



# Development of micro-solid phase extraction with titanate nanotube array modified by cetyltrimethylammonium bromide for sensitive determination of polycyclic aromatic hydrocarbons from environmental water samples

Yunrui Huang<sup>a,d</sup>, Qingxiang Zhou<sup>a,b,\*</sup>, Guohong Xie<sup>c</sup>

<sup>a</sup> School of Chemistry and Environmental Sciences, Henan Normal University, Henan Key Laboratory for Environmental pollution Control, Key Laboratory for Yellow River and Huaihe River Water Environment and Pollution Control, Ministry of Education, Xinxiang 453007, PR China

<sup>b</sup> State Laboratory of Petroleum Resource and Prospecting, College of Geosciences, China University of Petroleum Beijing, Beijing 102249, PR China

<sup>c</sup> College of Resources and Environment, Henan Institute of Science and Technology, Xinxiang 453003, PR China

<sup>d</sup> College of Chemistry and Pharmacy Engineering, Nan Yang Normal University, Nan Yang, 473061, PR China

## ARTICLE INFO

### Article history:

Received 11 March 2011

Received in revised form 4 July 2011

Accepted 7 July 2011

Available online 18 July 2011

### Keywords:

Micro-solid phase extraction

Polycyclic aromatic hydrocarbon

Ordered TiO<sub>2</sub> nanotube array

High performance liquid chromatography

## ABSTRACT

This paper described a simple and novel analytical technique for the determination of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. A micro-solid phase extraction ( $\mu$ -SPE) was developed utilizing cetyltrimethylammonium bromide modified ordered TiO<sub>2</sub> nanotube array. The experimental results indicated that modified TiO<sub>2</sub> nanotube arrays demonstrated an excellent merit on the preconcentration of PAHs, and there were excellent linear relationships between peak area and the concentration of PAHs in the range of 0.2–100  $\mu\text{g L}^{-1}$  and 1.0–100  $\mu\text{g L}^{-1}$ , respectively. The detection limits of proposed method for the targeted PAHs were in the range of 0.026–0.82  $\mu\text{g L}^{-1}$  ( $S/N=3$ ). The real-world environmental water samples were used to validate the applicability of the proposed method and good spiked recoveries were in the range of 75.0–114%. All these results demonstrated that this new  $\mu$ -SPE technique was a viable alternative to conventional enrichment techniques for the extraction and analysis of PAHs in complex samples.

© 2011 Elsevier B.V. All rights reserved.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a widely distributed group of organic pollutants, and are known to be strongly mutagenic and/or carcinogenic, especially for the PAHs containing four or more aromatic rings [1,2]. Some PAHs are suspected to be endocrine disrupters and much more attention has been focused on their possible biological effects on human health [3]. So far, over 100 PAHs have been known to occur naturally, and 16 of them are on the priority pollutant list of the US Environmental Protection Agency (EPA) on the basis of occurrence and carcinogenicity [4].

Many modern analytical techniques have been developed and subsequently applied for the monitoring of PAHs in the natural environment [5]. Their determination in water is difficult because their levels in water are very low due to their low solubility in water. In general, a preconcentration procedure is needed before

the analysis to assure the accuracy and sensitivity of the developed method. The selection of preconcentration technique is commonly on the basis of the extraction efficiency, selectivity, its simplicity of operation, low consumption of solvent, rapidity, the ease of automation, sample throughput and cost, etc. Current techniques for the preconcentration of PAHs from environmental samples are solvent extraction [6,7], solid phase extraction (SPE) [8–14], solid-phase microextraction (SPME) [15–20], pressurized liquid extraction (PLE) [21] and supercritical fluid extraction (SFE) [22]. When combined with HPLC, SPE is the most common technique of sample preparation with merits such as simplicity, high preconcentration efficiency and short time-consumption [10,23].

Many research groups [24–30] have explored the application of several nanosize SPE sorbents. Nanomaterials can offer several advantages over traditional SPE sorbents such as very large surface areas, which will result in high extraction capacity and high extraction efficiencies. However, the use of nanomaterials has some limitations. When packed column dynamic extraction mode is used, the nanosize sorbents packed SPE column exhibits high backpressure, which makes it very difficult to adopt high flow rates. When the disperse batch mode is used, the nanosize sorbents are often difficult to be separated and reused. Because of these disadvantages, it is necessary to develop new nanosize SPE methods that can be applied to preconcentrate and separate organic compounds

\* Corresponding author at: School of Chemistry and Environmental Sciences, Henan Normal University, Henan Key Laboratory for Environmental pollution Control, Key Laboratory for Yellow River and Huaihe River Water Environment and Pollution Control, Ministry of Education, Xinxiang 453007, PR China.  
Tel.: +86 10 89732300; fax: +86 10 89732300.

E-mail address: [zhouqx@henannu.edu.cn](mailto:zhouqx@henannu.edu.cn) (Q. Zhou).

from environmental water samples. Recently, a unique micro-solid-phase extraction ( $\mu$ -SPE) has been reported [31,32], and this method provided a new approach for method development.

Nowadays, highly ordered TiO<sub>2</sub> nanotube array, as a new nanomaterial of TiO<sub>2</sub> nanotubes, has been an attractive approach for many important engineering applications. These potential applications include photoelectrochemical hydrogen generation, solar cells, hydrogen storage, gas sensing, templates for growth of compound semiconductor nanowires for radiation sensing, substrate for high interfacial bond strength hydroxyl apatite coating in implants, biomedical applications, as catalyst supports and photoelectrocatalytic activity electrode for organic contaminant degradation [33–35]. However, to the best of our knowledge, there have very few reports using TiO<sub>2</sub> nanotube array on the enrichment and measurement of environmental pollutants, except that our group developed a new enrichment method with TiO<sub>2</sub> nanotube array for the determination of organochlorine pesticides, which had demonstrated that TiO<sub>2</sub> nanotube array earned excellent adsorption capacity for organochlorine pesticides [36]. TiO<sub>2</sub> nanotube array offer several advantages over the traditional microsize sorbents such as larger surface area, higher adsorption capacity, more easily to prepare large enrichment equipment, and higher possibility for cycle use.

The surfactants could be adsorbed to the surface of mineral oxides through attractive electrostatic interactions between the charged mineral oxide surface and the oppositely charged surfactant head group resulting in the formation of monolayers of adsorbed surfactant termed hemimicelles. After saturation of the mineral oxide surface, hydrophobic interactions between hydrocarbon chains of surfactant molecules result in the formation of admicelles [37–39]. In term of hemimicelles, the hydrophobic tails are exposed to aqueous solution, so the surfactant-coated TiO<sub>2</sub> nanotube surface will become hydrophobic, which favors the adsorption of non-ionic organic compounds onto the sorbents. Since possessing larger special areas and more ion-exchangeable OH groups on surface, TiO<sub>2</sub> nanotube materials are expected to have obvious advantage for the sorption of ionic surfactant, and behave remarkable adsorption capability to organic compounds correspondingly [40]. The present work was intended to assess the use of cetyltrimethylammonium bromide (CTAB) coated titanate nanotube array for the extraction of PAHs, and evaluate their applicability for the analysis of PAHs in natural waters.

## 2. Experimental

### 2.1. Chemicals and reagents

A mixed-PAH standard containing the Environmental Protection Agency (EPA) priority 16 PAHs was purchased from AccuStandard, Inc. (USA) including acenaphthene (Ace), acenaphthylene (Acy), anthracene (An), 1,2-benzoanthracene (BaA), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(ghi)perylene (BghiP), benzo(k)fluoranthene (BkF), chrysene (Chry), dibenzo(a,h)anthracene (DiahA), fluoranthene (Flt), fluorene (Flu), indeno(1,2,3-cd)pyrene (Inpy), naphthalene (Naph), phenanthrene (Ph), and pyrene (Pyr). The concentration of each compound in the mixture was 200 mg L<sup>-1</sup>. A working stock solution (20 mg L<sup>-1</sup>) of PAHs was prepared in HPLC grade methanol with the standard solution. All the standard solutions were stored at 4 °C in the refrigerator. The aqueous solutions were prepared daily by diluting the standard mixture with ultrapure water. The solubility of such compounds was listed in Table 1 [41]. HPLC grade methanol and acetonitrile were obtained from Jiangsu Guoda Chemical Reagent Co., Ltd. (Huaian, China). Cetyltrimethylammonium bromide was obtained from Beijing

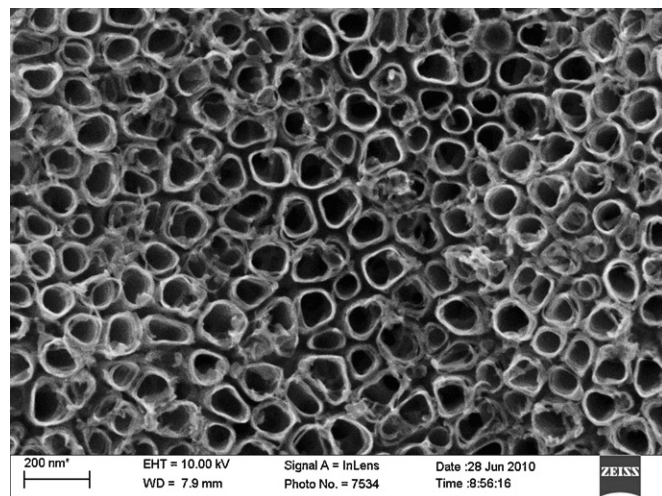


Fig. 1. FESEM images of top-view of TiO<sub>2</sub> nanotube arrays.

Xinjingke biotechnology Co., Ltd. (Beijing, China). Ultrapure water was prepared in the laboratory using a SZ-93 automatic double pure distillatory from Shanghai Yarong Biochemical Instrument Factory (Shanghai, China) and all the other solvents were analytical reagent grade unless otherwise stated. 1% sodium hydroxide and 1 mol L<sup>-1</sup> hydrochloric acid were used for adjusting the pH value of the water samples.

Titanium sheets (99.6% purity) from Beijing Hengli Taiye Co., Ltd. (Beijing, China), Pt electrode was obtained from Shanghai Ruosull Technology Co. Ltd. (Shanghai, China). A 30 V potentiostat was obtained from Shijiazhuang The Fourth Radio Factory (JWY-30G, Shijiazhuang, China)

### 2.2. Preparation and identification of TiO<sub>2</sub> nanotube array

Titanium sheets (0.2 mm thick, 20 × 20 mm size) with 99.6% purity (Beijing, China) were polished with metallographic abrasive paper, and then degreased by sonicating in acetone, isopropanol and methanol, respectively. The sheets were air-dried after rinsing with ultrapure water. The anodic oxidation was accomplished by using titanium sheet as anode and platinum as cathode. The distance between two electrodes was 3 cm in all experiments. The electrolyte was composed of 0.14 M NaF and 0.5 M H<sub>3</sub>PO<sub>4</sub>. The anodic oxidation was carried out at 20 V for 1 h. After electrolysis, titanium sheet was rinsed with ultrapure water and then air-dried. Prepared TiO<sub>2</sub> nanotube arrays were then analyzed with a field emission scanning electron microscope (SUPRA<sup>TM</sup> 55 FESEM, Germany) (see Fig. 1).

### 2.3. $\mu$ -SPE procedure

The TiO<sub>2</sub> nanotube array sheet was cleaned with organic solvent and water and then directly immersed in the 10 mL solution with a constant depth and then the sample vial was sealed. The extraction conditions were as the same of the optimized conditions. The stirring rate of the magnetic stirrer was set at 500 rpm. After the equilibrium between adsorption and desorption basically reached, the TiO<sub>2</sub> nanotube array sheet was taken out and rinsed with ultrapure water in order to remove co-adsorbed matrix substances and then air-dried. TiO<sub>2</sub> nanotube array sheet was directly immersed in a small amount of dichloromethane for complete desorption in an interval of 6 min. Afterwards, the TiO<sub>2</sub> nanotube array sheet was removed, and the dichloromethane was dried with mild stream of nitrogen gas. Then the residue was dissolved in 100  $\mu$ L methanol.

**Table 1**  
The solubilities of PAHs in water at 25 °C.

	Compounds							
	Naph	Acy	Ace	Flu	Ph	An	Flt	Pyr
Solubility (25 °C, mg L <sup>-1</sup> )	33.8	6.7	3.0	1.7	0.6	0.6	0.1	0.1
	Compounds							
	BaA	Chry	BbF	BkF	BaP	DiahA	BghiP	Inpy
Solubility (25 °C, mg L <sup>-1</sup> )	0.02	0.02	0.002	0.06	0.002	0.004	0.006	0

Finally, 20  $\mu\text{L}$  of the solution was injected for HPLC analysis. The schematic of  $\mu\text{-SPE}$  was demonstrated in Fig. 2.

#### 2.4. SPE procedure

A SPE procedure was performed for comparison and the enrichment conditions were as reported in Ref. [8]. The SPE cartridges (Agilent ZORBAX SPE C18 cartridge, 0.2 g, 3 mL polypropylene) were conditioned with 5 mL of dichloromethane, then 4 mL of methanol or 2-propanol, depending on the organic modifier of the sample, and finally 4 mL of methanol–water or 2-propanol–water mixture. Extraction of 10 mL solution, was carried out under vacuum at a flow rate of 5 mL min<sup>-1</sup>. Subsequently, the cartridge was washed with 3 mL of ultrapure water and dried under a certain negative pressure for 15 min. Analytes were eluted with 2 mL of dichloromethane. The eluents were dried under a stream of N<sub>2</sub> gas, and the residue was reconstituted with 100  $\mu\text{L}$  of methanol. 20  $\mu\text{L}$  of the solution was injected for HPLC analysis.

#### 2.5. HPLC analysis

A high-performance liquid chromatography system, which consisted of two LC-10ATvp pumps and an SPD-10Avp, ultraviolet Detector (Shimadzu, Japan) was used for the separation and analysis. A reversed-phase SunFire™ C18 column (150 mm  $\times$  4.6 mm, particle size 5  $\mu\text{m}$ , Waters Corporation) was used for separation at ambient temperature and Chromato-Solution Light Chemstation for LC system was employed to acquire and process chromatographic data. The mobile phase was obtained with methanol–water (80/20, v/v), and the flow rate, the injection volume and detection wavelength was 1.0 mL min<sup>-1</sup>, 20  $\mu\text{L}$  and 254 nm, respectively.

#### 2.6. Water samples

In this work, four environmental water samples such as rainwater, river water, canal water and water from the outlet of wastewater treatment plant were collected for validating

the proposed method. Rainwater samples were collected from Henan Normal University, Xinxiang, Henan Province, China. River water was collected from Baihe River, Nanyang, Henan Province, China. Canal water was collected from Gongchanzhuyi Canal, Xinxiang, Henan Province, China. The water sample from the outlet of wastewater treatment plant water sample was collected from Luotuowan Wastewater Treatment Plant, Xinxiang, Henan province, China. All the collected water samples were filtered through 0.45  $\mu\text{m}$  micropore membranes after sampling and were maintained in glass containers, then stored at 4 °C.

### 3. Results and discussion

#### 3.1. Optimization of $\mu\text{-SPE}$ procedure

In this  $\mu\text{-SPE}$  procedure, several factors affect the extraction. It is not as the same of conventional solid phase extraction. The adsorption of analytes onto the sorbents is a reversible procedure, and some of them may be desorbed at the same time. When these two steps reached the equilibrium, the best enrichment would be achieved. The parameters including concentration of CTAB, the type of organic solvents, sample pH, extraction time, desorption time, and salting-out effect would influence the enrichment efficiency. In order to obtain appropriate extraction efficiency, an optimization procedure was necessary.

#### 3.2. Effect of CTAB concentration

Surfactant molecules have a polar and non-polar moiety, so they can dissolve in water as monomers or be incorporated with other molecules to form a micelle. Critical micelle concentration (CMC), which is the concentration that they start to form a micelle, depends on various factors. When the hydrophobic part of the amphiphile is a hydrocarbon chain, the micelles will consist of a hydrocarbon core with polar groups at the surface, which serve to maintain solubility in water. In order to evaluate the effect of CTAB on the extraction efficiency, different concentration of CTAB from 0 to 150 mg L<sup>-1</sup>

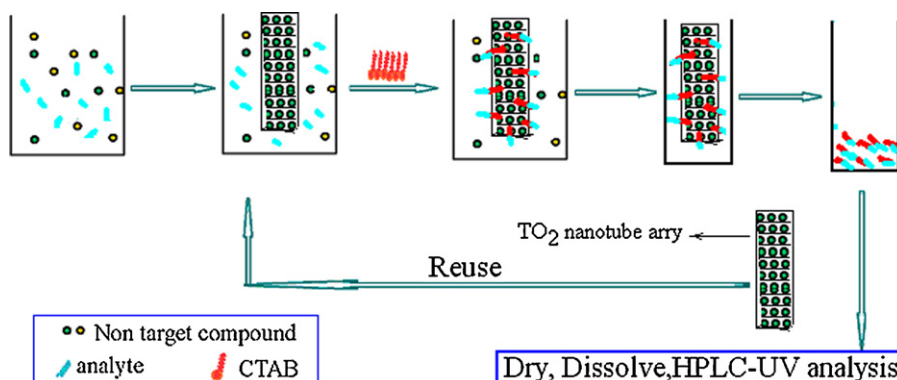
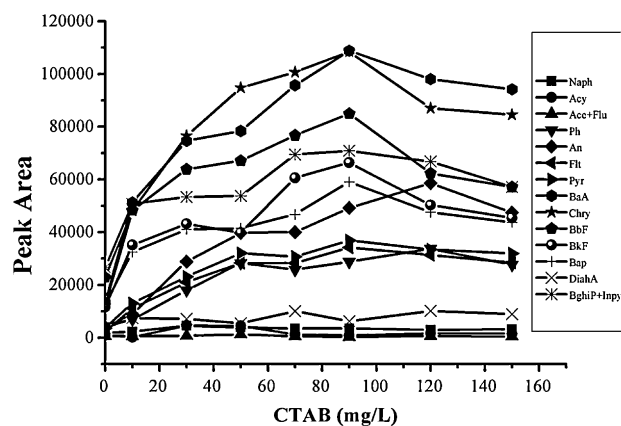


Fig. 2. Schematic of  $\mu\text{-SPE}$  procedure.



**Fig. 3.** Effect of CTAB concentration. Conditions: pH, 7; equilibrium time, 60 min; NaCl, 0%; organic solvent, dichloromethane; desorption time, 5 min; spiked sample concentration,  $10 \mu\text{g L}^{-1}$  for each compound.

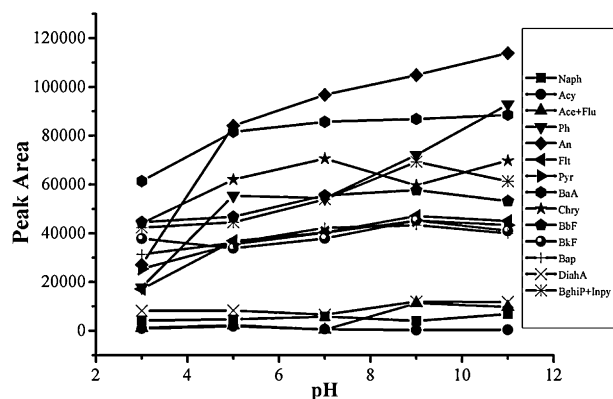
were added to a spiked ultrapure water sample and the experimental results were shown in Fig. 3. As can be seen that the maximum peak were obtained at a CTAB content of  $90 \text{ mg L}^{-1}$ . The reason is that CTAB is saturated on the surface of the  $\text{TiO}_2$  nanotubes. So  $90 \text{ mg L}^{-1}$  CTAB is adopted in further experiments.

### 3.3. Effect of the kind organic solvents

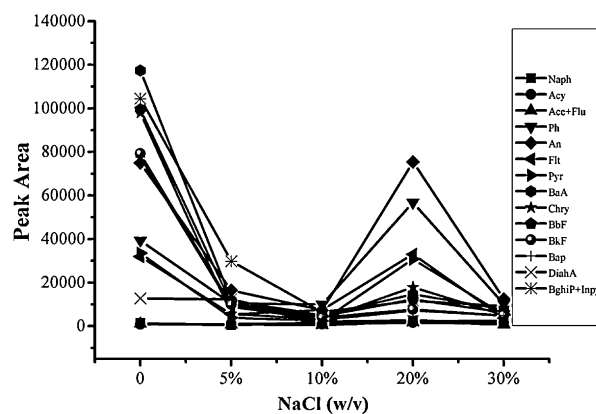
As far as a  $\mu$ -SPE procedure is concerned, different desorption efficiency would be obtained when different solvents are used because of the different physical and chemical properties of the organic solvents and the different characteristics of the target analytes. In this experiment, five types of solvents such as methanol, acetonitrile, acetone, hexane, dichloromethane and toluene were tested for the desorption of polycyclic aromatic hydrocarbons from the  $\text{TiO}_2$  nanotube array sheet. The results were exhibited that dichloromethane was the most effective solvent for the desorption of analytes. Moreover dichloromethane was easily evaporated in the concentration procedure. So it was used as the solvent for desorption.

### 3.4. Effect of sample pH

Sample pH plays an important role in the extraction procedure because pH value determines the existing form of the analytes, and then the sample pH affects the extraction efficiency. In this experiment, the effect of sample pH on the enrichment of polycyclic



**Fig. 4.** Effect of sample pH. Conditions: CTAB concentration,  $90 \text{ mg L}^{-1}$ ; organic solvent, dichloromethane; equilibrium time, 60 min; NaCl, 0%; desorption time, 5 min; spiked sample concentration,  $10 \mu\text{g L}^{-1}$  for each compound.

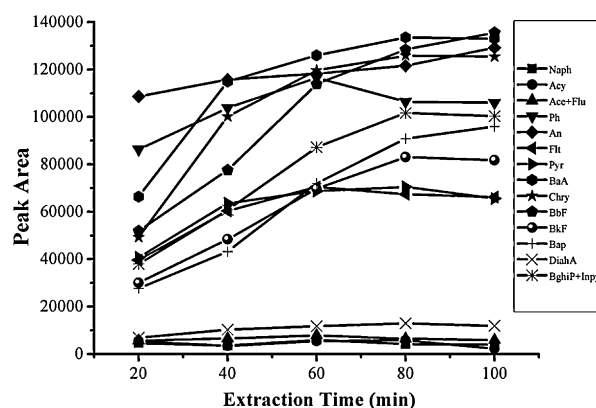


**Fig. 5.** Effect of salt effect. Conditions: CTAB concentration,  $90 \text{ mg L}^{-1}$ ; organic solvent, dichloromethane; equilibrium time, 60 min; pH, 7; desorption time, 5 min; spiked sample concentration,  $10 \mu\text{g L}^{-1}$  for each compound.

aromatic hydrocarbons was evaluated in the range of pH 3.0–11.0 (see Fig. 4). As can be seen, the peak area of polycyclic aromatic hydrocarbons was small, and the uptakes enhanced gradually with the increase of solution pH in the acidic solution. The maximum peak area for most analytes appeared at pH 7 on CTAB-titanate nanotube system. The reason is that  $\text{TiO}_2$  is an amphoteric material with the isoelectric point of 5, so it shows basic character in solutions of  $\text{pH} > 5$ . Since negative charges were favorable for the adsorption of cationic surfactant, the maximum uptake occurred when the pH value was higher than the isoelectric point of  $\text{TiO}_2$ . The highest retention for all analytes was obtained when the sample pH was near to pH 7. Generally, the adsorption was favored at high pH. Therefore, pH 7 is adopted in further experiments.

### 3.5. Salting-out effect

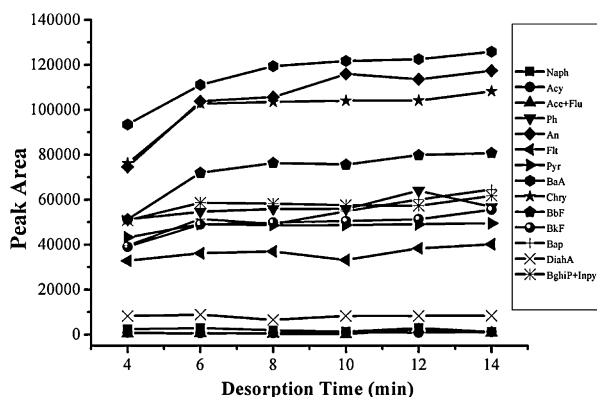
Salting-out effect is often an important factor in the enrichment procedure. In these experiments, it was optimized in the range of 0–30% (w/v), and the results were shown in Fig. 5. It can be seen from Fig. 5, the peak area increased with the increase of NaCl concentration, when the concentration of NaCl changed from 10% to 20%. However, the peak area decreased with the increase of NaCl concentration when the concentration of NaCl increased from 20% to 30%. When no NaCl was added in the sample solution, the peak area is much larger than that with the addition of NaCl. The reason is that the addition of NaCl suppressed the thickness of electrical adsorption layer at the  $\text{TiO}_2$  solution interface, which led to the decrease of mixed hemimicelles formed on the  $\text{TiO}_2$  surface.



**Fig. 6.** Effect of equilibrium time. Conditions: CTAB concentration,  $90 \text{ mg L}^{-1}$ ; organic solvent, dichloromethane; NaCl, 0%; pH, 7; desorption time, 5 min; spiked sample concentration,  $10 \mu\text{g L}^{-1}$  for each compound.

**Table 2**  
Linear ranges, correlation coefficients, precisions and detection limits (S/N = 3) of  $\mu$ -SPE.

Compound	Linear range ( $\mu\text{g L}^{-1}$ )	$R^2$	Intraday precision (RSD%, n = 6)	Interday precision (RSD%, n = 6)	LOD ( $\mu\text{g L}^{-1}$ )
Naph	0.2–100	0.989	5.5	7.8	0.18
Acy	0.2–100	0.987	3.8	4.6	0.1
Ace + Flu	0.2–100	0.985	5.4	5.2	0.12
Ph	0.2–100	0.999	8.6	10.1	0.026
An	0.2–100	0.997	9.5	11.2	0.058
Flt	0.2–100	0.999	6.6	8.5	0.12
Pyr	0.2–100	0.999	8.1	10.1	0.12
BaA	0.2–100	0.9873	5.7	7.2	0.033
Chry	0.2–100	0.996	9.3	11.0	0.082
BbF	0.2–100	0.998	7.4	8.9	0.043
BkF	0.2–100	0.988	7.8	7.5	0.047
BaP	0.2–100	0.991	9.5	12.0	0.10
DiahA	1–100	0.989	9.8	11.0	0.82
BghiP + Inpy	0.2–100	0.993	9.3	9.6	0.093



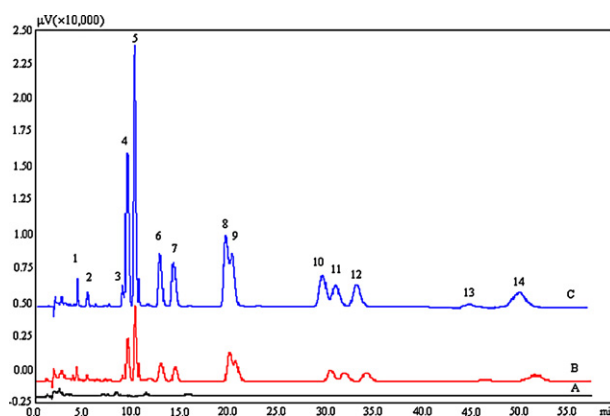
**Fig. 7.** Effect of desorption time. Conditions: CTAB concentration,  $90 \text{ mg L}^{-1}$ ; organic solvent, dichloromethane; NaCl, 0%; pH, 7; equilibrium time, 60 min; spiked sample concentration,  $10 \mu\text{g L}^{-1}$  for each compound.

### 3.6. Effect of equilibrium extraction time

As an equilibrium extraction step is concerned, an important factor is the equilibrium extraction time. If this time is short, good enrichment performance could not be obtained because the adsorption does not reach the equilibrium. But it will squander much time if the extraction time is too long. Hence, a series of experiments were designed for investigation of the effects of extraction time in the range of 20–100 min. The results were shown in Fig. 6. From Fig. 6, it could be seen that peak areas of polycyclic aromatic hydrocarbons increased with the increase of time up to 60 min. So 60 min was used as the extraction time. In fact, 60 min is sufficient

**Table 3**  
Linear ranges, correlation coefficients, precisions and detection limits (S/N = 3) of SPE.

Compound	Linear range ( $\mu\text{g L}^{-1}$ )	$R^2$	Intraday precision (RSD%, n = 6)	Interday precision (RSD%, n = 6)	LOD ( $\mu\text{g L}^{-1}$ )
Naph	0.5–100	0.982	8.3	8.9	0.27
Acy	0.5–100	0.981	9.2	6.8	0.19
Ace + Flu	0.2–100	0.994	5.6	7.9	0.081
Ph	0.2–100	0.994	8.4	5.2	0.013
An	0.2–100	0.995	4.3	6.1	0.011
Flt	0.2–100	0.997	1.7	4.6	0.048
Pyr	0.2–100	0.997	2.8	8.1	0.069
BaA	0.2–100	0.985	1.8	7.8	0.047
Chry	0.2–100	0.986	3.2	9.7	0.081
BbF	0.2–100	0.985	0.8	5.2	0.12
BkF	0.2–100	0.990	4.3	8.2	0.16
BaP	0.2–100	0.992	1.4	4.5	0.14
DiahA	0.5–100	0.988	4.8	6.8	0.48
BghiP + Inpy	0.5–100	0.988	2.2	4.6	0.18



**Fig. 8.** Typical chromatograms of river water samples. A. Blank of river water sample; B. river water sample spiked with  $5.0 \mu\text{g L}^{-1}$  for each compound; C. river water sample spiked with  $20 \mu\text{g L}^{-1}$  for each compound; Conditions: CTAB concentration,  $90 \text{ mg L}^{-1}$ ; organic solvent, dichloromethane; NaCl, 0%; pH, 7; equilibrium time, 60 min; desorption time, 6 min; 1. Naph; 2. Acy; 3. Ace + Flu; 4. Ph; 5. An; 6. Flt; 7. Pyr; 8. BaA; 9. Chry; 10. BbF; 11. BkF; 12. BaP; 13. DiahA; 14. BghiP + Inpy.

to achieve satisfactory extraction efficiency on the whole, and the equilibrium has almost reached. At the same time, with the consideration of the total operation time, the extraction time was set at 60 min.

### 3.7. Effect of desorption time

In the  $\mu$ -SPE procedure, two steps are very important, one is the adsorption of analytes on the surface of adsorbents, and the

**Table 4**  
Recoveries of real water samples spiked at two concentration levels of  $\mu$ -SPE.

Water samples	Added levels ( $\mu\text{gL}^{-1}$ )	Naph	Acy	Ace + Flu	Ph	An	Flt	Pyr	BaA	Chyr	BbF	BkF	BaP	DiahA	BghiP + Inpy
Rain water	Blank	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	114.0 $\pm$ 7.1	92.0 $\pm$ 3.0	93.7 $\pm$ 6.3	94.6 $\pm$ 5.2	91.7 $\pm$ 3.9	94.4 $\pm$ 8.2	98.0 $\pm$ 5.1	94.5 $\pm$ 1.4	96.3 $\pm$ 2.5	92.7 $\pm$ 6.7	90.0 $\pm$ 9.3	103.0 $\pm$ 9.8	97.9 $\pm$ 7.4	104.0 $\pm$ 3.9
	20	99.1 $\pm$ 6.3	105 $\pm$ 4.2	104.0 $\pm$ 0.5	98.2 $\pm$ 9.3	99.9 $\pm$ 6.4	102.0 $\pm$ 4.9	104.0 $\pm$ 3.5	97.5 $\pm$ 9.0	108.0 $\pm$ 2.6	101.0 $\pm$ 1.6	101.0 $\pm$ 4.9	96.4 $\pm$ 2.9	94.7 $\pm$ 4.7	105.0 $\pm$ 2.8
Luotuowan water	Blank	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	97.3 $\pm$ 5.2	88.2 $\pm$ 6.8	94.6 $\pm$ 2.8	89.3 $\pm$ 4.0	101.0 $\pm$ 1.7	84.8 $\pm$ 8.8	88.4 $\pm$ 2.5	92.9 $\pm$ 3.3	93.8 $\pm$ 4.5	85.6 $\pm$ 2.1	77.7 $\pm$ 4.5	77.8 $\pm$ 1.1	87.4 $\pm$ 2.8	81.9 $\pm$ 6.4
	20	77.9 $\pm$ 4.4	85.1 $\pm$ 6.5	97.3 $\pm$ 6.8	99.1 $\pm$ 3.3	95.7 $\pm$ 7.2	93.6 $\pm$ 5.5	82.8 $\pm$ 6.4	85.2 $\pm$ 4.3	89.6 $\pm$ 2.8	99.7 $\pm$ 3.8	75.0 $\pm$ 6.3	81.4 $\pm$ 9.2	93.2 $\pm$ 6.4	92.1 $\pm$ 9.2
Baihe River water	Blank	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	85.8 $\pm$ 5.4	78.0 $\pm$ 9.1	103.0 $\pm$ 2.2	98.5 $\pm$ 2.6	103.0 $\pm$ 6.3	91.0 $\pm$ 7.1	94.9 $\pm$ 4.7	105.0 $\pm$ 9.6	91.2 $\pm$ 9.2	97.7 $\pm$ 9.4	96.6 $\pm$ 8.8	104.0 $\pm$ 2.5	98.4 $\pm$ 5.9	96.4 $\pm$ 3.8
	20	88.2 $\pm$ 3.7	95.4 $\pm$ 9.7	102.0 $\pm$ 4.7	102.0 $\pm$ 5.0	106.0 $\pm$ 2.1	105.0 $\pm$ 0.9	99.2 $\pm$ 1.9	103.0 $\pm$ 3.5	101.0 $\pm$ 2.3	105.0 $\pm$ 4.2	101.0 $\pm$ 5.0	88.9 $\pm$ 6.9	105.0 $\pm$ 3.7	108.0 $\pm$ 4.8
Gongchanzhuyi Channel water	Blank	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	98.3 $\pm$ 4.6	76.6 $\pm$ 6.4	80.1 $\pm$ 7.7	94.0 $\pm$ 5.8	99.5 $\pm$ 3.1	94.2 $\pm$ 9.5	92.3 $\pm$ 7.6	83.4 $\pm$ 5.4	96.8 $\pm$ 3.5	82.8 $\pm$ 5.5	88.5 $\pm$ 6.7	99.7 $\pm$ 5.2	112.0 $\pm$ 7.0	112.0 $\pm$ 4.6
	20	96.7 $\pm$ 9.9	99.9 $\pm$ 5.7	96.9 $\pm$ 8.8	98.0 $\pm$ 4.5	79.7 $\pm$ 6.2	99.8 $\pm$ 1.2	91.3 $\pm$ 1.1	90.4 $\pm$ 9.8	83.2 $\pm$ 7.6	107.0 $\pm$ 7.1	106.0 $\pm$ 2.9	100.0 $\pm$ 1.1	101.0 $\pm$ 4.5	112.0 $\pm$ 8.6

**Table 5**  
Recoveries of real water samples spiked at two concentration levels of SPE.

Water samples	Blank	Added levels ( $\mu\text{gL}^{-1}$ )	Naph	Acy	Ace + Flu	Ph	An	Flt	Pyr	BaA	Chyr	BbF	BkF	BaP	DiahA	BghiP + Inpy
Rain Water	N.D.	5	59.5 $\pm$ 6.0	68.0 $\pm$ 5.1	67.8 $\pm$ 5.6	77.5 $\pm$ 2.8	71.7 $\pm$ 3.4	88.5 $\pm$ 5.4	98.0 $\pm$ 5.9	83.6 $\pm$ 5.6	95.3 $\pm$ 4.5	91.3 $\pm$ 5.2	91.8 $\pm$ 3.4	87.9 $\pm$ 2.7	90.0 $\pm$ 2.4	98.0 $\pm$ 1.0
	N.D.	20	56.2 $\pm$ 9.5	55.6 $\pm$ 5.2	71.8 $\pm$ 0.4	62.4 $\pm$ 1.3	85.2 $\pm$ 2.4	88.6 $\pm$ 1.9	94.6 $\pm$ 0.5	99.9 $\pm$ 9.0	108.0 $\pm$ 0.6	97.9 $\pm$ 1.8	95.7 $\pm$ 2.4	90.5 $\pm$ 6.1	93.0 $\pm$ 0.4	92.7 $\pm$ 0.5
Luotuowan Water	N.D.	5	52.2 $\pm$ 3.6	65.7 $\pm$ 0.4	69.5 $\pm$ 7.1	70.2 $\pm$ 5.4	80.8 $\pm$ 5.7	88.4 $\pm$ 4.0	89.3 $\pm$ 1.3	95.2 $\pm$ 1.4	92.8 $\pm$ 4.7	93.1 $\pm$ 1.4	104.5 $\pm$ 2.0	91.5 $\pm$ 1.4	98.6 $\pm$ 6.0	88.4 $\pm$ 1.9
	N.D.	20	53.8 $\pm$ 2.5	55.7 $\pm$ 2.4	61.5 $\pm$ 5.3	83.7 $\pm$ 1.1	86.1 $\pm$ 0.8	89.1 $\pm$ 1.4	91.0 $\pm$ 0.8	86.5 $\pm$ 3.8	85.1 $\pm$ 1.2	91.0 $\pm$ 5.3	86.6 $\pm$ 0.3	80.9 $\pm$ 4.5	86.4 $\pm$ 2.9	95.6 $\pm$ 0.8
Baihe River water	N.D.	5	51.7 $\pm$ 3.9	62.8 $\pm$ 2.1	58.9 $\pm$ 1.7	68.5 $\pm$ 2.6	76.2 $\pm$ 6.5	94.8 $\pm$ 1.1	95.6 $\pm$ 2.2	96.8 $\pm$ 0.2	87.2 $\pm$ 4.0	87.7 $\pm$ 1.3	81.3 $\pm$ 5.0	80.4 $\pm$ 2.7	87.0 $\pm$ 1.0	95.3 $\pm$ 1.4
	N.D.	20	51.1 $\pm$ 8.3	61.2 $\pm$ 2.7	67.0 $\pm$ 1.5	88.6 $\pm$ 0.8	83.6 $\pm$ 1.2	89.1 $\pm$ 2.7	94.8 $\pm$ 0.8	84.2 $\pm$ 2.1	82.5 $\pm$ 1.5	117.0 $\pm$ 0.8	82.5 $\pm$ 1.8	83.2 $\pm$ 2.5	84.5 $\pm$ 2.4	90.0 $\pm$ 1.6
Gongchanzhuyi Channel water	N.D.	5	54.2 $\pm$ 6.4	62.9 $\pm$ 9.7	67.0 $\pm$ 7.8	72.0 $\pm$ 8.6	78.1 $\pm$ 2.8	89.6 $\pm$ 1.5	94.6 $\pm$ 9.4	88.1 $\pm$ 2.5	112.0 $\pm$ 4.7	100.0 $\pm$ 3.1	99.6 $\pm$ 4.0	96.4 $\pm$ 2.5	87.1 $\pm$ 9.2	92.5 $\pm$ 6.9
	N.D.	20	57.7 $\pm$ 6.4	50.1 $\pm$ 5.3	63.8 $\pm$ 1.3	84.8 $\pm$ 0.5	82.2 $\pm$ 0.7	97.8 $\pm$ 1.0	100.0 $\pm$ 1.1	84.7 $\pm$ 1.1	87.5 $\pm$ 2.0	90.7 $\pm$ 2.7	85.4 $\pm$ 7.7	84.8 $\pm$ 8.1	75.0 $\pm$ 2.0	92.0 $\pm$ 2.2

other is the desorption of analytes from the adsorbents. Ideally these two procedures are very rapid. In fact, the procedure may be various due to different conditions. Desorption of polycyclic aromatic hydrocarbons from the TiO<sub>2</sub> nanotube array sheet with the dichloromethane is controlled by the time. In order to achieve complete desorption of PAHs, the desorption time was investigated in the range of 4–12 min and the results were exhibited in Fig. 7. It was found that the PAHs reached the best desorption in 6 min, so 6 min was optioned in subsequent experiments.

### 3.8. Features of the proposed method

As the optimum experimental conditions were determined, the parameters such as the linear range, correlation coefficients, limits of detection (LODs) and precisions were evaluated and the results were listed in Table 2. A comparison between SPE method and present method was carried out and the results were listed in Table 3. It was found that these two method have excellent linearity between the peak area and concentration over the range of 0.2–100 µg L<sup>-1</sup> for Naph, Acy, Ace + Flu, Ph, An, Flt, Pyr, BaA, Chry, BbF, BkF, BaP, BghiP + Inpy; 1.0–100 µg L<sup>-1</sup> for DiahA. The limits of detection of µ-SPE calculated on the basis of the ratio of signal to noise (S/N=3) were in the range of 0.026–0.82 µg L<sup>-1</sup> and close to the SPE. The precision of two analytical methods were investigated using six replicate experiments with 10 mL standard solution containing each of the PAHs at 5.0 µg L<sup>-1</sup>, and the relative standard deviations (RSD) were all below 10.0% (intraday).

### 3.9. Analysis of real water samples

Four samples of environmental water were extracted using µ-SPE procedures. No target analytes were detected. Thus, environmental water samples were spiked with target analytes at 5 and 20 µg L<sup>-1</sup> to assess matrix effects and the extraction performance was evaluated. The results were shown in Table 4. The typical chromatograms of real water sample were demonstrated in Fig. 8. The spiked recoveries were satisfied in the range of 75.0–114%. A comparison was made between present method and the conventional SPE, and the results were listed in Table 5. From the table, we can see that the merits of present method are obvious. The recoveries of most PAHs with C18 SPE were lower than that obtained with ordered TiO<sub>2</sub> nanotube array.

## 4. Conclusions

The present study established a new method for the enrichment and measurement of PAHs in water samples with ordered TiO<sub>2</sub> nanotube array. A micro-solid phase extraction (µ-SPE) was developed for the enrichment of PAHs prior to the analysis of high performance liquid chromatography. The experimental results indicated that a good separation of PAHs was achieved with an isostatic elution avoiding the baseline drift of the gradient elution. The CTAB modified TiO<sub>2</sub> nanotube arrays demonstrated excellent enrichment ability PAHs, and excellent linear relationships between peak area and the concentration of PAHs were obtained. The detection limits of proposed method for the targeted PAHs were in the range of 0.026–0.82 µg L<sup>-1</sup> (S/N=3). The real-world environmental water samples analysis validated the applicability of the proposed method and the spiked recoveries were in the range of 75.0–114%. All these indicated that this new µ-SPE technique would be a good selection and have a great prospect in the monitoring of environmental pollutants in complex samples.

## Acknowledgements

This work was supported by the Natural Science Foundation of China (20877022), Program for New Century Excellent Talents in University (NCET-10-0813), and the Natural Science Foundation of Henan Province (082102350022).

## References

- [1] C. Madichie, G.M. Greenway, T. McCreedy, The effects of surfactants on the analysis of organic pollutants in natural waters, *Anal. Chim. Acta* 392 (1999) 39–46.
- [2] P.J. Tsai, H.Y. Shieh, W.J. Lee, S.O. Lai, Characterization of PAHs in the atmosphere of carbon black manufacturing workplaces, *J. Hazard. Mater. A* 91 (2005) 5–42.
- [3] N. Kishikawa, M. Wada, N. Kuroda, S. Akiyama, K. Nakashima, Determination of polycyclic aromatic hydrocarbons in milk samples by high-performance liquid chromatography with fluorescence detection, *J. Chromatogr. B* 789 (2003) 257–264.
- [4] US Environmental Protection Agency, Guidelines establishing test procedures for the analysis of pollutants, Proposed regulations, Federal Register, vol. 49, no. 209, USEPA, Washington, DC.
- [5] T. Wenzl, R. Simon, J. Kleiner, E. Anklam, Analytical methods for polycyclic aromatic hydrocarbons (PAHs) in food and the environment needed for new food legislation in the European Union, *TrAC Trends Anal. Chem.* 25 (2006) 716–725.
- [6] S.G. Riddle, M.A. Robert, C.A. Jakober, M.P. Hannigan, M.J. Kleeman, Size distribution of trace organic species emitted from heavy-duty diesel vehicles, *Environ. Sci. Technol.* 41 (2007) 3850–3855.
- [7] Z. Zencak, J. Klanova, I. Holoubek, O. Gustafsson, Source apportionment of atmospheric PAHs in the western balkans by natural abundance radiocarbon analysis, *Environ. Sci. Technol.* 41 (2007) 3850–3855.
- [8] G. Kiss, Z. Varga-Puchony, J. Hlavay, Determination of polycyclic aromatic hydrocarbons in precipitation using solid-phase extraction and column liquid chromatography, *J. Chromatogr. A* 725 (1996) 261–272.
- [9] N. Li, H.K. Lee, Solid-phase extraction of polycyclic aromatic hydrocarbons in surface water: negative effect of humic acid, *J. Chromatogr. A* 921 (2001) 255–263.
- [10] L. Oliferova, M. Statkus, G. Tsysin, O. Shpigun, Y. Zolotov, On-line solid-phase extraction and HPLC determination of polycyclic aromatic hydrocarbons in water using fluorocarbon polymer sorbents, *Anal. Chim. Acta* 538 (2005) 35–40.
- [11] Y.Y. Zhou, X.P. Yan, K.N. Kim, S.W. Wang, M.G. Liu, Exploration of coordination polymer as sorbent for flow injection solid-phase extraction on-line coupled with high-performance liquid chromatography for determination of polycyclic aromatic hydrocarbons in environmental materials, *J. Chromatogr. A* 1116 (2006) 172–178.
- [12] W.D. Wang, Y.M. Huang, W.Q. Shu, J. Cao, Multiwalled carbon nanotubes as adsorbents of solid-phase extraction for determination of polycyclic aromatic hydrocarbons in environmental waters coupled with high-performance liquid chromatography, *J. Chromatogr. A* 1173 (2007) 27–36.
- [13] K. Li, H.F. Li, L.B. Liu, Y.K. Hashi, T. Maeda, J.M. Lin, Solid-phase extraction with C30 bonded silica for analysis of polycyclic aromatic hydrocarbons in airborne particulate matters by gas chromatography–mass spectrometry, *J. Chromatogr. A* 1154 (2007) 74–80.
- [14] R.M. Marcé, F. Borrull, Solid-phase extraction of polycyclic aromatic compounds, *J. Chromatogr. A* 885 (2000) 273–290.
- [15] M.S. García-Falcón, M. Pérez-Lamela, J. Simal-Gándara, Comparison of strategies for extraction of high molecular weight polycyclic aromatic hydrocarbons from drinking waters, *J. Agric. Food Chem.* 52 (2004) 6897–6903.
- [16] S.B. Hawthorne, C.B. Grabanski, D.J. Milier, J.P. Kreitinger, Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of *K<sub>DOC</sub>* values, *Environ. Sci. Technol.* 39 (2005) 2795–2803.
- [17] H. Bagheri, Z. Ayazi, A. Aghakhani, A novel needle trap sorbent based on carbon nanotube-sol-gel for microextraction of polycyclic aromatic hydrocarbons from aquatic media, *Anal. Chim. Acta* 683 (2011) 212–220.
- [18] J. López-Dariasa, V. Pinoa, Y.J. Meng, J.L. Anderson, A.M. Afonso, Utilization of a benzyl functionalized polymeric ionic liquid for the sensitive determination of polycyclic aromatic hydrocarbons; parabens and alkylphenols in waters using solid-phase microextraction coupled to gas chromatography-flame ionization detection, *J. Chromatogr. A* 1217 (2010) 7189–7197.
- [19] Y.J. Meng, J.L. Anderson, Tuning the selectivity of polymeric ionic liquid sorbent coatings for the extraction of polycyclic aromatic hydrocarbons using solid-phase microextraction, *J. Chromatogr. A* 1217 (2010) 6143–6152.
- [20] A. Ishizaki, K. Saito, N. Hanioka, S. Narimatsu, H. Kataoka, Determination of polycyclic aromatic hydrocarbons in food samples by automated on-line in-tube solid-phase microextraction coupled with high-performance liquid chromatography–fluorescence detection, *J. Chromatogr. A* 1217 (2010) 5555–5563.
- [21] M.R. Burkhardt, S.D. Zaugg, T.L. Burbank, M.C. Olson, J.L. Iverson, Pressurized liquid extraction using water/isopropanol coupled with solid-phase extraction cleanup for semivolatile organic compounds, polycyclic aromatic hydrocarbons

- (PAH), and alkylate PAH homolog groups in sediment, *Anal. Chim. Acta* 549 (2005) 104–116.
- [22] K. Hartonen, S. Bøwadt, H.P. Dybdahl, K. Nylund, S. Sparring, H. Lund, F. Orelid, Nordic laboratory intercomparison of supercritical fluid extraction for the determination of total petroleum hydrocarbon, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in soil, *J. Chromatogr. A* 958 (2002) 239–248.
- [23] F. Portet-Koltalo, K. Oukebdane, L. Robin, F. Dionnet, P.L. Desbène, Quantification of volatile PAHs present at trace levels in air flow by aqueous trapping-SPE and HPLC analysis with fluorimetric detection, *Talanta* 71 (2007) 1825–1833.
- [24] Q.X. Zhou, Y.J. Ding, J.P. Xiao, G.G. Liu, X.Y. Guo, Investigation of the feasibility of TiO<sub>2</sub> nanotubes for the enrichment of DDT and its metabolites at trace levels in environmental water samples, *J. Chromatogr. A* 1147 (2007) 10–16.
- [25] Y.R. Huang, Q.X. Zhou, J.P. Xiao, G.H. Xie, Determination of trace organophosphorus pesticides in water samples with TiO<sub>2</sub> nanotubes cartridge prior to GC-flame photometric detection, *J. Sep. Sci.* 33 (2010) 2184–2190.
- [26] Y.R. Huang, Q.X. Zhou, G.H. Xie, H.J. Liu, H.Y. Lin, Titanium dioxide nanotubes for solid phase extraction of benzoylurea insecticides in environmental water samples, and determination by high performance liquid chromatography with UV detection, *Microchim. Acta* 172 (2011) 109–115.
- [27] Q.X. Zhou, W.D. Wang, J.P. Xiao, Preconcentration and determination of nicosulfuron, thifensulfuron-methyl and metsulfuron-methyl in water samples using carbon nanotubes packed cartridge in combination with high performance liquid chromatography, *Anal. Chim. Acta* 559 (2006) 200–206.
- [28] Q.X. Zhou, J.P. Xiao, W.D. Wang, G.G. Liu, Q.Z. Shi, J.H. Wang, Determination of atrazine and simazine in environmental water samples using multiwalled carbon nanotubes as the adsorbents for preconcentration prior to high performance liquid chromatography with diode array detector, *Talanta* 68 (2006) 309–315.
- [29] Q.X. Zhou, J.P. Xiao, Y.J. Ding, Sensitive determination of fungicides and prometryn in environmental water samples using multiwalled carbon nanotubes solid-phase extraction cartridge, *Anal. Chim. Acta* 602 (2007) 223–228.
- [30] M. Trojanowicz, Analytical applications of carbon nanotubes: a review, *TrAC Trends Anal. Chem.* 25 (2006) 480–489.
- [31] C. Basheer, A.A. Alnedhary, B.S.M. Rao, S. Valliyaveetil, H.K. Lee, Development and application of porous membrane-protected carbon nanotube micro-solid-phase extraction combined with gas chromatography/mass spectrometry, *Anal. Chem.* 78 (2006) 2853–2858.
- [32] C. Basheer, H.G. Chong, T.M. Hii, H.K. Lee, Application of porous membrane-protected micro-solid-phase extraction combined with HPLC for the analysis of acidic drugs in wastewater, *Anal. Chem.* 79 (2007) 6845–6850.
- [33] K.S. Raja, M. Misra, V.K. Mahajan, T. Gandhi, P. Pillai, S.K. Mohapatra, Photo-electrochemical hydrogen generation using band-gap modified nanotubular titanium oxide in solar light, *J. Power Sources* 161 (2006) 1450–1457.
- [34] X. Quan, S. Yang, X. Ruan, H. Zhao, Preparation of titania nanotubes and their environmental applications as electrode, *Environ. Sci. Technol.* 39 (2005) 3770–3775.
- [35] Z. Zhang, Y. Yuan, G. Shi, Y. Fang, L. Liang, H. Ding, L. Jin, Photoelectrocatalytic activity of highly ordered TiO<sub>2</sub> nanotube arrays electrode for Azo Dye degradation, *Environ. Sci. Technol.* 41 (2007) 6259–6263.
- [36] Q.X. Zhou, Y.R. Huang, J.P. Xiao, G.H. Xie, Micro-solid phase equilibrium extraction with highly ordered TiO<sub>2</sub> nanotube array: a new approach for the enrichment and measurement of organochlorine pesticides at trace level in environmental water samples, *Anal. Bioanal. Chem.* 400 (2011) 205–212.
- [37] A. Moral, M.D. Sicilia, S. Rubio, D. Pérez-Bendito, Sodium dodecyl sulphate-coated alumina for the extraction/preconcentration of benzimidazolic fungicides from natural waters prior to their quantification by liquid chromatography/fluorimetry, *Anal. Chim. Acta* 569 (2006) 132–138.
- [38] A. Moral, M.D. Sicilia, S. Rubio, D. Pérez-Bendito, Determination of bisphenols in sewage based on supramolecular solid-phase extraction/liquid chromatography/fluorimetry, *J. Chromatogr. A* 1100 (2005) 8–14.
- [39] T. Saitoh, T. Kondo, M. Hiraide, Concentration of chlorophenols in water to dialkylated cationic surfactant-silica gel admicelles, *J. Chromatogr. A* 1164 (2007) 40–47.
- [40] H.Y. Niu, Y.Q. Cai, Y.L. Shi, F.S. Wei, S.F. Mou, G.B. Jiang, Cetyltrimethylammonium bromide-coated titanate nanotubes for solid-phase extraction of phthalate esters from natural waters prior to high-performance liquid chromatography analysis, *J. Chromatogr. A* 1172 (2007) 113–120.
- [41] Z.R. Liu, Photochemical degradation of selected polycyclic aromatic hydrocarbons on soil surface. Thesis for Master's degree of Dalian University of Technology, 2009.