Analyst

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/analyst

Natural cotton fibers as adsorbent for solid-phase extraction of polycyclic aromatic hydrocarbons in water samples

Jianping Wang, Shengquan Liu, Chunyan Chen, Ying Zou, Huiping Hu,

Qingyun Cai*, Shouzhuo Yao*

State Key Laboratory of Chemo/Biosensing & Chemometrics, College of Chemistry & Chemical Engineering, Hunan University, Changsha 410082, China

E-mail: szyao@hnu.edu.cn; caigroup@126.com; Tel: +86-731-88821968

Abstract

A kind of natural material, cotton fiber, has been applied as solid-phase extraction (SPE) adsorbent for sample preparation in the analysis of polycyclic aromatic hydrocarbons (PAHs) in water samples coupling with high-performance liquid chromatography (HPLC). The cotton fiber was directly used without any chemical modifications, which avoided complex synthesis process and large volume organic solvent consuming. The conditions affecting the extraction efficiency have been optimized to achieve high detection sensitivity, including elution solvent, ultrasonic elution time, extraction time, sample volume, salt concentration and organic modifier addition. Under the optimal conditions, the detection limits for seven PAHs compounds could reach up to 0.1 - 2.0 ng/L, correspondingly. Furthermore, the method accuracy was evaluated by recovery measurements in standard spiked samples and good recoveries of 70.69 – 110.04% with relative standard deviations (RSDs) less than 10% have been achieved. Consequently, the developed method was successfully applied for analyzing PAHs in environmental samples: snow water, metal-fabrication factory wastewater and Xiangjiang River water, with PAHs contents ranging from 13.2 to 83.1 ng/L, correspondingly. Therefore, the cotton fiber as new SPE absorbent showed easy preparation, low cost and great reusability, implying its promising application for sample preparation.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are formed originally during the incomplete combustion of hydrocarbons and are commonly released into the environment during fossil fuel combustion, oil refinement, and industrial and municipal discharges.[1] PAHs are recalcitrant and have high carcinogenicity and mutagenicity, especially after they are concentrated by biological chain.[2] They could induce oxidative stress and oxidative DNA damage through the metabolic activation and the generation of reactive oxygen species, so they have become appreciable environmental concerns around the world.[3-5]

Various analytical methods have been developed and applied for monitoring PAHs in the natural environment, such as high performance liquid chromatography with fluorescence detection (HPLC-FLD)[6, 7] and gas chromatography-mass spectrometry (GC-MS)[8, 9]. However, considering complicated sample matrices and trace amount of analytes existed in environment, sample clean-up and preconcentration become necessary to improve detection sensitivity and selectivity, so as to adapt to analytical instruments.

In last decades, a variety of extraction methods have been developed for preparing environmental samples, including solid-phase micro-extraction (SPME),[10, 11] liquid-phase micro-extraction (LPME),[12, 13] dispersive liquid–liquid micro-extraction (DLLME),[14] microwave-assisted headspace solid-phase micro-extraction (MA-HS-SPME), [15, 16] and solid-phase extraction (SPE).[17, 18] SPE has advantages of high recovery, short extraction time, high enrichment factor, low consumption of

organic solvents, and ease of automation and operation. However, adsorbents with superior properties play key role in SPE for enhancing enrichment efficiency and analytical performance. Nowadays, multiple materials have been synthesized and utilized as SPE sorbents, including multi-walled carbon nanotubes (MWCNTs),[19, 20] graphene,[21, 22] magnetic nanoparticle,[23, 24] and metal-organic framework[25]. However, the synthesis process of such materials are rather complex and often consume large amounts of organic solvents and time. Therefore, new materials with simple preparation process are still highly desired.

Natural fiber is a very important material and widely used in many areas. For example, hemp fiber is applied to absorb heavy metal ions from aqueous solutions.[26] Choi et al. reported that cotton, milkweed, and kenaf have great sorption capacities for oil with sorption properties 1.5-3 times better than that of polypropylene fibers.[27, 28] As a kind of natural fiber, cotton fiber mainly consists of cellulose which is polysaccharide composed mainly of carbon, oxygen, and hydrogen (scheme 1). Jonker and Zhang have reported that cellulose exhibited an ability to adsorb PAHs from water with cellulose–water partition coefficients ranging from 3.80 to 5.64.[29, 30] Liu et al. used cotton as a sorbent for on-line precolumn to enrich PAHs from waters,[31] however, only four kinds of PAHs have been investigated with high detection limits and PAHs had not been detected in the real sample. Takagai et al. applied blue cotton , cotton modified with blue pigment copper(II) phthalocyanine trisulfonate, as sorbent to enrich PAHs.[32]

In the present work, natural cotton fiber was used as SPE adsorbent to enrich

PAHs from real water samples. The green material was easy to get, without preparation and chemical modification, and convenient for usage in PAHs adsorption and desorption with only by acetonitrile. Under optimal conditions, highly sensitive detection for seven PAHs was achieved, and to the best of our knowledge, it is the first time for such material to be successfully applied for real environmental samples analysis. Thereby, natural cotton fiber proves its promising application in sample enrichment and analysis.

2. Experimental

2.1. Chemicals and materials

The certified reference standards of fluorine (Flu), anthrance (Ant), fluoranthene (FlA), pyrene (Pyr), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF) and benzo[k]fluoranthene (BkF) were purchased from Acros Organics (NJ, USA). Stock solutions of these PAHs at the concentration of 100 μg/mL (Flu, Ant, Pyr), 1000 μg/mL (FlA, BaA) and 50 μg/mL (BbF, BkF) were prepared in methanol. To achieve a response at the same level in HPLC-FLD detection, the standard mixture of PAHs was composed of Flu (1.5 μg/mL), Ant (4 μg/mL), FlA (8 μg/mL), Pyr (4 μg/mL), BaA (1.5 μg/mL), BbF (1.5 μg/mL) and BkF (0.4 μg/mL) which were diluted from their stock solutions with methanol. n-Hexane and dichloromethane were purchased from Sinopharm Chemical Reagent (Shanghai, China), while HPLC grade methanol and acetonitrile were purchased from Merck (Darmstadt, Germany). The cotton fiber was purchased from Zhenxiang Labor Protection Product Company (Changsha, China).

Titanium wire was obtained from Lihua Non-ferrous Metals Co., Ltd (Baoji, China). Ultrapure water was prepared by MilliQ system (Bedford, USA). Working solutions were freshly prepared by diluting mixed standard solution with methanol to required concentrations. All standards and working solutions were stored at 4 ºC.

2.2. Instrumentation

HPLC analysis of PAHs was performed with a Shimadzu (Tokyo, Japan) LC-20AT liquid chromatograph equipped with a Shimadzu RF-10A XL fluorescence detector and a CTO-10AS VP column oven. A Diamonsil C_{18} column (250 mm × 4.6 mm, particle size 5 μm; Dikma Technologies, China) was used for separation. Ultrasonic wash and elution were operated by a B5500S-DTH ultrasonic machine (Branson, USA).

2.3. Water samples collection

The water samples selected for the investigation included river water sample collected from the Xiangjiang River (Changsha, China), snow water sample collected from Yuelu Mountain (Changsha, China) and factory waste water collected from a metal-fabrication factory (Changsha, China). Before experiments, all the water samples were filtered through 0.22 μm micropore membranes and stored at 4 ºC in refrigerator.

2.4. Preparation of cotton fibers

The cotton fibers were cut into 5 cm of each section (55 ± 2 mg，Φ：1.80 mm) by scissors and fixed at a titanium wire. To increase the contact area between the fiber and the sample to improve the enrichment efficiency, the cotton fibers were unraveled

until each cotton are separated as shown in scheme 1, and then ultrasonic washed by acetonitrile for about 10 min at room temperature.

2.5. SPE Procedure

The SPE procedure is schematically shown in scheme 1. Briefly, extraction process was performed in a 50 mL glass vial containing 50 mL of sample solution. A cotton fiber was directly immersed in the sample solution for 1 h under constant stirring at room temperature. After extraction, the extracted PAHs were ultrasonically eluted from the cotton fibers by 3×2 mL of acetonitrile. The eluate was collected and dried to about 200 μL under a gentle nitrogen stream, and then reconstituted to 500 μL by acetonitrile. Finally, 20 μL of this solution was injected directly into the HPLC system for analysis.

2.6. HPLC-FLD analysis

Determination of PAHs was carried out by a HPLC-FLD system. Chromatographic analysis was performed using a Diamonsil C_{18} column maintained at 30 ºC. The mobile phase consisted of water (solvent A) and acetonitrile (solvent B) and the flow rate was 1 mL min^{-1}. The gradient elution program was set as follows: maintained 75% B for 15 min; then increased B to 90% in 3 min, and kept from 18 min to 26 min; at last, decreased B to 75% at 27 min and kept for 5 min to equilibrate the column. The time program of fluorescence detection is given in Table S1.

3. Results and discussion

3.1. Optimization of SPE procedure

In order to achieve accurate and sensitive chromatographic quantification of trace PAHs in samples, the optimum conditions for SPE using cotton fibers were investigated. Several conditions affecting the extraction efficiency were optimized, including elution solvent, ultrasonic elution time, extraction time, sample volume, volume of organic modifier, and salt concentration. Optimization experiments were performed using standard aqueous solution of PAHs containing 0.75 μg/mL Flu, 2 μg/mL Ant, 4 μg/mL FlA, 2 μg/mL Pyr, 0.75 μg/mL BaA, 0.75 μg/mL BbF, and 0.2 μg/mL BkF to ensure relatively the same level of responses to each compound.

3.1.1. Optimization of desorption conditions

As far as SPE method is concerned, analyte desorption from adsorbent can significantly affect analyte extraction sensitivity. Thereby, proper elution solvent plays key role in the process. According to the properties of PAHs, methanol, dichloromethane, n-hexane and acetonitrile were selected as possible solvents in this experiment. As shown in Fig. 1, n-hexane has a poor eluting power toward the targets. Dichloromethane yields the highest recovery for BaA, while acetonitrile is preferable to Flu, Ant, FlA, Pyr, BbF and BkF. Therefore, acetonitrile was chosen as elution solvent and used for further studies.

Meanwhile, the elution efficiency also relies on the volume of elution solvent. As shown in Fig. S1, for most of PAHs, the recovery increased with eluent volume increasing from 2 to 6 mL, which remains nearly unchanged with volume further increasing from 6 to 8 mL. Considering the elution solvent consumption and time consuming, 6 mL (2 mL each for three times) of acetonitrile was selected for

desorption.

In order to resolve any possible carryover problem and avoid the loss of PAHs, the ultrasonic desorption time was further optimized. The process of desorption was carried out in an ultrasonic mode with desorption times of 1, 3, 5 and 10 min, respectively. The results shown in Fig. S2 prove that peak areas of PAHs increased with desorption time increasing from 1 to 5 min, while remain unchanged with desorption time elongation. Thus 5 min was sufficient to achieve maximum desorption. Mosier et al. reported that Trypan blue, a polyaromatic, planar molecule was irreversibly adsorbed to cotton cellulose at temperatures of <120ºC [33], probably induced by amino, sulfo and aromatic group of Trypan blue. Thereby, PAHs desorption from cotton fibers with only poly-aromatic groups, was rather easy to happen. That is why 5 min was enough for PAHs desorption, which was chosen as optimized desorption time.

3.1.2. Effect of salt concentration and organic modifier

Salt ion in sample might also affect SPE by the competitive interaction between the salting-out and the salting-in effect, a widely accepted mechanism. The salting-out effect induces analyte solubility decreasing in water and enhances its partition onto the fiber, while salting-in effect leads to an opposite result. Hence, the effect of the addition of salt to the samples was investigated. As shown in Fig. S3, no obvious change was observed for the recoveries with KCl at 0 – 200 mM, indicating salt ion addition does not affect extraction efficiency. Salt ion had been reported to enhance polar compounds recoveries.[34] Considering low polarity of seven PAHs, the reason

for above results was understandable. Thereby, no salt was added in the following experiments.

Meanwhile, organic modifier addition, such as methanol might also promote SPE extraction efficiency, by avoiding carbon chains from cross-linking and completely contact with target analytes[7]. Thereby, organic modifier volume was investigated. However, methanol of 0 to 3 mL addition results in no actual changes in extraction efficiency as shown in Fig. S4. It probably resulted from that cellulose with hydrophilic groups spreading out well in water. Therefore, no organic modifier is needed.

The above results indicated that the cotton fiber as sorbent was stable in various solutions, and the extraction efficiency was independent of the salinity and organic modifier.

3.1.3. Effect of sample volume

To obtain high concentration factors and satisfactory recoveries for all analytes, as well as reliable analytical results, sample initial volume as large as possible was recommended. Therefore, a series of aqueous solution volume (20 – 250 mL) were investigated. It was found the highest extraction efficiency was obtained with sample volume of 50 mL, as shown in Fig. 2. In contrast, only below 50% recoveries of PAHs was achieved with sample volume increasing up to 100 mL, inferring its insufficient extraction efficiency. Thereby, initial sample volume was set at 50 mL for further SPE process.

3.1.4. Optimization of extraction time

Furthermore, extraction time as another key factor was also investigated. Extraction time was set ranging from 15 to 90 min. As shown in Fig. 3, recoveries of all targets increased with extraction time altering from 15 to 60 min, and remain unchanged even when time up to 90 min, inferring extraction equilibrium achieved at about 60 min, which was selected for this work.

3.2. Regeneration and reusability

The durability of cotton fiber was also investigated by extracting PAHs from water sample for 30 times. The cotton fiber was regenerated ultrasonically in 10 mL acetonitrile for 10 min. The extraction efficiency was almost unchanged for the cotton fiber after 30 times extractions, and the results are shown in Fig. 4. The results indicate that the cotton fibers can be repeatedly used for extraction.

3.3. Method performance

Under the optimized extraction conditions, the performance of the proposed SPE method was evaluated using 50 mL ultrapure water samples spiked with different analytes concentrations. Quantitative parameters of the proposed method including linear range, correlation coefficients (R^2), limit of detections (LODs), and RSDs are listed in Table 1. The linear range from 0.025 to 30 mg/L with R^2 ranging from 0.9964 to 0.9999 for all target analytes were obtained. The LODs calculated on the basis of a signal/noise (S/N) ratio of 3 were 0.38 ng/L for Flu, BaA and BbF, 2.00 ng/L for Ant, 0.80 ng/L for FlA, 1.00 ng/L for Pyr, and 0.10 ng/L for BkF, respectively. According the Drinking Water Directive (98/83/EC) of the European Union and the Standards for Drinking Water Quality (GB 5749—2006) from China,

the total content of PAHs must under 100 ng/L in drink water. Thus, the method of this paper meets the requirement for real water analysis.

3. 4 Environmental water sample analysis

Subsequently, the method developed was applied for PAHs detection in environmental real water samples: river water，snow water and factory waste water. Quintuplicate analyses were performed and the recoveries, concentrations found for the target compound and RSD are summarized in Table 2. Among the three kinds of environmental samples, PAHs were not detected in snow water; Only Flu was detected in the metal-fabrication factory waste water with a concentration of 22.6 ng/L. Then seven river water samples were analyzed, collected from different spots in Xiangjiang River with detail spots shown in Fig. 5. In (A) point at the outlet of wastewater, Flu, Pyr, BaA, BbF and BkF were detected at 31.9 ng/L, 50.3 ng/L, 83.1 ng/L, 79.4 ng/L, 21.3 ng/L, respectively (shown in Table 3); while in (F) point of a dock, BbF and BkF were also detected at 41.5 ng/L, and 13.2 ng/L, respectively, suggesting PAHs mainly come from the wastewater. Method accuracy was evaluated by relative recovery of spiked real water samples at three concentration levels. Relative recoveries in range of 70.69 – 110.04% have been successfully achieved. These above results indicated that our established method could be successfully applied in PAHs analysis in real water samples. The typical chromatograms of the snow water, waste water, river water samples and standard spiked solution were presented in Fig. 6.

3.5 Comparison with other methods

The present method with the cotton fiber as absorbent was also compared with other materials reported in literatures (as shown in Table 4).[35-37] The time and organic solvent required in sorbent preparation and limits of detection (LOD) were contrasted. LODs achieved in present paper are lower or comparable with that of reported. Furthermore, cotton fiber as sorbent has obvious advantages: considering previous SPE sorbent synthesis requires several days and dozens or hundreds mL of organic solvent, resulted in time-consuming and environment pollution, cotton fiber without any modification needs only 10 min ultrasonic washing with several mL of acetonitrile. Therefore, cotton fiber is proven to be a green, convenient, efficient and reliable material for the pre-concentration of trace PAHs from environmental water samples.

4. Conclusion

In summary, we directly and successfully applied cotton fiber as SPE adsorbent for PAHs analysis in real environmental water samples. LODs of the developed method for seven PAH compounds was achieved at 0.1 – 2 ng/L, correspondingly. Compared to traditional SPE methods, the present sorbent is easy to prepare and simple to regenerate, which can meet the need for rapid analysis. In addition, cost in cotton fiber adsorbent preparation is much lower than reported methods, with much less organic solvent consumption; Furthermore, cotton fiber can be regeneration and re-usage for more than 30 times, considering its degradable, which is friendly to

environment. Thereby, the green and inexpensive material implied great potential for analyzing PAHs in environmental water samples.

Acknowledgments

This work was supported by the National Science Foundation of China (NSFC, Grants No. 21175038, 21235002) and the Foundation for Innovative Research Groups of NSFC (Grant No. 21221003).

References

1. M. L. Nahorniak and K. S. Booksh, *Analyst*, 2006, **131**, 1308-1315.
2. Y. Wan, X. Jin, J. Hu and F. Jin, *Environ. Sci. Technol.*, 2007, **41**, 3109-3114.
3. A. S. Gunasekara, M. J. Simpson and B. Xing, *Environ. Sci. Technol.*, 2003, **37**, 852-858.
4. H. Nakata, Y. Sakai, T. Miyawaki and A. Takemura, *Environ. Sci. Technol.*, 2003, **37**, 3513-3521.
5. M. T. O. Jonker, S. A. van der Heijden, J. P. Kreitinger and S. B. Hawthorne, *Environ. Sci. Technol.*, 2007, **41**, 7472-7478.
6. A. Ishizaki, K. Saito, N. Hanioka, S. Narimatsu and H. Kataoka, *J. Chromatogr. A* 2010, **1217**, 5555-5563.
7. D. Pan, C. Chen, F. Yang, Y. Long, Q. Cai and S. Yao, *Analyst*, 2011, **136**, 4774-4779.
8. M. R. Mannino and S. Orecchio, *Atmos. Environ.* , 2008, **42**, 1801-1817.
9. Y. Liu, Y. Hashi and J.-M. Lin, *Anal. Chim. Acta* 2007, **585**, 294-299.
10. A. N. Dias, V. Simão, J. Merib and E. Carasek, *Anal. Chim. Acta* 2013, **772**, 33-39.
11. H. Bagheri, E. Babanezhad and A. Es-haghi, *J. Chromatogr. A* 2007, **1152**, 168-174.
12. N. Ratola, A. Alves, N. Kalogerakis and E. Psillakis, *Anal. Chim. Acta* 2008, **618**, 70-78.
13. A. Sarafraz-Yazdi and A. Amiri, *TrAC, Trends Anal. Chem.* , 2010, **29**, 1-14.
14. V. Ghasemzadeh-Mohammadi, A. Mohammadi, M. Hashemi, R. Khaksar and P. Haratian, *J. Chromatogr. A* 2012, **1237**, 30-36.
15. M.-C. Wei and J.-F. Jen, *Talanta*, 2007, **72**, 1269-1274.
16. H.-P. Li, C.-H. Lin and J.-F. Jen, *Talanta*, 2009, **79**, 466-471.
17. P. W. Crozier, J. B. Plomley and L. Matchuk, *Analyst*, 2001, **126**, 1974-1979.
18. S. Zhang, H. Niu, Z. Hu, Y. Cai and Y. Shi, *J. Chromatogr. A* 2010, **1217**, 4757-4764.
19. J. Ma, R. Xiao, J. Li, J. Yu, Y. Zhang and L. Chen, *J. Chromatogr. A* 2010, **1217**, 5462-5469.
20. Q. Zhou, J. Xiao and W. Wang, *J. Chromatogr. A* 2006, **1125**, 152-158.
21. Q. Liu, J. Shi, L. Zeng, T. Wang, Y. Cai and G. Jiang, *J. Chromatogr. A* 2011, **1218**, 197-204.

22. Q. Liu, J. Shi, J. Sun, T. Wang, L. Zeng and G. Jiang, *Angew. Chem. Int. Ed.* , 2011, **50**, 5913-5917.
23. H. Heidari, H. Razmi and A. Jouyban, *J. Chromatogr. A* 2012, **1245**, 1-7.
24. J. Ding, Q. Gao, D. Luo, Z.-G. Shi and Y.-Q. Feng, *J. Chromatogr. A* 2010, **1217**, 7351-7358.
25. S. Yang, C. Chen, Z. Yan, Q. Cai and S. Yao, *J. Sep. Sci.* , 2013, **36**, 1283-1290.
26. B. Pejic, M. Vukcevic, M. Kostic and P. Skundric, *J. Hazard. Mater.* , 2009, **164**, 146-153.
27. H.-M. Choi, H.-J. Kwon and J. P. Moreau, *Text. Res. J.* , 1993, **63**, 211-218.
28. H. M. Choi and R. M. Cloud, *Environ. Sci. Technol.*, 1992, **26**, 772-776.
29. M. T. O. Jonker, *Chemosphere*, 2008, **70**, 778-782.
30. M. Zhang and L. Zhu, *Environ. Sci. Technol.*, 2009, **43**, 2740-2745.
31. J.-f. Liu, Y.-g. Chi, G.-b. Jiang, C. Tai and J.-t. Hu, *Microchem. J.* , 2004, **77**, 19-22.
32. Y. Takagai, R. Akiyama and S. Igarashi, *Anal. Bioanal.Chem.* , 2006, **385**, 888-894.
33. N. S. Mosier, J. J. Wilker and M. R. Ladisch, *Biotechnol. Bioeng.* , 2004, **86**, 756-764.
34. X. Jiang, C. Basheer, J. Zhang and H. K. Lee, *J. Chromatogr. A* 2005, **1087**, 289-294.
35. X. Song, J. Li, S. Xu, R. Ying, J. Ma, C. Liao, D. Liu, J. Yu and L. Chen, *Talanta*, 2012, **99**, 75-82.
36. Y. Long, Y. Chen, F. Yang, C. Chen, D. Pan, Q. Cai and S. Yao, *Analyst*, 2012, **137**, 2716-2722.
37. H. Zhang, W. P. Low and H. K. Lee, *J. Chromatogr. A* 2012, **1233**, 16-21.

Tables:

Table 1 Linear range, linearity curve, correlation coefficient and LOD for the determination of PAHs (n=3)

Table 2 Recoveries of PAHs in spiked water samples (n = 5)

Table 3 The detected PAHs concentration in real water samples (n = 5).

Table 4 Comparisons of analytical performances of the developed method with those in literature.

Scheme:

Scheme 1. Structural formula of cellulose and the SPE procedure.

Figure Legends:

Figure 1. Effect of different eluting solvent on SPE performance. Extraction conditions: sample volume, 50 mL; extraction time: 60 min; eluent volume, 2 mL; ultrasonic desorption time, 10 min.

Figure 2. Effect of sample volume. Extraction conditions: extraction time: 60 min; eluent solvent, acetonitrile; volume of elution solvent, 3×2 mL; ultrasonic desorption time, 5 min.

Figure 3. Effect of extraction time on SPE performance. Extraction conditions: sample volume, 50 mL; eluent solvent, acetonitrile; volume of elution solvent, 3×2 mL; ultrasonic desorption time, 5 min.

Figure 4. Regeneration and reusability. Extraction conditions: extraction time: 60 min; eluent solvent, acetonitrile; volume of elution solvent, 3×2 mL; ultrasonic desorption time, 5 min.

Figure 5. The seven water sample spots in Xiangjiang.

Figure 6. Chromatograms of PAHs in samples: (a) factory waste water spiked with 0.75μg/L Flu, 2 μg/L Ant, 4 μg/L FlA, 2 μg/L Pyr, 0.75 μg/L BaA, 0.75 μg/L BbF and 0.2 μg/L BkF. Peaks: (1) Flu; (2) Ant; (3) FlA; (4) Pyr; (5) BaA; (6) BbF; (7) BkF; (b) Xiangjiang River water; (c) factory waste water; (d) snow water.

Table 1 Linear range, linearity curve, correlation coefficients, LODs and RSDs for the determination of PAHs (n=3)

Analyte	Linear range (μg/L)	Linearity curve※	R^2	LOD (ng/L)	RSD (%)
Flu	0.015-3.8	$Y=8.01\times10^5X+1.78\times10^5$	0.9998	0.38	7.41
Ant	0.040-10	$Y=6.98\times10^5X+9.66\times10^4$	0.9998	2.00	6.08
FlA	0.080-20	$Y=4.02\times10^5X+1.05\times10^5$	0.9997	0.80	5.64
Pyr	0.040-10	$Y=8.37\times10^5X+9.23\times10^4$	0.9998	1.00	4.73
BaA	0.015-3.8	$Y=1.95\times10^6X+2.31\times10^4$	0.9997	0.38	8.09
BbF	0.015-3.8	$Y=2.03\times10^6X+5.08\times10^4$	0.9969	0.38	6.47
BkF	0.040-1.0	$Y=8.65\times10^6X+4.31\times10^4$	0.9968	0.10	6.68

※： X is compound concentration (mg/L) and Y is peak area.

Table 2 Recoveries of PAHs in spiked water samples (n = 5)

Analyte	Spiked (μg/L)	River water		Snow water		Factory waste water	
		Recoveries (%)	RSD (%)	Recoveries (%)	RSD (%)	Recoveries (%)	RSD (%)
Flu	0.06	94.59	3.34	86.02	4.85	94.11	8.00
	0.15	75.74	4.80	77.95	5.36	75.87	3.12
	0.75	109.85	6.55	110.04	4.90	91.47	1.44
Ant	0.16	81.14	5.09	83,20	5.77	70.69	4.81
	0.4	91.69	7.05	82.97	8.72	91.59	8.10
	2	102.39	7.93	101.19	5.40	91.11	2.66
FLA	0.32	76.50	8.30	81.38	7.56	86.93	5.75
	0.8	94.93	9.91	95.67	7.93	109.55	4.55
	4	97.59	7.07	98.72	8.28	92.85	2.36
Pyr	0.16	84.74	8.83	78.40	5.52	101.99	8.70
	0.4	85.47	8.35	92.67	6.80	105.42	7.60
	2	83.54	3.37	99.90	5.40	87.83	4.74
BaA	0.06	73.44	7.42	80.29	9.61	95.21	8.49
	0.15	95.87	5.50	83.25	5.57	99.31	4.61
	0.75	74.78	4.63	89.34	4.91	78.26	2.01
BbF	0.06	99.13	6.32	77.72	7.92	74.82	7.23
	0.15	83.52	5.85	72.19	7.82	76.56	3.69
	0.75	79.09	8.69	89.24	2.04	80.21	1.50
BkF	0.016	91.36	3.19	75.89	6.99	73.41	3.37
	0.04	88.82	4.36	74.65	8.38	80.57	4.07
	0.2	71.07	8.04	90.74	2.45	82.31	0.61

Table 3 The detected PAHs concentration in real water samples (n=3).

Sample	Flu (ng/L)	Ant (ng/L)	FLA (ng/L)	Pyr (ng/L)	BaA (ng/L)	BbF (ng/L)	BkF (ng/L)
(A)	31.9 ± 1.5	nd[a]	nd	50.3± 2.6	83.1 ± 8.0	79.4 ± 5.1	21.3 ± 1.1
(B)	nd	nd	nd	nd	nd	nd	nd
(C)	nd	nd	nd	nd	nd	nd	nd
(D)	nd	nd	nd	nd	nd	nd	nd
(E)	nd	nd	nd	nd	nd	nd	nd
(F)	nd	nd	nd	nd	nd	41.5 ± 2.3	13.2 ± 1.0
(G)	nd	nd	nd	nd	nd	nd	nd
(H)[b]	nd	nd	nd	nd	nd	nd	nd
(I)[c]	22.6 ± 1.0	nd	nd	nd	nd	nd	nd

(a): Not detected

(b): sample (H) was snow water sample collected in Yuelu Mountain

(c): sample (I) was waste water collected in a metal-fabrication factory

Table 4 Comparisons of analytical performances of the developed method with those in literature.

Method	Sorbent preparation cost (per time)			Number of analytes	LOD (ng L^{-1})	References
	Material	Time(h)[(a)]	Organic solvent(ml) [(b)]			
MIPs-SPE	imprinted sol–gel adsorbent	38	90	16	5.2–12.6	[35]
MSPE	TPA-functionalized MNPs	37．5	104	6	0.04-3.75	[36]
μ-SPE	functionalized graphene sheet	29.5	-	7	0.8 –3.9	[37]
SPE	Cotton fiber	0.5	-	7	0.1-2	Proposed method

(a) Experiment operation time was not counted.

(b) Wash solvent was not counted.

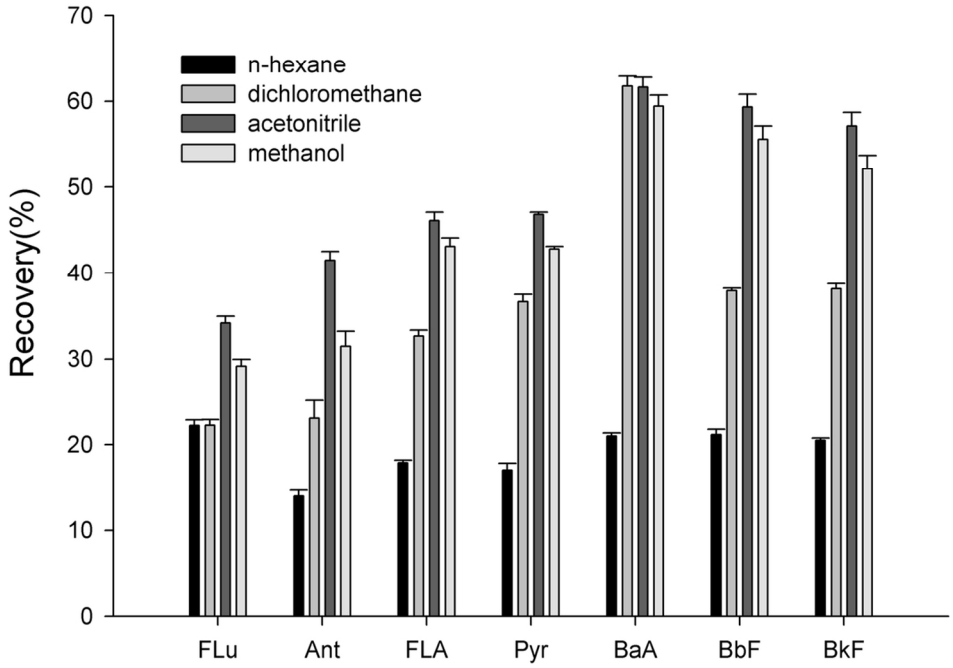


Figure 1. Effect of different eluting solvent on SPE performance. Extraction conditions: sample volume, 50 mL; extraction time: 60 min; eluent volume, 2 mL; ultrasonic desorption time, 10 min.
109x80mm (300 x 300 DPI)

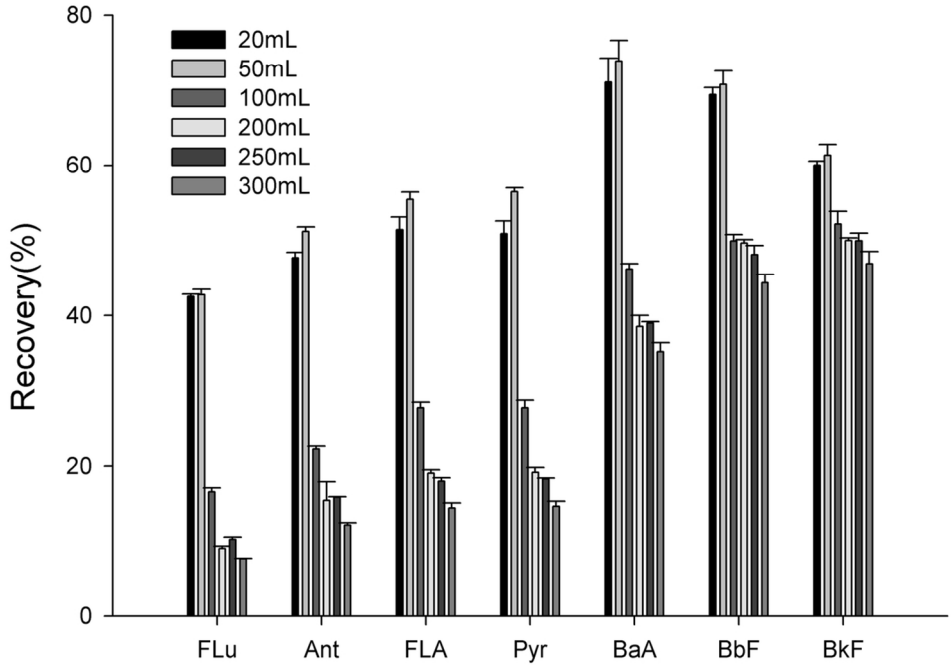


Figure 2. Effect of sample volume. Extraction conditions: extraction time: 60 min; eluent solvent, acetonitrile; volume of elution solvent, 3×2 mL; ultrasonic desorption time, 5 min.
109x80mm (300 x 300 DPI)

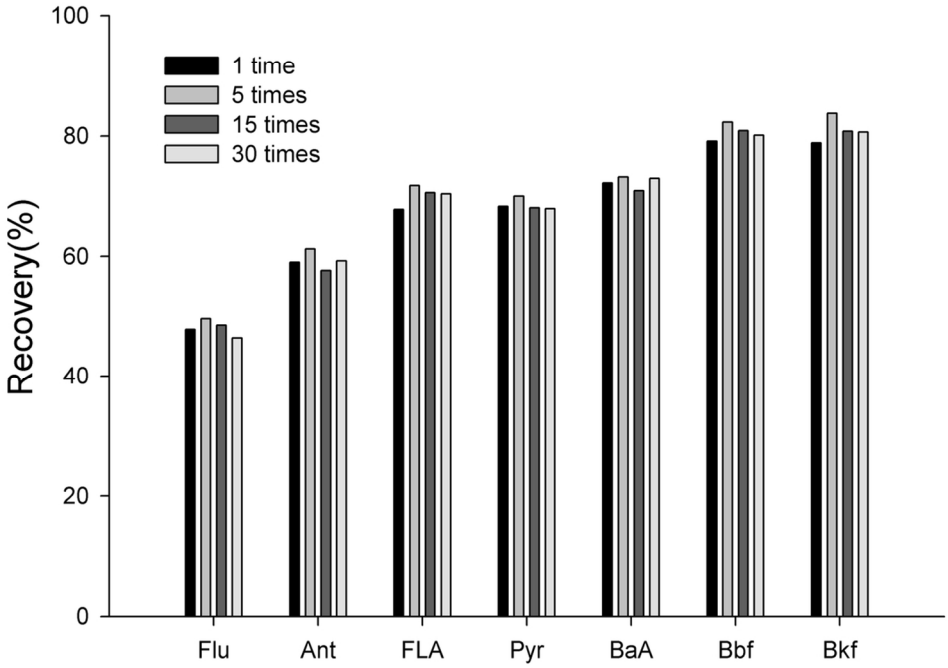


Figure 4.Regeneration and reusability. Extraction conditions: extraction time: 60 min; eluent solvent, acetonitrile; volume of elution solvent, 3×2 mL; ultrasonic desorption time, 5 min.
109x80mm (300 x 300 DPI)

Figure 5. The seven water sample spots in Xiangjiang.
39x30mm (300 x 300 DPI)

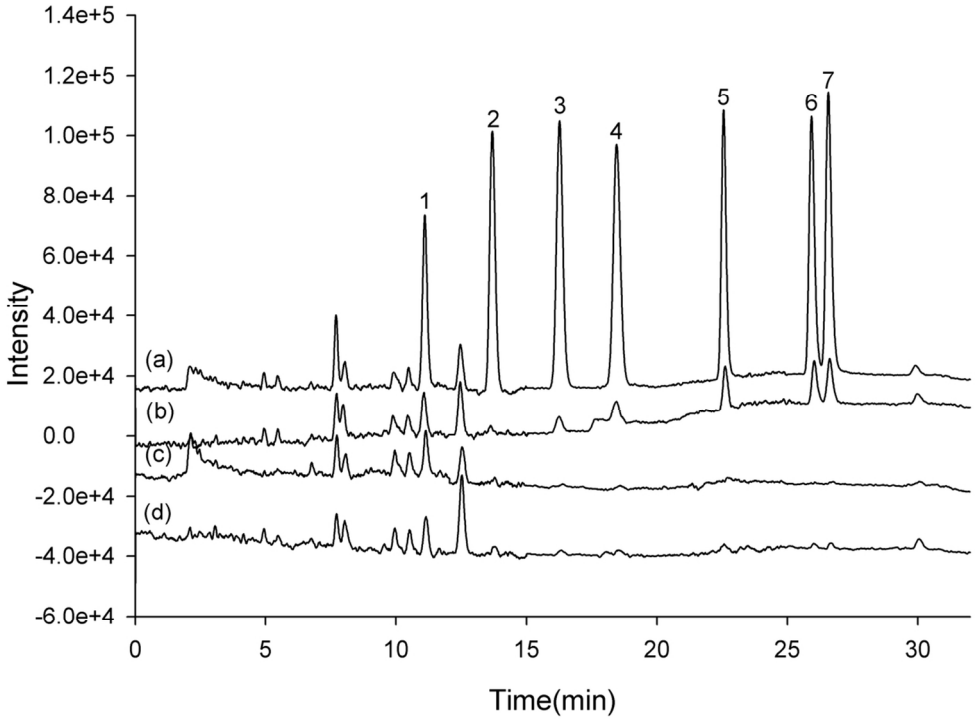
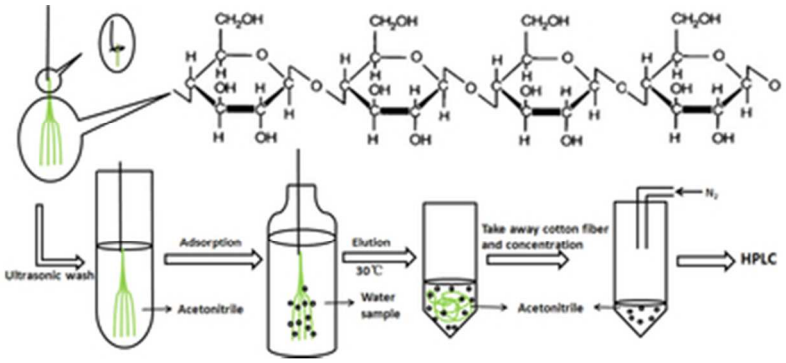


Figure 6.Chromatograms of PAHs in samples: (a) factory waste water spiked with 0.75μg/L Flu, 2 μg/L Ant, 4 μg/L FlA, 2 μg/L Pyr, 0.75 μg/L BaA, 0.75 μg/L BbF and 0.2 μg/L BkF. Peaks: (1) Flu; (2) Ant; (3) FlA; (4) Pyr; (5) BaA; (6) BbF; (7) BkF; (b) Xiangjiang River water; (c) factory waste water; (d) snow water.
109x80mm (300 x 300 DPI)



Scheme 1. Structural formula of cellulose and the SPE procedure.
34x14mm (300 x 300 DPI)