Evaluation of sulfonated graphene sheets as sorbent for micro-solid-phase extraction combined with gas chromatography–mass spectrometry

Hong Zhang, Wei Ping Low, Hian Kee Lee*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

ABSTRACT

This report describes the use of sulfonated graphene sheets as sorbent in micro-solid-phase extraction (μ-SPE), together with gas chromatography–mass spectrometry, for the determination of polycyclic aromatic hydrocarbons (PAHs) in water. In this study, for the first time, graphene sheets were used as a sorbent material for this mode of microextraction. The modified graphene sheets were characterized by transmission electron microscopy, Fourier transform infrared spectroscopy, and elemental analysis. μ-SPE parameters such as extraction time, desorption time and desorption solvent were optimized. The method showed good precision, reproducibility and linear response for PAH analysis over a concentration range of 0.05–100 μg/L for naphthalene and 0.01–100 μg/L for the remaining PAHs (acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) with coefficient of determination (r^2) of higher than 0.992. Limits of detection of from 0.8 to 3.9 ng/L for 7 PAHs were achieved. The developed method was successfully applied to determine PAHs in river water samples.

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1. Introduction

Microextraction techniques for aqueous samples have been developing rapidly over the past few years to overcome some of the limitations of classical techniques such as liquid–liquid extraction (LLE) and, to some extent, solid-phase extraction (SPE). LLE requires relatively large volumes of samples and solvents. SPE needs relatively less solvent but still generally involves multi-step extraction and clean-up procedures that are tedious and time consuming. The development of relatively simple and fast sampling techniques that require reduced amount of solvents is very important and allows convenient monitoring of trace levels of aqueous contaminants. An example of such a simple, fast and completely solvent-free sample preparation device is solid-phase microextraction (SPME), which was developed in the 1990s by Arthur and Pawliszyn [1]. It is an excellent alternative to the above mentioned classical methods that incorporates extraction, concentration and extract introduction to an analytical system into a single step. In the rapid development of SPME, various sorbents are now available commercially or are prepared in-house, to permit a reasonable range of sensitivity and selectivity, for various classes of analytes. Several other similar miniaturized sample enrichment procedures have been reported such as in-needle sampling by Saito et al. [2], and needle trap for air sampling by Gong et al. [3], Wang et al. [4] and Koziel et al. [5].

Another approach to achieve high extraction efficiency while reducing the amount of solvent needed is micro-solid-phase extraction (μ-SPE) [6]. Basheer et al. reported the use of μ-SPE comprising C18 [6–8] and carbon nanotubes (CNTs) [9] held within a polypropylene membrane envelope for extracting persistent organic pollutants and acidic drugs. Since the porous membrane afforded protection of the sorbent, no further cleanup of the extract was required, which simplified the extraction procedure, i.e. clean up and extraction involve a single step. Besides affording satisfactory analytical results, these μ-SPE devices have some other advantages over traditional SPE such as cost-effectiveness, shorter extraction time, and much reduced solvent consumption [6].

In recent years, a large number of allotropic carbon nanoparticles have been investigated as sorbents, including nanodiamonds [10], fullerene C60 [11], graphite fibers [12] and CNTs [13], etc., as well as their functionalized forms. Graphene, the first two-dimensional atomic crystal, which was first experimentally produced in 2004 [14], is a conceptually new class of carbon material. It consists of a monolayer of sp^2 hybridized carbon atoms packed into a dense honeycomb crystal structure. Graphene sheets can be prepared by various techniques including mechanical exfoliation (peeling off sheet by sheet) of graphite [14], and reduction of exfoliated graphite oxide [15]. Exfoliation of graphite oxide can be obtained by rapid thermal expansion [16] or by ultrasonic dispersion [17]. The functionalization of graphene has been considered to be important for improving their solubility and stability to avoid aggregation. Its unique planar nanostructure and a wide range of

unusual properties have promised potential applications in a large number of areas such as electronics, sensors, and energy storage [14,18]. As the basic structural element of CNTs, graphene has been reported to possess a theoretical high specific surface area (2630 m^2/g) [19,20], which may make them attractive as sorbents if stable dispersion of graphene sheets is feasible [21]. For example, graphene-based gas sensors were reported to be capable of detecting individual gas molecules [22]. Also, graphene-based composites have been successfully used to fabricate an electrochemical glucose biosensor [23]. In addition, recent reports on hydrogen storage by well-defined graphene sheets [24] are of great interest. Very recently, the extraction capacity of graphene in kinds of forms of extraction techniques [25–29] was investigated. For example, Chen et al. [25] evaluated graphene-based SPME fiber coating for the extraction of pyrethroid pesticides. Liu et al. [26] used graphene powder as novel SPE absorbent for the preconcentration of chlorophenols. We have recently demonstrated the use of graphene-based sol–gel coating as sorbent for plunger-in-needle SPME to determine polybrominated diphenyl ethers [27]. The extensive delocalized π-electron system of graphene can interact strongly with benzene rings [30].

In the present work, a procedure previously reported by Si and Samulski [31] was used to prepare functionalized graphene sheets, and for the first time, these materials were used as a μ-SPE sorbent. Although mechanical exfoliation of graphite can provide pristine graphene, the yield of the product is so limited that it is not suitable for large-scale application. The reduction of exfoliated graphite oxide is one approach to obtain (functionalized) graphene in bulk. During this process, the prevention of aggregation is of particular importance for processability and applications of graphene, because most of its attractive properties are only associated with individual graphene sheets. In Samulski's method, the reduction of exfoliated graphite oxide can realize bulk production; in addition, the introduction of a small number of *p*-phenyl-SO$_3$H groups can result in water-soluble graphene which did not aggregate [31], which is also the reason that we chose sulfonated graphene rather than graphene for direct use as a μ-SPE sorbent. Polycyclic aromatic hydrocarbons (PAHs) were used as test compounds to determine the feasibility of this novel microextraction approach. After optimization of the extraction conditions, the developed method was applied to river water in combination with gas chromatography–mass spectrometric (GC–MS) analysis.

2. Experimental

2.1. Chemicals and reagents

Analytical-grade sulfanilic acid, sodium nitrite, hydrochloric acid (37%) and HPLC-grade dichloromethane were purchased from Merck (Darmstadt, Germany). Sodium borohydride, hydrazine hydrate 100% (hydrazine, 64%) and sodium carbonate were obtained from ACROS Organics (Geel, Belgium). HPLC-grade methanol, toluene, hexane and acetonitrile were obtained from Fisher (Loughborough, UK). The PAHs (naphthalene (Nap), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt) and pyrene (Pyr)) were purchased from Supelco (Bellefonte, PA, USA). Ultrapure water was obtained from ELGA Purelab Option-Q (High Wycombe, UK).

Graphite (325 mesh) was obtained from Asbury Carbons (Asbury, NJ, USA). Accurel polypropylene sheet (0.2-μm pore size) was bought from Membrana (Wuppertal, Germany). Commercial sorbents C8 and C18 were purchased from Alltech (Deerfield, IL, USA) and Waters (Milford, MA, USA) respectively.

2.2. Synthesis of functionalized graphene sheets

The functionalized graphene sheets were prepared from natural graphite flakes using a chemical exfoliation method, which has been reported in detail by Si and Samulski [31]. The complete procedure is provided in Supplementary materials section. For analysis of the graphene material, the following instruments were utilized: Philips CM300 transmission electron microscopic (TEM) system (Amsterdam, The Netherlands), Varian 3100 Fourier transform infrared spectroscopic (FT-IR) system (Santa Clara, CA, USA), and an Elementar Vario Micro Cube elemental analysis (EA) system (Hanau, Germany).

2.3. Sample preparation

Stock PAH solutions (0.2 mg/mL each of analytes) were prepared in pure methanol and stored in the dark at 4 °C. Water samples were prepared by spiking ultrapure water with the analytes at known concentrations (generally 100 μg/L) to study extraction performance under different conditions.

Fresh genuine water samples were collected from the Singapore River and stored in aluminium foil-wrapped glass bottles in the dark at 4 °C. They were processed and analyzed directly or after being spiked with PAHs at a concentration of 5 μg/L. Samples were not filtered prior to processing.

2.4. Preparation of μ-SPE device

The μ-SPE device consists of sorbent materials enclosed within a polypropylene membrane sheet envelope (∼1.0 cm × 0.8 cm) as previously described [6,9]. Briefly, a membrane sheet was folded and 2 of its open edges were then heat-sealed, leaving one opening. Sorbent (1 mg) was introduced into the resulting membrane envelope via the remaining open end that was then heat-sealed to secure the contents. Each device was cleaned by ultrasonication in methanol for 10 min and stored in clean methanol until use. Before use, the device was conditioned by ultrasonication in dichloromethane for 1 min and then in ultrapure water for 2 min [9]. The μ-SPE envelope was then placed in a 20 mL water sample, whose container was sealed with a cap, and stirred at 1000 rpm at room temperature. After extraction (30 min), the μ-SPE device was removed, rinsed in ultrapure water, gently dabbed dry with lint-free tissue and transferred to a micro-vial containing 150 μL desorption solvent and sonicated in a ultrasonic water bath to desorb the analytes from the sorbent. This final extract was directly introduced (1 μL injection) into the GC–MS system for analysis.

2.5. GC–MS analysis

GC–MS analysis was carried out using a Shimadzu (Kyoto, Japan) QP2010 system equipped with a Shimadzu AOC-20i auto sampler and a DB-5 fused silica capillary column (30 m × 0.25 mm I.D., film thickness 0.25 μm) (Agilent Technologies, Santa Clara, CA, USA). Helium was used as carrier gas at a flow rate of 1.8 mL/min. The GC conditions were as follows: initial oven temperature 80 °C for 4 min, increased to 260 °C at the rate of 10 °C/min, then held at 260 °C for 3 min. The injector and interface temperature was set at 280 °C. All injections were in splitless mode. All standard and samples were analyzed in selective ion monitoring (SIM) mode at least in triplicate.
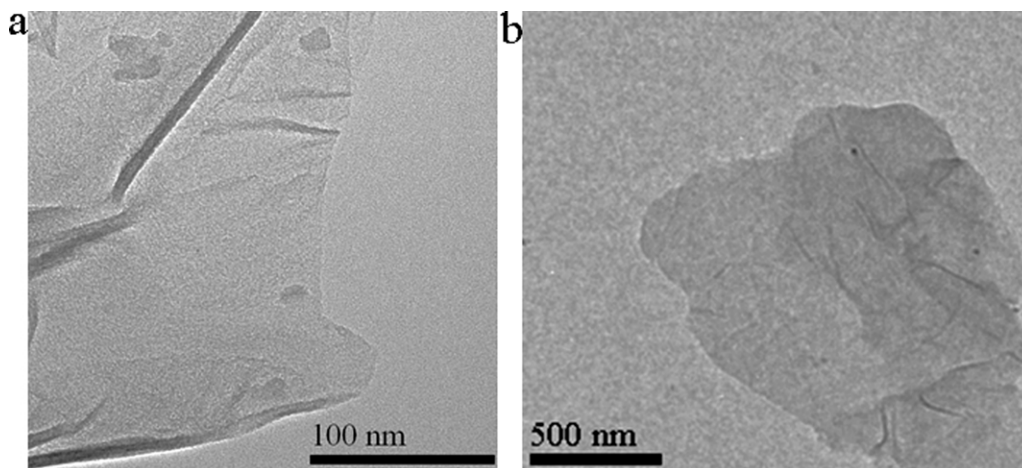
Fig. 1. TEM images of partially folded sulfonated graphene sheets. (a) G1 and (b) G2.

3. Results and discussion

3.1. Characteristics of functionalized graphene sheets

The morphology of the as-synthesized sulfonated graphene sheets was examined using TEM. The surface composition of the samples was investigated by FT-IR spectroscopy.

TEM images of a single graphene sheet for G1 and G2 are shown in Fig. 1(a and b, respectively). They appear transparent and are a little folded with isolated small fragments of graphene on their surfaces. The FT-IR spectra of the prepared materials are shown in Fig. 2. The spectrum of graphite oxide illustrates the presence of C–O (υ_{C-O} at 1055 cm^{-1}), C–O–C (υ_{C-O-C} at 1223 cm^{-1}), C–OH (υ_{C-OH} at 1369 cm^{-1}), and C=O in carboxylic acid and carbonyl moieties ($\upsilon_{C=O}$ at 1725 cm^{-1}) [31]. The peak at 1622 cm^{-1} could be due to skeletal vibrations of unoxidized graphitic domains [32]. After pre-reduction, sulfonation and the final reduction with hydrazine, the peaks at 1055 cm^{-1}, 1223 cm^{-1} and 1369 cm^{-1} are weakened in sulfonated graphene (G1 and G2). The small peaks at 1170 cm^{-1} and 1120 cm^{-1} (two υ_{S-O}) and 1034 cm^{-1} ($\upsilon_{S-phenyl}$) indicate the presence of a sulfonic acid group in G1 and G2 [31,33]. EA confirmed the presence of a small sulfur content in both G1 and G2, with S:C atomic ratios of 1:28 and 1:44 respectively. After post-reduction with hydrazine, a slight loss of sulfonic acid groups occurred in that there was a decrease of the S:C ratios from 1:23 to 1:28 and from 1:35 to 1:44 for G1 and G2 respectively, which is consistent with Si and Samulski's result [31]. These results indicate that graphite oxide was reduced and modified into sulfonated graphene with some oxygen and sulfur functionalities.

3.2. Comparison with C8 and C18

Two kinds of sulfonated graphene sheets named G1 and G2, differing in sulfur content, were compared with commercially available sorbents, C8 and C18. From Fig. 3, it can be clearly seen that for all analytes, the graphene sorbents show higher chromatographic signals among these sorbents.

The graphene sheets possess a planar hexagonal array of carbon atoms, thereby providing a larger surface and higher π–π electrostatic interactions with the benzene rings of the PAHs, in a similar way as the strong interactions between dioxin and the surface of carbon nanotubes [13]. Furthermore, the introduction of *p*-phenyl-SO$_3$H groups into graphene oxide before it is fully reduced to graphene, can improve the solubility of graphene in water and the presence of negatively charged – SO$_3^-$ group introduces electrostatic repulsion that prevents any aggregation [31]. From the EA results, the sulfur content in G1 was found to be higher than that in G2, which indicated a higher degree of sulfonation in G1. This could lead to increased surface area available for adsorption of PAHs, resulting in better extraction efficiency for G1 compared to G2 as indicated in Fig. 3. Based on the discussion above, G1 was chosen as sorbent in μ-SPE for further experiments.
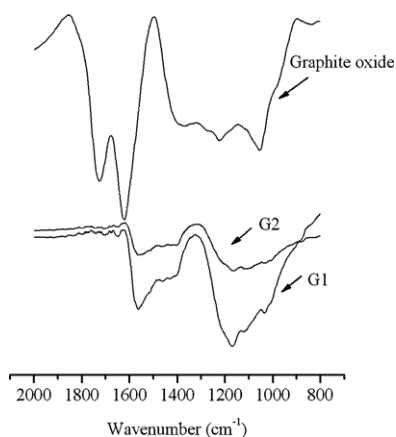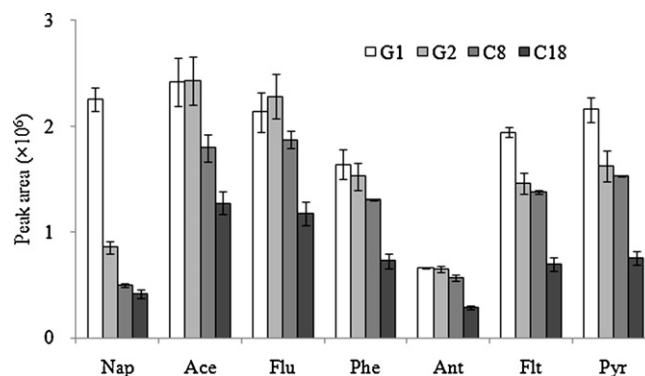

Fig. 2. FT-IR spectra of graphite oxide, G1 and G2.

Fig. 3. Comparison of the extraction efficiency of sulfonated graphene (G1 and G2) with commercial C8 and C18 for PAHs at 100 μg/L. Conditions: sample volume, 20 mL; extraction time, 30 min; desorption time, 10 min; desorption solvent, 150 μL toluene; magnetic stirring, 1000 rpm. Error bars show the standard deviation (n = 3).
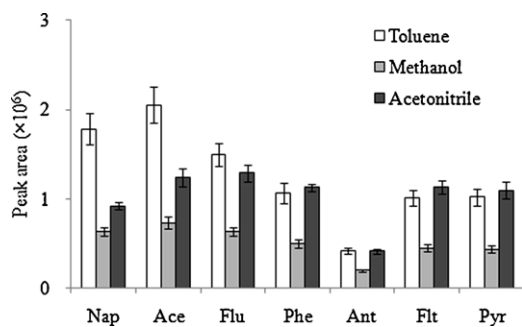
Fig. 4. Effect of desorption solvent on μ-SPE. Extraction conditions: 100 μg/L PAHs spiked solution; sample volume, 20 mL; extraction time, 30 min; desorption time, 10 min; magnetic stirring, 1000 rpm. Error bars show the standard deviation (*n* = 3).

3.3. Optimization of μ-SPE

The objective of the optimization procedure was to obtain maximum analyte recovery. The parameters investigated here were types of desorption solvent, extraction time, and desorption time. Optimization experiments were performed at least in triplicate.

3.3.1. Effect of the desorption solvent

Methanol, acetonitrile, hexane and toluene were investigated as desorption solvent for the PAHs after μ-SPE. μ-SPE was conducted on a 20 mL aqueous solution spiked at 100 μg/L of each analyte at a stirring speed of 1000 rpm. The results are shown in Fig. 4. Possibly, due to the high volatility of hexane (vapor pressure of 128 mm Hg, as compared to 23.2 mm Hg for toluene at 21 °C [34]), this solvent gave variable results (not shown). It may be observed from Fig. 4 that toluene gave better desorption results in terms of peak areas of analytes, though acetonitrile may also be considered (since it is more compatible with reversed-phase high-performance liquid chromatography (HPLC)). The strong interaction between the analytes and toluene may be attributed to the hydrophobic interactions between them. Generally, PAH hydrophobicity increases with an increase in number of fused benzene rings [35]. The hydrophobicity of the solvents may be compared in terms of the log *n*-octanol/water partition coefficient (log P_{ow}). Toluene has a log *P* value of 2.69, compared to that of −0.82 and −0.34 for methanol and acetonitrile, respectively [34]. Hence, toluene was conceivably able to solubilize hydrophobic PAHs better than methanol and acetonitrile for lighter PAHs (Nap to Flu with log *P* = 3.29–4.18 [36]). For heavier PAHs, acetonitrile was observed to be comparable to toluene in terms of desorption efficiency. This may be due to the π–π interaction between its lower unoccupied molecular orbital and the higher occupied molecular orbital of the PAH aromatic rings [37]. For heavier PAHs, with more fused benzene rings, the π–π interaction between PAHs and acetonitrile may be more favorable than the hydrophobic interaction between PAHs and toluene, leading to a slightly better desorption efficiency. Based on the above discussion, toluene was chosen as the desorption solvent due to better stability and desorption efficiency for the lighter PAHs.

3.3.2. Effect of the extraction time

μ-SPE, like SPME, is an equilibrium-based rather than exhaustive extraction procedure. The extraction time profile was studied from 10 to 60 min, as shown in Fig. 5. It can be seen that different compounds exhibited varying responses to different extraction times because, based on their molecular weights, they likely have different diffusion coefficients [38]. Most of the analytes achieved high extraction efficiency after 60 min except for Nap, which showed a drop in the peak area response. This could be due to the volatility of Nap, which has the lowest molecular weight among
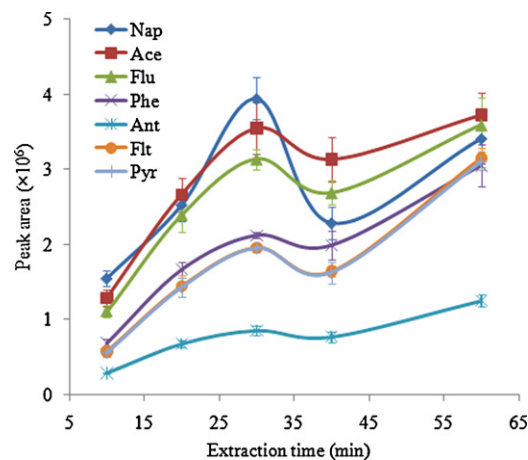

Fig. 5. Effect of extraction time on μ-SPE. Extraction conditions: 100 μg/L PAHs spiked solution; sample volume, 20 mL; desorption time, 10 min; desorption solvent, 150 μL toluene; magnetic stirring, 1000 rpm. Error bars show the standard deviation (*n* = 3).

the PAHs. All of the analytes showed a decrease in extraction efficiency when the extraction was performed for 40 min (compared to 30 min). The reduction in extraction efficiency may be contributed by the effect of back-extraction that arises due to prolonged period of extraction [39]. The reduction was observed to vary with different analytes according to the molecular weight. Lighter PAHs, such as Nap, Ace and Flu, were observed to show a greater reduction in extraction efficiency at 40 min while heavier PAHs, such as Phe, Ant, Flt and Pyr, displayed a smaller extent of reduced extraction efficiency. This may be reflective of the different solubility and volatility of the PAHs with different molecular weights.

Although 60 min gave the highest extraction efficiency for the analytes, for reasons of practicality, 30 min was selected as extraction time for subsequent experiments, since the difference between extraction at 30 min and 60 min was not significant.

3.3.3. Effect of the desorption time

A series of desorption times from 5 to 60 min was investigated. Fig. 6 depicts the relationship between chromatographic signal and desorption time. A 10-min desorption time appeared to be the optimum for all analytes. A longer period of desorption time did not yield any significant increase in the response, which became
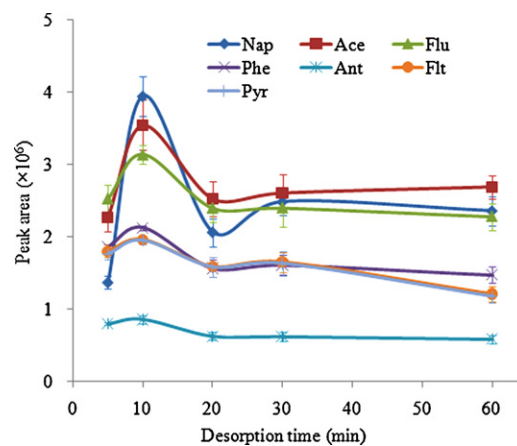

Fig. 6. Effect of desorption time on μ-SPE. Extraction conditions: 100 μg/L PAHs spiked solution; sample volume, 20 mL; extraction time, 30 min; desorption solvent, 150 μL toluene; magnetic stirring, 1000 rpm. Error bars show the standard deviation (*n* = 3).

Table 1
Regression data, LODs and LOQs of analytes.

Analyte	Linearity (μg/L)	Coefficient of determination (r^2)	Intra-day RSD[a] (%, $n = 5$)	Inter-day RSD[a] (%, $n = 3$)	LOD (ng/L)	LOQ (ng/L)
Nap	0.05–100	0.9958	1.0	2.9	3.9	12.9
Ace	0.01–100	0.9925	6.5	8.8	2.1	7.0
Flu	0.01–100	0.9931	6.6	10.5	2.7	8.8
Phe	0.01–100	0.9959	9.0	11.2	1.4	4.7
Ant	0.01–100	0.9964	2.6	6.6	2.6	8.7
Flt	0.01–100	0.9974	6.8	7.3	0.8	2.7
Pyr	0.01–100	0.9970	4.3	7.4	1.5	4.9

[a] Calculated from a sample spiked at a level of 5 μg/L.

Table 2
Analytical results for the determination of PAHs in river water samples.

Analyte	River water without spiking		River water spiked at 5 μg/L	
	Concentration (μg/L)	RSD (%, $n = 3$)	Relative recovery (%)	RSD (%, $n = 3$)
Nap	0.11	11.1	113.5	4.1
Ace	<LOQ[a]		112.1	4.7
Flu	<LOQ		106.5	3.0
Phe	<LOQ		91.3	9.5
Ant	<LOQ		96.3	1.2
Flt	<LOQ		81.6	5.7
Pyr	<LOQ		84.8	11.3

[a] Below the limit of quantification.

relatively constant after 30 min. Therefore, 10 min was chosen as desorption time.

Based on the above discussion, the most suitable extraction conditions were: 20 mL sample solution, 30 min extraction time, and desorption by toluene (150 μL) with sonication for 10 min. All the following experiments were carried out under these conditions.

3.4. Method evaluation

Linearity, repeatability, precision, limits of detection (LODs) and limits of quantitation (LOQs) were evaluated in order to assess the performance of μ-SPE with the graphene sorbent, as illustrated in Table 1. The calibration study was performed using spiked ultra-pure water samples. The coefficient of determination (r^2) values were higher than 0.992 in the concentration range of 0.05–100 μg/L for naphthalene and 0.01–100 μg/L for the remaining PAHs, so a directly proportional relationship between the extracted amount of compounds and the initial concentration in the sample was demonstrated. The precision of the procedure was evaluated at 5 μg/L spiked concentration level by calculating the percentage relative standard deviation (%RSD). The intra-day and inter-day RSD values were lower than 9.0% and 11.2%, respectively. LODs were calculated based on peak height and at a signal-to-noise (S/N) ratio of 3 by progressively decreasing the analyte concentration in the spiked sample, which were from 0.8 to 3.9 ng/L. LOQs were calculated at an S/N ratio of 10, ranging from 2.7 to 12.9 ng/L. These results were compared with previously reported values [40–43], in which PAHs were extracted by solid-phase nanoextraction (SPNE) [40] and SPE [41–43], with HPLC or GC–MS analysis, as summarized in Table 3. The present method gave comparable LODs with a relatively small amount of the graphene sorbent.

3.5. Genuine sample analysis

Natural water from the Singapore River was used as samples for evaluating the μ-SPE approach developed in this work. The results are shown in Table 2. The concentration of Nap was found to be 0.11 μg/L. Other PAHs were also detected, although not quantified. Their presence was further confirmed by spiking PAH standards

into a river water sample at concentration levels of 5 μg/L of each compound and reanalyzing it after μ-SPE (Fig. 7).

To evaluate the accuracy of the proposed method, the relative recovery test was performed by spiking PAH standards into river water at 5 μg/L levels of each compound. As shown in Table 2, the relative recoveries ranged from 81.6% to 113.5%. The RSDs for them were less than 11.3%, implying the established method is reliable for, and applicable to, real sample analysis.
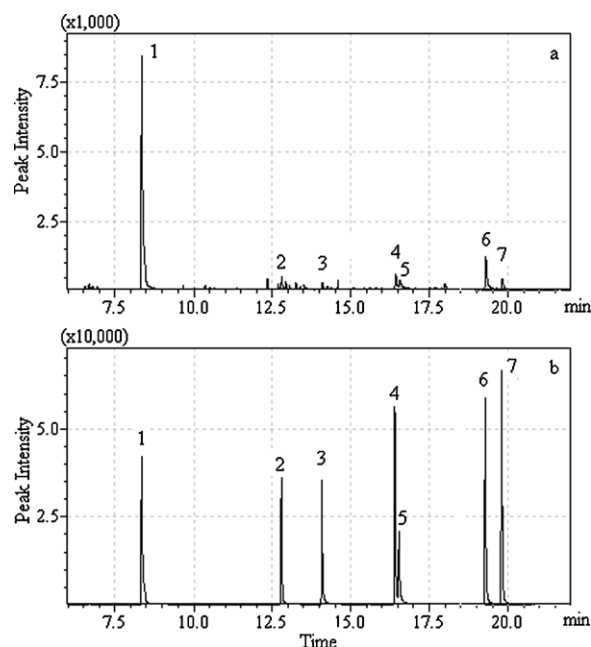

Fig. 7. GC–MS-SIM traces of river water extracts of (a) unspiked river water sample and (b) river water sample spiked with PAH standards at concentration levels of 5 μg/L of each compound. Conditions: sample volume, 20 mL; extraction time, 30 min; desorption time, 10 min; desorption solvent, 150 μL toluene; magnetic stirring, 1000 rpm. Peak identities: 1, Nap; 2, Ace; 3, Flu; 4, Phe; 5, Ant; 6, Flt; and 7, Pyr.

Table 3
Comparative data of the developed method with other solid-phase extraction approaches and HPLC or GC–MS analysis of PAHs in water samples.

Parameters	SPNE [40]	SPE [41]	SPE [42]	SPE [43]	Present study
Extraction sorbent	Gold nanoparticles	MWCNTs/C18[b]	C30	MWCNTs	Sulfonated graphene
Sorbent consumption (mg)	–	100/500[b]	500	150	1
Determination technique	HPLC-fluorescence	HPLC-UV	GC–MS	GC–MS	GC–MS
LODs (ng/L)	0.9–58	5–36/9–49[b]	7–210	2.0–3.5	0.8–3.9
Number of PAHs[a]	7	6	7	7	7

[a] Number of PAHs studied in each approach; only those studied in the present work were considered.
[b] C18 as a comparative sorbent.

4. Conclusions

In the current work, sulfonated graphene sheets (in powder form) were synthesized and preliminarily investigated as a novel sorbent for μ-SPE. Although small quantities (1 mg) of sorbent were used, this new material exhibited excellent extraction capability for 7 PAHs used as test compounds from water samples. Satisfactorily low LODs and good repeatability (RSD < 9.0%) could be obtained when μ-SPE was coupled with GC–MS. The enrichment by Graphene 1, with slightly higher sulfur content, was significantly higher than what was achieved by C8 and C18 sorbents under the most favorable extraction conditions. The results in this preliminary study indicate that sulfonated graphene sheets can be used as a μ-SPE sorbent for hydrophobic compounds such as PAHs in water. Therefore, we can expect that graphene-based materials would show high extraction ability toward other hydrophobic benzenoid-form compounds via strong π–π interaction if well dispersed graphene sheets are available. To increase the extraction performance of graphene, structural and compositional modifications are required to retain its intrinsic high surface area. Further development relating to this is being conducted in our laboratory.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.02.020.

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