



Determination of 16 polycyclic aromatic hydrocarbons in environmental water samples by solid-phase extraction using multi-walled carbon nanotubes as adsorbent coupled with gas chromatography–mass spectrometry

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ABSTRACT

A solid-phase extraction (SPE) using multi-walled carbon nanotubes (MWCNTs) as adsorbent coupled with gas chromatography–mass spectrometry (GC–MS) method was developed for the determination of 16 polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. Several condition parameters, such as extraction adsorbents, elution solvents and volumes, and sample loading flow rate and volume were optimized to obtain high SPE recoveries and extraction efficiency. 150 mg MWCNTs as sorbent presented high extraction efficiency of 16 PAHs due to the large specific surface area and high adsorption capacity of MWCNTs compared with the commercial C18 column (250 mg/2 mL). The calibration curves of 16 PAHs extracted were linear in the range of 20–5000 ng L⁻¹, with the correlation coefficients (*r*²) between 0.9848 and 0.9991. The method attained good precisions (relative standard deviation, RSD) from 1.2% to 12.1% for standard PAHs aqueous solutions; method recoveries ranged in 76.0–125.5%, 74.5–127.0%, and 70.0–122.0% for real spiked samples from river water, tap water and seawater, respectively. Limits of detection (LODs, *S*/*N*=3) of the method were determined from 2.0 to 8.5 ng L⁻¹. The optimized method was successfully applied to the determination of 16 PAHs in real environmental water samples.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) consisting of two or more fused aromatic rings, are ubiquitous in the aquatic environment. PAHs are mainly produced by incomplete combustion of organic matter; they are recalcitrant and have high carcinogenicity and mutagenicity, especially after they are concentrated by biological chain [1]. They could induce oxidative stress and oxidative DNA damage through the metabolic activation and the generation of reactive oxygen species [2]. Therefore, PAHs have aroused great attention to their influences on environment especially aquatic environment. The Environmental Protection Agency (EPA) has taken 16 PAHs as priority pollutants [3]. In China, 6 PAHs in surface water are forced to test according to the rule of State Environmental Protection Administration (SEPA) [4]. Due to their trace level concentration and wide distribution in complex water environment, it is required and vital to develop efficient precon-

centration procedures and high selective and sensitive separation and analysis techniques.

The most common analytical methods for PAHs in water were high performance liquid chromatography–fluorescence detection (HPLC–FLD) [5,6] or ultraviolet diode-array detection (HPLC–UV–DAD) [7,8]; gas chromatography–mass spectrometry (GC–MS) [9–11], GC [12], and HPLC coupled to electrospray ionization mass spectrometry (HPLC–ESI–MS) [13] have also often been applied to detect PAHs in water. In this study, GC–MS was employed because it could provide structural information in total ion current mode and high sensitivity for quantification in selected ion monitoring (SIM) mode. However, even so, because of the complexity of matrix in water, and the low content of PAHs, clean-up and enrichment procedures were required prior analysis. Current techniques for the extraction and concentration of PAHs from environmental water samples were liquid–liquid extraction (LLE) [14], stirring bar sorptive extraction (SBSE) [5,6,15], solid-phase microextraction (SPME) [11], hollow fibre liquid-phase microextraction (HF–LPME) [16] and so on. Solid-phase extraction (SPE), because of its advantages of high recovery, short extraction time, high enrichment factor, low consumption of organic solvents, and ease of automation and operation, was universally used for concentration of PAHs in water samples. In a SPE procedure, the choice of adsorbents was a very

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important factor for obtaining high enrichment efficiency. There are many materials used as SPE adsorbents for preconcentration of PAHs in water samples, including porous organoclay composite [17], matrix-immobilized organoclay [18], polyvinylidene fluoride [19], and bamboo charcoal [20]. But C18 is the most common adsorbent chosen for extracting PAHs in water samples [7,21–23]. Oleszczuk and Baran [24] applied C18 as the SPE sorbent to determine PAHs in sewage sludge extracts. However, the recoveries of high ring PAHs were not satisfactory in some cases and thus improvements were still needed.

Carbon nanotubes (CNTs) have attracted much interest that was directed toward exploiting their unique thermal, mechanical, electronic and chemical properties [25] since discovered. The multi-walled CNTs (MWCNTs) composed of several rolled-up graphite sheets [26] displayed large specific surface areas [27] and high adsorption capacity [28], which was primarily owe to their dramatically hydrophobic surface and unique structure with internal tube cavity [29]. Cai et al. [30] indicated that the hexagonal arrays of carbon atoms in graphene sheets of the surface of CNTs have strong interaction with the two benzene rings of dioxin, and therefore, it was easily concluded that MWCNTs also have the ability to adsorb PAHs containing two or more fused benzene rings (2–6). Many facts show that MWCNTs might have great analytical potentials as effective SPE adsorbent for some compounds. The MWCNTs as effective SPE adsorbent displayed very strong adsorption effects to bisphenol A, 4-n-nonylphenol, 4-tert-octylphenol [30], phthalate esters [31], and chlorophenols [21]. Wang et al. [8] applied MWCNTs as SPE adsorbent to extract and determine 10 PAHs in the environmental water samples, obtaining good repeatability and precision, however, the PAHs with more rings such as benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[*a,h*]anthracene and benzo[*ghi*]perylene were not taken into account. These 5–6 rings and highly non-polar PAHs have more carcinogenicity and mutagenicity than others. Because their polarity decreases with the increase of their molecular weight, these PAHs are not always easy to be adsorbed by common SPE materials.

In this study, a SPE procedure using the novel material of MWCNTs as sorbent was developed coupled with GC–MS for the determination of 16 PAHs including high rings PAHs. The properties of MWCNTs as a SPE sorbent was investigated; several key influence factors including flow rate of sample loading, elution solvents and volumes, and sample loading volume were studied in detail for excellent SPE efficiency. The method was demonstrated to be applicable for the analysis of 16 PAHs in real environmental water samples.

2. Experimental

2.1. Chemical reagents and materials

Sixteen PAHs standards dissolved in *n*-hexane were purchased from Supelco (Bellefonte, PA, USA), which were defined and nominated as priority pollutants by EPA, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Ph), anthracene (An), fluoranthene (Flt), pyrene (Py), benz[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (InPy), dibenz[*a,h*]anthracene (DiahA) and benzo[*ghi*]perylene (BghiP). The concentration of each compound in the mixture was 2000 mg L⁻¹. Stock solutions at the concentration of 10 mg L⁻¹ were prepared in *n*-hexane, and working solutions were prepared daily by appropriate dilution of the stock solutions with water before use. All solvents, including methanol, ethyl acetate, dichloromethane and *n*-hexane were of HPLC grade and purchased from Tianjin Kermel Chemical Co. (Tianjin, China). A model Synergy 185 ultrapure water system (Millipore, USA) was used to purify water. MWCNTs (60–100 nm i.d., 5–15 μm length, 40–300 m² g⁻¹) were obtained from Nanotech Part Co. (Shenzhen, China). Before use, MWCNTs were dried at 120 °C for 2 h. The C18 SPE extraction columns (250 mg × 2 mL⁻¹) were purchased from Supelco (St. Louis, MO, USA).

Tap water samples were collected from our laboratory. River water samples were collected from Qingdao Baisha River, and sea-water samples were collected from Coastal Seawater of Qingdao. Before use, all the water samples were filtered through 0.45 μm membrane (Tianjin Jinteng Experiment Equipment Ltd., Co., Tianjin, China) and stored in brown glass bottles at 4 °C prior to analysis.

2.2. Solid-phase extraction procedures

A MWNTs-packed cartridge was prepared by modifying Supelclean SPE LC-18 (250 mg × 2 mL⁻¹) cartridge. The C18 packing of the cartridge was evacuated, then MWCNTs (150 mg) were packed into the cartridge after a polypropylene frit was set at the cartridge bottom. In the front of the cartridge, another polypropylene frit was set to hold the height of MWCNTs at about 1.0 cm. Each MWCNTs SPE cartridge was used only once. Then the outlet tip of the cartridge was connected to Visiprep™ Solid-Phase Extraction Vacuum Manifolds (Supelco, USA), and the inlet end of cartridge was connected to PTFE suction tube of which other end was inserted

Table 1
Analytical performances of the developed method.

PAHs	Retention time (min)	<i>m/z</i> ^a	Regression equation ^b	<i>r</i> ²	Linear range (ng L ⁻¹)	LODs (ng L ⁻¹)
Nap	8.4	128	$y = 226.6x + 15.8$	0.9983	20–5000	2.1
Ace	12.1	152	$y = 251.5x - 3.5$	0.9985	20–5000	3.0
Acy	12.5	153	$y = 207.5x - 9.7$	0.9957	20–5000	2.3
Flu	13.7	166	$y = 157.9x - 8.6$	0.9981	20–5000	2.0
Ph	16.0	178	$y = 200.9x + 34.6$	0.9872	20–5000	3.4
An	16.2	178	$y = 230.0x + 31.7$	0.9859	20–5000	3.5
Flt	18.9	202	$y = 215.8x - 23.3$	0.9991	20–5000	3.2
Py	19.4	202	$y = 224.7x + 31.9$	0.9848	20–5000	3.0
BaA	23.3	228	$y = 208.6x - 65.0$	0.9955	20–5000	4.1
Chry	23.5	228	$y = 184.1x - 16.8$	0.9984	20–5000	3.2
BbF	28.0	252	$y = 162.1x - 54.1$	0.9957	20–5000	5.3
BkF	28.1	252	$y = 165.4x - 45.5$	0.9976	20–5000	5.0
BaP	29.5	252	$y = 169.9x - 71.1$	0.9972	20–5000	4.7
InPy	34.8	276	$y = 118.2x - 68.8$	0.9925	20–5000	8.5
DiahA	35.10	278	$y = 124.5x - 22.5$	0.9914	20–5000	5.1
BghiP	36.0	276	$y = 129.7x - 33.8$	0.9983	20–5000	4.6

^a Quantitation ion of each PAH for SIM.

^b x = Concentration (ng L⁻¹); y = area. Calibration results were obtained referring to the selective ions listed.

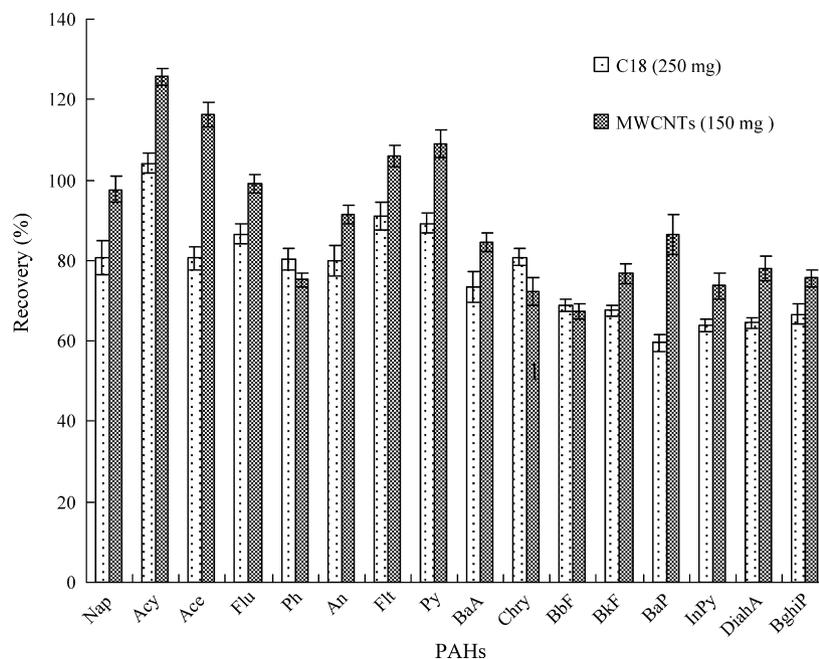


Fig. 1. Effects of sorbents on extraction recoveries of PAHs. Elution solvent: 15 mL *n*-hexane, 5.0 mL min⁻¹ flow rate of sample loading, and 0.2 μg L⁻¹ of 16 PAHs in 500 mL water samples.

into sample solution. Before loading samples, the cartridge was first conditioned with 10 mL *n*-hexane, then 10 mL methanol to remove air and leach impurity, and then with 10 mL ultrapure water to equilibrate the phase. Next, a 500 mL water sample was loaded at the flow rate of 5.0 mL min⁻¹. After loading, the cartridge was kept vacuum for 30 min to remove residual water. The objects retained on the cartridge were eluted with 15 mL *n*-hexane at the flow rate of 1 mL min⁻¹. The effluents were collected into a test tube and condensed to dryness under a gentle flow of nitrogen at room temperature and re-dissolved with 1 mL *n*-hexane. The resulting solution was then transferred to double layer silicone-Teflon sept vials for automatic sampling and GC–MS analysis.

2.3. GC–MS analysis

Analyses were performed by using a gas chromatograph of Thermo Finnigan Trace GC (Thermo Electron Co., Waltham, MA, USA) equipped with an AI/AS3000 autosampler, coupled to a mass spectrometer of Thermo Finnigan Automass quadrupole (Thermo Electron). A DB-5MS fused-silica column was used with 30 m × 0.25 mm i.d. and 0.25 μm film thickness (5% phenyl/methylsiloxane, J&W Scientific, Folsom, CA, USA). The temperature program for the chromatographic run, after optimization, was as follows: initial temperature 70 °C held for 2 min, increased to 240 °C at a rate of 10 °C min⁻¹, afterwards increased to

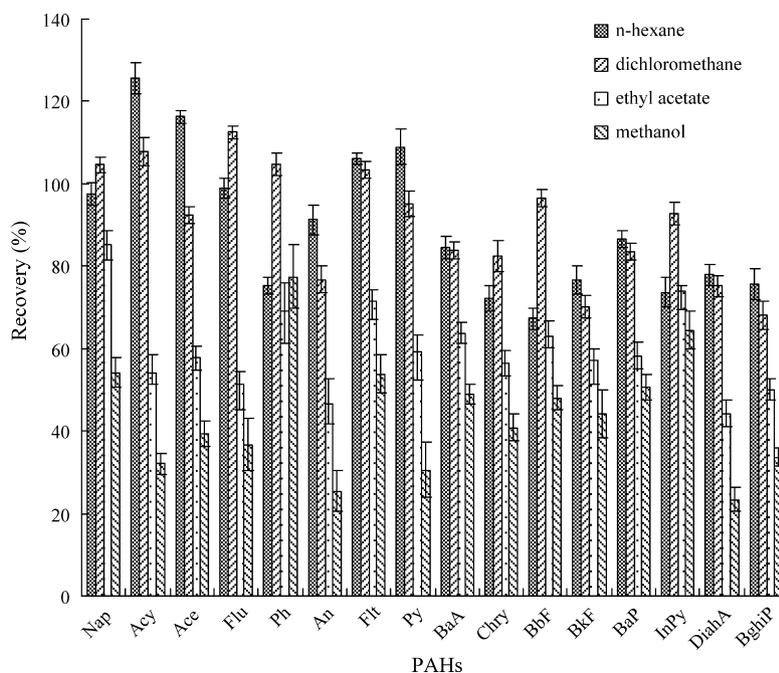


Fig. 2. Effects of different elution solvents on recoveries of PAHs using MWCNTs. Other extraction conditions were the same as those described in Fig. 1.

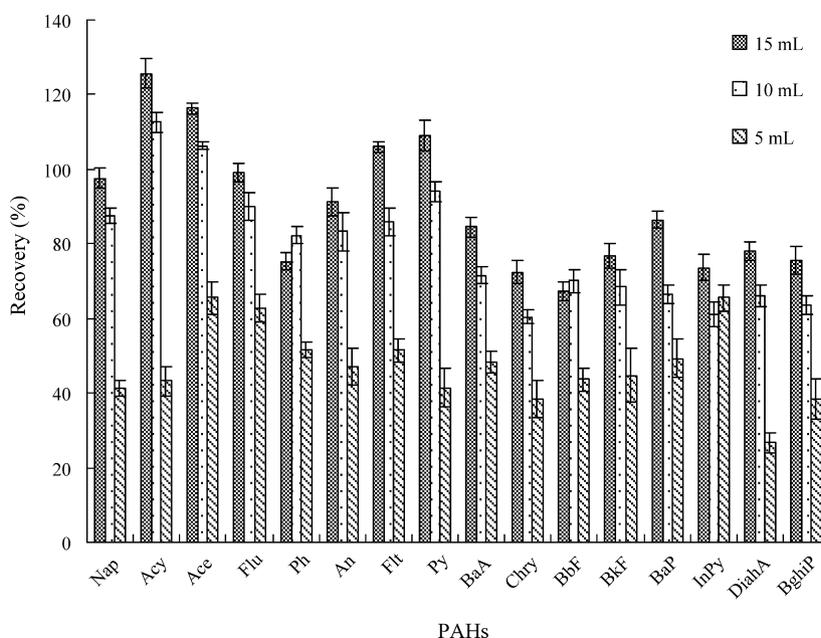


Fig. 3. Effects of *n*-hexane volumes on recoveries of 16 PAHs in 500 mL water samples extracted by MWCNTs. Other extraction conditions were the same as those described in Fig. 1.

290 °C at 3 °C min⁻¹, and eventually held for 5 min, and the solvent delayed for 4 min. Helium (99.999%) was used as carrier gas, at a flow rate of 1.0 mL min⁻¹. The injection with the volume of 1.0 μL was set on a splitless mode at 280 °C. The MS was operated in electron impact (EI) mode with an ion source temperature of 250 °C. The MS transfer-line temperature was 280 °C. A mass range of *m/z* 50–650 was recorded in the full-scan mode. Peak identification of objects was based on the retention times and full scan spectra of the standards. For better sensitivity, SIM mode was employed to quantify the analytes.

The retention time of each PAH and the quantitation ion were obtained under the optimized GC–MS conditions, shown in Table 1. Five standard solutions with different concentrations (20, 50, 100, 500, and 5000 ng L⁻¹ for individual PAH) were obtained by serial dilution with *n*-hexane from a stock solution (10 mg L⁻¹ of each

PAH). Limits of detection (LODs) were determined based on the signal-to-noise ratio of 3.

3. Results and discussion

3.1. Optimization of SPE procedure

Recovery is the best indicator of SPE method and the recoveries of PAHs in SPE process are mainly subjected to several factors such as the SPE adsorbent, the flow rate of sample loading, eluent and elution volume, and the sample solution volume. In this study, these five major factors were investigated using a spiked ultrapure water sample (0.2 μg L⁻¹), and all the optimization experiments were conducted three times.

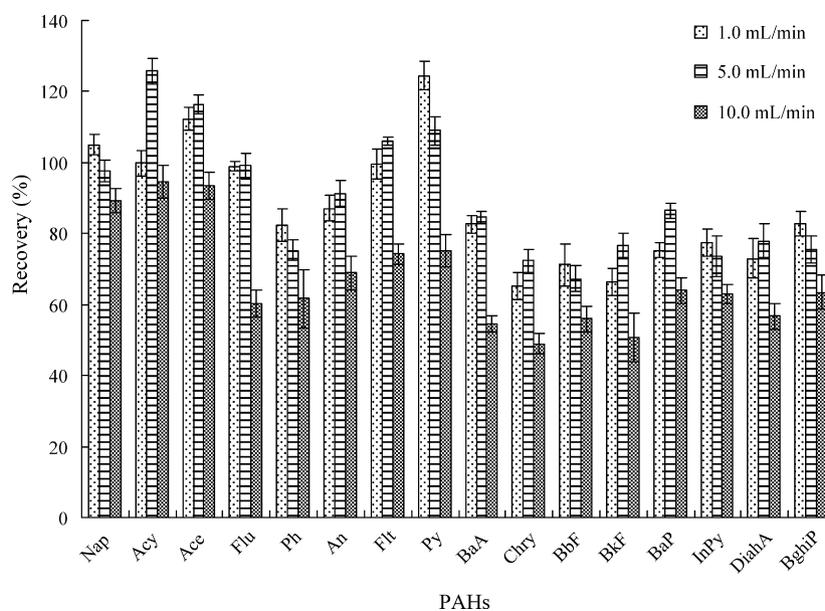


Fig. 4. Effects of flow rate of sample loading on recoveries of 16 PAHs in 500 mL water sample extracted by MWCNTs. Other extraction conditions were the same as those described in Fig. 1.

3.1.1. Comparison of different SPE adsorbents

Selection of suitable sorbents is crucial for SPE efficiency. 16 PAHs in water were extracted using C18 and MWCNTs as SPE sorbents, respectively. As can be seen from Fig. 1, the recoveries of low rings PAHs extracted by 150 mg MWCNTs were obviously higher than those by C18. MWCNTs effectively adsorbed the PAHs (4–6 rings) with recoveries of 75.3–125.7%. The relative standard deviation (RSD, $n=3$) ranged from 1.17% to 4.84%. For C18, the recoveries became lower about 10% than those of MWCNTs, especially low to 59.5%, which obviously could not work satisfactorily. So, higher extraction yields were obtained by 150 mg MWCNTs than those by C18. The reason may be as the following: C18 SPE material (octadecyl-bonded silica gel) is suitable to extract non-polar, weak polar and medium polar compounds in water samples by hydrophobic interaction. 16 PAHs were all non-polar compounds considering their $\lg K_{ow}$ values of 3.35–6.90. With the increase of ring numbers of PAHs, the hydrophobic interaction between PAHs and C18 was enhanced. So it was seen that PAHs with 4 or 5 rings were not easily desorbed from C18 adsorbent. Alternatively, MWCNTs were preferred as adsorbent, which composed of several rolled-up graphite sheets and hexagonal arrays of carbon atoms [28,32]. MWCNTs adsorbed PAHs by the coaction of delocalized pi bond interaction and physical adsorption [32]. The delocalized pi bond interaction between PAHs and MWCNTs is much stronger than the hydrophobic interaction between PAHs and C18. Because of the different functional structure and adsorption mechanism between C18 and MWCNTs, PAHs can be adsorbed more easily on MWCNTs than on C18. Therefore, 150 mg MWCNTs were selected as SPE sorbent in further studies.

3.1.2. Effect of the elution solvent and elution volume

The type and volume of elution solvent are vital for the extraction efficiency. So the choice of elution solvent and its optimum volume should be carefully taken into account. Fig. 2 shows the recoveries obtained from four different organic solvents including methanol, ethyl acetate, dichloromethane and *n*-hexane tested as elution solvents. The recoveries of PAHs eluted by *n*-hexane were in the range of 67.3–125.7% with RSD ($n=3$) ranging from 1.37% to 4.18%. For dichloromethane, the recoveries obtained were 68.1–112.5% with RSD ($n=3$) of 1.50–3.45%. For ethyl acetate and methanol as elution solvents, the recoveries were both much lower, only 44.1–85.1% with RSD of 1.56–6.9% and 23.4–77.4% with RSD of 2.40–7.74%, respectively. Among the four solvents, dichloromethane and *n*-hexane provided the comparable results

for PAHs, about 30–40% higher than those by using methanol or ethyl acetate. Considering the toxicity of dichloromethane, *n*-hexane was chosen as elution solvent. Moreover, the influence of volume of *n*-hexane was tested (Fig. 3). Finally, 15 mL *n*-hexane was adopted for eluting the PAHs for further work.

3.1.3. Effect of flow rate of sample loading

Flow rate of sample loading was also considered in the SPE procedure. Generally, sample loading time can be saved at a high flow rate while the possible analytes loss happens owing to an incomplete adsorption of PAHs by the sorbents; complete adsorption can be achieved at a low flow rate but it is time consuming. Therefore, a suitable flow rate for loading sample should be investigated to achieve high recovery and short loading time. As shown in Fig. 4, at the flow rate of 1.0 mL min^{-1} , the recoveries obtained for 16 PAHs were 65.2–124.5% with RSD of 1.25–5.99%. At 5.0 mL min^{-1} , the recoveries ranged from 67.3% to 125.7% with RSD of 1.73–5.66%. At 10.0 mL min^{-1} , the recovery for each PAH decreased compared to their corresponding values at 1.0 and 5.0 mL min^{-1} , even lower to 48.9%; meanwhile, the RSD increased even up to 8.29%. Considering that all the 16 PAHs could be efficiently adsorbed by 150 mg MWCNTs in acceptable time span, the sample loading flow rate of 5.0 mL min^{-1} was the optimal choice.

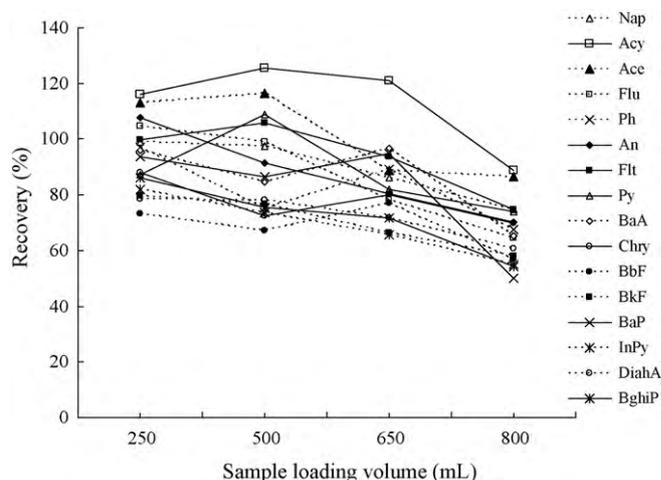


Fig. 5. Effects of sample loading volume on recoveries of 16 PAHs extracted by MWCNTs in 500 mL water sample. Other extraction conditions were the same as those described in Fig. 1.

Table 2
Method precisions and recoveries of PAHs.

PAHs	RSD ^a (%)	Add ($\mu\text{g L}^{-1}$)	Found ^b	Recovery (%)	Found ^c	Recovery (%)	Found ^d	Recovery (%)
Nap	10.2	0.2	0.161	80.5	0.172	86.0	0.185	92.5
Acy	12.1	0.2	0.178	89.0	0.190	95.0	0.179	89.5
Ace	9.2	0.2	0.189	94.5	0.190	95.0	0.217	108.5
Flu	2.6	0.2	0.203	101.5	0.166	83.0	0.163	81.5
Ph	6.8	0.2	0.197	98.5	0.231	115.5	0.140	70.0
An	6.5	0.2	0.149	74.5	0.177	88.5	0.107	83.5
Flt	2.7	0.2	0.210	105.0	0.175	87.5	0.185	92.5
Py	9.9	0.2	0.101	80.5	0.171	85.5	0.133	66.5
BaA	5.7	0.2	0.172	86.0	0.187	93.5	0.188	94.0
Chry	5.2	0.2	0.164	82.0	0.166	83.0	0.203	101.5
BbF	1.4	0.2	0.169	84.5	0.160	80.2	0.183	91.5
BkF	3.8	0.2	0.164	82.0	0.152	76.0	0.194	97.0
BaP	3.9	0.2	0.188	94.0	0.193	96.5	0.189	94.5
InPy	1.2	0.2	0.254	127.0	0.251	125.5	0.244	122.0
DiahA	7.4	0.2	0.175	87.5	0.169	84.5	0.171	85.5
BghiP	5.6	0.2	0.170	85.0	0.174	87.0	0.176	88.0

^a Spiked ultrapure water samples ($0.2 \mu\text{g L}^{-1}$), $n=5$.

^b Spiked tap water samples ($0.2 \mu\text{g L}^{-1}$), $n=3$.

^c Spiked river water samples ($0.2 \mu\text{g L}^{-1}$), $n=3$.

^d Spiked seawater samples ($0.2 \mu\text{g L}^{-1}$), $n=3$.

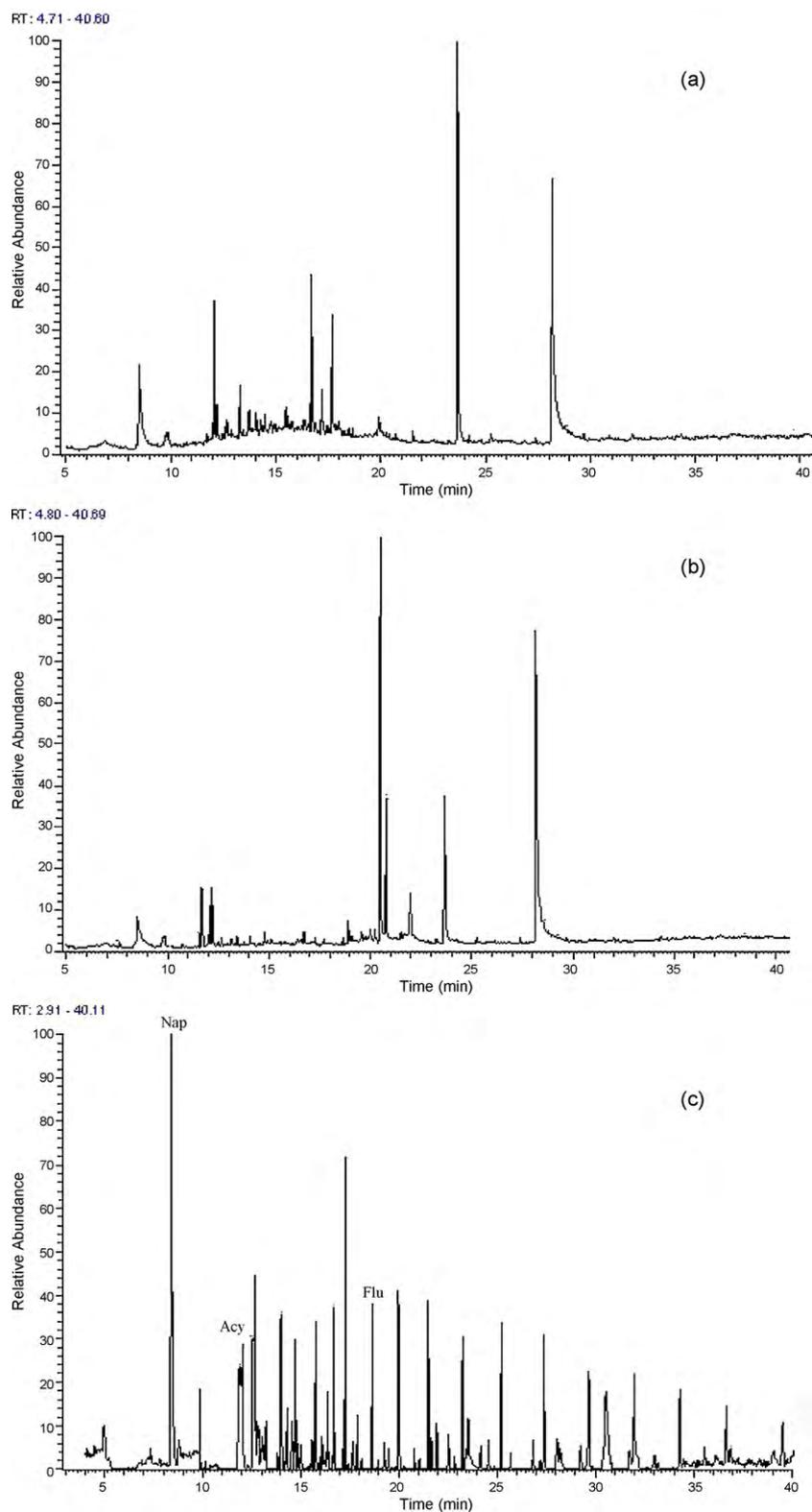


Fig. 6. GC–MS chromatograms under SIM mode of PAHs in (a) tap water, (b) sea water and (c) river water. Extraction conditions: sorbent, MWCNTs; elution solvent, *n*-hexane (15 mL); flow rate of sample loading, 5.0 mL min^{-1} ; sample loading volume, 500 mL.

3.1.4. Effect of sample loading volume

To obtain reliable analytical results and high concentration factors, it was very important to get satisfactory recoveries for all analytes in as large volume of sample solutions as possible. And therefore it was necessary to obtain the breakthrough volumes in the SPE process. Four different volumes (250, 500, 650 and 800 mL)

of water samples were investigated three times for the breakthrough volume; each one was spiked with 100 ng of individual PAH. The results of recoveries for 16 PAHs in water samples are presented in Fig. 5. It was believed that the breakthrough volume of 16 PAHs in water sample was more than 650 mL at least. So, the loaded sample volume of 500 mL was selected for further work. More-

Table 3
Method comparisons for analysis of PAHs.

	Ref. [6]	Ref. [11]	Ref. [23]	Ref. [9]	Ref. [8]	Present study
PAHs ^a	15	16	16	16	10	16
Pretreatment method	SBSE	SPME	C18-SPE	C30-SPE	MWCNTs	MWCNTs
Analytical method	HPLC-FLD	GC-MS	HPLC-UV	GC-MS	HPLC-UV	GC-MS
LODs (ng L ⁻¹)	0.2–1.5	1–29	0.07–3.0 ^b	7–210	5–58	2–8
RSD (%)	3.2–12.8	<20	5–14	1.4–9.2	1.7–4.8	1.2–12.1
Recoveries (%)	60.1–86.8	N/A ^c	63–101	61–116	78.7–118.1	75.8–125.3 ^d
Advantages	Low LODs	Solvent free	Universal	Effective for heavy PAHs	Good precision	Good repeatability, especially for heavy PAHs with low LODs
Disadvantages	Poor reproducibility	Poor precision, expensive SPME fibers	High LODs	High LODs	Not detected heavy PAHs, high LODs	High solvent consumption

^a The number of PAHs detected.

^b mg kg⁻¹.

^c Not available.

^d Recoveries of PAHs from river water.

over, the loading amounts, namely herein the dynamic adsorption capacities of MWCNTs, could be calculated for the 16 PAHs between 15.08 and 27.56 mg g⁻¹. It is rarely reported that pollutant sorption by CNTs in natural water systems where multiple organic contaminants are present [33]. Different adsorption capacities of the multiple PAHs are possibly attributed to their competitive sorption on a MWCNT material [33]. Also, it can be concluded that the dynamic adsorption capacities of MWCNTs were higher than those of common adsorbents such as C18 [34].

3.2. Analytical performance and application

Under the optimal conditions mentioned above, the analytical performance of the proposed method was assessed, by virtue of the precision (RSD) obtained by spiked standard solutions with 0.2 µg L⁻¹ individual PAH, and repeatability (recovery) obtained by spiked real water samples with 0.2 µg L⁻¹ individual PAH. The results of RSD were calculated by adopting five replicate runs and the recoveries of three real water samples were averaged from three replicate runs, shown in Table 2. The RSDs of PAHs were in the range of 1.2–12.1%. The recoveries of 16 PAHs ranged from 76.0% to 125.0% for river water samples, 74.5–127.0% for tap water samples, and 70.0–122.0% for seawater samples. In most cases, low recoveries were obtained particularly for heavy PAHs with more rings. It is because that with the increase of ring number of PAHs, the interaction between PAHs and MWCNTs increased. Therefore, PAHs adsorbed on MWCNTs were eluted more difficultly, resulting in lower recovery. On the other hand, some factors can lead to high recoveries even up to 127%, such as matrix effect, operation errors, method errors, and so on, but still acceptable.

To further evaluate the method applicability, three real water samples were also analyzed. As seen in Fig. 6, no PAHs were found in either the tap water (a) or sea water samples (b), while Nap, Acy and Flu were detected in the river water sample (c) at 159, 73 and 54 ng L⁻¹, respectively.

The method comparisons for the analysis of PAHs with others reported [6,11,23,9,8] are summarized in Table 3. It can be concluded that the coupling of novel sorbent of MWCNTs for SPE procedure with GC-MS detection exhibited excellent sensitivity, selectivity and repeatability, simplicity, rapidity, and ease of operation. Especially for the heavier PAHs containing more rings, the present method displayed more excellent and unique analytical merits for complex matrices.

4. Conclusions

A novel material of MWCNTs was developed as SPE sorbent to extract 16 PAHs from water samples, presenting robust extraction capacity for PAHs especially for more rings ones. The combination

of SPE with GC-MS enabled selective and sensitive analysis of PAHs at very low levels in complex water environment, and easy identification of the individual compounds. The method was demonstrated to be greatly applicable for the routine analysis of the PAHs in surface waters.

Acknowledgments

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