

Analytical Methods

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

**Determination of polycyclic aromatic hydrocarbons in water samples by hollow fiber extraction
coupled with GC-MS**

Jun-Fang Guo*, Qing-Zhong Guo, Guo-ping Yan

School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430073, China

*Corresponding author: Tel: +8615327199693; E-mail address: guojunfang2013@gmail.com

Analytical Methods Accepted Manuscript

Abstract

An octadecyl silica hollow fiber (OSHF) was prepared by a template method. The characteristics of the OSHF were evaluated by scanning electron microscopy, elemental analysis and pore size analyzer. It was an idea material for solid phase microextraction. The performance of it was thus studied by extracting polycyclic aromatic hydrocarbons (PAHs) in water samples. The results demonstrated that, under the optimal extraction condition, the linearities were 0.6-60, 1-60 and 2-60 ng/mL for different PAHs with all regression coefficients higher than 0.976. The limits of detection were in the range from 31.5 to 97.9 pg/mL for these analytes.

Keywords: Silica; Fiber; Extraction; SPME; PAHs

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1. Introduction

With the development of chemical industrial, many harmful substances have been exposed to environment, leading to serious threat to human being. Among these, polycyclic aromatic hydrocarbons (PAHs), one kind of persistent pollutants, have drawn much attention.^{1,2} The determination of them in environment is thus of great importance. Currently, instruments of gas chromatography (GC) and high performance liquid chromatography (HPLC) are the most commonly used techniques for their determination. However, since in the environment PAHs are generally present in trace level and accompanied by diversified matrices, they cannot be directly handled by instruments. Sample preparation, which aims to concentrate the analytes as well as eliminate or decrease the interference, is unavoidable.³

For a considerable time, liquid-liquid extraction (LLE) and solid phase extraction (SPE) are common sample preparation methods. Although these techniques are very useful in many applications, some drawbacks cannot be conquered, including time consuming, requiring large amounts of sample solutions, high cost of sorbent materials, etc.. The efforts in the past decades were devoted to developing suitable sample preparation methods, which may be simple, economical, time and chemical saving, etc.. Miniaturization can satisfy most of these purposes. Therefore, development of miniaturized sample preparation methods, e.g. solid phase microextraction (SPME),⁴⁻⁶ stir-bar sorptive extraction^{7,8} and liquid phase microextracion⁹⁻¹¹, has drawn much attention in recent years. Among these, SPME is very promising. Since its invention, SPME has gained tremendous progress and found broad applications in biological, environmental and pharmaceutical analyses¹²⁻¹⁴. Development of new SPME method in terms of novel sorbent phase and/or flexible operation mode is an interesting

task.

The conventional SPME was performed on the coating of the silica fiber, which had the disadvantage of low extraction capacity. To address the problem, some strategies were adopted. For examples, carbon monolith was prepared as an individual SPME extractant. Using phenols as the probe analytes, the carbon monolith exhibited higher extraction capacity than the commercial coated fiber¹⁵. In addition, sulfonated polyvinyl chloride fibers were proposed as cation-exchange microextraction extractant, which was demonstrated to be effective for the extraction of anaesthetics from urine sample¹⁶. Here, we reported a new SPME method based on a silica hollow fiber. The silica hollow fiber was prepared by a template method and derivatized with octadecyl to gain functional moieties. The hollow fiber had porous structure and high surface area, which was an ideal extraction media for SPME. Using PAHs as model analytes, the extraction conditions were optimized systematically and the extraction performance was evaluated.

2. Experimental Section

2.1. Chemicals

The polypropylene hollow fiber (PPHF) membrane (1000- μm in outer diameter, 200- μm in wall thickness and 0.2- μm pores in the walls) was purchased from Membrana (Wuppertal, Germany). Tetraethoxysilane (TEOS) was bought from WD Silicone Company (Wuhan, China). Acetic acid, cetyltrimethylammonium bromide (CTAB) and polyethyleneglycol (PEG, Mw = 10 000) were bought from Sinopharm Chemical Reagent Company (Shanghai, China). Methanol, toluene and acetonitrile of HPLC-grade were purchased from Fisher (Loughborough, UK). The PAH standards (naphthalene

1
2
3 99 (Nap), acenaphthylene (Acp), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene
4
5 100 (Ant), fluoranthene (Flt), pyrene (Pyr), chrysene (Cry), benzo[*a*]anthracene (BaA),
6
7
8 101 benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP),
9
10
11 102 indeno[*1,2,3-cd*]pyrene (InP), dibenzo[*a,h*]anthracene (DBA), benzo[*g,h,i*]perylene (BPe)) were
12
13
14 103 purchased from Supelco (Bellefonte, PA, USA).
15
16 104
17
18

19 105 **2.2 Synthesis of the octadecyl derivatized silica hollow fiber (OSHF)**

20
21 106 The PPHF was cut into small pieces (3.0 cm in length) and used as hard templates. They were
22
23
24 107 immersed into 10.0 mmol/L CTAB solution (in water) for 20 min to obtain CTAB-PPHF composite.
25
26
27 108 The silica sol was prepared by mixing TEOS (2.0 mL), PEG (1.0 g) and acetic acid (0.01mol/L, 5.0
28
29
30 109 mL) under water bath at 60°C for 60 min. Then the CTAB-PPHF was immersed into the sol for 20 min.
31
32 110 The silica sol infiltrated into the pores of the CTAB-PPHF. When the CATB-PPHF was taken out and
33
34
35 111 put into an oven at 40°C, the silica sol underwent sol-gel transition, forming silica ingredient
36
37
38 112 adsorbing onto the wall of the PPHF. The immersion and reaction process were repeated twice. Then
39
40 113 the composite was calcined in a muffle furnace under elevated temperature (1 °C /min from 25 to
41
42
43 114 600°C, kept at 600°C for 2 h). During the high temperature treatment, the organic part was removed,
44
45
46 115 leaving silica species. As the pores in the PPHF were continuous, the resultant silica also
47
48 116 demonstrated hollow fibrous structure.
49
50
51 117
52
53
54 118 Derivatization of the silica hollow fiber with octadecyl was achieved according to previous reports.
55
56 119 Briefly, the silica hollow fiber was first activated under refluxing with concentrated hydrochloric acid
57
58
59 120 (6 mol/L). Then it was washed to neutral and dried thoroughly at 160°C for 6 h. To the silica hollow
60

fiber (0.2 g), octadecyltrichlorosilane (0.1 g) and toluene (5.0 mL) were added. The mixture was heated at 110°C for 24 h. After being washed with copious toluene and methanol, octadecyl derivatized silica hollow fiber was obtained.

2.3 Characterization

The as-prepared OSHF was characterized by scanning electron microscopy (SEM), elemental analysis (EA) and nitrogen sorption measurement. SEM experiments were performed on a JSM-6701F SEM instrument (JEOL, Tokyo, Japan). Prior to observation, the OSHF was sputtered with gold film. EA was carried out on a Thermo Finnigan (CA, USA) 1112 instrument. Nitrogen sorption experiment was carried out on a Coulter (Florida, USA) SA 3100 Plus instrument. The OSHF was activated by evacuating in vacuum and heating to 120°C for 4 h before analysis. The surface area was calculated according to the BET (Brunauer-Emmett-Teller) equation at P/P_0 between 0.05-0.2. The pore volume and mean pore size were evaluated from the desorption branch of isotherm based on BJH (Barrett-Joyner-Halenda) model.

2.4. Sample preparation

PAH stock solutions (containing 5 µg/mL of every analyte) were prepared by diluting the standard analytes with methanol. Water samples were prepared with analytes at known concentrations to evaluate the extraction performance under different conditions. Real water samples were collected from a local lake.

2.5. Extraction procedures

1
2
3 143 The OSHF was glued onto a SPME holder by epoxy resin. Twenty hours later, the epoxy resin dried
4
5 144 and the fiber was firmly immobilized. For extraction, the OSHF was immersed in the sample solution
6
7
8 145 of 50 mL in a 60-mL vial at a fixed position. A stirring bar was in the vial and a magnetic stirrer was
9
10
11 146 used to agitate aqueous sample solution at different stirring rates. After extraction for a prescribed
12
13
14 147 time, the OSHF was taken out and immersed in acetonitrile (0.2 mL) for desorption of the analytes.
15
16 148 After desorption, 1 uL of the elution was injected into the gas chromatography - mass spectrometric
17
18
19 149 (GC-MS) instrument for analysis.
20
21
22 150
23

24 151 **2.6 GC-MS**

25
26
27 152 GC-MS analysis was carried out on a Shimadzu (Tokyo, Japan) QP2010 system. A RTX-5MS fused
28
29
30 153 silica capillary (30 m × 0.25 mm I.D., film thickness 0.25 µm) was used as the separation column
31
32 154 (J&W Scientific, Folsom, CA, USA). Helium was used as carrier gas at a flow rate of 1.7 mL/min. All
33
34
35 155 injections were in splitless mode and in selective ion monitoring (SIM) mode. The masses monitored
36
37
38 156 by the detector were set as follows: 6-8 min, m/z 128, 129, 127, 102; 8-9.5 min, m/z 152, 153, 151, 154;
39
40 157 9.5-10.8 min, m/z 166, 165, 167, 139; 10.8-13 min, m/z 178, 176, 179, 152; 13-16 min, m/z 202, 203,
41
42
43 158 200, 101; 16-20 min, m/z 228, 226, 229, 227, 252; 20-23 min, m/z 253, 252, 250, 126; 23-28 min, m/z
44
45 159 276, 278, 277, 138.
46
47
48 160
49
50

51 161 The injector temperature was 260 °C. The GC oven was firstly kept at 70°C for 2 min and then ramped
52
53
54 162 to 190°C at 15 °C/min. After being kept for 1 min, the temperature was increased to 260°C at
55
56 163 10 °C/min. Then it increased to 285 °C at 5 °C/min and held at that temperature for 5 min.
57
58
59 164
60

3. Results and discussion

3.1 Characterization of OSHF

As a porous polymer, PPHF was an ideal template for synthesis of inorganic hollow fibers. However, most of the inorganic precursors were aqueous solution, which was difficult to adsorb onto the hydrophobic PPHF. Here, amphoteric CTAB, which possesses both hydrophobic and hydrophilic moieties, was used to modify the PPHF first. When the PPHF was immersed in the CTAB/water solution, the CTAB self-assembled onto the PPHF by hydrophobic interaction, leaving the hydrophilic moieties towards the outside, which can endow the hollow fiber with hydrophilic nature. Moreover, CATB is a cationic surfactant, which was beneficial for adsorbing negative silica sol. By this method, the silica sol can be easily assembled onto the hollow fiber. After repeated adsorption and gelation, the silica species stuffed the pores in the wall of PPHF. By calcination, the PPHF and CATB were burned off, leaving silica skeletons in the mixture. Since the pores in the PPHF were continuous, the as-prepared silica demonstrated a continuous structure, which was a negative template of the PPHF.

Figure 1 shows the scanning electron micrographs of the PPHF (Figure 1 (a). (b)) and OSHF (Figure 1 (c), (d), (e) and (f)) at different magnifications and different view-angles. Figure 1 (a) and (b) were cross-sectional and longitudinal images of PPHF, respectively. From these two images, it can be found that the PPHF possessed fibrous frameworks and structural pores. The latter provided channels for hosting inorganic species. Figure 1 (c) and (d) displayed the cross-sectional images of the OSHF at different magnifications. Figure 1 (e) and (f) presented the longitudinal images of the OSHF at different magnifications. Apparently, the OSHF was totally porous, which was beneficial for extraction application.

1
2
3 187 Elemental analysis on the OSHF revealed that the carbon content of it was 12.2%. The surface area and
4
5 188 mean pore size of it were found to be 286 m² g⁻¹ and 4 nm, respectively. Obviously, the surface area
6
7
8 189 was relatively high, which can provide much adsorption site for target analytes.
9
10

11 190
12
13 191 **3.2 Optimization of extraction performance of the OSHF**
14
15
16 192 The extraction performance of the OSHF for PAHs was evaluated. To achieve best result, the extraction
17
18
19 193 time, stirring speed, ionic strength, desorption solvent and desorption time were evaluated in detail.
20
21
22 194

23
24 195 **3.2.1 Extraction time**
25
26
27 196 Extraction time is important for equilibrium of the analytes between the OSHF and the sample
28
29
30 197 solution. In this study, the extraction time was investigated from 15 to 60 min. Figure 2 demonstrates
31
32 198 that, as the time increased up to 45 min, the peak areas for all of the analytes increased gradually.
33
34
35 199 From 45 to 60 min, the increase was neglectable. Therefore, 45 min was chosen as the optimized
36
37
38 200 extraction time.
39
40 201

41
42
43 202 **3.2.2 Stirring speed**
44
45
46 203 Agitation is an effective method for accelerating the mass transfer of the analytes from sample
47
48 204 solution onto the extraction media, especially when large volume of sample solution was used. In this
49
50
51 205 study, a stirring bar and a magnetic stirrer were used to agitate the sample solution. The stirring speed
52
53
54 206 was investigated from 0 to 1800 rpm. The result (Figure 3) displays that, when the stirring was turned
55
56 207 off (0 rpm), the peak areas for the analytes were quite small, indicating that the extraction
57
58
59 208 performance was poor. As the stirring speed increased, the peak areas increased gradually. However,
60

as the speed was higher than 1200 rpm, the intensive swirling of the solution broke the OSHF, which generally led to unsuccessful extraction. As a result, 1200 rpm was selected as the acceptable extraction speed.

3.2.3 Ionic strength

Usually the presence of salt and its concentrations may influence the extraction performance via increasing or decreasing the solubility of the analytes in sample solution. In this study, sodium chloride, a most easily available salt, was selected for evaluating salt effect. Four concentrations (0, 15, 30 and 45 mmol/L) were compared. The results were shown in Figure 4. It is obvious that, in the range of 0-30 mmol/L of sodium chloride in water, the extraction performance increased steadily; after that value, the extraction performance decreased. Therefore, 30 mmol/L of sodium chloride in sample solution was selected as the suitable condition for extraction.

3.2.4 Desorption Solvent and desorption time

Acetonitrile and methanol were investigated for their suitability as the desorption solvent, as compared in Figure 5. It can be observed that both solvents can desorb the PAHs from the OSHF and the performance of acetonitrile was a little better. Therefore, acetonitrile was selected as the suitable desorption solvent. The desorption time was also studied in the range of 1-10 min. The results indicated that the peak areas for most of the PAHs increased with the increase in desorption time, up to 8 min. So the desorption time of 8 min appeared to be the most suitable.

Based on the above discussion, the optimal extraction conditions were extraction time of 45 min, a

1
2
3 231 stirring speed of 1200 rpm, 30 mmol/L NaCl adding into the sample solution, acetonitrile as the
4
5 232 desorption solvent and 8 min for the desorption.
6
7

8 233

10
11 234 **3.3 Method evaluation**

12
13 235 A series of experiments related to the linearity, limits of detection (LODs) and reproducibility was
14
15
16 236 performed to validate the proposed method at the optimized extraction conditions. The results obtained
17
18
19 237 are listed in Table 1. The linearity of the method was tested over a range of 0.6 and 60.0, 1.0 and 60.0,
20
21
22 238 or 2.0 and 60.0 ng/mL, depending on the analytes. The calibration curves were obtained by plotting the
23
24 239 mean peak area versus sample concentration. The regression coefficients (r^2) were higher than 0.976
25
26
27 240 for all the analytes. The LODs for the PAHs ranged from 31.5 to 97.9 pg/mL.
28
29

30 241

31
32 242 The reproducibility was studied on six pieces of OSHF from different batches. Under the same
33
34
35 243 extraction conditions, the RSDs of them for Nap, Pyr and Phe (selected arbitrarily from the PAH series)
36
37
38 244 were 3.7%, 5.3% and 4.2%, respectively. Apparently, the reproducibility was fairly good, which was
39
40 245 suitable for practical usage.
41
42

43 246

44
45
46 247 **3.4 Applications**

47
48 248 The OSHF was investigated to extract possible PAHs in real water from a local lake. To eliminate
49
50
51 249 matrix effects, the standard addition method was adopted for the quantitative determination of the
52
53
54 250 PAHs. The results are listed in Table 2. Several PAHs were detected in the samples, indicating
55
56 251 extraction based on the OSHF was suitable for real environmental application.
57
58

59 252

60

4. Conclusion

In the present study, octadecyl silica hollow fibers (OSHF) were prepared by a template method. The characteristics of the OSHF were studied in detail. Its application as an extraction media was attempted. The results demonstrated that the OSHF can be successfully used to extract polycyclic aromatic hydrocarbons (PAHs) from water samples. Under the optimal extraction condition, the limits of detection were as low as in the pg/mL range for PAHs. Good linearity and reproducibility were also achieved. In conclusion, the proposed extraction technique was a simple and effective method for sample preparation.

Acknowledgments

The authors gratefully acknowledge the financial support of this research by the Nature Science Foundation of China (No. 21001085).

References

1. Z.-G. Shi and H.K. Lee, *Anal. Chem.*, 2010, **82**, 1540-1545.
2. L. Xu and H.K. Lee, *J. Chromatogr. A*, 2008, **1192**, 203-207.
3. M. Cruz-Vera, R. Lucena, S. Cárdenas and M. Valcárcel, *J. Chromatogr. A* **1216**, 6459-6465.
4. F. Svec, *J. Chromatogr. B*, 2006, **841**, 52-64.
5. C. Dietz, J. Sanz and C. Camara, *J. Chromatogr. A*, 2006, **1103**, 183-192.
6. M.M. Zheng, B. Lin and Y.Q. Feng, *J. Chromatogr. A*, 2007, **1164**, 48-55.
7. E. Baltussen, P. Sandra, F. David and C. Cramers, *J. Micro. Sep.*, 1999, **11**, 737-747.
8. F. David and P. Sandra, *J. Chromatogr. A*, 2007, **1152**, 54-69.
9. A. Sarafray-Yazdi and A. Amiri, *J. Mem. Sci.* 2010, **360**, 334-340.
10. C. Zidi, R. Tayeb, M.B.S. Ali and M. Dhahbi, *TrAC Trends Anal. Chem.*, 2010, **29**, 1-14.
11. L. Farina, E. Boido, F. Carrau and E. Dellacassa, *J. Chromatogr. A* 2007, **1157**, 46-50.
12. A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namiesnik, *J. Chromatogr. A* 2013, **1321**, 1-13.
13. A. Mehdinia, M. O. Aziz-Zanjani, *Trends-Trend Anal. Chem.* 2013, **51**, 13-22.

1
2 281 14. J. Deng, Y. Yang, X. Wang, T. Luan, Trends-Trend Anal. Chem. 2014, **55**, 55-67.
3 282 15. Z.-G. Shi, F. Chen, J. Xing and Y.-Q.Feng, J. Chromatogr. A 2009, **1216**, 5333-5339.
4 283 16. L. Xu and H.K. Lee, J. Chromatogr. A 2009, **1216**, 6549-6553.
5
6
7 284
8
9
10 285
11
12 286
13
14
15 287
16
17
18 288
19
20 289
21
22
23 290
24
25
26 291
27
28 292
29
30
31 293
32
33
34 294
35
36 295
37
38
39 296
40
41
42 297
43
44 298
45
46
47 299
48
49
50 300
51
52 301
53
54
55 302
56
57
58 303
59
60

Figure captions

Figure 1. Scanning electron micrographs of PPHF and OSHF. (a) cross-sectional image of PPHF; (b) longitudinal image of PPHF; (c) and (d) cross-sectional images of OSHF; (e) and (f) longitudinal images of OSHF.

Figure 2. Extraction time profiles for PAHs.

Figure 3. Stirring speed profiles for PAHs.

Figure 4. Profiles of salt concentration for PAHs.

Figure 5. Comparison of desorption solvent for PAHs.

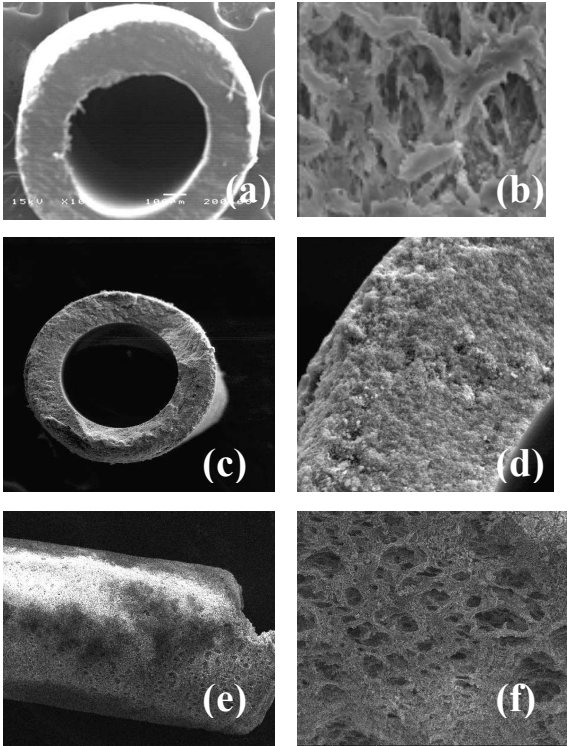


Fig. 1

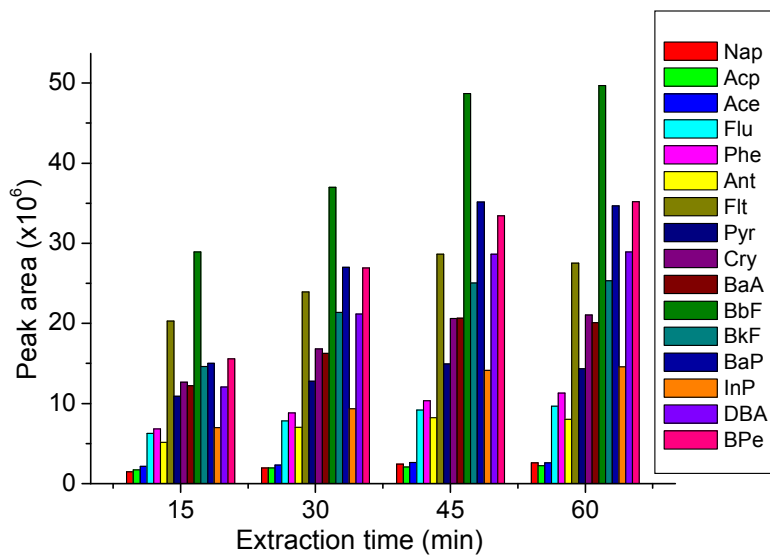


Fig. 2

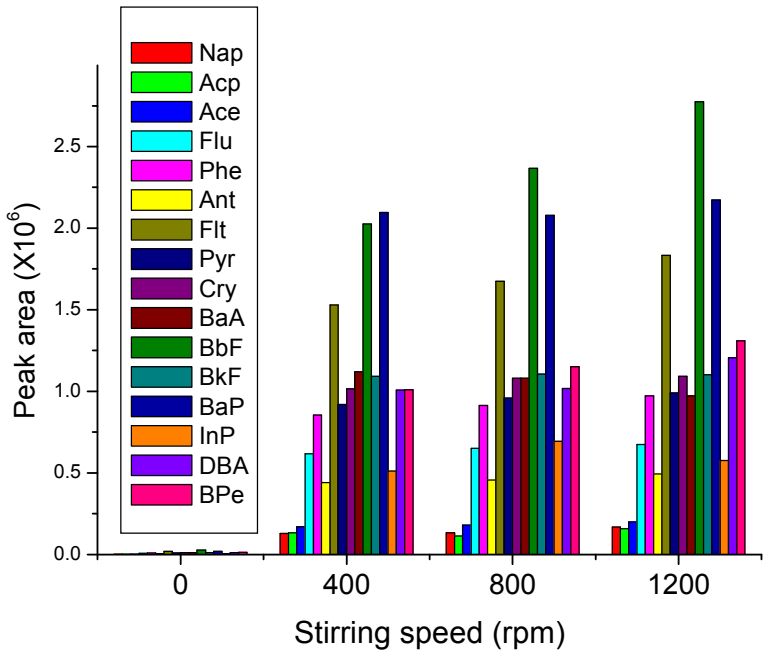


Fig. 3

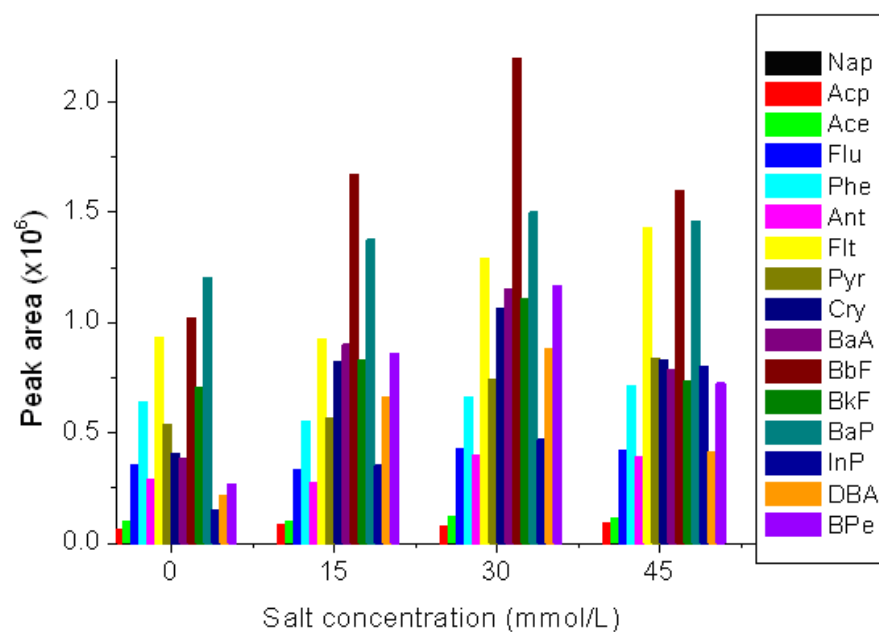


Fig. 4

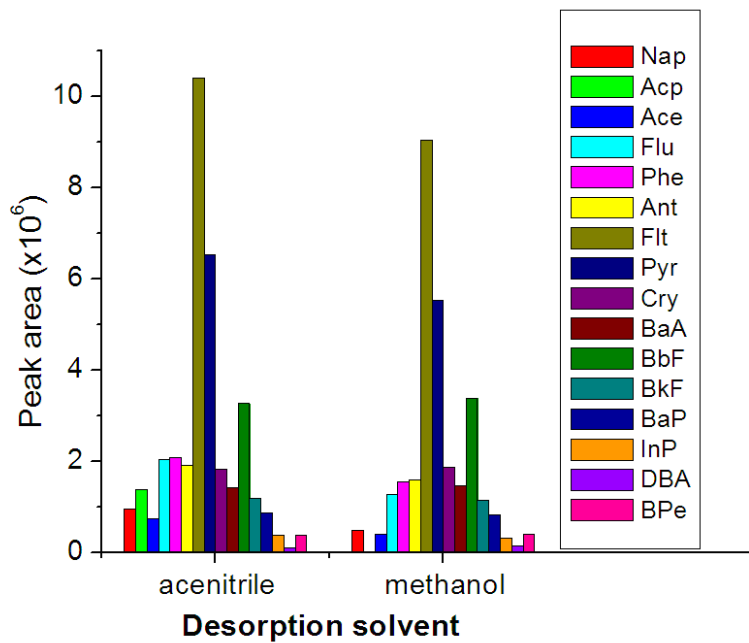


Fig. 5

Table 1. Linear range, regression data and LODs of the PAHs of this extraction method.

Analytes	Linear range (ng/mL)	r^2	LOD (pg/mL)
Nap	1.0-60.0	0.993	94.7
Acp	1.0-60.0	0.987	86.2
Ace	0.6-60.0	0.985	43.3
Flu	0.6-60.0	0.991	51.5
Phe	0.6-60.0	0.993	40.6
Ant	0.6-60.0	0.994	44.5
Flt	0.6-60.0	0.981	31.5
Pyr	0.6-60.0	0.986	35.6
Cry	0.6-60.0	0.989	56.1
BaA	2.0-60.0	0.987	49.6
BbF	2.0-60.0	0.985	52.5
BkF	2.0-60.0	0.986	66.2
BaP	2.0-60.0	0.976	76.2
InP	2.0-60.0	0.981	86.4
DBA	2.0-60.0	0.979	91.4
BPe	2.0-60.0	0.979	97.9

Table 2 The PAHs in the lake water determined by this method.

Analyte	Quantity (ng/mL)	RSD (% n=3)
Nap	3.11	6.1
Acp	1.13	6.7
Ace	1.28	6.9
Flu	1.87	8.4
Phe	0.99	9.9
Ant	0.75	7.6
Flt	1.12	7.8
Pyr	1.34	7.9
Cry	n.d	--
BaA	n.d	--
BbF	n.d	--
BkF	n.d	--
BaP	n.d	--
InP	n.d	--
DBA	n.d	--
BPe	n.d	--

n.d=not detected.