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Supplementary Information

Gas-Cycle-Assisted Headspace Solid-Phase Microextraction Coupling with Gas Chromatography for Rapid Analysis of Organic Pollutants

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1. Experimental section

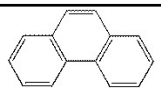
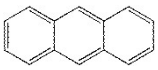
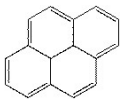
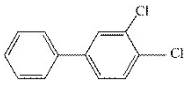
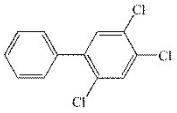
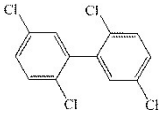
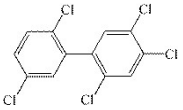
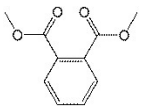
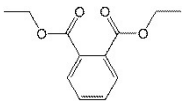
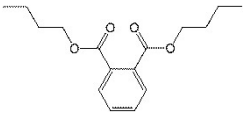
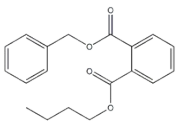
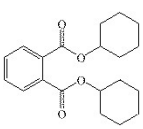
1.1 Reagents and materials

PAHs including phenanthrene (PHE), anthracene (ANT), pyrene (PYR), PCBs containing 3,4-dichlorobiphenyl (PCB-12), 2,4,5-trichlorobiphenyl (PCB-29), 2,2',5,5'-tetrachlorobiphenyl (PCB-52), 2,2',4,5,5'-pentachlorobiphenyl (PCB-101), PAEs consisting of dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), dicyclohexyl phthalate (DCHP) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China), the properties of these analytical targets are listed in Table S1. HPLC grade acetone (ACE) was obtained from Merck KGaA (Darmstadt, Germany). Ultrapure water（18.2 MΩ cm^{-1}）purified with a Milli-Q purification system (Millipore, Bedford, MA, USA) was used throughout the experiments. All other chemicals were of analytical grade.

Single stock standard solutions of PAHs, PCBs, and PAEs were prepared in ACE at a concentration of 1 mg·mL^{-1}. The mixed stock standard solution was obtained by diluting each single stock solution with ACE stepwise into 100 μg·mL^{-1}. The working standard solutions were prepared by a suitable dilution of the mixed stock standard solution with ultrapure water. Above mentioned standard solution were stored at 4 ℃ in the darkness.

SPME fibers with 100 μm polydimethylsiloxane (PDMS), 65 μm PDMS/divinylbenzene (PDMS/DVB) were purchased from Supelco (Bellefonte, PA, USA). All the fibers were conditioned before being used in the GC injector according to the instructions provided by the manufacturer.

Table S1. Physical-chemical properties of organic pollutants including PAHs, PCBs and PAEs that used in this work.

Analyte	Structure	Molecular weight	logK_{ow}[a]	Boiling point (℃)
PHE		178.229	4.46	337.4±9.0
ANT		178.229	4.45	337.4±9.0
PYR		202.251	4.88	404.0±0.0
PCB-12		223.098	5.41	323.7±22.0
PCB-29		257.543	5.77	331.6±37.0
PCB-52		291.988	6. 26	344.9±37.0
PCB-101		326.433	6. 85	371.0±37.0
DMP		194.184	1.66	282.7±8.0
DEP		222.237	2.65	294.0±0.0
DBP		278.344	4.61	337.0±10.0
BBP		312.360	4.84	408.3±20.0
DCHP		330.418	6.20	425.8±18.0

[a]logK_{ow}: n-octanol/water partition coefficients, indicator for hydrophobicity. Data taken from RSC publishing Home: http://www.chemspider.com/

1.2 Circulating device

The device primarily consisting of a mini-pump and a speed controller was purchased from Kamoer (Shanghai, China), which was used to circulate and control the flow rate of gas. A silicone tube (25, 20, and 15 cm length) and a needle were obtained to constitute the circulating system. Three-port glass vial (250, 100, 50, and 25 mL) with a PTFE-coated septum from Lianhua Labware (Jiangsu, China) was used to HS-SPME.

1.3 Apparatus

All chromatographic analysis were performed on an Agilent 7890B gas chromatography (Agilent, China) system coupled with a flame ionization detector (FID). A HP-5 capillary column (30 m×0.32 mm×0.25 μm) was used to separate PAH. PCBs and PAEs were separated by a DB-5 capillary column (30 m×0.32 mm×0.25 μm). High purity nitrogen (99.99%) was used as carrier gas in splitless mode at a constant flow rate of 1 $mL \cdot min^{-1}$.

The parameters to analysis PAHs was set according to the literature.[1] Briefly, temperature initially maintained at 60 ℃ for 1 min, then rapidly increased to 190 ℃ by 65 $℃ \cdot min^{-1}$ and held for 1 min, after that arrived at 220 ℃ at a ramp of 6 $℃ \cdot min^{-1}$ and held for 0.5 min. Finally, the oven temperature was heated to 300 ℃ with a rate of 80 $℃ \cdot min^{-1}$ and kept for 7 min. The injector temperature was set at 290 ℃ and the detector temperature was 300 ℃.

For separation of PCBs, the GC oven temperature program was modified according to the previous reference.[2] Firstly, the initial temperature was set at 60 ℃

and maintained for 0.5 min. Then rapidly increased to 190 ℃ at 65 ℃·min^{-1} and held for 1 min. Secondly, the temperature reached 220 ℃ at a rate of 6 ℃·min^{-1} and kept for 1 min. Finally, the oven temperature was heated to 300 ℃ with a ramp of 80 ℃·min^{-1} and kept for 2 min. The injector temperature was set at 290 ℃ and the detector temperature was 300 ℃.

The GC oven temperature program of PAEs was set and slightly modified according to the previously reported study.[3] The initial temperature was 60 ℃, then arrived at 220 ℃ with a rate of 40 ℃·min^{-1} (held for 1 min), after that arrived at 300 ℃ with 20 ℃·min^{-1} and held for 4 min. The injector temperature and the detector temperature were 300 ℃.

1.4 Sample collection and preparation

The surface natural soil (NS, 0-5 cm depth) was collected from a lawn in Henan University, the road-deposited soil (RDS, 0-5 cm depth) was obtained from Zhengkai road of Kaifeng, and the chemical-deposited soil (CDS, 0-5 cm depth) was collected from Jiyuan nearby a chemical plant. The soil samples were air-dried at room temperature and sifted through a 60-mesh sieve prior to use.

1.5 GCA HS-SPME procedures

For GCA HS-SPME mode, 10 μL mixed stock standard solution or 10.0 g soil samples diluted with 10.0 mL ultrapure water was placed into 25 mL three-port glass vial, one port was immediately sealed with PTFE-coated septum, the other two were connected to the air inlet and the air outlet of the mini-pump respectively to form a circulation path (Fig. S2). A thermostatic water bath was chosen to control the

extraction temperature. During the extraction, the fiber was carefully introduced directly into the air inlet of the device for a certain time, the mini-pump and speed controller were utilized to circulate and regulate the flow rate of gas. After extraction, the fiber was immediately inserted into GC injector for thermal desorption.

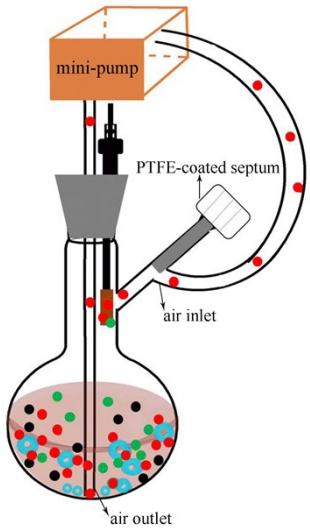


Fig. S2. Schematic illustration of the GCA HS-SPME.

1.6 Determination of enrichment factors

Enrichment factor (EF) defined as the ratio of the peak area of analytes after GCA HS-SPME extraction to that before extraction under the same condition, which is used to represent the adsorption ability of the method toward each analyte.[4,5] The following formula is used to calculate the enrichment factor:

$EFs=A_f/A_s$

Where A_f is the chromatography peak area of analyte after GCA HS-SPME extraction, A_s is the chromatography peak area of analyte before extraction of this method.

1.7 Determination of relative recoveries

To determine the relative recoveries of the method, the standard solutions with three different concentrations (1.0, 10.0, 50.0 ng·mL^{-1}) were added to soil samples. The spiked samples were analyzed by GCA HS-SPME coupled with GC-FID under the optimized conditions. The recoveries were calculated based on the following equation:

$$\frac{PAHs\ total\ -\ PAHs\ originally\ in\ soil}{PAHs\ spiked} \times 100\%$$

where "PAHs total" and "PAHs originally in soil" refer to the concentrations determined by HS-SPME GC-FID in spiked and unspiked samples, respectively. The "PAHs spiked" refers to the concentration of spiked standard solutions.

1.8 GC-MS conditions

The GC-MS QP2010 SE system (Shimadzu, Japan) using a Rtx-5 capillary column (30 m length × 0.25 mm i.d. × 0.25 μm film thickness) was used for comparative experiments. The GC conditions were set as follows: the injector temperature was 280 ℃. The column temperature was increased from 100 °C to 240 °C at a rate of 5 °C min^{-1}, maintained for 1 min, then 30 °C min^{-1} to 280 °C for 3 min. Splitless injections were used throughout. The high-purity helium (99.999%) was used as carrier gas with the flow rate of 1.79 mL min^{-1}. The MS was operated in the EI mode ionizing energy of 70 eV. The source temperature was set at 230 °C. Full scan mass spectra were acquired in the mass range within 45 to 700 (m/z).

2. Results and discussion

2.1 *Optimization of GCA HS-SPME procedures*

To achieve better performance of the GCA HS-SPME coupled with GC-FID

method, the experimental parameters including volume of three-port glass vial, length of silicone tube, position of the fiber, gas flow rate, extraction temperature, desorption time, desorption temperature, and salt concentration were investigated for the analysis of PAHs with a concentration of 100 $ng \cdot mL^{-1}$. The extraction time was used as 11 min based on previously investigation.

2.1.1 *The volume of three-port glass vial and length of silicone tube*

The effect of volume of three-port glass vial on enrichment of three PAHs was investigated. Four volumes of three-port glass vial including 250, 100, 50, and 25 mL were selected. Experimental results demonstrated that the enrichment ability of the analytes was improved with reducing the size of the three-port glass vial (from 250 to 25 mL) by keeping the volume of sample solution constant. In other words, the volume of headspace is reduced with reducing the size of the three-port glass vial. The similar conclusion was achieved by vacuum-assisted HS-SPME and predicted by the theory in regular HS-SPME.[6,7] The length of silicone (25, 20, and 15 cm) was investigated. The results indicated that the length of silicone has not obvious effect on enrichment of the analytes. The possible reason can be attributed that the length of silicone has not obvious effect on headspace.

2.1.2 *The position of fiber*

The position of fiber from the air inlet may have significate effect on adsorption efficiency. As shown in Fig. S3, three different positions (A, B, and C) were investigated. The Experimental results are given in Fig. S4. The highest adsorption efficiencies were achieved for three PAHs when the fiber coating placed at air inlet

(position B). The possible reason is that the target analytes may have more contact chance at position B than that of position A and position C. Hence, position B was selected in the following experiments.

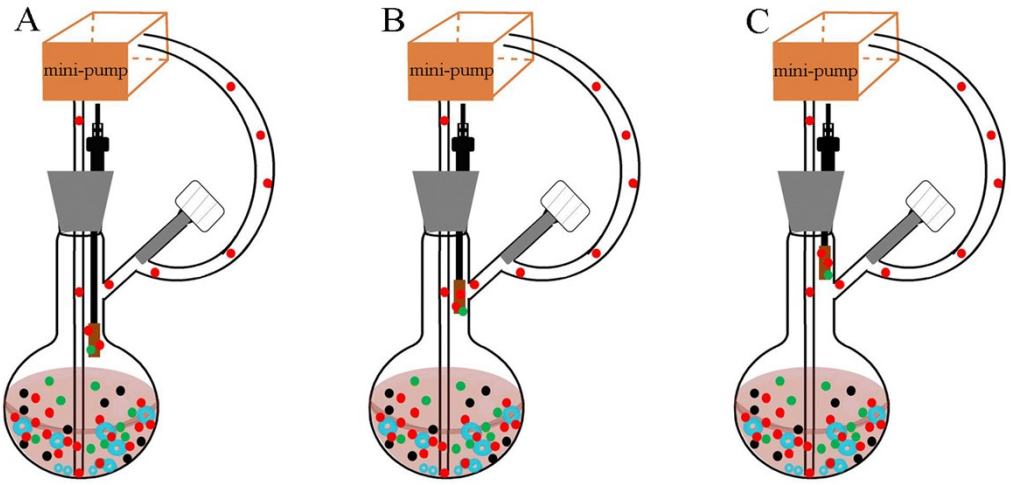


Fig. S3. The position of the fiber from the air inlet.

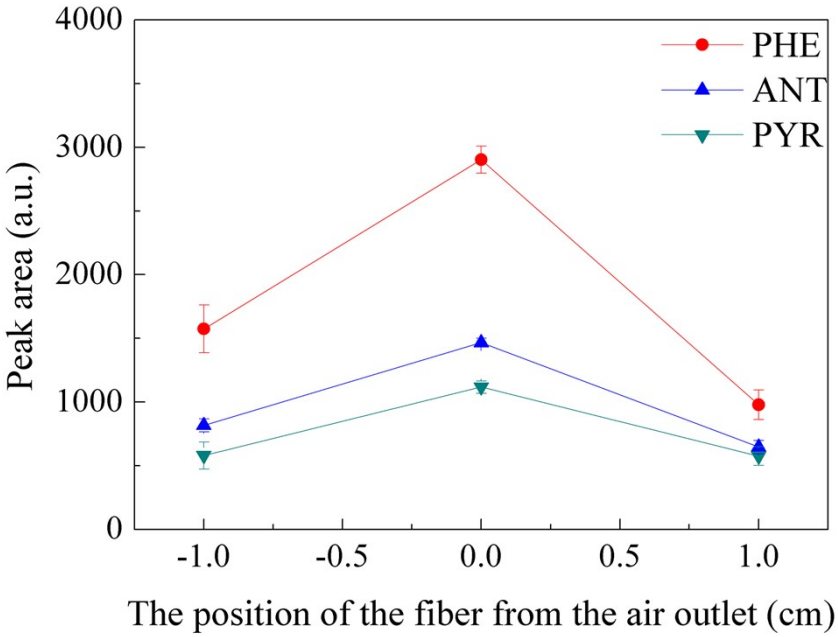


Fig. S4. The effect of position of the fiber on extraction efficiency. Experimental conditions: Fiber coating, 100 μm PDMS fiber; *v*olume of three-port glass vial, 25 mL; gas flow rate, 2 L·min^{-1}; extraction temperature, 50 ℃; desorption temperature, 280 ℃; desorption time, 2 min; salt concentration, 0; concentration of analytes, 100 ng·mL^{-1}.

2.1.3 *Gas flow rate*

In GCA HS-SPME, the equilibrium times can be greatly shortened with increasing transfer rates of analytes from sample matrix to headspace. The enhancement of gas flow rate is favorite to increase evaporation rates of analytes at sample/headspace interface. However, the contact time of analytes and fiber coating was also shortened with increasement of gas flow rate. With limitation of device, the flow rate of assisted-gas from 2 to 6 $L \cdot min^{-1}$ were studied. Experimental results demonstrated that the peak areas of all analytes reached the maximum when the gas flow rate was 2 $L \cdot min^{-1}$ (Fig. S5). Therefore, the gas flow rate of 2 $L \cdot min^{-1}$ was chosen for the following experiments.

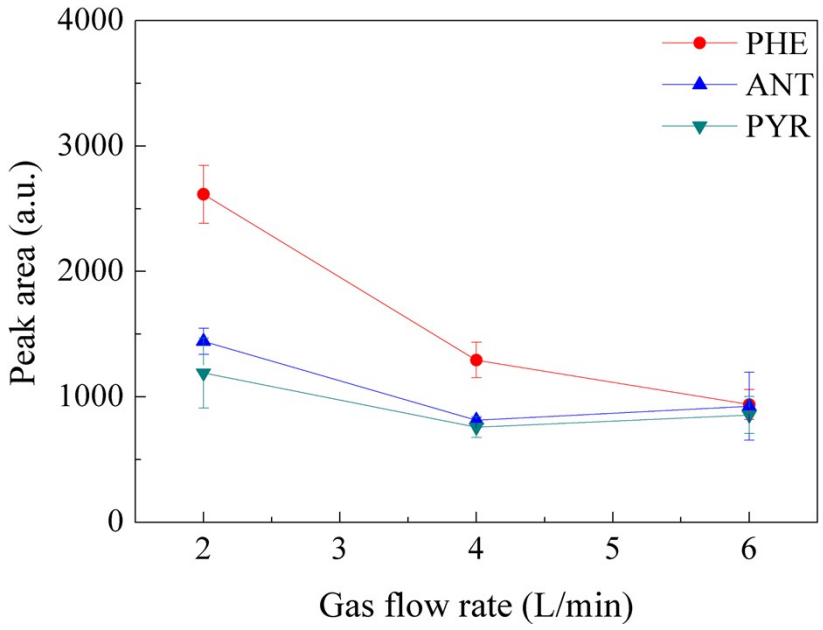


Fig. S5. The effect of gas flow rate on extraction efficiency. Experimental conditions: Fiber coating, 100 μm PDMS fiber; *v*olume of three-port glass vial, 25 mL; extraction temperature, 50 ℃; desorption temperature, 280 ℃; desorption time, 2 min; salt concentration, 0; concentration of analytes, 100 $ng \cdot mL^{-1}$.

2.1.4 *Extraction temperature*

High temperature provides enough energy for PAHs to overcome energy barriers that bind them in the matrixes and increases the vapor pressure during mass transfer. The effect of extraction temperature on extraction efficiency was investigated in the range of 20 to 70 ℃ by monitoring peak areas with GC-FID. As the results showed in Fig. S6, the maximum extraction ability for PHE and ANT were achieved at 50 ℃. While, the peak area of PYR was increased with further enhancing temperature to 70 ℃. Considering that higher extraction temperature can decrease the partition coefficients because of the exothermic nature of the adsorption. Thus, 50 ℃ was selected as extraction temperature in the following experiments.

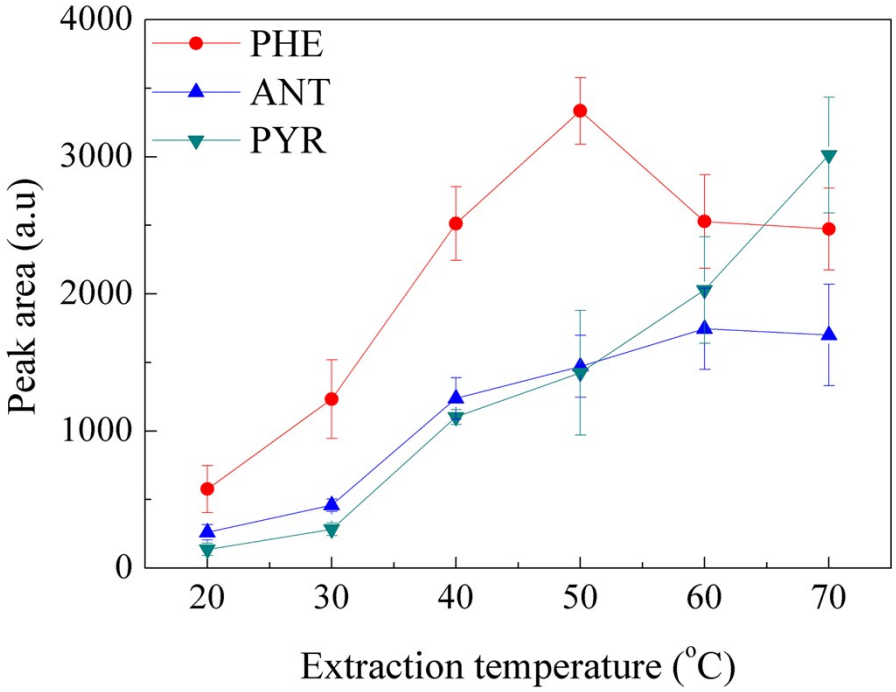


Fig. S6. The effect of extraction temperature on extraction efficiency. Experimental conditions: Fiber coating, 100 μm PDMS fiber; *v*olume of three-port glass vial, 25 mL; gas flow rate, 2 L·min^{-1}; desorption temperature, 280 ℃; desorption time, 2 min; salt concentration, 0; concentration of analytes, 100 ng·mL^{-1}.

2.1.5 *Desorption temperature*

Desorption temperature is another key parameter that affects the efficiency of GCA HS-SPME. As we all know, the analytes can be completely released from the fiber coating at high desorption temperature. Thus, enhancement of desorption temperature is favorite to achieve better sensitivity. However, the fiber coating may be destroyed at high desorption temperature, which will result in shorten life-time of fiber coating. To achieve an appropriate desorption temperature, the temperature of the GC injector between 240 to 290 ℃ were systematically studied. It can be obviously observed from Fig. S7 that the response areas of analytes showed an upward trend with increasing temperature from 250 to 280 ℃. When the desorption temperature higher than 280 ℃, the response areas of three target PAHs have slightly decreased. Subsequently, the desorption temperature was set at 280 ℃.

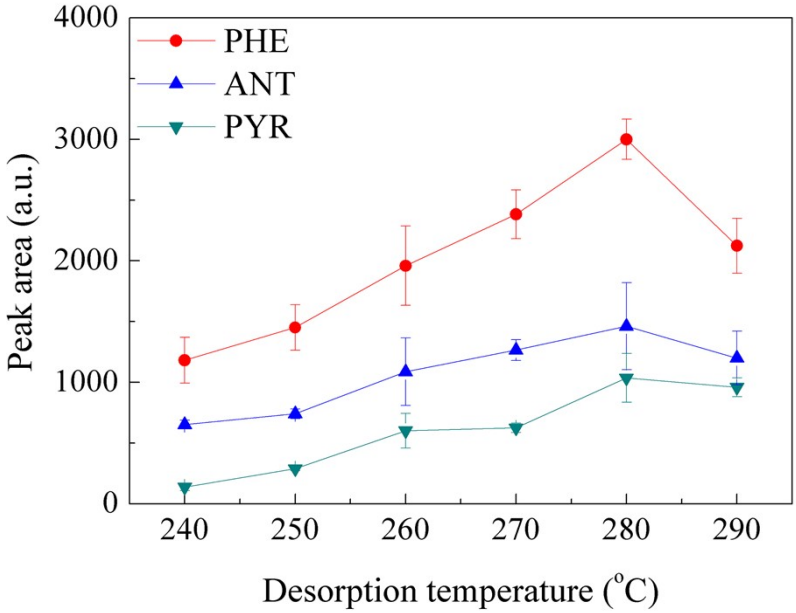


Fig. S7. The effect of desorption temperature on extraction efficiency. Experimental conditions: Fiber coating, 100 μm PDMS fiber; *v*olume of three-port glass vial, 25 mL; gas flow rate, 2 $L \cdot min^{-1}$; extraction temperature 50 ℃; desorption time, 2 min; salt concentration, 0; concentration of analytes, 100 $ng \cdot mL^{-1}$.

2.1.6 *Desorption time*

The desorption time is another factor that would impact extraction performance of HS-SPME. Proper desorption time can not only ensure the analytes completely released from the fiber, but also can avoid the cross-contamination in subsequent experiments. Therefore, the effect of desorption time on extraction performance was investigated from 0.5-2.5 min. The results (Fig. S8) reveal that the desorption efficiency was enhanced with the increasing desorption time from 0.5 to 2.0 min and subsequent slightly decreased. Consequently, the desorption time of 2.0 min was chosen in the following experiment.

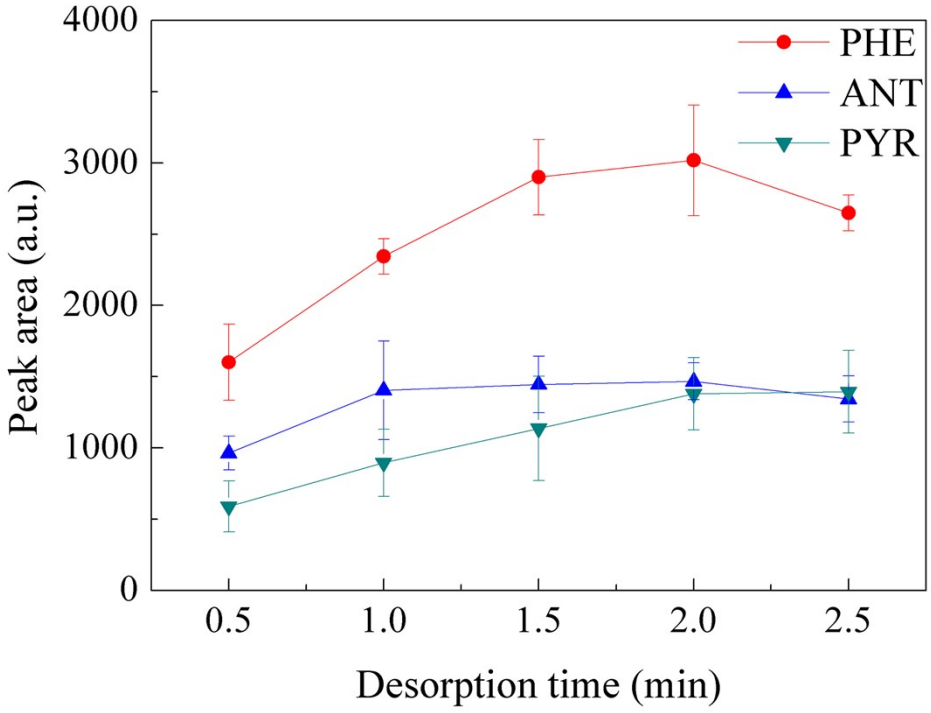


Fig. S8. The effect of desorption time on extraction efficiency. Experimental conditions: Fiber coating, 100 μm PDMS fiber; *v*olume of three-port glass vial, 25 mL; gas flow rate, 2 $L \cdot min^{-1}$; extraction temperature, 50 ℃; desorption temperature, 280 ℃; salt concentration, 0; concentration of analytes, 100 $ng \cdot mL^{-1}$.

2.1.7 *Ionic strength*

The influence of ionic strength of the sample solution on extraction efficiency was investigated. Usually, the extraction efficiency was enhanced with increasing ionic strength because of salting-out effect. To evaluate the effect of ionic strength on extraction efficiency, different concentrations of NaCl from 0 to 25% (w/v) were investigated. As shown in Fig. S9, when NaCl concentration from 0% to 20% (w/v), the extraction efficiency has not obvious change with increasing the ion strength. This phenomenon can be attributed to the fact that the GCA device accelerates the transfer rate of semi-volatile analytes through producing large amount of air bubbles at the interface of solution and headspace, which is similarity to the effect of increasing ionic strength to reduce the solubility of the target analytes and promote evaporation. The phenomenon for decreasing at high concentration of ion strength (from 20% to 25%) can be explained as following. The viscosity of solution was improved with increasing ion strength, which result in enhancement of mass transfer and electrostatic interaction between the analyte and salt ions. Therefore, the extraction efficiency was decreased with further improving ion strength from 20% to 25%.[8] So, no salt was added in this work.

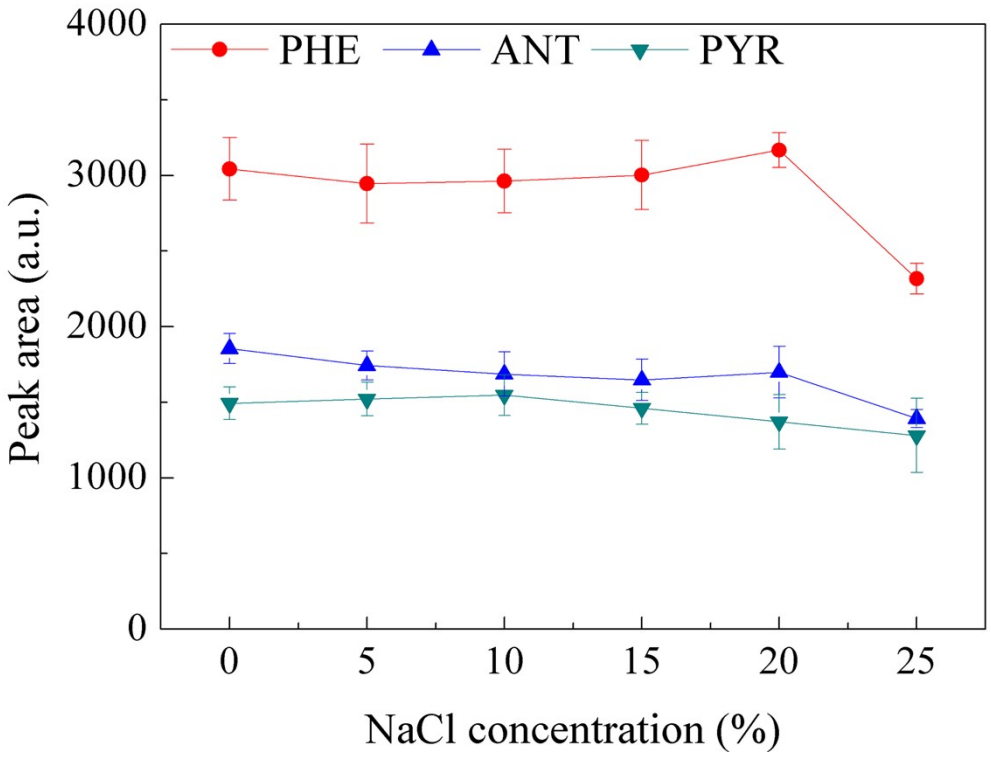


Fig. S9. The effect of position of the fiber on extraction efficiency. Experimental conditions: Fiber coating, 100 μm PDMS fiber; *v*olume of three-port glass vial, 25 mL; gas flow rate, 2 L·min^{-1}; extraction temperature, 50 ℃; desorption temperature, 280 ℃; desorption time, 2 min; salt concentration, 0; concentration of analytes, 100 ng·mL^{-1}.

2.2 *Validation of the method*

Analytical parameters including linearity, limits of detection (LODs), and intraday/interday precision were investigated under the optimal conditions. The linearity was investigated in the range of 0.002-100 ng·mL^{-1}. The linearity plot of PHE, ANT, and PYR are presented in Fig. S10. The results are listed in Table S2.

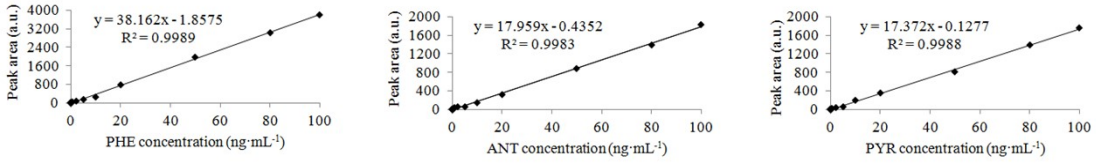


Fig. S10. The linearity plots of PHE, ANT, and PYR achieved by GCA HS-SPME GC-FID. All analysis were performed under the optimized conditions.

Table S2. The linear range, LODs, correlation coefficients (R^2), enrichment factors (EFs) and device precision parameters of the method for the analysis of PAHs.

Analytes	Linear range (ng·mL^{-1})	LOQs (pg·mL^{-1})	LODs (pg·mL^{-1})	R^2	EFs	RSD(%), n=5	
						Intra-day	Inter-day
PHE	0.002-100	2.00	0.49	0.9989	3030	2.94	10.48
ANT	0.005-100	5.00	1.35	0.9983	4166	2.54	7.75
PYR	0.005-100	5.00	1.51	0.9988	1339	5.88	7.05

2.3 *Analysis of real samples and recoveries of the method*

The recoveries of the method were investigated with adding three different concentrations to soil samples. The results are summarized in Table S3. The recoveries were obtained in the range from 79.84 to 122.4% with the RSDs (n = 5) between 1.58 and 12.0%.

Table S3. The results for analysis of soil samples by GCA HS-SPME GC-FID and recoveries.

Analytes	NS, 0-5 cm depth			RDS, 0-5 cm depth			CDS, 0-5 cm depth		
	Found (ng·mL^{-1})	Add (ng·mL^{-1})	Recovery% (RSD)	Found (ng·mL^{-1})	Add (ng·mL^{-1})	Recovery% (RSD)	Found (ng·mL^{-1})	Add (ng·mL^{-1})	Recovery% (RSD)
PHE	N.D.[a]	1.0	110.7±6.45	0.21	1.0	90.42±8.89	2.36	1.0	89.43±6.75
		10.0	96.66±5.35		10.0	84.85±5.52		10.0	115.3±3.49
		50.0	93.12±1.58		50.0	84.81±12.0		50.0	108.8±11.7
ANT	N.D.	1.0	97.48±6.99	0.54	1.0	87.80±1.92	2.17	1.0	90.10±4.99
		10.0	95.68±3.86		10.0	102.0±7.00		10.0	122.4±9.00
		50.0	96.19±4.05		50.0	79.84±1.67		50.0	98.68±9.48
PYR	N.D.	1.0	85.95±4.20	0.30	1.0	83.63±3.71	1.88	1.0	90.17±5.72
		10.0	103.2±8.82		10.0	110.1±8.65		10.0	92.92±3.14
		50.0	99.53±10.4		50.0	106.5±2.24		50.0	106.1±11.0

[a] Not detected

2.4 *Comparison with other sample pretreatment methods*

The comparison with other sample pretreatment methods to extract PAHs in soil samples were listed in Table S4. It can be seen from Table S4 that short extraction time and low extraction temperature were achieved with GCA HS-SPME technique. Moreover, this technique also can provide low LODs. This phenomenon can be attributed to the gas cycle assisted device facilitating the volatilization of semi-

volatile PAHs to headspace. It overcomes the shortcoming of conventional HS-SPME technology in pretreatment of semi-volatile target analytes.

Table S4. The comparison of this work with other reported method for the analysis of PAHs in soil sample.

Fiber Coating material	Extraction time (min)	Extraction temperature (℃)	LODs ($ng \cdot g^{-1}$/$ng \cdot mL^{-1}$)	Matrix	Analytical method	Refs.
OMC-ZSM-5[a]	30	60	0.5-1.6	Soil	HS-SPME-GC/FID	7
PDMS[b]	30	300	4.2-8.5	Soil	CA-SPME-GC/MS[c]	8
CNT–TiO_2[d]	40	50	0.002–0.004	Water	SPME-GC/FID	9
Nanoporous silica	20	80	0.4-3.5	Soil	NTD-SPME-GC/FID[e]	10
PDMS	120	80	0.8-8	Sediments	HS-SPME-GC/FID	11
PDMS	11	50	0.00049-0.0051	Soil	HS-SPME-GC/FID	This work

- [a] Ordered mesoporous carbon- zeolite socony mobil-5
- [b] Polydimethylsiloxane
- [c] Cooling-assisted headspace-SPME-GC/MS
- [d] carbon nanotubes–titanium oxide
- [e] Needle trap device headspace-SPME-GC/FID

2.5 Confirmation with GC-MS

To verify results obtained from GCA HS-SPME coupled with GC-FID, the chemical-deposited soil (CDS) sample was analyzed with GC-MS (Fig. S11). The results obtained from GC-MS were searched in chromatographic library (NIST17s.lib). Three target analytes including PHE (retention time, 16.930 min), ANT (retention time, 17.171 min), and PYR (retention time, 23.630 min) were detected in CDS sample. It can be concluded that the results of GCA HS-SPME coupled with GC-FID are consistent with that of GC-MS.

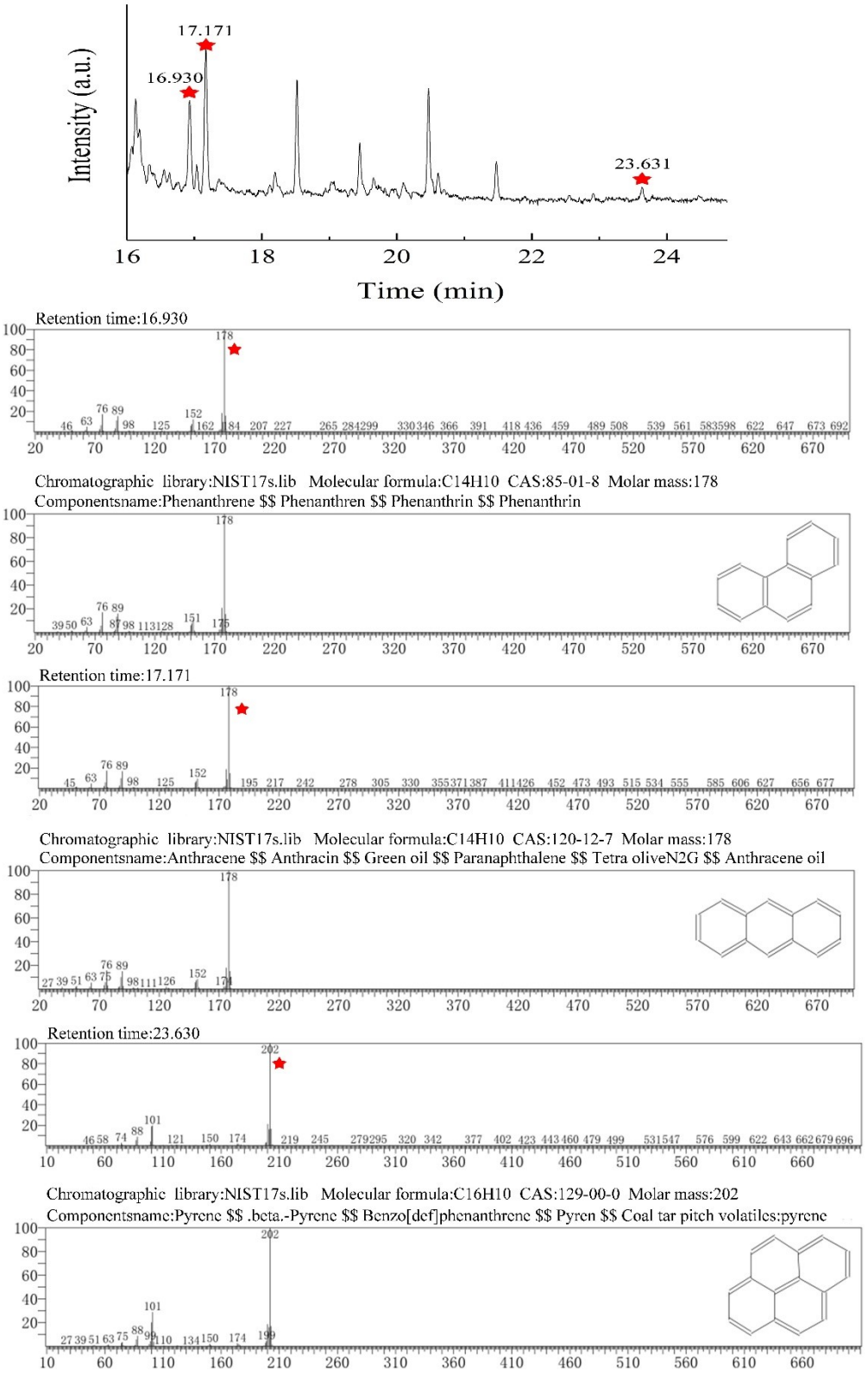


Fig. S11. The GC-MS chromatograms for the analysis of chemical-deposited soil.

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