Quantitative Determination of 16 Polycyclic Aromatic Hydrocarbons in Soil Samples Using Solid-Phase Microextraction

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Research Article

Quantitative determination of 16 polycyclic aromatic hydrocarbons in soil samples using solid-phase microextraction

A method for the determination of polycyclic aromatic hydrocarbons (PAHs) in soil samples using ultrasonic-assisted extraction with internal surrogates combined with solid-phase microextraction and GC-MS has been developed. Five kinds of commercial solid-phase microextraction fibers, 100 μm PDMS, 30 μm PDMS, 65 μm PDMS/DVB, 50 μm DVB/CAR/PDMS and 85 μm PA, were compared to choose the optimal SPME fiber for extraction of PAHs. One hundred micrometers of PDMS fiber was found to be more suitable for the determination of PAHs due to its wider linear range, better repeatability, lower detection and more satisfactory efficacy than the other fibers. Under the recommended conditions, 100 μm PDMS fiber could provide low nanogram level detection limits with correlation coefficient greater than 0.98. The method was also applied to determine PAHs in a spiked soil sample, obtaining recoveries higher than 79.3%. A field study with naturally contaminated samples from local contaminated sites was carried out. The proposed method was found to be a reliable, inexpensive and simple preparation method for quantitative determination of 16 PAHs in soil samples.

Keywords: Internal standard / Polycyclic aromatic hydrocarbons / Soil sample / Solid-phase microextraction / Ultrasonic extraction
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1 Introduction

Widespread contamination of polycyclic aromatic hydrocarbons (PAHs) in environment received great attention due to their toxicity and potential carcinogenic properties. Generally, the PAHs' level in environmental matrix is relatively low; therefore, preconcentration is necessary for the efficient determination of PAHs. Conventional methods such as liquid–liquid extraction and SPE have been widely applied to extract the PAHs in the aquatic and soil systems. However, these techniques are generally time-consuming and require large amounts of organic solvents. In addition, a highly tedious purification of the extracted solution before analysis is needed, which might reduce the recovery rates of PAHs. Consequently, alternative sample preparation methods are explored; one such method is solid-phase microextraction (SPME). SPME technique, as the rising pretreatment technique, has been proved to be a useful tool for extraction of PAHs in different matrix, such as water [1], human blood serum [2], urine [3], milk [4] and food matrix [5].

For PAHs determinations, especially in solid samples, headspace SPME has proved to be an efficient method to extract the low-ring PAHs, while the high-ring PAHs are difficult to be extracted because of their low volatility and strong adsorption to the particles [5–7]. However, most high-ring PAHs, such as benzo[a]pyrene and benzo[ghi]perylene are more toxic and have higher risk of carcinogenesis and mutagenesis than low-ring PAHs [8]. Restrictive legislation of the PAHs has been developed by various governments. In addition, high-ring PAHs are prone to accumulate in solid matrix due to their lipophilic character. Thus, it is imperative to accurate quantification for high-ring PAHs in the soil samples. Direct immersion SPME (DI-SPME) was commonly applied to the high-ring PAHs in the aquatic samples [4, 8–10]. However, DI-SPME cannot be directly used to extract the PAHs in the soil samples. It can be used

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Abbreviations: AcP, acenaphthene; **AcPY,** acenaphthylene; **BaA,** benz[a]anthracene; **BaP,** benzo[a]pyrene; **BbFL,** benzo[b]fluoranthene; **BghiP,** benzo[ghi]perylene; **BkFL,** benzo[k]fluoranthene; **Chr,** chrysene; **DBA,** dibenz[a,h]anthracene; **DI-SPME,** direct immersion-SPME; **FID,** flame ionization detector; **Flu,** fluorene; **FL,** fluoranthene; **InP,** indeno[1,2,3-cd]pyrene; **IS,** internal standard; **Nap,** naphthalene; **PAH,** polycyclic aromatic hydrocarbon; **Phe,** phenanthrene; **Pyr,** pyrene; **SPME,** solid-phase microextraction

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in combination with other extraction methodologies, such as ultrasonic extraction [11–13], microwave-assisted extraction [14] and subcritical water extraction [15]. For example, with the help of micellar media, microwave-assisted extraction combined with SPME, ten of the 16 PAHs in soil sample were quantified [16].

For SPME applications, selection of SPME fiber is important. Many studies have been conducted to assess the applicability of different commercial SPME fibers to extract PAHs [10, 17]. However, these studies usually take extraction efficiency as the sole criteria to choose optimal SPME fiber. Other parameters, such as the method's sensitivity, reproducibility, selectivity and linearity range are usually ignored. Therefore, it is necessary to pay attention on them. Therefore, it is very necessary to find the optimal SPME fiber by comparison of different fibers in terms of various parameters.

In this paper, an in-depth study on the applicability of SPME to 16 PAHs determination in soil samples was carried out. Five commercially available SPME fibers were selected to determine PAHs. Labeled internal standard (IS) method was introduced, which was expected to compensate casual errors (*e.g.* losses to glassware or volatilization) and reduce matrix effect (*e.g.* adsorption to particulate). Ultrasonic extraction was employed prior to SPME procedure. Matrix effect of soil on determination of PAHs was investigated. A field analysis was performed and validated for real samples.

2 Materials and methods

2.1 Reagents

The standard mixture of 16 PAHs (each at 200 μg/mL) in dichloromethane/methanol (1:1, v:v), containing 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 (BbFL), benzo[k]fluoranthene (BkFL), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenz[a,h]anthracene (DBA) and benzo[ghi]perylene (BghiP), was purchased from AccuStandard (USA). Deuterated ISs containing [2H10] AcP-d10, [2H10] phenanthrene (Phe-d10), and [2H12] chrysene (Chr-d12) at 500 μg/mL were purchased from Supelco (Bellefonte, PA, USA). For SPME study, working solutions of 16 PAHs and IS solution at a concentration of 10 mg/L were prepared, respectively, by diluting with methanol every week. All standards and working solutions were stored at 4°C in silanized brown glass bottles with Teflon-lined caps. Copper filings were activated by 6 M HCl solution and consecutively rinsed with distilled water, acetone and *n*-hexane, respectively, prior to use. Deionized water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Methanol, dichloromethane and *n*-hexane of HPLC grade were obtained from Merk (Darmstadt, Germany).

2.2 Choice of SPME fibers

Commercial SPME holders for manual use and fiber assembly for manual sampling were purchased from Supelco. Five SPME fibers were selected according to the literature and also recommended by Supelco: 100 μm PDMS, 30 μm PDMS, 65 μm PDMS/DVB, 50 μm DVB/CAR/PDMS and 85 μm PA. These fibers were selected to compare and evaluate their extraction performance of PAHs. All fibers were conditioned according to the instructions provided by the manufacturer.

2.3 Collection of the samples

A total of four soil samples were collected. Soil 1 which was used to construct calibration curves was obtained from Zijin mountain (Nanjing, Jiangsu, China). Soil 2, used as spiked sample to investigate the matrix effect of the proposed method, was collected from Chengde (Chengde, Hebei, China). Both soil 1 and soil 2 were free of PAHs contamination. Soil 3 and soil 4 used as real samples were taken from Heilongjiang province and a heavy traffic area located in Jiangning district in Nanjing city of Jiangsu province, respectively. The physicochemical characteristics of the soil samples are given in Table 1.

2.4 Preparation of spiked soil samples

The soil samples were air-dried at ambient temperature (25°C) for 1 wk and sieved through 0.154-mm mesh. The samples were spiked as follows: 1 g of each soil was immersed in 2 mL acetone, then spiked with a mixed standard solution of 75 ng/g IS and calibration PAHs, shaking for 2 h. Finally, the spiked samples were left at ambient temperature for 24 h for drying and aging. All samples were kept in brown glass bottles.

2.5 SPME procedure

All analyses were performed in 22-mL amber glass vials with PTFE silicone septa obtained from Supelco. The solutions were stirred with a magnetic stirrer (Jingfeng Instrument, Shanghai, China) using PTFE-coated magnetic stir bars (Sigma-Aldrich). Ultrasonic extractions were

Table 1. Physicochemical characteristics of the soil samples

Properties	Soil 1	Soil 2	Soil 3	Soil 4
pH	5.78	8.05	5.64	5.65
Sand (%)	36.8	43.6	38.8	39.3
CEC[a)] (cmol/kg)	24.55	17.73	32.47	22.38
Organic matter (%)	2.59	1.85	2.68	2.04

a) Cation exchange capacity.

carried out in a digital-controlled ultrasonic bath (Kunshan Ultrasonic Instrument, Kunshan, China).

Generally, higher desorption temperature facilitates complete desorption of PAHs, especially for high-ring PAHs. In this study, the temperatures which were 10°C lower than maximum operation temperatures were used as desorption temperatures as a compromise of the fiber life-span and desorption efficiency. Ten minutes in splitless mode was selected to desorb the PAHs. Possible carryover was removed by keeping the fiber in another injector for an additional 5 min with the inlet in the split mode.

For preliminary choice of SPME fibers, the SPME procedure was performed in water samples. DI-SPME mode was employed because the headspace SPME was inefficient for incapable of extraction of the high-ring PAHs [4, 8–10]. Extraction parameters used in this study were based on previous literature [10] except that the extraction time was fixed at 60 min instead of 90 min as a compromise of GC time and enough sensitivity. In detail, 15 mL of water was extracted at 60°C for 60 min with DI-SPME mode under magnetic stirring; neither pH adjustment nor ionic strength correction was applied.

For soil samples, there are two separate off-line steps: ultrasonic extraction of PAHs from the soil and then SPME over soil extract. The literature procedure [12] for ultrasonic extraction was used. In detail, 1 g spiked soil sample was added to 0.2 g copper filings, and then extracted by a 10-mL aliquot of hexane/dichloromethane (1:1) with ultrasonic agitation for 10 min. Suspensions were separated by centrifugation for 15 min at 3500 rpm and then another fresh 10 mL aliquot organic solvent was used to extract for another two 10 min. The combined extracts were reduced to approximately 5 mL with a vacuum rotary evaporator at 35°C and then evaporated to almost dryness under a gentle stream of nitrogen. The residues were reconstituted with 100 μL acetone and 15 mL water in sequence. Then, it was subjected to SPME extraction with 100 μm PDMS fiber under the conditions described previously for water samples.

2.6 Analytical process of GC and GC/MS

Agilent 6890N GC system with flame ionization detector (FID) and DSQ II Single Quadrupole GC-MS (Thermo-Quest, San Jose, CA, USA) were used for the determination of PAHs. Primary analysis for SPME fiber selection was conducted using GC-FID, and confirmatory analysis for method establishment was carried out using GC-MS. The conditions of GC-FID were as follows: a DB-5 capillary column (30 m × 0.32 mm id, 0.25 μm film thickness) was used for separation. Oven temperature program started at 50°C, held for 5 min, then up to 160°C at 20°C/min, to 265°C at 5°C/min and finally to 300°C at 3°C/min and held for 5 min. The carrier gas was nitrogen with a flow rate of 1.5 mL/min. The detector flow rates were 400 mL/min for air, 30 mL/min for hydrogen and 25 mL/min for nitrogen (makeup gas). The detector was maintained at 320°C. The injector was maintained between 250 and 310°C, depending on the desorption temperature used. For GC-MS, a fused-silica DB-35 MS capillary column (30 m × 0.32 mm id, 0.25 μm film thickness) was used. Oven temperature program started at 50°C, held for 5 min, then up to 160°C at 20°C/min, to 265°C at 3°C/min and finally to 325°C at 5°C/min and held for 5 min. Helium was the carrier gas at a constant flow of 1.0 mL/min. The interface line and ion source temperature were maintained at 300 and 230°C, respectively. The ionization was carried out in electron impact mode at 70 eV. The mass range scanned was from 50 to 550 amu under full scan acquisition mode. Retention times and molecular ions were used as the key criteria for identification, shown in Table 2.

Table 2. Retention time, *m/z* value and surrogate standards for each analyte

Compound	Retention time (min)	*m/z*	Surrogate
Nap	11.06	128	AcP-d_{10}
AcPY	14.95	152	AcP-d_{10}
AcP-d_{10}	15.32	164	
AcP	15.46	154	AcP-d_{10}
Flu	17.54	166	AcP-d_{10}
Phe-d_{10}	23.1	188	
Phe	23.26	178	Phe-d_{10}
Ant	23.54	178	Phe-d_{10}
FL	31.85	202	Phe-d_{10}
Pyr	33.83	202	Phe-d_{10}
BaA	43.5	228	Chr-d_{12}
Chr-d_{12}	43.8	240	
Chr	44.05	228	Chr-d_{12}
BbFL	51.1	252	Chr-d_{12}
BkFL	51.24	252	Chr-d_{12}
BaP	53.18	252	Chr-d_{12}
InP+DBA[a)]	58.26	278, 276	Chr-d_{12}
BghiP	59.71	276	Chr-d_{12}

a) Under the proposed GC-MS conditions, InP and DBA were hard to be separated and thus integrated together.

3 Results and discussion

3.1 Primary choice of five fibers

To choose the optimal SPME fibers, the extraction efficiency was used as the primary criteria to compare the PAHs extraction ability for five commercial fibers. Five micrograms per liter PAHs in the spiked water samples were extracted. Figure 1 shows the extraction efficiency of 16 PAHs for five fibers. As shown in the figure, 85 μm PA fiber gave relatively low extraction efficiency, which might be due to its polar character. 50 μm DVB/CAR/PDMS fiber gave satisfactory extraction efficiency towards low-ring PAHs, but it is

incapable for the high-ring PAHs. On the contrary, for 30 μm PDMS fiber, only high-ring PAHs were effectively extracted.

One hundred micrometers PDMS fiber and 65 μm PDMS-DVB fiber could synchronously extract the low-ring and high-ring PAHs in the aqueous phase. Previous studies have also proved that, from the perspective of extraction efficiency, 100 μm PDMS [1, 10, 18, 19] and 65 μm PDMS-DVB [4, 5, 9, 17, 20] could be considered as the optimal fibers for the PAHs extraction. Moreover, 100 μm PDMS gave excellent affinity to high-ring PAHs, while 65 μm PDMS-DVB gave better extraction toward low-ring PAHs. This can be explained by their different extraction mechanism, *i.e.* absorption (100 μm PDMS) *versus* adsorption (65 μm PDMS-DVB) [21]. For 100 μm PDMS, the distribution coefficients (K) increase with the increasing analyte hydrophobicity, expressed by the octanol-water partitioning coefficient (K_{ow}) [22]. For 65 μm PDMS-DVB the analytes extraction is a competitive process, which would result in concentration-dependent and mixture-dependent responses. The number of effective surface sites is limited for adsorption to occur. Low molecular compounds diffuse into the pores of the sorbents more easily. Therefore, 100 μm PDMS and 65 μm PDMS-DVB were chosen as SPME candidates to extract PAHs and evaluated roundly in the following study.

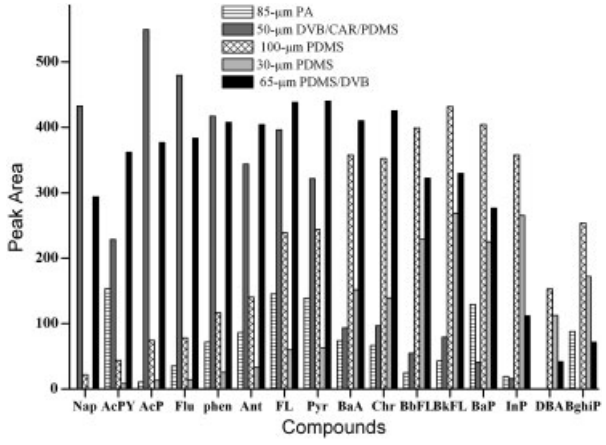

Figure 1. Comparison of extraction efficiency of five SPME fibers.

3.2 Determination of the optimal fiber

One hundred micrometers PDMS and 65 μm PDMS-DVB were compared in terms of method detection limits, repeatability, linearity range, lifespan and anti-interference ability other than extraction efficiency alone. Detection limits were calculated at a signal to noise ratio (S/N) of 3. The method precision was evaluated by six repetitive analysis of standard solutions at a concentration of 5 μg/L ($n = 6$). All these studies were carried out using GC-FID.

The features of proposed method using the both fibers are presented in Table 3. Slope of the linearity equation could reflect the extraction efficiency. Similar to Fig. 1, higher slope of the high-ring PAHs was obtained for 100 μm PDMS, while that of the low-ring PAHs for 65 μm PDMS-DVB. The lowest LOD for most of the PAHs, especially for high-ring PAHs were obtained by using the 100 μm PDMS fiber. For repeatability, 100 μm PDMS fiber was superior to 65 μm PDMS-DVB for most PAHs except for Acp, Inp and BghiP. Considering linear range, 100 μm PDMS fiber also showed wider range with excellent correlation coefficients.

Table 3. Analytical parameters for the analysis of PAHs using 100 μm PDMS and 65 μm PDMS-DVB SPME fiber performed on GC-FID

	DRL[a)] (ng/mL)		Slope		Correlation coefficient (R^2)		R.S.D. (%)		LOD (μg/mL)	
	100 μm PDMS	65 μm PDMS-DVB	100 μm PDMS	65 μm PDMS-DVB	100 μm PDMS	65 μm PDMS-DVB	100 μm PDMS	65 μm PDMS-DVB	100 μm PDMS	65 μm PDMS-DVB
Nap	0.5–150	0.2–10	5.0664	38.136	0.9975	0.9961	1.45	6.64	0.1	0.05
AcPY	0.2–150	0.1–50	9.0502	47.787	0.9984	0.9942	1.77	6.56	0.05	0.02
AcP	0.2–150	0.1–50	17.24	63.829	0.9981	0.9991	6.49	5.94	0.05	0.02
Flu	0.2–150	0.1–50	18.741	71.617	0.9979	0.9995	3.24	5.94	0.05	0.02
Phe	0.2–150	0.1–100	27.085	71.467	0.9986	0.9943	2.25	5.61	0.05	0.02
Ant	0.2–150	0.1–100	28.771	62.38	0.9999	0.9906	1.84	5.19	0.05	0.02
FL	0.2–150	0.2–100	49.342	73.803	0.9999	0.9958	2.44	4.67	0.05	0.05
Pyr	0.2–150	0.2–100	52.134	74.815	0.9998	0.9957	3.37	6.62	0.05	0.05
BaA	0.2–30	0.2–10	66.432	74.328	0.9997	0.9997	3.31	14.23	0.02	0.05
Chr	0.1–30	0.2–10	64.497	75.822	0.9996	0.9991	3.36	4.95	0.01	0.05
BbFL	0.1–100	0.2–10	71.386	56.543	0.9995	0.9998	3.28	7.39	0.01	0.05
BkFL	0.1–100	0.2–10	70.648	50.295	0.9989	0.9961	3.28	6.46	0.01	0.05
BaP	0.1–100	1–10	68.073	43.079	0.9993	0.9987	5.59	8.158	0.01	0.2
InP	0.2–10	1–10	55.12	14.86	0.9985	0.9932	6.52	3.94	0.01	0.2
DBA	0.2–50	2–50	12.867	2.3482	0.9903	0.9990	5.62	6.56	0.03	0.5
BghiP	0.2–50	2–50	14.169	2.6558	0.9802	0.9832	9.26	5.91	0.03	0.5

a) Dynamic linearity range.

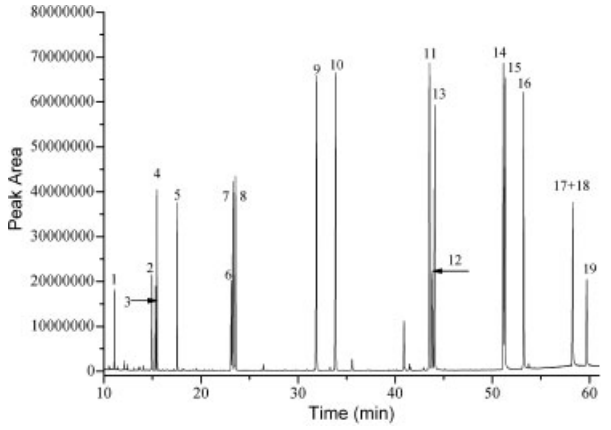

Figure 2. Chromatogram of 16 PAHs (10 μg/L) and three internal surrogates (5 μg/L) analyzed under the proposed method. Peak numbers correspond to (1) Nap, (2) AcPY, (3) AcP-d_{10}, (4) AcP, (5) Flu, (6) Phe-d_{10}, (7) Phe, (8) Ant, (9) FL, (10) Pyr, (11) BaA, (12) Chr-d_{12}, (13) Chr, (14) BbFL, (15) BkFL, (16) BaP, (17+18) InP+DBA and (19) BghiP.

Table 4. Analytical parameters for 16 PAHs in soil samples with proposed method performed on GC-MS

Compound	DLR (ng/g)	R^2	LOD (ng/g)	RSD (%)
Nap	15–1200	0.9910	10	11.8
AcPY	15–1200	0.9946	2	3.2
AcP	25–1500	0.9952	5	5.6
Flu	30–1500	0.9987	5	6.8
Phe	30–1200	0.9942	5	2.6
Ant	20–1200	0.9938	5	5.4
FL	20–1200	0.9901	2	9.7
Pyr	30–750	0.9953	2	10.9
BaA	15–750	0.9980	5	8.47
Chr	15–750	0.9998	5	3.4
BbFL	15–750	0.9835	5	9.3
BkFL	15–750	0.9858	5	10.54
BaP	15–750	0.9820	5	11.4
InP+DBA	45–450	0.9726	20	10.62
BghiP	45–450	0.9685	20	12.37

In terms of lifespan, 40–50 sample injections are required in direct immersion mode for 65 μm PDMS-DVB [4], while over 100-time injections are required for 100 μm PDMS in this study. Considering matrix interference, absorption mechanism based SPME fiber (*e.g.* 100 μm PDMS) is more selective than adsorption mechanism based fiber (65 μm PDMS-DVB) [23], so it may be more resistant to matrix composition, which is especially beneficial for analysis of complex real samples. Based on the above qualities, 100 μm PDMS fiber was selected as the most appropriate SPME fiber for determining PAHs because it provided lower LOD, better repeatability, a broader linear range with excellent correlation coefficients and longer lifespan.

3.3 Determination of PAHs in the soil samples

All the following studies were carried out using GC-MS. Under the recommended SPME conditions using 100 μm PDMS, satisfactory extraction efficiency was obtained in aqueous sample, as shown in Fig. 2. However, an attempt to construct calibration curves by external method in soil samples failed because of the serious matrix effect and casual operation errors. It was recommended by Pawliszyn *et al.* [24] that ISs can be used to compensate for the matrix effect, losses of analytes during sample preparation and irreproducibility in parameters. As expected, when labeled IS was introduced, it made the accurate quantification of PAHs in soil samples. The results are illustrated in Table 4. However, it is worthy to notice that the recoveries of spiked sample, correlation coefficient (column 3 in Table 4) and RSD (column 5 in Table 4) of calibration sample for Nap and higher ring PAHs are worse. It can be explained that in IS calibration method the physicochemical properties of the standard should be similar to the target analyte. The closer physicochemical properties of the native analyte and ISs, the better results will be obtained. Although calibration with isotope-labeled standards can produce a satisfactory result [25], internal surrogates are not available for all analytes of interest. It was observed that the properties of the Nap and higher ring PAHs are more different from selected surrogate compounds, leading to their different partition behavior.

3.4 Investigation of the matrix effect

The influence of soil characteristics on the proposed method was determined using spiked soil 2 sample whose properties were much different from soil 1 sample (Table 1) to further evaluate the applicability of the proposed method. As shown in Fig. 3, the GC resolution and peak shapes are acceptable. In general, the recovery rates are satisfactory for all compounds, ranging from 79.3% to 88.6%, which is comparable or superior to previous study [16]. Especially, the proposed method is independent of soil characteristic, which is very useful in field analysis. It may be due to the joint effect of exhaustive extraction (ultrasonic extraction) and IS addition. Thus, the proposed method could be expected to determine PAHs in sediment, atmospheric particulate and so on. These results demonstrated that isotope dilution method is indispensable and feasible to accurately quantify the PAHs in complex environmental matrix.

3.5 Application to real samples

The proposed methods were carried out to determine the PAHs levels in the real soil samples. Each was performed in

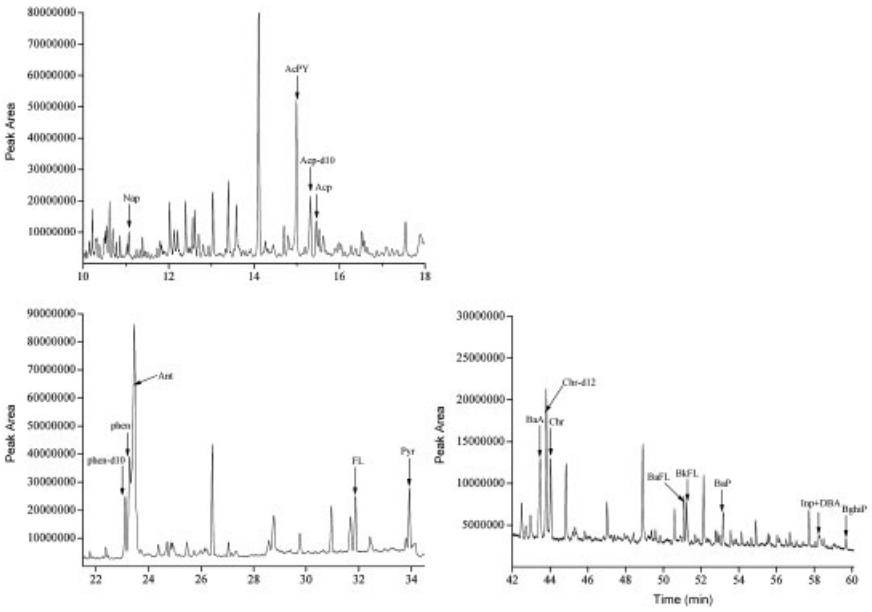

Figure 3. Mass chromatograms obtained after SPME of spiked soil 2.

triplicate. The soil samples were treated as described in Section 2.3, except for addition of native 16 PAHs. Because the concentrations for most of the detected compounds (AcPY, AcP, Chr, BbFL, BkFL and Bap) in soil 4 sample exceeded the linearity range, quantitative information was not obtained by the proposed method. The soil 3 sample was abundant in Nap (21.5 ng/g), FL (79.5 ng/g), Pyr (64.8 ng/g), BaA (83 ng/g) and Chr (52.4 ng/g), indicating that the PAHs widely existed in natural environment. Especially, high-ring PAHs (*i.e.* BaA, Chr, BbFL, BkFL and Bap) are detected out, which is incapable for headspace-SPME [6].

4 Concluding remarks

One hundred micrometers PDMS and 65 μm PDMS-DVB SPME fibers were compared in terms of extraction efficiency, LOD, RSD, DLR, *etc*. and the results showed that the 100 μm PDMS was the most suitable fiber for PAHs analysis. A method based on SPME-GC-MS has been developed and validated for determining 16 PAHs in soil samples. The proposed method enables the quantification of PAHs at nanogram level in soil matrix. It has been demonstrated that matrix effects especially for soils determination make the use of isotope-labeled surrogates necessary to get reliable quantification results. Good recoveries were obtained in spiked experiments. Three surrogates employed in this study are commercially available and cheap, and ultrasonic extraction is common and economic preliminary method, which is applicable in routine analysis. Some target PAHs were found in real-world samples under proposed method.

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