated that good reproducibility can be achieved by the method.

The present method was compared with other previous extraction methods that were used for the determination of PAHs. The results are summarized in Table 3. The method developed in our current study gave the lower LODs, indicating the highly sensitive detection of PAHs. The SPE time was also compared to other methods with rapid detection. The analysis time by our method was less than most methods by SPE and it can be comparable with the microextraction, suggested a rapid method.

### 3.4 Analysis of environmental water samples

The optimized GC-MS method coupled a sample preparation with graphene-based SPE disk was applied for the analysis of several environmental water samples, including tap water and river water. Each sample (1000 mL) was filtered through microporous membranes, and then spiked with the PAHs at two different concentration levels and analyzed by the proposed method to estimate the influence of the matrix. Figure 7 presents typical total ion chromatograms obtained from unspiked river water samples and the samples spiked with the analytes. As listed in Table 4, the recoveries were in the range of 72.8–106.2% for tap water samples and 73.7–102.2% for river water samples. These satisfactory recoveries indicated no significant effects from the matrix composition of the environmental water samples.

## 4 Conclusions

In this work, a graphene-based SPE disk was manufactured first for the fast separation and preconcentration of trace polycyclic aromatic hydrocarbons from environmental water samples. The prepared disks exhibited high loading rate and anticlogging. The SPE time was shortened

**Table 4.** Recoveries of real water samples spiked with the target analytes ( $n = 3$ )

Analyte	Concentration added (ng/mL)	Tap water samples		River water samples	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Nap	0.2	96.3	3.9	100.8	9.4
	2	103.2	6.4	93.2	7.3
Ace	0.2	89.7	5.3	85.2	3.4
	2	85.3	5.7	94.0	3.7
Fle	0.2	98.5	7.3	96.2	5.6
	2	106.2	6.9	102.2	4.8
Phe	0.2	79.4	5.1	83.6	6.6
	2	92.2	4.7	96.7	5.8
Flu	0.2	86.6	5.3	93.7	4.2
	2	94.7	4.6	85.4	3.8
Pyr	0.2	101.4	7.6	73.7	7.6
	2	99.6	10.2	82.9	8.6
BaA	0.2	78.1	9.3	74.5	10.3
	2	80.5	10.5	85.2	5.6
BbF	0.2	92.5	6.3	90.3	7.5
	2	83.2	7.3	87.4	6.6
BaP	0.2	80.6	12.6	92.1	11.4
	2	72.8	8.4	79.8	5.7

significantly and the reusability was improved greatly. The strong adsorption property of graphene for PAHs makes the excellent performance in SPE. Under the optimized conditions, a rapid, sensitive, and cost-effective method for the determination of PAHs from environmental water was established by the coupling of graphene-based SPE disk with GC-MS. The obtained results showed that the LODs were much lower and the analysis time was shortened, which demonstrated that the graphene-based SPE disk has great potential for fast separation and preconcentration of trace pollutants in environmental water samples.

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