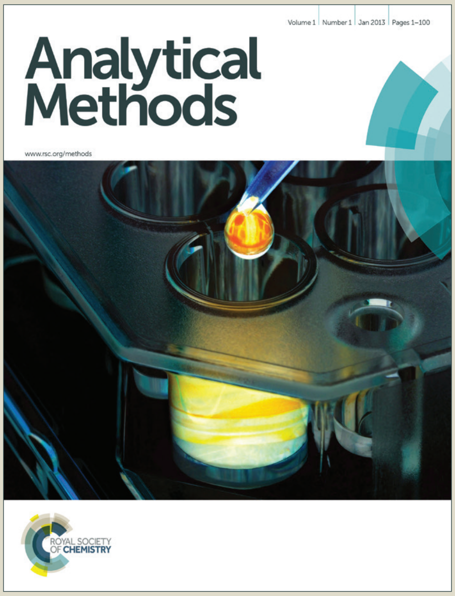
Analytical Methods

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/methods

Rapid Determination of Polycyclic Aromatic Hydrocarbons in Environmental Water Based on Magnetite Nanoparticles/Polypyrrole Magnetic Solid-Phase Extraction

Sheng-Nan Xu[1], Qin Zhao[1], Hai-Bo He[1,2], Bi-Feng Yuan[1], Yu-Qi Feng[1], Qiong-Wei Yu[*1]

1. Key Laboratory of Analytical Chemistry for Biology and Medicine (Ministry of Education), Department of Chemistry, Wuhan University, Wuhan 430072, China

2. Department of Chemistry, Shanghai University, Shanghai, 200444, P.R. China

[*] Corresponding author. Tel: +86-27-68755595; Fax: +86-27-68755595.

E-mail address: qwyu@whu.edu.cn (Q.-W. Yu).

Abstract

Polypyrrole (PPy)-functionalized Fe_3O_4 magnetic nanoparticles (Fe_3O_4–PPy) were prepared and applied as magnetic solid-phase extraction (MSPE) sorbent for the extraction of polycyclic aromatic hydrocarbons (PAHs) from environmental water samples. To achieve optimum extraction performance, several parameters were investigated, including the amounts of sorbent, volume of desorption solvent, extraction and desorption time, inorganic salt and organic solvent content of the sample matrix. Coupled with gas chromatography/mass spectrometry (GC/MS) analysis, a rapid, sensitive and cost-effective method for the analysis of PAHs in aqueous samples was established. The low detection limits (LODs) for the target PAHs in the proposed method were in the range of 0.38 to 5.01 ng/L, which are much lower than those LODs reported in previous methods. Good linearities of the detection method were obtained with correlation coefficients (R) between 0.9904 and 0.9992. Satisfactory reproducibility was also achieved with the relative standard deviations (RSDs) being less than 13.3% by intra- and inter-day precision evaluation. The recoveries of the 10 PAHs in several environmental water samples ranged from 72.4 to 115.7% with the RSDs being less than 9.7%.

Keywords: Polypyrrole; Magnetic solid-phase extraction (MSPE); Polycyclic aromatic hydrocarbons (PAHs); Environmental water; Gas chromatography/mass spectrometry (GC/MS).

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one category of the most widespread organic pollutants. They consist of two or more benzene rings and originate from incomplete combustion of organic compounds. PAHs are mutagenic, carcinogenic, and teratogenic [1-2], therefore monitoring PAHs in environmental samples has received great attention [3-5]. As we known, PAHs with more aromatic rings are more toxic. Moreover, the German Society for Fat Science has recommended maximum residue limits of 5 μg/L for heavy PAHs[6]. Therefore it is highly necessary to monitor the heavy PAHs.

The most widely used methods to analyze PAHs are chromatographic techniques such as gas chromatography (GC) and high performance liquid chromatography (HPLC) coupled with various detectors [7-10]. Due to the semi-volatile, thermostable, and nonpolar properties of most PAHs, they can be conveniently analyzed by gas chromatography/mass spectrometry (GC/MS). However, environmental samples are extremely complex and the concentrations of PAHs are normally low. Thus, effective sample pretreatment is indispensable prior to GC-MS analysis to achieve sensitive and reliable analysis of PAHs.

Several sample pretreatment techniques, such as solid-phase extraction (SPE) [11-13], solid-phase microextraction (SPME) [14-18], stir rod sorptive extraction (SRSE)[19], cloud point extraction (CPE)[20-21], pressurized liquid extraction[22-23] and supercritical fluid extraction[23], have been developed for the extraction of PAHs from environmental water samples. Among these methods, SPE is the most widely used technique due to its high enrichment factor and recovery, rapid phase separation and low cost. However, because of the limited rate of diffusion and mass transfer, the extraction time of ordinary SPE processes is usually long when extracting low amount of the target compounds from large volume of water samples.

Magnetic solid-phase extraction (MSPE), as a new SPE mode, has some additional advantages. In MSPE mode, the adsorbents are not required to be packed into the SPE cartridge and they can disperse in large volumes of water samples solution or suspension. Compared with tedious centrifugation and filtration procedures, the separation process by MSPE can be performed directly using an external magnet, which makes the separation much convenient. In addition, due to the dispersive extraction mode, MSPE is suitable for direct analysis of samples containing particles or microorganisms that widely exist in food and environmental samples. Up to date, several materials have been prepared as MSPE adsorbents to extract PAHs from water samples by modifying magnetic nanoparticles (MNPs) with some hydrophobic compounds such as n-octadecylphosphonic acid (OPA)[24], carbon, octadecyl (C_{18})[25], triphenylamine (TPA)[26], graphene[27], tetrabenzyl (TBCD)[28] and metal–organic framework MIL-101[29]. In this respect, high enrichment factor and extraction capacity of PAHs from water samples can be achieved by MSPE based on hydrophobic interaction between PAHs and MSPE adsorbents. Whereas, OPA, carbon and C_{18} modified MNPs normally show low extraction selectivity; TPA modified MNPs have poor dispersal capability. In addition, the preparation of magnetic microsphere-confined graphene requires multiple steps, which is a tedious and time-consuming. Thus, novel magnetic sorbents with better dispersal capability, easier preparation process and higher extraction selectivity are highly desirable.

Polypyrrole (PPy) is one of the most important conductive polymers. Due to the versatile properties such as hydrophobility, large π-conjugated structure, hydrogen bonding, ion exchange property[30], it has been used as SPE packing materials or SPME coating materials to extract organic contaminants or inorganic ions from various sample[31-33]. In recent years, polypyrrole (PPy) has been introduced into the MSPE and some polypyrrole (PPy)-functionalized Fe_3O_4 magnetic nanoparticles (i.e., Fe_3O_4–PPy) have been prepared using *in situ* polymerization or co-mixing method. We recently also prepared Fe_3O_4–PPy by a simple and environment-friendly *in situ* polymerization method and the Fe_3O_4–PPy was successfully used to extract estrogens in milk samples[34] and pesticide residues in beverage and environmental water samples[30].

The Fe_3O_4–PPy has not been used to extract PAHs from environmental waters yet, but PPy is favor for selective extraction of aromatic compound[35] by taking advantage of the charge-transfer and hydrophobic interaction between PPy and analytes. Based on this, in this study, Fe_3O_4–PPy was expanded to extract PAHs in environmental waters. The extraction conditions were investigated and optimized to achieve best performance. Under the optimal conditions, a rapid, simple and convenient MSPE−GC/MS method for the determination of PAHs in water samples was established.

2. Experimental

2.1. Reagents

Acetone (HPLC grade) was obtained from J.T. Baker Chemical Company (Phillipsburg, NJ, USA). Ethylene glycol (EG), ethanol, toluene, ethylene diamine (ED), ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent (Shanghai, China). Before use, toluene was purified through distillation. All the other chemicals were used directly without further purification.

PAHs standard solution and chrysene-d12 (internal standard (I.S.), 2 mg/mL in CH_2Cl_2) were bought from J&K Chemical Ltd. (Tianjin, China). Benzo[a]pyrene-d12 (I.S., BaP-d12$\geqslant$98%) was bought from Sigma-Aldrich (St. Louis, MO, USA). The PAHs standard solution contains fluoranthene (FLT), pyrene (PYR), chrysene (CHRY), benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (INPY), dibenzo[a,h]anthracene (DiahA) and benzo[g,h,i]perylene (BghiP), each at 0.2 mg/mL in n-hexane/methylene dichloride (1/1, v/v). The PAHs stock solution was prepared in methanol at the concentration of 10 μg/mL. The I.S. stock solution was prepared in acetone at the concentrations of 1 μg/mL. All the stock solutions were kept at

4 °C in darkness.

2.2. Preparation of Fe_3O_4–PPy

The preparation of Fe_3O_4–PPy was according to our previously described procedure [34]. Briefly, $FeCl_3 \cdot 6H_2O$ (5.0 g) was dissolved in EG (100 mL), and then NaAc (15.0 g) and ED (50 mL) were added to the solution. After vigorous stirring for 30 min, the homogeneous mixture was sealed in a Teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to 200 °C, maintained for 8 h, and allowed to cool to room temperature. The product was magnetically collected, washed with water/ethanol for several times, and vacuum-dried at 60 °C for 6 h. Then, the resultant Fe_3O_4 magnetic nanoparticles were PPy-coated. 1.0 g of Fe_3O_4, 9.1 g of $FeCl_3$, and 100 mL of deioned water were added to a 250 mL flask. To accumulate the Fe^{3+} ions on the surface of MNPs by the common ion effect, the mixture was continuously shaken in a water bath at 25 °C for 3 h. Then, 20 mL of SDS solution (5.85 wt %) and 0.5 mL of PPy monomers were rapidly added, and the mixture was kept shaking for additional 12 h. The products (i.e., Fe_3O_4–PPy) were magnetically collected, washed by water/ethanol successively and repeatedly, and then vacuum-dried at 60 °C for 6 h.

2.3. The Extraction Procedure

The MSPE procedures are schematically described in Fig. 1. Fe_3O_4–PPy (20 mg) was placed in a 15 mL vial, and then 10 mL of spiked PAHs solution was added into the vial. The mixture was vortexed vigorously for 1 min and then discarded the supernatant. Meanwhile the sorbent was gathered to the vial bottom by placing a strong magnet on the bottom of the vial. After the supernatant solution was discarded, PAHs were eluted from the sorbents with 0.3 mL desorption solvent (acetone/toluene, 1/1, v/v) by vagarious vortex for 2 min. The desorption solution was collected, and 1 μL of the desorbed solution was used for analysis.

2.4. Apparatus

The MNPs and Fe_3O_4–PPy were characterized by JEM-100CXII transmission electron microscope (TEM, Jeol, Japan). In addition, FTIR spectra were determined by using a T hermo Nicolet 670FT-IR (Boston, USA) equipped with a diffuse reflectance accessory. The gas chromatography-mass spectroscopy (GC/MS) analysis was performed on a Shimadzu GCMS-QP2010Plus which is equipped with an AOC-20i autosampler (Kyoto, Japan). The GC separation was achieved on an Rxi^{TM}-5ms column (30 m × 0.25 mm× 0.25 μm) (Restek, USA). The oven temperature was held at 70 ^{o}C for 2.0 min, then increased to 190 ^{o}C at a rate of 20 ^{o}C /min and held for 8.0 min, then increased to 260 ^{o}C at a rate of 10 ^{o}C /min and to 290 ^{o}C at a rate of 5 ^{o}C /min. Finally it was held at 290 ^{o}C for another 10.0 min. The injection volume was 1.0 μL in splitless mode. Helium (purity ≥ 99.999%) was used as carrier gas at a flow rate of 1.2 mL/min. The temperatures of injection port, detector and interface were held at 290 ^{o}C, 220 ^{o}C and 280 ^{o}C, respectively. Selective ion monitoring (SIM) mode was adopted for the quantitative analysis. The qualitative and quantitative ions for each PAH are listed in Table 1.

2.5. Samples

Tap water, industrial wastewater, lake water and hospital sewage were selected as real water samples for investigation. Tap water sample was taken from our laboratory. Industrial wastewater sample was collected from Wuhan Iron and Steel (Group) Corp in Wuhan (Hubei, China). Lake water sample was collected from the East Lake in Wuhan. Hospital sewage was obtained from the sewer exit pipe of Zhongnan hospital (Wuhan, China). All the water samples were filtered through a 0.22 μm membrane and stored at 4 ^{o}C before use.

3. Results and discussion

3.1. Characterization of Fe_3O_4–PPy

The size and shape of the prepared microspheres were observed by transmission electron microscopy (TEM). Fig. 2 shows the TEM images of MNPs and Fe_3O_4–PPy. MNPs were nearly mono-dispersed and sphere-like with a mean diameter of about 65 nm (Fig. 2a). In Fig.

2b, the microspheres shows additional light gray phases on the edges of black MNPs, demonstrating the encapsulation of PPy on the surface of MNPs and the formation of core-shell architecture.

Fig. 3 shows the IR spectra of MNPs (a), Fe_3O_4–PPy (b) and PPy (c). The peaks of Fe_3O_4–PPy at 1552 and 1040 cm^{-1} can be assigned to the C–N ring stretching vibrations of the pyrrole ring, and the peaks at 1175, 894, and 785 cm^{-1} are related to the C–H in-plane and out-plane vibrations. These results demonstrate the existence of PPy on the Fe_3O_4 particles.

3.2. Optimization of MSPE

Several experimental conditions, including the amounts of sorbent, desorption solvent and volume, extraction and desorption time, the organic solvent content and salt concentration of sampling solution were optimized to achieve the best extraction efficiencies of PAHs.

3.2.1. Effect of the amounts of sorbent

To achieve good extraction efficiency, different amounts of Fe_3O_4–PPy sorbent ranging from 5 to 50 mg were applied to the extraction of ten PAHs. As shown in Fig. 4a, with the increase of the sorbent amount, the peak areas of four PAHs (FLT, PYR, CHRY, BaA) enhanced. The peak areas of other analytes increased as sorbent ranging from 5 mg to 20 mg and then decreased as the sorbent amount further increased. The effect of sorbent amounts on peak areas was primarily caused by the difference of adsorptive affinity of PAHs on Fe_3O_4–PPy. Due to the hydrophobic interaction and π-π interaction between PAHs and Fe_3O_4–PPy, PAHs with more π electrons and more aromatic rings (BbF, BkF, BaP, INPY, DiahA, BghiP) have relatively stronger affinity to Fe_3O_4–PPy than the four smaller PAHs (FLT, PYR, CHRY, BaA). For those PAHs with more π electrons and more aromatic rings, the adsorptive affinity are too strong and then they could not be completely eluted with 2.5 mL desorption solvent in 5 min as more than 20 mg sorbents were used, which led to the decreased peak areas. Thus 20 mg was used in the following experiments.

3.2.2. Effect of desorption solvent and volume

Acetone, acetonitrile, n-hexane, toluene and their mixture were studied as desorption solvent to examine their effects on the extraction efficiencies of PAHs. Our results showed the best extraction efficiencies of PAHs were obtained with acetone/toluene (1/1, v/v) as desorption solution. The effect of desorption solution volume was also investigated in the range of 0.3 to 1.0 mL. As shown in Fig. 4b, the smaller volume used, the higher extraction efficiencies of PAHs can be obtained. Finally, 300 μL desorption solvent was used in the following experiments.

3.2.3. Effect of extraction and desorption time

The effect of extraction and desorption time were examined in the range of 30 s to 5 min. As shown in Fig. 4c and 4d, the peak area of analytes of PAHs increased with increasing the extraction and desorption time to 1 min and 2 min, respectively. The peak area of analytes decreased little with further increasing the extraction and desorption time. Thus the extraction and desorption time were fixed at 1 min and 2 min, respectively.

3.2.4. Effects of organic solvent content and salt concentration

Various amount of methanol was added to the matrix solution to evaluate the effect of organic solvent on the extraction efficiencies of PAHs. As shown in Fig. 5a, with the increase of methanol content, the extraction efficiencies for most PAHs decreased. Therefore, no organic solvent was added in the following experiments.

The effect of ionic strength was investigated by adding NaCl to the matrix solution in the range of 0 mM to 80 mM (Fig. 5b). The results indicated that salt addition had a slightly negative effect on the extraction efficiencies, which could be explained by the “oil effect” [24]. The addition of salt into the matrix solution would reduce the interaction between PAHs and Fe_3O_4–PPy, which led to poor extraction efficiencies. So no salt was added in the following experiments.

On the basis of the above discussion, the optimal extraction conditions were 20 mg Fe_3O_4–PPy, 1 min of extraction time and 2 min of desorption time, 0.3 mL acetone/toluene (1/1, v/v) as the desorption solvent. And no salt was added in the sample solution.

3.3. Evaluation of the reproducibility of Fe_3O_4–PPy adsorbent

In this study, we investigated the batch-to-batch reproducibility of Fe_3O_4–PPy adsorbent. Three batches of Fe_3O_4–PPy prepared under the same conditions were used for the extraction of PAHs. As shown in Table 2, the RSDs ranged from 4.6 to 12.9%, indicating that the Fe_3O_4–PPy adsorbent possessed acceptable reproducibility.

3.4. Validation of the MSPE-GC/MS method

Under the optimal conditions, PAHs were quantitatively analyzed using chrysene-d12 and benzo[a]pyrene-d12 as I.S. A series of experiments were performed to validate the developed MSPE-GC/MS method using ultrapure water samples spiked with different concentrations of analytes. The calibrations were obtained by plotting peak areas ratio versus concentrations. As shown in Table 3, good linearity is observed for all analytes, with correlation coefficients (R) ranging from 0.9904 to 0.9992. The limits of detection (LODs) and limits of quantification (LOQs) were calculated at concentrations at which signal-to-noise ratios were equal to 3 and 10, respectively. The LODs and LOQs were in the range 0.38−5.01 ng/L and 1.29−16.70 ng/L, respectively.

The recoveries and intra- and inter-day RSDs of the proposed method were measured with ten PAHs spiked at three different concentrations in tap water samples. The recoveries were determined by comparing the calculated amounts of PAHs (using calibration curves in ultrapure water) with the spiking amounts of PAHs in tap water samples. The recoveries and RSDs data for PAHs spiked in tap water samples are summarized in Table 4. The intra- and inter-day recoveries were in the range of 79.6-114.3%. These results clearly demonstrate that the method for determination of PAHs in tap water samples is suitable and reliable. The intraand inter-day precision for recoveries of ten PAHs were evaluated with the resulting RSDs less than 13.3%, illustrating the good reproducibility of the method.

3.5. Applications

The proposed method was used to analyze some water samples included tap water, Donghu lake water, hospital sewage and industrial wastewater. The total ion chromatograms of blank and spiked industrial wastewater sample extracted by Fe_3O_4–PPy were shown in Fig. 6. In order to demonstrate the reliability of the proposed method in some water samples besides tap water, the spiked recoveries of PAHs in the water samples were investigated. They are determined by comparing the measured amounts of spiked PAHs in real samples with the total amounts of spiked PAHs. As listed in Table 5, the recoveries of the PAHs from various real samples were in the range of 72.4% to 115.7% with the RSDs being less than 9.7%. The results demonstrated that the accuracy of the present method was acceptable in these water samples. As can be seen in Table 5, the tested PAHs were not detected in tap water. In Donghu lake water, only BaP was found. In the hospital sewage water samples, FLT, PYR and DiahA were detected at concentration of 50 ng/L, 40 ng/L, 40 ng/L, respectively. In industrial wastewater untreated by the company, all PAHs were detected except BbF and BghiP. For those industrial wastewater treated by the company, some PAHs can also be detected.

A comparison of our developed method with previously reported methods (including the US EPA 8272 method[36]) was performed and the results are listed in Table 6. It can be seen that our method has a better sensitivity (except Fe_3O_4–TBCD sorbent), less sorbent and less time-consuming.

4. Conclusions

In this study, magnetic nanoparticles functionalized with PPy were synthesized and, for the first time, applied to the extraction of trace level PAHs from water samples. Combined with GC/MS, a rapid and efficient method for the determination of PAHs in environmental water samples was established. The LODs and LOQs of the target compounds were in the range of 0.38−5.01 ng/L and 1.29−16.70 ng/L, respectively. The recoveries in several real samples were in the range of 72.4–115.7% with RSDs <9.7%. The inter- and intra-day precisions were less than 13.3%. Moreover, Fe_3O_4–PPy exhibited a good batch-to-batch reproducibility with RSDs less than 12.9%.

Acknowledgments

The authors thank the financial support from the National Key Basic Research Foundation of China (973 Program) (2013CB910702, 2012CB720601), the National Natural Science Foundation of China (91017013, 91217309, 21005057, 21205091), the Key Laboratory of Analytical Chemistry for Biology and Medicine of Wuhan University awarded by the Ministry of Education（ACBM2014002).

Reference

1. Y. C. Chen and B. H. Chen, *Journal of Agricultural and Food Chemistry*, 2003, 51, 4162-4167.
2. J. L. Zhou and K. Maskaoui, *Environmental Pollution*, 2003, 121, 269-281.
3. W. Wilcke, *Geoderma*, 2007, 141, 157-166.
4. G. Li, X. Xia, Z. Yang, R. Wang and N. Voulvoulis, *Environmental Pollution*, 2006, 144, 985-993.
5. B. H. Chen and Y. C. Chen, *Journal of Agricultural and Food Chemistry*, 2001, 49, 5238-5243.
6. D. Luo, Q.-W. Yu, H.-R. Yin and Y.-Q. Feng, *Anal. Chim. Acta*, 2007, 588, 261-267.
7. Q. Zhao, F. Wei, Y.-B. Luo, J. Ding, N. Xiao and Y.-Q. Feng, *Journal of Agricultural and Food Chemistry*, 2011, 59, 12794-12800.
8. H. C. Menezes and Z. de Lourdes Cardeal, *Journal of Chromatography A*, 2011, 1218, 3300-3305.
9. Y. J. Huang, J. Wei, J. Song, M. F. Chen and Y. M. Luo, *Chemosphere*, 2013, 92, 1010-1016.
10. E. H. Denis, J. L. Toney, R. Tarozo, R. S. Anderson, L. D. Roach and Y. S. Huang, *Org. Geochem.*, 2012, 45, 7-17.
11. H. Bagheri and A. Mohammadi, *Journal of Chromatography A*, 2003, 1015, 23-30.
12. K.-J. Huang, J. Li, Y.-M. Liu and L. Wang, *Journal of Separation Science*, 2013, 36, 789-795.
13. I. Limam and M. R. Driss, *Int. J. Environ. Sci. Technol.*, 2013, 10, 973-982.
14. Y.-l. Hu, Y.-l. Fu and G.-K. Li, *Anal. Chim. Acta*, 2006, 567, 211-217.
15. A. Mohammadi, Y. Yamini and N. Alizadeh, *Journal of Chromatography A*, 2005, 1063, 1-8.
16. E. Rianawati and R. Balasubramanian, *Physics and Chemistry of the Earth, Parts A/B/C*, 2009, 34, 857-865.
17. S. Maghsoudi and E. Noroozian, *Chromatographia*, 2012, 75, 913-921.
18. M. B. Gholivand, M. M. Abolghasemi and P. Fattahpour, *Anal. Chim. Acta*, 2011, 704, 174-179.
19. Y.-B. Luo, J.-S. Cheng, Q. Ma, Y.-Q. Feng and J.-H. Li, *Analytical Methods*, 2011, 3, 92-98.
20. C. F. Li, J. W. C. Wong, C. W. Huie and M. M. F. Choi, *Journal of Chromatography A*, 2008, 1214, 11-16.
21. I. Y. Goryacheva, S. N. Shtykov, A. S. Loginov and I. V. Panteleeva, *Anal. Bioanal. Chem.*, 2005, 382, 1413-1418.
22. M. Lund, L. Duedahl-Olesen and J. H. Christensen, *Talanta*, 2009, 79, 10-15.
23. M. A. Amezcua-Allieri, M. A. Ávila-Chávez, A. Trejo and J. Meléndez-Estrada, *Chemosphere*, 2012, 86, 985-993.
24. J. Ding, Q. Gao, D. Luo, Z.-G. Shi and Y.-Q. Feng, *Journal of Chromatography A*, 2010, 1217, 7351-7358.
25. Y. Liu, H. Li and J.-M. Lin, *Talanta*, 2009, 77, 1037-1042.
26. Y. Long, Y. Chen, F. Yang, C. Chen, D. Pan, Q. Cai and S. Yao, *Analyst*, 2012, 137, 2716-2722.
27. W. Wang, R. Ma, Q. Wu, C. Wang and Z. Wang, *Journal of Chromatography A*, 2013, 1293, 20-27.
28. Y. Zou, Y. Chen, Z. Yan, C. Chen, J. Wang and S. Yao, *Analyst*, 2013, 138, 5904-5912.
29. S.-H. Huo and X.-P. Yan, *Analyst*, 2012, 137, 3445-3451.
30. Q. Zhao, Q. Lu and Y.-Q. Feng, *Anal. Bioanal. Chem.*, 2013, 405, 4765-4776.
31. M. B. Gholivand, M. M. Abolghasemi and P. Fattahpour, *Anal. Chim. Acta*, 2011, 704, 174-179.
32. H. Bagheri and A. Mohammadi, *Journal of Chromatography A*, 2003, 1015, 23-30.
33. H. Bagheri, E. Babanezhad and F. Khalilian, *Anal. Chim. Acta*, 2009, 634, 209-214.
34. Q. Gao, D. Luo, M. Bai, Z.-W. Chen and Y.-Q. Feng, *Journal of Agricultural and Food Chemistry*, 2011, 59, 8543-8549.
35. E. Tahmasebi, Y. Yamini, S. Seidi and M. Rezazadeh, *Journal of Chromatography A*, 2013, 1314, 15-23.

36 http://www.caslab.com/EPA-Method-8272/

Table 1. The qualitative and quantitative ions for the analysis of PAHs.

Analytes	Qualitative ions	Quantitative ion
FLT	200, 202, 203	202
PYR	200, 202, 203	202
CHRY	226, 228, 229	228
BaA	226, 228, 229	228
BbF	250, 252, 253	252
BkF	250, 252, 253	252
BaP	250, 252, 253	252
INPY	276, 277, 278	276
DiahA	276, 277, 278	276
BghiP	276, 277, 278	278
Chrysene-d12 (I.S.)	240	240
benzpyrene-d12 (I.S.)	264	264

Table 2. The RSDs of the extracted PAHs with three different batches of Fe_3O_4–PPy.

Analyte	Batch-to-batch reproducibility (RSD, n = 3)
FLT	5.3
PYR	4.6
CHRY	8.3
BaA	4.7
BbF	12.9
BkF	10.5
BaP	8.2
INPY	10.1
DiahA	5.1
BghiP	8.4

Table 3. Calibration curves, LODs and LOQs of the PAHs in aqueous samples.

Analytes	Linear dynamic range (ng/L)	regression line		LODs (ng/L)	LOQs (ng/L)
		Calibration curve	R value		
FLT	10-2000	Y = -0.0233+0.0278 X	0.9977	0.39	1.33
PYR	10-2000	Y = 0.0366+0.02248 X	0.9904	0.38	1.29
CHRY	10-2000	Y = -0.0165+0.0172 X	0.9986	0.45	1.51
BaA	10-2000	Y = 0.0236+0.0204 X	0.9989	0.51	1.72
BbF	20-2000	Y = 0.0991+0.0089 X	0.9974	5.01	16.70
BkF	20-2000	Y = 0.0509+0.0090X	0.9992	4.74	15.81
BaP	20-2000	Y = 0.1774+0.0069X	0.9988	4.33	14.43
INPY	20-2000	Y = -0.0224+0.0027X	0.9992	4.98	16.60
DiahA	10-2000	Y = 0.0126+0.0041X	0.9958	3.04	10.13
BghiP	20-2000	Y = 0.0013+0.0037X	0.9991	3.98	13.27

Table 4 The method accuracies (expressed as recoveries) and precisions at three different concentrations of the ten PAHs in tape water samples.

Analytes	Intraday recoveries (%RSD%, n=3)			Inter-day recoveries (%RSD%, n=3)		
	100 ng/L	500 ng/L	1000 ng/L	100 ng/L	500 ng/L	1000 ng/L
FLT	84.5(2.5)	87.3(1.6)	79.8(0.6)	82.7(4.5)	90.2(2.5)	79.6(2.5)
PYR	97.2(2.0)	100.2(3.7)	99.1(1.4)	89.5(3.1)	105.8(1.7)	87.9(5.0)
CHRY	92.2(2.3)	93.7(3.5)	102.0(7.2)	98.0(5.6)	86.3(5.1)	114.3(3.2)
BaA	85.0(4.1)	103.4(2.1)	80.9(1.3)	85.6(9.2)	99.5(6.3)	83.7(2.7)
BbF	80.4(5.2)	98.3(3.9)	112.8(1.4)	79.9(5.2)	107.1(7.8)	109.6(8.1)
BkF	102.3(9.4)	92.1(3.4)	94.4(3.3)	112.3(13.3)	83.2(10.2)	106.5(9.8)
BaP	97.6(3.2)	87.7(3.7)	92.1(5.5)	105.0(6.2)	87.4(6.5)	93.5(4.4)
INPY	92.8(6.5)	112.4(5.4)	97.3(6.8)	102.2(5.2)	109.7(1.1)	99.3(11.0)
DiahA	103.5(5.1)	105.3(4.8)	100.3(2.9)	97.8(7.1)	106.4(2.8)	107.2(7.5)
BghiP	82.7(4.5)	90.6(9.5)	84.8(0.7)	80.8(8.6)	96.5(1.9)	97.1(9.2)

Table 5. Analysis of real samples.

Analytes	**Tap water**		**Donghu water**		**Hospital sewage**		**Wugang water(import)**		**Wugang water(export)**	
	Concentration (ng/L, RSD %, n =3)	Recovery (%, RSD %, n =3)	Concentration (ng/L, RSD %, n =3)	Recovery (%, RSD %, n =3)	Concentration (ng/L, RSD %, n =3)	Recovery (%, RSD %, n =3)	Concentration (ng/L, RSD %, n =3)	Recovery (%, RSD %, n =3)	Concentration (ng/L, RSD %, n =3)	Recovery (%, RSD %, n =3)
FLT	Nd	79.8(0.6)	Nd	97.6(4.3)	50(4.1)	97.8(5.6)	300(5.1)	85.4(1.8)	30(1.4)	87.0(2.4)
PYR	Nd	99.1(1.4)	Nd	115.7(1.7)	40(3.1)	110.7(5.9)	500(6.1)	107.5(3.2)	30(1.3)	111.3(2.7)
CHRY	Nd	102.0(7.2)	Nd	76.9(4.5)	Nd	97.4(3.5)	400(6.8)	102.4(4.1)	20(1.8)	111.5(3.5)
BaA	Nd	80.9(1.3)	Nd	77.7(3.4)	Nd	72.4(5.0)	300(7.2)	90.3(4.0)	20(2.6)	95.2(3.5)
BbF	Nd	112.8(1.4)	Nd	114.0(2.4)	Nd	110.2(8.0)	Nd	100.8(5.5)	Nd	90.3(4.7)
BkF	Nd	94.4(3.3)	Nd	99.6(4.2)	Nd	88.2(1.7)	50(2.7)	88.9(2.7)	Nd	91.1(4.4)
BaP	Nd	92.1(5.5)	Nd	100.6(5.4)	Nd	100.9(3.0)	200(3.3)	113.6(2.4)	10(9.9)	95.5(3.4)
INPY	Nd	97.3(6.8)	Nd	95.5(6.1)	Nd	85.8(7.4)	200(2.8)	100.3(2.7)	Nd	107.7(4.9)
DiahA	Nd	100.3(2.9)	Nd	89.8(6.6)	40(4.5)	85.8(9.7)	100(2.9)	96.5(1.5)	20(2.4)	97.5(3.9)
BghiP	Nd	84.8(0.7)	Nd	86.7(1.4)	Nd	87.7(2.6)	Nd	97.8(1.8)	Nd	96.4(3.7)

The concentrations of the spiked PAHs were 1000 ng/L.

Nd, Not detected.

Table 6. Comparison of our method with other pretreatment methods.

Extraction technique	Sorbent	Matrix	Loading volumn (mL)	Sorbent amount (mg)	Extraction time (min)	Elution volume (mL)	LOD (ng/L)	Instrumental analysis	Ref.
US EPA 8272(SPME)	PDMS	Pore water	1.5				60-9000	GC-MS	36
MSPE	Fe_3O_4–octadecylphosphonic	Tap water and hospital sewage	10	50	5	0.5	14.1-64.4	GC-MS	23
MSPE	Fe_3O_4–C18 MNPs	aqueous samples	20	50	6	4.5	800-36000	GC-MS	24
MSPE	Fe_3O_4–TBCD	Sea and snow water	200	80	5	8	0.03-1.2	HPLC-FLD	27
MSPE	Fe_3O_4–SiO2–graphene	Sea and tap water	250	40	5	0.3	0.5-5.0	HPLC-FLD	26
MSPE	Fe_3O_4–SiO_2–MIL-101	Lake water	20	1.6	20	0.5	2.8-27.2	HPLC-PDA	28
SPME	PDMS	Rainwater and stormwater	10		60		4-41	GC-MS	15
SPME	PPy/SBA	Water samples	10		40		7-20	GC-MS	16
SPME	MWCNTs	Water samples	5		60		40-60	GC-MS	17
MSPE	Fe_3O_4–PPy	Tap and lake water hospital sewage	10	20	1	0.3	0.3-5.0	GC-MS	this work

PDMS, polydimethylsiloxane (PDMS)-coated fused silica, PPy/SBA, polypyrrole/hexagonally ordered silica nanocomposite, MWCNTs, multiwalled carbon nanotubes,

Captions

Fig. 1. Schematic illustration of the MSPE process using the Fe_3O_4–PPy.

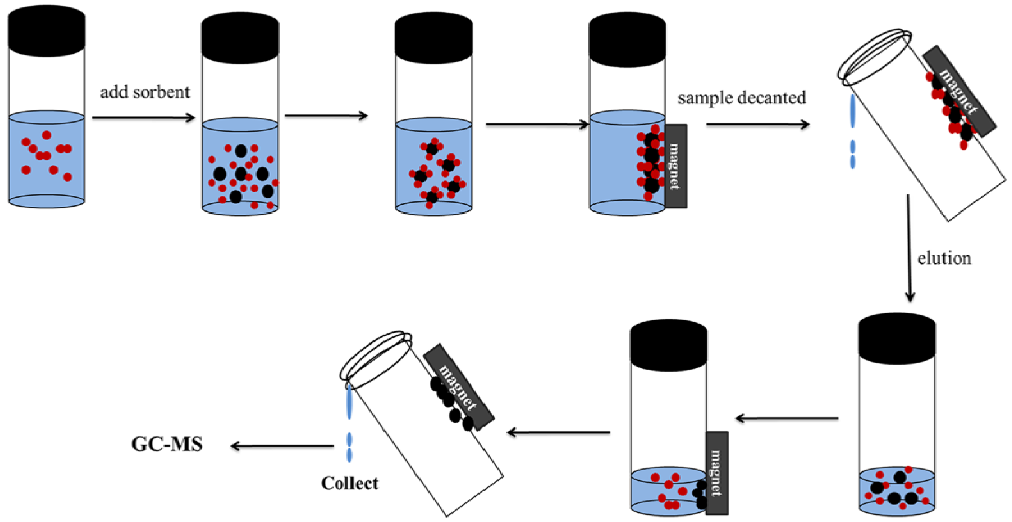


Fig. 2. TEM images of MNPs (A) and Fe_3O_4–PPy (B).

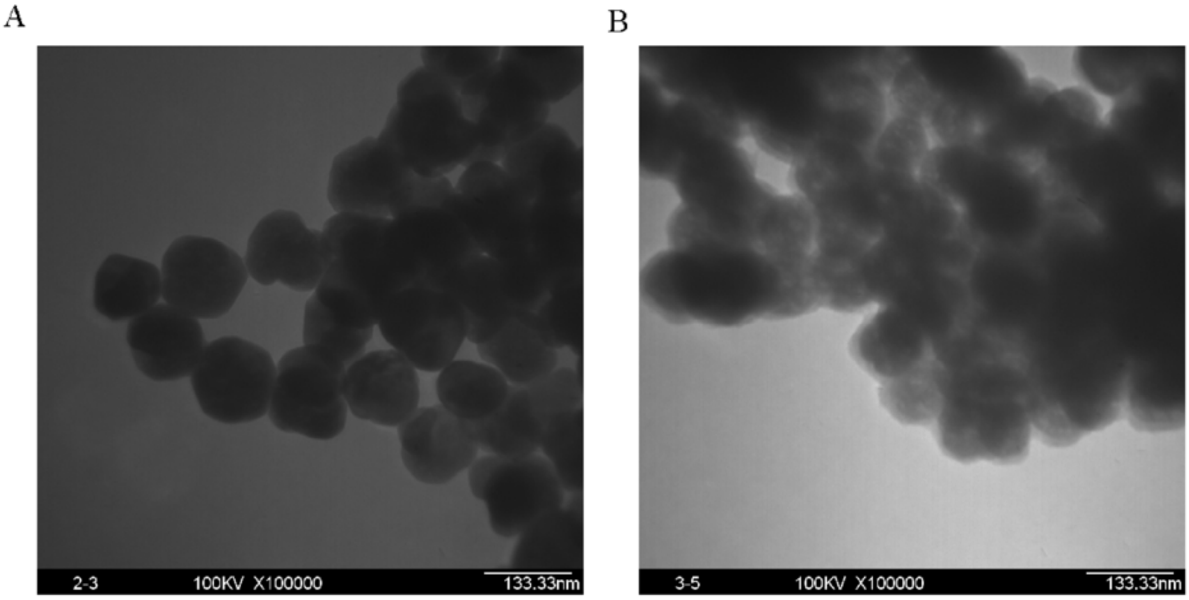


Fig. 3. IR spectra of MNPs (a), Fe_3O_4–PPy (b) and PPy (c).

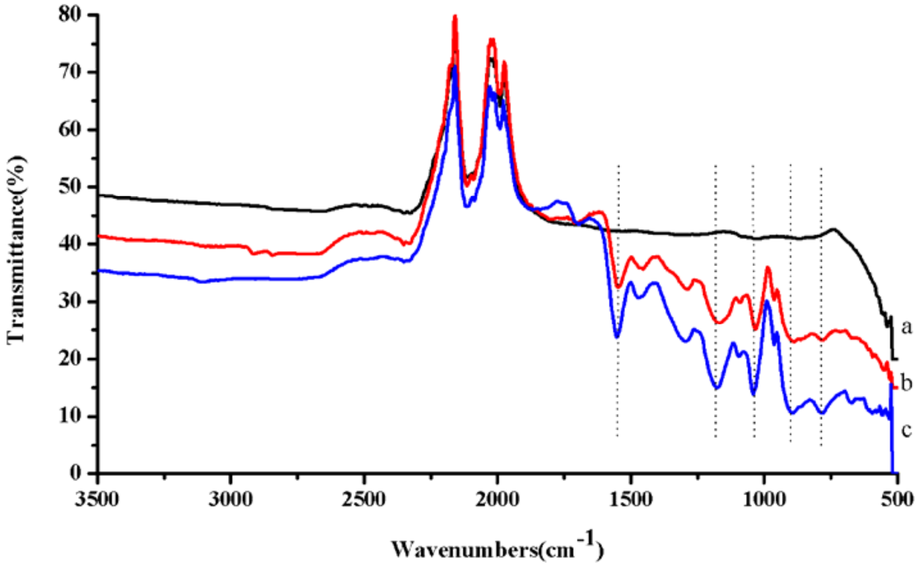


Fig. 4. Optimization of the MSPE parameters. (a). Effect of the amount of the sorbent on extraction performance. (b). Effect of the volume of the desorption solvent. (c). Effect of the extraction time. (d). Effect of the desorption time.

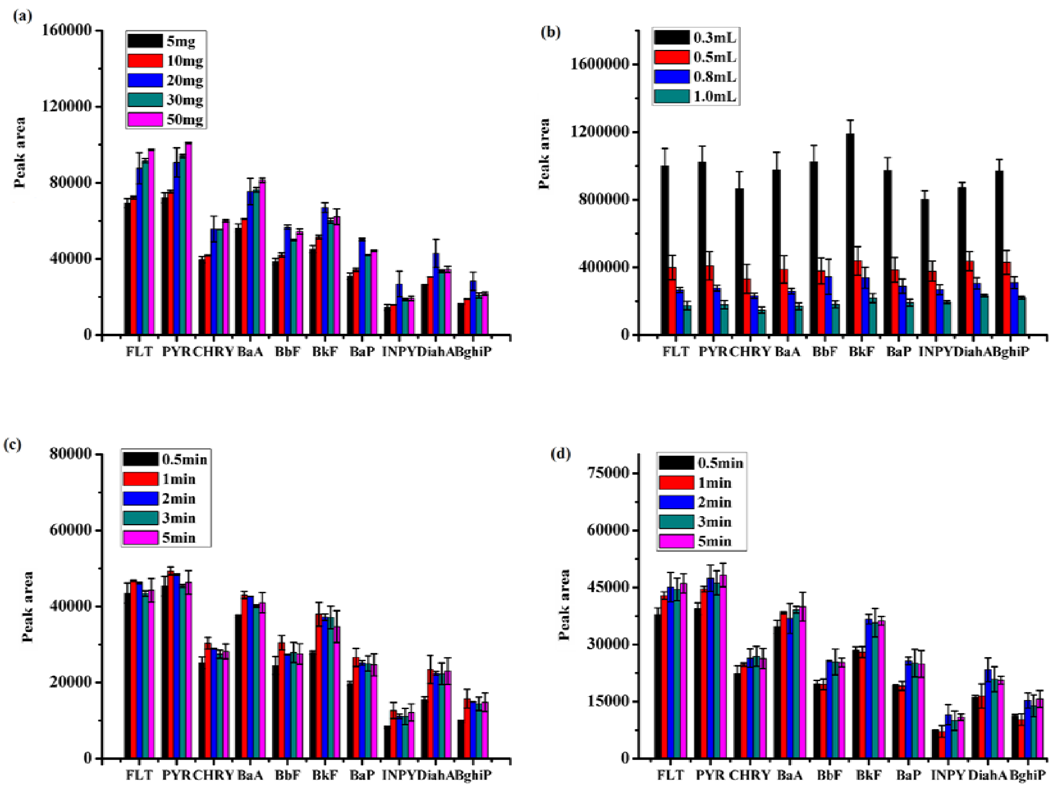


Fig. 5. (a) Effect of organic solvent in sample matrix. (b). Effect of salt addition in sample matrix.

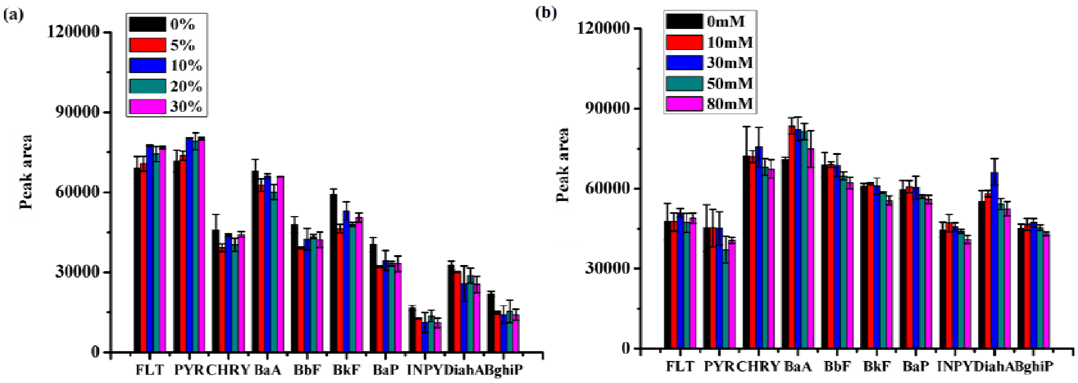


Fig. 6. (a) The total ion chromatogram of industrial wastewater sample (import) extracted directly by Fe_3O_4–PPy. (b) The total ion chromatogram of industrial waster sample (import) spiked with 1000 ng/mL of each PAHs and extracted by Fe_3O_4–PPy. Peaks identification: (1) (FLT), (2) (PYR), (3) (CHRY), (4) (BaA), (5) (BbF), (6) (BkF), (7) (BaP), (8) (INPY), (9) (BghiP), (10) (DiahA).