ENVIRONMENTAL CHEMICAL CONTAMINANTS

QuEChERS with Ultrasound-Assisted Extraction Combined with High-Performance Liquid Chromatography for the Determination of 16 Polycyclic Aromatic Hydrocarbons in Sediment

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Abstract

Background: Polycyclic aromatic hydrocarbons (PAHs) have attracted worldwide attention due to their carcinogenic, teratogenic, and mutagenic effects, environmental persistence, and bioaccumulation characteristics. Therefore, the sensitive, reliable, and rapid detection of PAHs in sediment is of great importance.
Objective: To develop a high-performance liquid chromatography (HPLC) with fluorescence and ultraviolet detection after Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) treatment for simultaneous determination of 16 U.S. Environmental Protection Agency priority PAHs in sediment samples.
Method: The samples were ultrasonically extracted with acetone and then the supernatant was purified with a modified QuEChERS method. After centrifugation, the supernatant was injected into the HPLC system for analysis. The separation was accomplished on a ZORBAX Eclipse PAH column (150 × 4.6 mm, 3.5 μm) and the column temperature was set at 30 °C. The flow rate of the mobile phase consisting of water and acetonitrile in gradient elution mode was fixed at 0.9 mL/min. Detection was conducted on an ultraviolet detector and a fluorescence detector simultaneously. The qualitative analysis was based on retention time and the quantification was based on standard curves.
Results: Under the optimal conditions, this method showed good linearities in the range of 10–200 μg/L with correlation coefficients greater than 0.9993. The method had LODs ranging from 0.00108 to 0.314 ng/g. The mean recoveries ranged from 78.4 to 117% with intra-day and inter-day RSDs of 0.592–10.7% and 1.01–13.0%, respectively. The proposed method was successfully applied to the detection of 16 PAHs in sediment samples collected from the Funan River in Chengdu, China with total contents of 431–2143 ng/g·dw.
Conclusions: The established method is simple, rapid, environmentally friendly, and cost-effective. It can be applied to the analysis of 16 PAHs in sediment samples.
Highlights: A method of QuEChERS with ultrasound-assisted extraction combined with HPLC has been established for the analysis of 16 PAHs in sediment samples and the proposed method has been successfully applied to the analysis PAHs in real sediment samples.

Polycyclic aromatic hydrocarbons (PAHs), a large category of persistent organic pollutants (POPs) composed of two or more fused benzene rings, are ubiquitous in the environment. They mainly come from the incomplete combustion of fossil fuels and biomass, as well as volcanic eruptions and forest fires (1). PAHs can be classified into low molecular weight (LMW) and high molecular weight (HMW) ones (2). The physical and chemical properties of PAHs including boiling points, and melting points depend on their molecular weights, and their lipophilicity will increase with increasing molecular weight. They have attracted wide attention worldwide because of their carcinogenic, teratogenic, and mutagenic effects, environmental persistence, and bioaccumulation. The U.S. Environmental Protection Agency (EPA) and the European Union (EU) have listed partially different 16 PAHs as priority control pollutants. These PAHs are highly toxic, widely distributed, and harmful to human health (3). Numerous studies have shown that human lung cancer, skin cancer, breast cancer, and colon cancer are associated with PAH exposure (4). According to the International Agency for Research on Cancer (IARC), benzo[a]pyrene is a group 1 human carcinogen. Naphthalene, dibenzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[a, h]anthracene, and indeno[1,2,3-cd]pyrene are group 2B carcinogens, i.e., probable human carcinogen, and other PAHs are classified into suspected human carcinogens (group 3) (5). Because of the high lipophilicity and hydrophobicity of PAHs, they can be easily adsorbed on suspended particles in water and finally deposited in the river sediment. They are chemically stable and not easily degradable, so they can persist in sediment for a long time. The PAHs in sediment can be transferred into animal and plant tissue and eventually to the human body through the food chain. They pose a potential threat to human health, so it is essential to identify and quantify the PAHs in sediment for the accurate evaluation of the ecological risk to the water environment (6).

Due to the trace level of PAHs and matrix interferences in sediment samples, extraction and clean-up procedures are necessary for their separation and quantification. At present, a variety of techniques have been applied to the sample preparation, e.g., Soxhlet extraction (7, 8), ultrasonication-assisted extraction (UAE) (9, 10), microwave-assisted extraction (MAE) (11), supercritical fluid extraction (SFE) (12), pressurized liquid extraction (PLE) (13), solid-phase extraction (SPE) (14), magnetic solid-phase extraction (MSPE) (15), solid-phase microextraction (SPME) (16), dispersive liquid-liquid microextraction (DLLME) (17), and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) (18). Soxhlet extraction has high extraction efficiency, but it is time-consuming and requires large amounts of organic solvents. As modern extraction techniques UAE, MAE, SFE, and PLE can shorten the extraction time and reduce the consumption of organic solvents, and also have good extraction efficiency, but they require additional equipment. DLLME sometimes uses toxic halogenated solvents in the extraction procedure (6). The above-mentioned methods have some problems such as a time-consuming, high-cost, and tedious operation .

In 2003, Anastassiades et al. (19) initially developed the QuEChERS method based on dispersive solid phase extraction (d-SPE) for the analysis of pesticides in vegetables and fruits. Compared with other sample preparation methods, QuEChERS has the advantages including being simple, rapid, environmentally friendly, and cost-effective, and it can effectively reduce the matrix effect and has high recovery. Therefore, it has been widely used for the analysis of pesticides in the food (20), environmental, and biological samples. But there is only one report on its application for analysis of PAHs in different matrices (21). In QuEChERS, acetonitrile is commonly used to extract the target analytes, and $MgSO_4$ (desiccant) and NaCl (to reduce the effect of polarity interference) are added. Finally, primary secondary amine (PSA) is used as an adsorbent to eliminate polar interfering substances, such as fumic acids, organic acids, sugars, and pigments. Since the dried sediment sample has very low water content, it is necessary to add water in advance to hydrate the sample and promote phase separation. Considering that the analytes in the sediment sample are more firmly bound to the matrix, an ultrasonic-assisted method is used instead of the traditional manual agitation (21–25).

High-performance liquid chromatography–fluorescence detection (HPLC–FLD) (26), high-performance liquid chromatography–ultraviolet detection (HPLC–UVD) (9), liquid chromatography–mass spectrometry (LC–MS) (27), gas chromatography–flame ionization detection (GC–FID) (28), and gas chromatography–mass spectrometry (GC–MS) (29) have been applied to the separation and detection of PAHs in different samples. Fluorescence detection has similar sensitivity to MS detection (6).

In this study, a modified QuEChERS method coupled with HPLC with ultraviolet and fluorescence detection was established for simultaneous determination of 16 EPA priority PAHs in sediment. The established method has been applied to the determination of 16 PAHs in sediment samples collected from Funan River, Chengdu, China for the first time, which is beneficial to accurately evaluate the PAHs pollution level of the river and its potential impact on human health.

Experimental

Samples

The surface sediment samples (0–5 cm, $n = 23$) were collected from the Funan River in Chengdu, China (Figure 1 shows the sampling sites). The surface sediments were collected and stored in pre-cleaned and dried glass bottles. The sediment samples were homogenized and air-dried at ambient temperature (25°C) for one week, and then passed through 150 μm mesh sieves and stored in glass bottles in a -4°C freezer before analysis (18). The water contents of the sediment samples were measured separately by drying at 105°C for 4 h to constant weight. Because the water contents were all less than 1% for the air-dried sediment samples, they were neglected in the calculation of contents of PAHs in the sediment samples.

Apparatus

(1) *LC system*.—Dionex Ultimate 3000 HPLC system with a VWD-3100 variable wavelength detector and a FLD-3100 Dual-PMT fluorescence detector (Thermo Fisher Scientific, MA, USA).

(2) *LC column*.—ZORBAX Eclipse PAH column (150 × 4.6 mm, 3.5 μm; Agilent Technologies, USA).

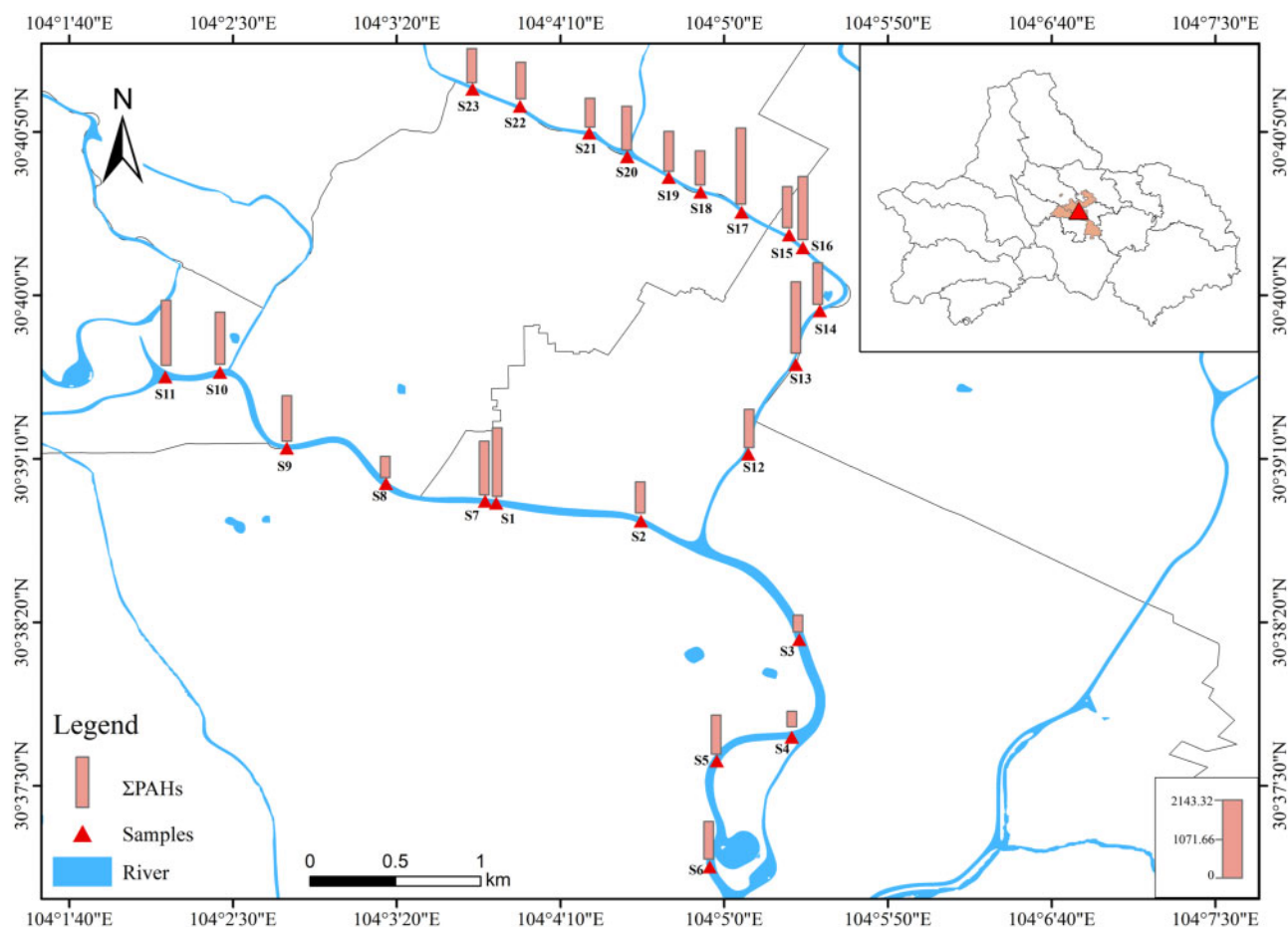(3) *Ultrasonic cleaner*.—KQ-250 ultrasonic cleaner (40 kHz; Kunshan Ultrasonic Instruments, Kunshan, China).

Figure 1. Sampling locations in the Funan River, Chengdu, China.

(4) *Centrifuge.*—TDL-80-2B centrifuge (Anting, Shanghai, China).

(5) *Vortex mixer.*—ZX4 advanced IR vortex mixer (VELP, Milan, Italy).

(6) *Analytical balance.*—BSA224S analytical balance (Sartorius, Gottingen, Germany).

Reagents

(a) *PAHs standard solution (200 mg/L, in acetonitrile).*— Naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IND), dibenz[a, h]anthracene (DBA), and benzo[g, h, i]perylene (BghiP) were obtained from O2si smart solutions (New Orleans, LA).

(b) *Solvent.*—Acetonitrile (HPLC grade) purchased from the Sigma Aldrich Company (St. Louis, MO). Acetone, dichloromethane, *n*-hexane, and ethylacetate of HPLC grade were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd, China.

(c) *Salt.*—Magnesium sulfate ($MgSO_4$) and sodium chloride (NaCl) of analytical grade purchased from Ruijinte Chemical Reagent Co. Ltd (Tianjin, China).

(d) *Adsorbents.*—Primary secondary amine (PSA, 40–63 μm, 60 A) and octadecylsilane (C18) were purchased from Anpel Experimental Technology Co. Ltd (Shanghai, China).

(e) *Water.*—Ultrapure water (18.2 MΩ·cm) was produced by a Millipore Milli-Q system (Bedford, MA).

Preparation of Standard Solutions

(a) *Working solution of 16 PAHs (20.0 mg/L).*—The working solution was prepared weekly by diluting stock solutions with acetonitrile.

(b) *Standard solutions for calibration curve (10–200 μg/L).*—The standard series of solutions were prepared by diluting the working solution with acetonitrile before use. All stock solutions were sealed and stored in a -20°C freezer.

Chromatographic Conditions

(a) *Mobile phase.*—Acetonitrile (A) and water (B).

(b) *Flow rate and gradient elution.*—The gradient elution program is shown in Table 1.

(c) *Column temperature.*—30°C.

(d) *Injection volume.*—10 μL.

(e) *Wavelength of detection.*—The wavelength switching program is shown in Table 2 and the UV detection wavelength was set at 230 nm.

Sample Preparation

One gram air-dried sediment was accurately weighed into a 15 mL centrifuge tube. After 1 mL of ultrapure water and 4 mL extraction solvent (acetone) was added, the tube was vortexed at 3000 rpm for 30 s, then ultrasonically extracted for 15 min and centrifuged at 4000 rpm for 5 min. Afterward, 1.00 mL of the supernatant was transferred into another 2 mL centrifuge tube containing 25 mg PSA and 90 mg $MgSO_4$. The tube was vortexed at 3000 rpm for 30 s and centrifuged for 5 min at 12 000 rpm. Finally, 10 μL supernatant was drawn and injected into the HPLC system for analysis.

Results and Discussion

Optimization of HPLC Conditions

The excitation wavelength and emission wavelength of each analyte are different. To detect each analyte under its corresponding best excitation wavelength and emission wavelength as much as possible, the corresponding wavelength switching was carried out according to their retention time, and the final wavelength switching program is shown in Table 2. Since acenaphthylene cannot emit fluorescent signal, it is detected with an ultraviolet detector at 230 nm.

For better chromatographic separation of the target PAHs, the separation efficiencies of methanol–water and acetonitrile–water were compared. Acetonitrile–water had better separation and elution efficiencies, so it was chosen as the mobile phase. The gradient elution program was optimized, and the satisfactory gradient elution program was shown in Table 1.

The flow rate and column temperature affect the separation efficiencies, retention time, and sensitivities of the analytes as well. Therefore, the flow rate of the mobile phase was optimized and the results indicated that a flow rate of 0.9 mL/min was appropriate for the separation of 16 PAHs within 28 min. The column temperature was investigated within 20 to 40°C, and 30°C was the most optimal for all the analytes' separation.

Table 1. The gradient elution program for separation of PAHs

Time, min	Flow rate, mL/min	Acetonitrile, %	Water, %
0.0	0.9	60	40
12.0	0.9	60	40
18.0	0.9	100	0
28.5	0.9	100	0
28.5	0.9	60	40
32.0	0.9	60	40

Figure 2 shows the chromatogram of a 200 ng/mL of 16 PAHs standard solution under the optimal HPLC conditions.

Optimization of QuEChERS Procedure

Selection of extraction solvent.—Acetonitrile is the most commonly used extraction solvent for a majority of organic chemicals in vegetables, melons, and fruits with high water content. So far, the extraction techniques for the PAHs in sediment samples are mainly Soxhlet extraction, UAE, and MAE, in which dichloromethane, acetone, *n*-hexane, ethyl acetate, or the mixed solvent of acetone and *n*-hexane are used as the extraction solvent (18, 30–33). The extraction efficiencies of acetonitrile, acetone, *n*-hexane, dichloromethane, ethyl acetate, and *n*-hexane–acetone (1:1 and 3:7, v/v) for PAHs in sediment were compared. As shown in Figure 3A, the highest extraction efficiencies were obtained by using acetone as the extraction solvent. The extraction efficiencies of different volumes (2.00–5.00 mL) of acetone showed that 4.00 mL acetone yielded the highest extraction efficiency, therefore, 4.00 mL acetone was used as the extraction solvent in the subsequent experiments. The effect of ultrasonic extraction time (5, 10, 15, 20, and 30 min) on the recoveries was also investigated, and it was found that ultrasonic extraction of 15 min had the highest recoveries. We tried to concentrate the supernatant using a stream of nitrogen, and then redissolving the residue, but the recovery rates of low-molecular-weight PAHs were not satisfactory. Considering that direct injection could meet the analytical requirements and simplify the procedure as well, we did not conduct the concentration procedure.

Selection of adsorbing materials.—PSA and octadecylsilane (C18) are commonly used as adsorption materials for the clean-up in the QuEChERS procedure. We compared the clean-up performances of these sorbents for PAHs in sediment, and the results (Figure 3B) indicated that PSA could remove the co-existent interfering substances from the extract more effectively and have less loss of PAHs. Thus, PSA was selected as the adsorbing material.

The amount of adsorbent.—PSA amounts (10–30 mg) on the clean-up performance were compared. As shown in Figure 3C, 25 mg PSA were adequate to clean-up the sediment's extract. At the same time, 90 mg of magnesium sulfate was added to dehydrate.

Method Performance

As shown in Table 3, the linearities of the method were investigated in the range 10–200 μg/L for all the PAHs with satisfactory correlation coefficients (between 0.9993 and 1,000). The LODs

Table 2. The excitation and emission wavelength switching program

PAHs	Retention time, min	Excitation wavelength, nm	Emission wavelength, nm
Nap, Acp, Flu	0.00	280.0	324.0
Phe	12.50	254.0	350.0
Ant	14.50	254.0	400.0
FL	16.80	290.0	460.0
Pyr	17.25	336.0	376.0
BaA, CHR	19.50	275.0	385.0
BbF, BkF, BaP, DBA, BghiP	21.20	305.0	430.0
IND	27.00	305.0	500.0

and LOQs of the method were calculated as three times the signal-to-noise (S/N = 3) and ten times the signal-to-noise (S/N = 10), respectively. From Table 3, we can see that the LODs and the LOQs of the method were $0.108–31.4 \times 10^{-2}$ and $0.360–104 \times 10^{-2}$ ng/g·dry weight (dw), respectively. Satisfactory recoveries and relative standard deviations (RSDs) were obtained for the PAHs spiked at three levels (50, 100, 200 ng/g)

in the sediment sample (prepared with 23 mixed and homogenized air-dried samples). The mean recoveries ranged from 78.4 to 117% with the intra-day and inter-day RSDs of 0.592–10.7% and 1.01–13.0%, respectively (Table 4). We analysed the method blank, but no PAHs were detected. Figure 4 shows the chromatogram of a 50 µg/L mixed-PAH standards solution (a) and the chromatogram of the method blank (b).
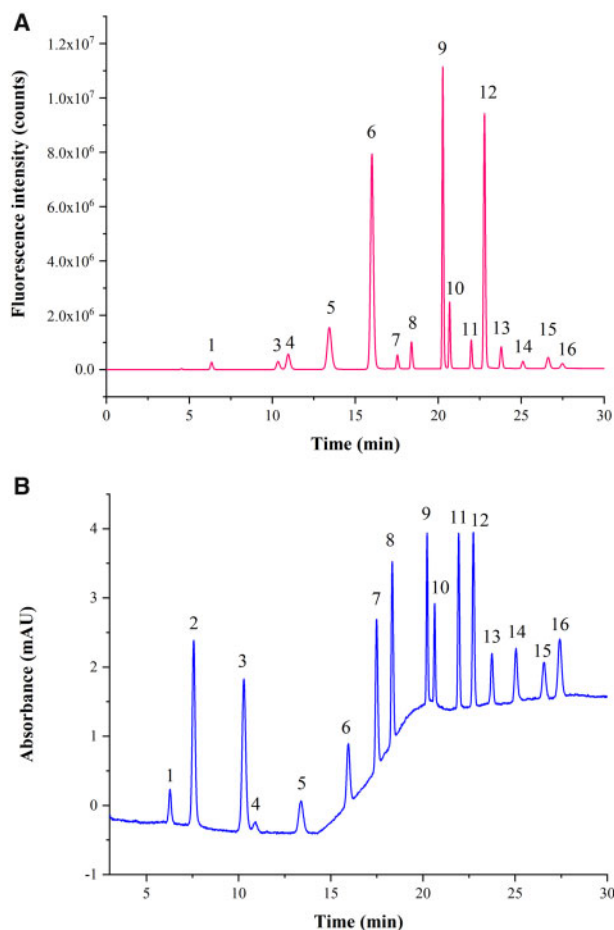
Comparison of the Proposed Method with Other Methods

The proposed method was compared with the reported methods for the analysis of PAHs in sediment in terms of analysis time, linear ranges, LODs, RSDs, and recoveries (Table 5). There are some reports on PAH analysis in sediment so far. For instance, Shamsipur et al. (34) established a miniaturized homogeneous liquid–liquid extraction (MHLLE) followed by HPLC–FLD method for determination of 13 PAHs in sediment samples. The samples were ultrasonically extracted with methanol and then the supernatant solution was re-extracted with n-hexane. The recovery range was 81–92%, and the RSDs were less than 7%. Rocha et al. (35) applied MAE to the extraction of 16 US EPA priority PAHs in sediment samples and then purified the sample solution by using SPME, followed by GC–MS analysis. This method gave recoveries of 70.0–109.6%, with RSDs less than 15.1%. Geng et al. (36) combined vortex-assisted extraction (VAE) with DLLME for extraction of 15 PAHs in sediment samples determined by HPLC–FLD. Mean recoveries of the method were 72.9–97.8%, with RSDs less than 8%. Rezaee et al. (37) developed an SFE–DLLME–GC–FID method for the determination of 9 PAHs in sediment samples. The recoveries varied between 82.9% and 100% with RSDs less than 10.3%. Compared with those reported methods, our proposed method is simple to operate, uses fewer organic solvents, takes less analysis time, more PAHs are detected, and has similar sensitivities and recoveries.

The Application of the Method

The established method has been successfully applied to the determination of 16 PAHs in 23 sediment samples collected from the Funan River in Chengdu, China. We qualitatively confirmed the results of this method by GC–MS (see supplemental information). Figure 5 shows the chromatograms of a sample and the sample spiked with 200 ng/g PAHs. The PAHs contents in 23 samples are listed in Table 6. The results show that 16

Figure 2. Chromatograms of a 200 µg/L mixed-PAH standards solution (A) fluorescence chromatogram and (B) ultraviolet chromatogram. (1) Nap, (2) AcPy, (3) Acp, (4) Flu, (5) Phe, (6) Ant, (7) FL, (8) Pyr, (9) BaA, (10) CHR, (11) BbF, (12) BkF, (13) BaP, (14) DBA, (15) BghiP, and (16) IND.
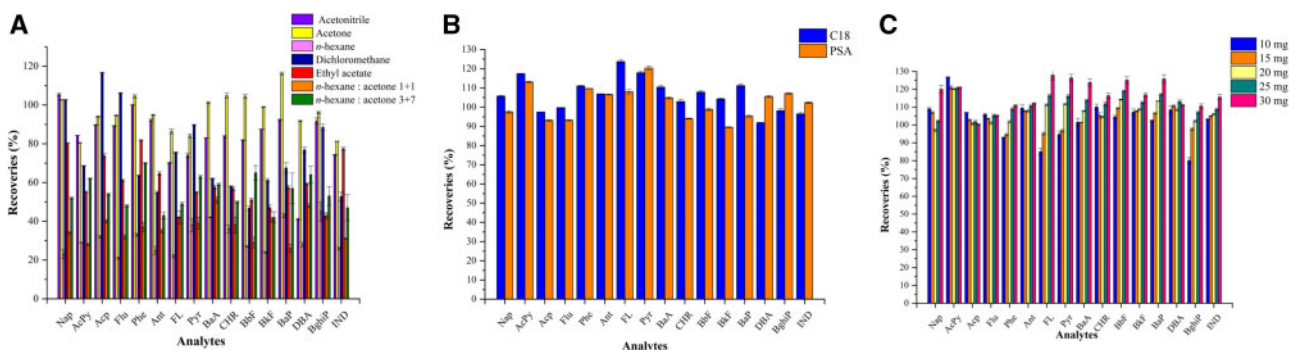

Figure 3. Optimization of the QuEChERS parameters: effects of (A) the extraction solvent, (B) the adsorbing materials, and (C) the amount of adsorbent.

Table 3. Linear ranges, correlation coefficients, LODs, and LOQs of the method

PAHs	Linear ranges, µg/L	Linear regression equations	Correlation coefficients	LODs, ng/g	LOQs, ng/g
Nap	10–200	$y = 2.36 \times 10^2\, x + 1.20 \times 10^2$	0.9998	0.0365	0.122
AcPy	10–200	$y = 2.60 \times 10^{-3}\, x - 2.10 \times 10^{-3}$	0.9993	0.314	1.04
Acp	10–200	$y = 3.74 \times 10^2\, x - 8.26$	0.9999	0.0239	0.0795
Flu	10–200	$y = 7.65 \times 10^2\, x - 4.52 \times 10^2$	0.9999	0.0120	0.0401
Phe	10–200	$y = 2.47 \times 10^3\, x - 3.29 \times 10^3$	0.9999	0.00379	0.0126
Ant	10–200	$y = 8.54 \times 10^3\, x - 8.05 \times 10^3$	0.9999	0.00108	0.00360
FL	10–200	$y = 399 \times 10^2\, x - 3.60 \times 10^2$	1.0000	0.0228	0.0763
Pyr	10–200	$y = 6.91 \times 10^2\, x - 8.46 \times 10^2$	0.9999	0.0136	0.0455
BaA	10–200	$y = 5.60 \times 10^3\, x - 6.33 \times 10^3$	0.9999	0.00166	0.00553
CHR	10–200	$y = 1.28 \times 10^3\, x - 1.78 \times 10^3$	0.9999	0.00733	0.0245
BbF	10–200	$y = 6.20 \times 10^2\, x - 6.69 \times 10^2$	0.9999	0.0150	0.0501
BkF	10–200	$y = 6.33 \times 10^3\, x - 5.93 \times 10^3$	0.9999	0.00146	0.00488
BaP	10–200	$y = 6.31 \times 10^2\, x - 8.27 \times 10^2$	0.9998	0.0150	0.0501
DBA	10–200	$y = 2.51 \times 10^2\, x - 3.74 \times 10^2$	0.9999	0.0377	0.126
BghiP	10–200	$y = 4.69 \times 10^2\, x - 6.13 \times 10^2$	0.9999	0.0199	0.0664
IND	10–200	$y = 2.20 \times 10^2\, x - 1.75 \times 10^2$	0.9999	0.0422	0.142

Table 4. The recoveries and RSDs of the method ($n = 6$)

	Spiked 50 ng/g			Spiked 100 ng/g			Spiked 200 ng/g		
PAHs	Recovery, %	Intra-day RSD, %	Inter-day RSD, %	Recovery, %	Intra-day RSD, %	Inter-day RSD, %	Recovery, %	Intra-day RSD, %	Inter-day RSD, %
Nap	117	1.79	1.01	83.4	10.7	10.9	95.8	0.926	4.20
AcPy	98.1	5.98	13.0	91.9	3.06	5.34	92.0	5.61	2.67
Acp	101	3.97	8.36	102	3.39	3.71	101	3.73	1.98
Flu	115	1.37	7.84	110	0.592	1.36	99.3	2.85	1.65
Phe	108	8.14	7.94	92.0	8.28	8.93	100	1.73	1.14
Ant	111	1.18	5.00	93.4	5.27	4.97	100	2.95	4.73
FL	78.4	5.59	8.30	84.9	3.66	3.08	88.4	4.64	2.75
Pyr	85.1	5.74	6.89	94.3	2.62	5.25	94.2	3.80	2.32
BaA	95.6	0.680	4.85	92.9	2.14	2.87	94.1	2.65	1.09
CHR	98.8	2.26	3.04	84.3	2.44	4.10	86.4	2.22	1.47
BbF	90.3	4.03	4.87	94.2	4.42	6.89	97.6	2.46	2.23
BkF	83.3	1.24	1.68	82.0	3.85	5.66	97.1	0.923	2.67
BaP	107	1.51	7.65	83.8	1.36	9.53	93.7	2.64	1.12
DBA	87.6	2.62	4.10	91.2	0.72	6.49	108	4.16	2.20
BghiP	81.0	2.69	6.57	94.6	1.34	4.44	92.3	3.55	2.36
IND	93.2	3.07	4.14	82.1	4.60	3.03	90.8	3.38	1.48

PAHs were all detected in the samples with the total contents of 431–2.14×10^3 ($1.22 \times 10^3 \pm 463$) ng/g·dw. Nap had the highest contents of 23.1–898 ng/g·dw among the PAHs in most samples. BaP, the powerful carcinogen, had a content range of 15.2–126 ng/g·dw and a ratio of BaP/BghiP in the range of 0.58–1.38. The ratio of BaP/BghiP > 0.6 indicates traffic emissions, and the ratio < 0.6 indicates non-traffic emissions (38). Since the selected sampling points were located near densely populated living areas, a large amount of domestic sewage was discharged daily into the Funan River, and the increase of PAH contents in the airborne particulates caused by automobile exhaust emission can also lead to the increase of PAH content in river sediment. Therefore, the contents of the PAHs were higher than the other researchers' reports, i.e., the Yellow River, China (100–197 ng/g·dw) (39), Bohai Sea (149–1.21×10^3 ng/g·dw) and northern part of the Yellow Sea, China (148.28–907.47 ng/g·dw) (40), Okobo-Enjema, Nigeria (10–70 ng/

g·dw) (41), and Paranagua Bay in Southern Brazil (0.11–12 ng/g·dw) (42), so they have potential adverse effects on the residents' health. Cecinato et al. (43) introduced benzo[a] pyrene equivalent carcinogenicity (BaPE) as an indicator to quantitatively evaluate the potential toxicity of PAHs in suspended particulate matter. From Table 6, we can see that the BaPE of PAHs in the Funan River sediments ranged from 26.7 to 205 ng/g·dw. Up to now, there is no report on BaPE in sediment samples, therefore we did not conduct an evaluation of the toxicity of PAHs in the Funan River.

Conclusions

In this study, a simple, rapid, environmentally friendly, and cost-effective QuEChERS coupled with the HPLC method was established for simultaneous determination of 16 U.S. EPA priority PAHs in sediment samples. Compared with the conventional QuEChERS,
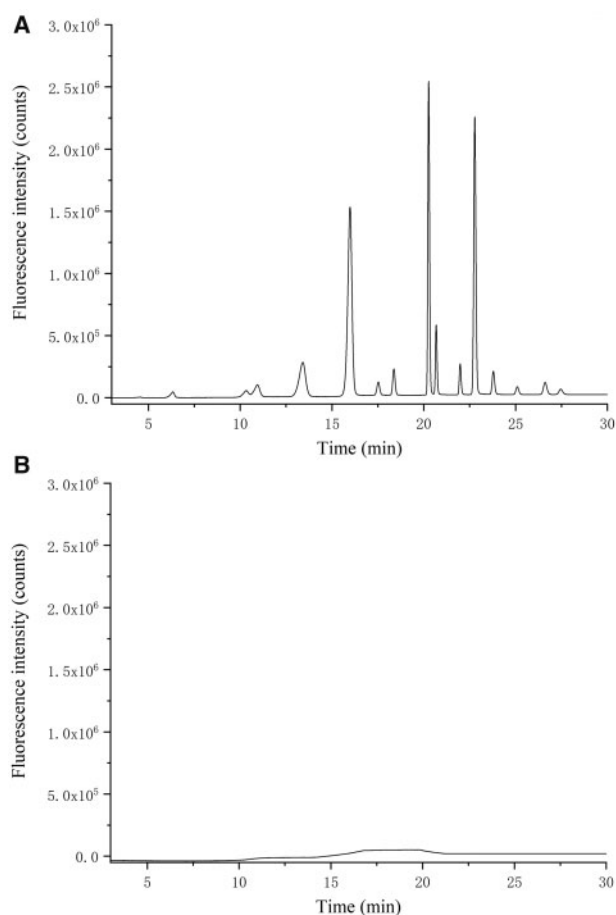
Figure 4. (A) Chromatogram of a 50 µg/L mixed-PAH standards solution and (B) the chromatogram of the method blank.

ultrasound-assisted extraction was used instead of manual agitation to improve the extraction efficiency. In the whole sample preparation process, only an ultrasonic cleaner and a small amount of organic solvents were used. Under optimal conditions, this method has satisfactory linearities, recoveries, sensitivity, and precisions. The developed method was applied to analyze 23 sediment samples collected from the Funan River in Chengdu, China. Sixteen PAHs, including BaP, were detected in all samples, and the highest content was Nap with contents of 23.1–898 ng/g·dw and BaP content were 15.2 to 126 ng/g·dw.

Supplemental Information

Supplemental information is available on the *J. AOAC Int.* website.

Acknowledgments

References

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Table 5. Comparison of the proposed method with other methods for determination of PAHs in sediment samples

Analytes	Sample pretreatment method[a]	Detection techniques	Analysis time, min	Linear ranges	LODs	RSDs, %	Recoveries, %	Ref.
Acy, Fl, Phe, Ant, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, BghiP, INDnP	UAE (methanol), MHLLE (hexane)	HPLC-FLD	35	0.01–4.5 ng/g	0.003–0.04 ng/g	<7	81–92	[34]
Nap, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, BghiP, IND	MAE (acetone), SPME	GC-MS	60	-	0.07–0.76 ng/g	<15.1	70.0–109.6	[35]
Nap, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, BghiP, IND	VAE (acetonitrile), DLLME (dichloromethane)	HPLC-FLD	35	20–2100 ng/g	2.3–6.8 ng/g	<8	72.9–97.8	[36]
Nap, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, Chr	SFE (CO2), DLLME (acetonitrile, chlorobenzene)	GC-FID	30	0.4–41.6 ng/g	0.2 ng/g	<10.3	82.9–100	[37]
Nap, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, BghiP, IND	QuEChERS (acetone, PSA)	HPLC-FLD-UV	28	10–200 µg/L	0.00108–0.314 ng/g	<13	78.4–117	This method

[a]MHLLE, miniaturized homogenous liquid–liquid extraction; VAE, vortex-assisted extraction.
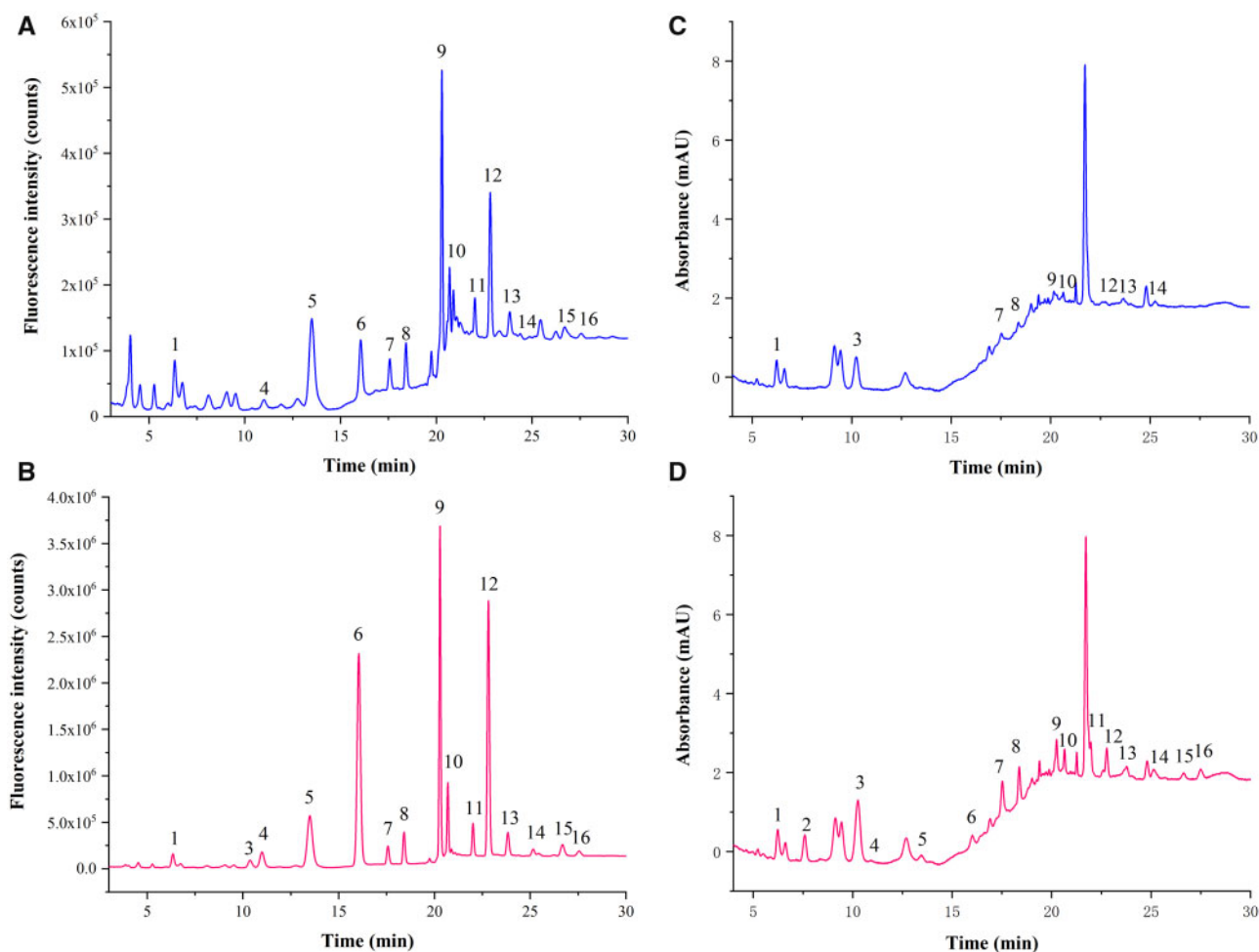
Figure 5. Fluorescence chromatograms of (A) a sample and (B) the sample spiked with 200 ng/g PAHs. (C) Ultraviolet chromatogram of a sample and (D) the sample spiked with 200 ng/g PAHs. (1) Nap, (2) AcPy, (3) Acp, (4) Flu, (5) Phe, (6) Ant, (7) FL, (8) Pyr, (9) BaA, (10) CHR, (11) BbF, (12) BkF, (13) BaP, (14) DBA, (15) BghiP, and (16) IND.

Table 6. The PAHs contents (ng/g·dw) in sediment samples by the proposed method

Samples	Nap	AcPy	Acp	Phe	Ant	FL	Pyr	BaA	CHR	BbF	BkF	BaP	DBA	BghiP	IND	ΣPAHs[a]	BaPE[b]
S1	649	4.77	3.47	133	19.4	210	185	91.9	76.8	97.4	51.0	103	83.2	134	73.4	1.93×10^3	175
S2	456	6.00	29.6	41.6	7.94	49.8	41.0	24.1	25.3	24.9	14.7	28.4	50.1	49.0	19.1	874	64.2
S3	168	3.85	5.26	37.7	6.64	35.4	31.4	19.6	17.9	21.5	12.0	33.0	24.4	23.9	16.8	470	52.5
S4	205	7.85	5.18	37.2	6.35	25.8	23.2	14.1	13.2	13.1	8.50	15.2	14.0	18.9	9.77	431	26.7
S5	377	7.96	2.40	71.0	13.8	115	102	48.6	54.7	29.9	57.2	32.3	64.8	43.4	43.4	1.10×10^3	89.6
S6	268	7.08	4.22	90.4	19.3	126	97.9	61.2	76.6	58.0	28.2	54.7	43.4	66.7	35.2	1.06×10^3	93.3
S7	514	9.08	0.743	126	17.5	174	137	71.5	77.1	68.0	36.8	71.6	48.8	89.9	51.7	1.51×10^3	116
S8	23.1	9.18	1.09	61.8	10.7	74.6	63.0	43.1	45.9	44.5	22.4	43.4	48.5	58.4	29.1	593	82.1
S9	492	5.69	0.161	86.9	12.7	122	101	57.0	68.0	63.2	30.8	58.6	49.6	77.9	42.7	1.28×10^3	102
S10	401	8.77	3.16	105	18.6	185	143	80.3	83.6	85.1	40.8	81.6	65.1	95.4	54.7	1.47×10^3	139
S11	590	4.62	2.37	153	15.1	202	172	85.7	120	116	48.2	85.3	54.3	110	59.0	1.84×10^3	139
S12	434	5.85	0.156	65.8	9.50	92.2	77.4	42.8	61.2	58.0	25.6	42.3	50.6	62.7	33.7	1.08×10^3	83.8
S13	898	5.85	2.00	115	16.0	161	143	82.5	99.0	100	45.6	87.4	64.4	110	63.7	2.01×10^3	146
S14	505	8.31	5.67	70.7	10.3	87.0	73.8	41.5	61.6	55.4	23.9	43.4	54.7	69.2	34.4	1.17×10^3	87.0
S15	610	5.69	0.153	102	18.1	190	161	100	98.7	99.1	47.6	96.0	71.9	96.6	64.1	1.78×10^3	161
S16	341	5.23	5.83	108	16.9	127	108	58.7	61.3	56.7	26.4	53.5	47.7	72.4	34.2	1.15×10^3	94.2
S17	424	5.54	5.38	258	39.8	293	234	120	114	132	62.7	126	85.4	124	86.8	2.14×10^3	205
S18	403	4.00	3.74	61.4	9.03	73.0	60.3	34.5	40.9	40.5	21.3	43.3	48.3	75.0	26.4	962	80.8
S19	530	5.69	5.23	70.3	13.1	86.9	73.2	43.9	50.9	40.6	22.8	43.6	32.8	47.9	28.2	1.12×10^3	72.6
S20	738	5.08	3.41	70.6	8.57	61.4	53.5	30.6	41.6	37.9	18.0	37.4	35.0	47.2	22.6	1.23×10^3	66.0
S21	286	6.00	0.873	66.9	9.77	73.5	60.9	37.0	38.5	45.5	20.2	38.0	36.8	46.2	26.6	811	69.0
S22	379	5.08	5.04	90.6	10.7	91.5	78.1	41.7	53.0	53.3	25.0	50.2	32.7	55.8	35.0	1.03×10^3	80.6
S23	383	4.62	3.18	74.9	13.1	76.9	66.2	39.8	49.4	38.7	21.3	44.0	32.9	56.2	31.5	958	72.8

[a] ΣPAHs, the sum of 16 PAHs listed above.

[b] Benzo[a]pyrene-equivalent carcinogenic power (BaPE = BaA × 0.06 + BbkF × 0.07 + BaP + DBahA × 0.6 + Inc × 0.08).

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