



## Original Paper

# Fast analysis of derivatives of polycyclic aromatic hydrocarbons in soil by ultra-high performance supercritical fluid chromatography after supercritical fluid extraction enrichment



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## ABSTRACT

An efficient and environment-friendly method for simultaneous determination of 13 typical derivatives of polycyclic aromatic hydrocarbon (PAH) in petroleum-polluted soil with nitro-, oxy- and alkyl-functional group was developed using supercritical fluid extraction (SFE) followed by ultra-high performance supercritical fluid chromatography (UHPSFC). Parameters of UHPSFC, including type of stationary phase and mobile phase modifiers, gradient elution process, backpressure, column temperature, and the flow rate of mobile phase, were systematically optimized, achieving a fast separation within 4.2 min. Limits of detection (LOD) were 0.005–0.1  $\mu\text{g mL}^{-1}$  or 0.1–2.0  $\text{ng g}^{-1}$ , respectively, with a good repeatability (RSD<5.0%). Before UHPSFC-PDA analysis, the PAH-derivatives in soil samples were effectively enriched in 15.0 min using SFE with an online carbon nanotubes (CNTs) collection trap. The soil samples were analyzed by the proposed method and the results were verified by GC-MS. Thus, SFE equipped with an online CNTs trap followed by UHPSFC-PDA analysis, which only consumed about 2.0 mL organic solvent for a whole run, has been demonstrated to be an efficient way for screening and quantitative analysis of trace-level PAH-derivatives in soil samples.

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## 1. Introduction

Along with the rapid development of petroleum industries, petroleum exploitation activities are growing intensively, whereas oil spills also occur from time to time (Du et al., 2011). As a result, large quantities of the surrounding soils have been contaminated by petroleum or its products (Wang et al., 2008). Oil contamination in soils is becoming a big environmental issue. Environmental screening is an important task of pollution monitoring and control, and it is also one area where rapid and high-throughput analysis is highly required (Zhou et al., 2015). There are thousands of pollutants in oil-contaminated soils. Among them, polycyclic aromatic hydrocarbons (PAHs) have attracted worldwide attention because they have potential risks of carcinogenesis and mutagenesis.

Derivatives of polycyclic aromatic hydrocarbon (PAH), primarily including alkyl-, oxy- and nitro-PAHs, are also widespread in oil-contaminated soils. Compared with PAHs, PAH-derivatives were proved to possess higher toxicity (Durant et al., 1996) and stronger resistant to biodegradation, but they were paid less attention to because most current regulations only monitor residual PAHs (Cai et al., 2009; Hollosi and Wenzl, 2011; Tian et al., 2018). For PAH-derivatives with a wide range of polarity, it is a challenging task to achieve fast separation in one-run analysis.

The most common techniques used to separate PAH-derivatives in environmental matrix are gas chromatography (GC) and liquid chromatography (LC). The highly concerned species of PAH-derivatives have been analyzed separately or simultaneously by GC coupled with mass spectrometry (MS) in many studies with high sensitivity up to 1–40  $\text{ng mL}^{-1}$  (Niederer, 1998a; Meyer et al., 1999; Cochran et al., 2012; Qiao et al., 2013; Han et al., 2015). However, it often takes more than 1 h to analysis 5–13 typical PAH-derivatives, which is time consuming and limits high throughput

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analysis. In addition, GC method has proven less useful for compounds with high molecular weight (>300 amu) and low volatilities (Cai et al., 2009; Lung and Liu, 2015). Nitro-PAHs are prone to decompose at high temperatures, and thus a cool on-column injection is preferred (Niederer, 1998b). But on-column injection is not favored when other species of PAH-derivatives are present, decreasing the sensitivity of nitro-PAHs analysis. To overcome these shortcomings, high performance liquid chromatography (HPLC) and ultra-high performance liquid chromatography (UPLC), coupled with fluorescence, UV, and MS detectors were employed. Nyiri et al. (2016) analyzed 11 nitro-PAHs in particulate matter samples taking 19 min using LC-atmospheric pressure chemical ionization (APCI) MS. Gimeno et al. (2002) determined 6 PAHs and 4 sulfur containing PAH-derivatives in seawater and sediment samples by HPLC with both fluorescence detection (FD) and APCI-MS in 35 min and 18 min, respectively. To further improve the separation efficiency, UPLC was currently introduced. Based on UPLC-APPI-MS, Lung et al. (2015) analyzed 20 PAHs and 9 nitro-PAHs in aerosols taking 15 min and 11 min, respectively, only one half of the analysis time by GC-MS or even HPLC-MS.

A promising alternative to UPLC method for PAHs/PAH-derivatives analysis is supercritical fluid chromatography (SFC). Using supercritical fluid CO<sub>2</sub> (sc-CO<sub>2</sub>) instead of organic solvent as mobile phase, SFC is classified as a green separation technique and particularly ideal for non- or low-polarity compounds (Gong et al., 2014; Guo et al., 2015; Liu et al., 2017). It possesses evident benefits in fast and high throughput separation since supercritical fluid with low viscosity and high diffusivity, which could accelerate diffusion and mass transfer of analytes. SFC has been applied to analysis of sulphonamides residues in food (Perkins et al., 1991), triterpenoids in plant (Huang et al., 2016), chiral separation in pharmaceutical industry (Plotka et al., 2014), and so on. Most of the separation could be completed in less than 10 min. However, SFC has not been extensively used since developed because its backpressure is hard to keep as stable as HPLC, resulting in poor controllability and reproducibility. Ultra-high performance supercritical fluid chromatography (UHPSFC), a new generation of SFC, integrating the benefits of SFC technology with the performance of UPLC technology, has successfully overcome the technical challenge of poor backpressure control. Moreover, usage of UPLC columns with sub-2 μm particles packing provides improved separation efficiency. Thus, the analytical time and consumption of organic solvent could be drastically reduced, which makes its application more attractive in routine or high-throughput analysis. UHPSFC has been explored in pharmaceutical industry (Grand-Guillaume et al., 2012; Zhang et al., 2015), food safety (Berger and Berger, 2013; Ji et al., 2014; Li et al., 2015), environmental screening (Chen et al., 2014) and so on. For example, Zhou et al. (2014) determined 17 disperse dyes in textile within 5 min; Zhang et al. (2015) separated 15 sulfonamides and metabolites in serum samples within 7 min; Li et al. (2015) analyzed 9 carotenoids in dietary supplements within 10 min; Tang et al. (2018) analyzed 16 PAHs in rubber within 5 min.

Sample preparation is also a critical and time-consuming step. A supercritical fluid extraction (SFE) method with carbon nanotubes (CNTs) as solid collection trap has been developed in our previous work, which has been proved a green, effective and efficient method for PAH-derivatives enrichment from soil matrix (Han et al., 2015).

Therefore, the aim of this work is to develop a fast and reliable method for simultaneous determination of 13 typical alkyl-, oxy- and nitro-PAH derivatives (Fig. 1) in soil samples based on SFE-CNTs pretreatment and UHPSFC separation.

## 2. Material and methods

### 2.1. Chemicals and materials

Standard compounds of PAH-derivatives, 2,6-dimethylnaphthalene (2,6-DMN), 1,4-naphthoquinone (1,4-NQ), 2-methyl-1-nitronaphthalene (2-M-1-N), 1-nitronaphthalene (1-NA), 1,5-dinitronaphthalene (1,5-DNN), 1-methylpyrene (1-Mpy), 9-fluorenone (9-Fl), 2-nitrofluorene (2-NF), anthraquinone (Antr), 9-nitronaphthalene (9-NA), benzo[*a*]anthracene-7,12-dione (BaA-7,12-Q), 1-nitropyrene (1-Npyr) and benzanthrone (BAQ) were purchased from Acro Organics, Inc. New Jersey, USA. Dichloromethane (DCM), hexane, toluene and methanol were all of HPLC-reagent grade and supplied by Fisher Scientific, USA. The names and structures of the PAH-derivatives are shown in Fig. 1. A stock solution was prepared in toluene as 1 mg mL<sup>-1</sup> each of PAH-derivatives and stored at 4 °C.

Multi-wall carbon nanotubes were synthesized according to the arc discharge method using graphite as raw material. The external diameter of the CNTs was between 10 and 40 nm with the length in the range of 10–30 μm.

### 2.2. Instruments

UHPSFC analysis was performed using an ACQUITY UPC<sup>2</sup> system (Waters, USA) which consists of a convergence manager, a sample manager, a binary solvent manager, a back pressure regulator, a column manager and a photo-diode array detector (PDA). The UHPSFC-PDA system was controlled by MassLynx version 4.1 software (Waters). The quantitative analysis was performed at 50 °C using an ACQUITY UPC<sup>2</sup> BEH 2-Ethyl-Pyridine column (100 mm × 3.0 mm i. d., 1.7 μm, Waters, USA). The mobile phase A was supercritical carbon dioxide and the mobile phase B was toluene. The elution gradient was: 100% A (initial), 100–99.9% A (0–3.0 min), 99.9–70% A (3.0–3.4 min), 70–70% A (3.4–4.0 min), 70–100% A (4.0–4.2 min), providing a total analysis time 4.2 min. The flow rate was set at 1.65 mL min<sup>-1</sup>. The back pressure was set at 1500 psi. The injection volume was 1 μL. Each analyte was monitored at its wavelength of maximum absorbance. The PDA detector set at 222 nm for 2,6-DMN, 243 nm for 1,4-NQ, 218 nm for 2-M-1-N, 209 nm for 1-NA, 227 nm for 1,5-DNN, 238 nm for 1-Mpyr, 251 nm for 9-Fl, 316 nm for 2-NF, 246 nm for Antr, 243 nm for 9-NA, 279 nm for BaA-7, 12-Q, 232 nm for 1-Npyr and 226 nm for BAQ.

Supercritical fluid extraction was performed on an ASFE instrument (Waters, USA). The extraction temperature and pressure were set at 40 °C and 300 bar, respectively. DCM was used as the co-solvent of supercritical CO<sub>2</sub> with a volume ratio of 10%. The flow rate was 1.0 mL min<sup>-1</sup> and the dynamic extraction time was 15 min. The extraction cell was 10 mL, which could be fully filled with 5 g soil sample. Detailed information has been described in our previous work (Han et al., 2015).

### 2.3. Soil samples and sample pretreatment

The soil samples were collected, crushed and sieved to 100–200 mesh. After checked by GC-MS (The limit of detection of GC-MS for 13 PAH-derivatives was between 1 and 10 ng mL<sup>-1</sup>) to be free of PAH-derivatives, the soil samples were used as blank matrix and stored at 4 °C before use. The blank soil sample was spiked with the standard solution of PAH-derivatives at three different concentration levels.

Sample pretreatment were performed using the online SFE extraction-CNTs trap method (Han et al., 2015). The target analytes

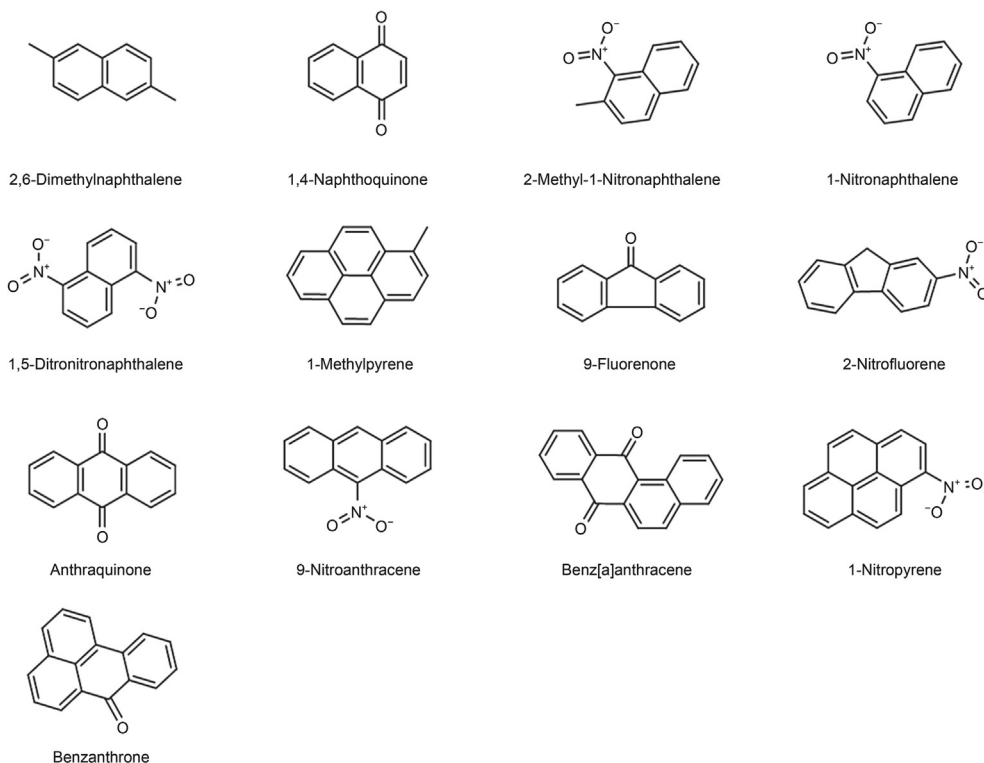


Fig. 1. Chemical structures of the investigated PAH-derivatives.

absorbed on the CNTs adsorbent were eluted by 1 mL of DCM for three times. The eluate was nearly dried under a gentle stream of nitrogen and re-dissolved in toluene to a final volume of 100  $\mu$ L for UHPSFC analysis.

### 3. Results and discussion

#### 3.1. Optimization of UHPSFC conditions

For efficient resolution of PAH-derivatives, four kinds of stationary phases with different retention properties were tested, i.e., BEH (hybrid silica without bonding), BEH 2-Ethyl-pyridine (hybrid silica with a 2-ethylpyridine bonding, BEH 2-EP for short), HSS C18 SB (classical silica bonded with C18) and CSH Fluorophenyl (charged surface hybrid silica bonded with a fluorophenyl group). Unlike PAHs, PAH-derivatives are not only different in the benzene skeleton, but also in the polarity of the substituents. BEH 2-EP column, which could offer  $\pi$ - $\pi$  interaction and dipole induced dipole interaction between PAH-derivatives and the stationary phase, was demonstrated effective. Modifiers are usually added to supercritical fluids to change its eluent strength and improve peak shape. Four modifiers including hexane, toluene, dichloromethane and methanol were evaluated and the best result was obtained using toluene. During the screening experiments, the gradient conditions, auto back pressure regulator (ABPR) backpressure, column temperature and flow rate were found to be the critical factors effecting separation efficiency, peak shape, resolution, and sensitivity of the analyzed compounds, and thus should be systematically optimized.

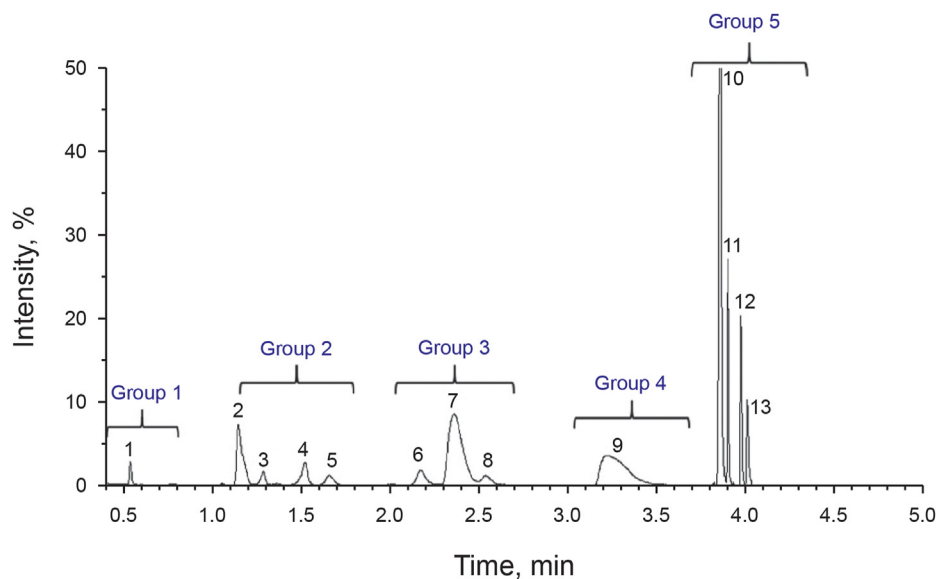
#### 3.2. Optimization of the gradient conditions

For the 13 PAH-derivatives containing a wide range of polarity, gradient elution is required to achieve fast separation. 13 PAH-

derivatives can be roughly divided into 5 groups based on their retention behavior (refer to Fig. 2 and Table 1 for detailed groups information). The objective of gradient optimization is to ensure a baseline separation within each group and the time gap between groups is as short as possible. When no organic modifier was added, only the first 3 groups could be eluted by pure supercritical CO<sub>2</sub> around 3.0 min but with poor peak symmetry, while the rest 2 groups could be eluted after 3.0 min only when no less than 10% toluene was added. Therefore, the point of 3.0 min is critical for it divided the optimization process into two sections: section 1 including the first 3 groups only needs a weak elution whereas section 2 including the rest 2 groups requires a strong elution.

As for section 1, to obtain a baseline separation with better peak shape, the initial percentage of toluene was 0 and the final percentage was varied. Since subtle changes in toluene amount can result in obvious change in resolution of peaks, toluene amount was varied over a narrow range from 0 to 1% in 0.1% increment as shown in Fig. 3a, and 0.1% was selected, which also demonstrated the outstanding controllability of this SFC system. Then, conditions for section 2 was optimized in the same way as shown in Fig. 3b. 0.1% was used as the initial percentage of toluene and the final percentage was optimized in the range of 10%–40% within the time section of 3.0–4.0 min. Considering the resolution as well as symmetrical factors of all peaks, condition f was selected.

To further shorten the separation time, the time section for gradient elution was further evaluated using the optimized modifier concentrations. Generally, the narrower the time section is, the steeper the gradient is, the more effective the elution is. As shown in Fig. 3c, the gradient elution for section 2 started at 3.0 min, and the length of time section varied from 0.1 min to 1.0 min with 0.1 min increment. The resolution of 12 pairs of adjacent peaks was plotted as a function of length of time sections ( $a = 3.0$ – $3.1$  min,  $b = 3.0$ – $3.2$  min, ...,  $j = 3.0$ – $4.0$  min). Both condition d (time section = 3.0–3.4 min) and condition e (time



**Fig. 2.** The chromatogram of a standard mixture of 13 PAH-derivatives by UHPSFC with PDA detector. Peaks numbering: 1 = 2,6-DMN, 2 = 1,4-NQ, 3 = 2-M-1-N, 4 = 1-NA, 5 = 1,5-DNN, 6 = 1-Mpyr, 7 = 9-Fl, 8 = 2-NF, 9 = Antr, 10 = 9-NA, 11 = BaA-7,12-Q, 12 = 1-Npyr, 13 = BAQ. Acquity UPC<sup>2</sup> BEH 2-EP 100 mm × 3.0 mm, 50 °C, 1500 psi backpressure, 1 μL injected, 246 nm, gradient: 100% A (initial), 100–99.9% A (0–3.0 min), 99.9–70% A (3.0–3.4 min), 70–70% A (3.4–4.0 min), 70–100% A (4.0–4.2 min) at 1.65 mL min<sup>-1</sup>.

**Table 1**

Retention time, linear range, LODs, LOQs of PAH-derivatives analyzed by UHPSFC with PDA detector.

No.	Analyte	Retention time, min	Group	Linear range, μg mL <sup>-1</sup>	Correlation coefficient (r)	LOD <sup>a</sup> , μg mL <sup>-1</sup>	LOQ <sup>a</sup> , μg mL <sup>-1</sup>	LOD <sup>b</sup> , ng g <sup>-1</sup>
1	2,6-DMN	0.54	1	0.02–10	0.9997	0.005	0.02	0.1
2	1,4-NQ	1.15	2	0.3–100	0.9999	0.1	0.3	2.0
3	2-M-1-N	1.30	2	0.5–30	0.9991	0.1	0.5	2.0
4	1-NA	1.51	2	0.3–100	0.9990	0.1	0.3	2.0
5	1,5-DNN	1.64	2	0.3–100	0.9999	0.1	0.3	2.0
6	1-Mpyr	2.20	3	0.3–50	0.9997	0.1	0.3	2.0
7	9-Fl	2.40	3	0.2–50	0.9998	0.08	0.2	1.6
8	2-NF	2.55	3	0.3–100	0.9999	0.1	0.3	2.0
9	Antr	3.30	4	0.3–100	0.9999	0.1	0.3	2.0
10	9-NA	3.86	5	0.03–10	0.9991	0.01	0.03	1.0
11	BaA-7,12-Q	3.90	5	0.2–30	0.9999	0.08	0.2	1.6
12	1-Npyr	3.98	5	0.2–20	0.9999	0.05	0.2	1.0
13	BAQ	4.02	5	0.2–80	0.9996	0.05	0.2	1.0

<sup>a</sup> Obtained from UHPSFC-PDA method.

<sup>b</sup> Obtained from SFE- CNTs-UHPSFC-PDA method.

section = 3.0–3.5 min) could ensure a baseline separation with all the resolution greater than 1.5. Considering the peak symmetry, condition d was selected.

### 3.3. Effects of ABPR backpressure

In UHPSFC, ABPR backpressure can affect the retention behavior and chromatographic separation of analytes by changing the density of supercritical fluid. Generally, the density of supercritical fluid increases with the increase of pressure. Thus, the higher the ABPR backpressure is, the larger the solvation power of supercritical fluid is, and the shorter retention time is. Here, a back pressure changing from 1500 to 1650 psi were evaluated. The effect of ABPR backpressure on the resolution of the 12 peak pairs is shown in Fig. 3d. All analytes were separated completely when a pressure of 1500, 1520, or 1550 psi was applied. Finally, 1500 psi was selected in order to prolong instrument life and reduce energy consumption.

### 3.4. Effects of flow rate and column temperature

The flow rate of the mobile solvents is another important factor that affects both the separation efficiency and the analysis speed.

Here, different flow rates varied from 1.5 to 1.9 mL min<sup>-1</sup> with an increment of 0.05 mL min<sup>-1</sup> were investigated as shown in Fig. 3e. All analytes could be baseline separated when the flow rates between 1.55 and 1.75 mL min<sup>-1</sup> were applied. Considering the column efficiency and peak symmetry, 1.65 mL min<sup>-1</sup> was selected.

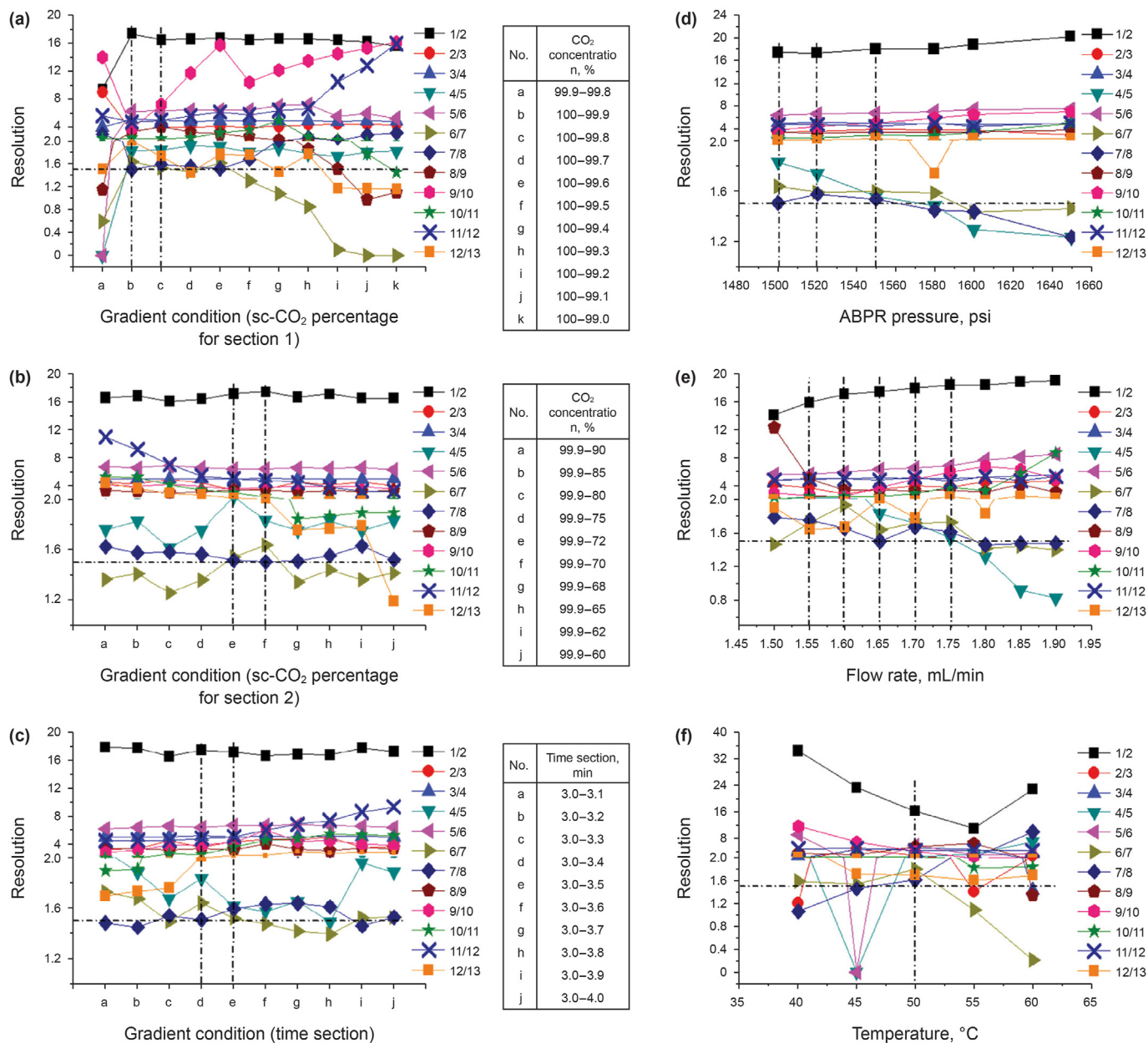
The increase of temperature causes an increase in the vapor pressure of supercritical fluid and a decrease of solvent density. The former could enhance the solvation power of supercritical fluid, while the latter is the opposite. Here, the effect of temperature was optimized between 40 and 60 °C in 5 °C increments. As shown in Fig. 3f, considering the observed separation, the ultimate temperature was selected as 50 °C.

Under the optimal conditions, 13 PAH-derivatives can be separated in 4.1 min (Fig. 2).

### 3.5. Matrix interference and method validation

To study the matrix interference in the quantitative analysis, three samples were compared for each type of soil (sand type and clay type). Two of the three were the spiked samples whose matrix were the SFE extracts of soil. The other one was the standard sample whose matrix was pure solvent, toluene. The concentration





**Fig. 3.** Effect of gradient conditions, ABPR backpressure, mobile phase flow rate and column temperature on the resolution of 12 pairs of PAH-derivatives detected by UHPSFC with PDA detector. (a) Effect of liquid CO<sub>2</sub> concentration on gradient section 1; (b) Effect of liquid CO<sub>2</sub> concentration on gradient section 2; (c) Effect of gradient time section; (d) Effect of ABPR backpressure; (e) Effect of mobile phase flow rate; (f) Effect of column temperature. Note: “sc-CO<sub>2</sub>” is the abbreviation of “supercritical carbon dioxide”.

of PAH-derivatives was the same for all the samples for comparison. No signal enhancement or suppression was observed for all the targets, indicating that the UHPSFC-PDA quantification of PAH-derivatives was not influenced by the soil matrix, guaranteeing the feasibility of the external standard quantitation method in this case. In fact, the SFE-CNTs pretreatment can significantly reduce matrix interference to a large extent, on the one hand because of the use of weak polarity extraction solvent (supercritical CO<sub>2</sub> with 10% dichloromethane) which can filter out the polar interference; on the other hand, CNTs can further filter out the compounds with the non-conjugated structures.

The optimized UHPSFC procedure was evaluated in terms of repeatability, sensitivity and linear range. Intraday repeatability of the method was estimated by measuring of 5 μg mL<sup>-1</sup> standard mixture six times during the day. Interday repeatability was

calculated from analysis the same standard mixture in six different days. Since all the values of RSD were below 5.0%, the method was considered repeatable. For the developed UHPSFC-PDA method, limits of detection (LOD, calculated as three times the signal to noise ratio) and limits of quantification (LOQ, calculated as ten times the signal to noise ratio) were 0.005–0.1 μg mL<sup>-1</sup> and 0.02–0.5 μg mL<sup>-1</sup>, respectively (as listed in Table 1), whose sensitivity is a little lower than GC-MS (LOD, 1–40 ng mL<sup>-1</sup>) (Niederer, 1998a; Cochran et al., 2012; Qiao et al., 2013; Han et al., 2015) and LC-MS/MS (LOD, 1–10 ng mL<sup>-1</sup>) (Mirivel et al., 2010; Lung and Liu, 2015). But in this study, an effective enrichment method, SFE using CNTs trap, was applied before the UHPSFC-PDA analysis, which can make up for the shortcomings, realizing the analysis of trace PAH-derivatives in soil samples. Therefore, for the overall method, SFE-CNTs-UHPSFC-PDA, the sensitivity is comparable or

even higher with the LOD as low as  $0.1 \text{ ng g}^{-1}$  (Table 1). In addition, the developed UHPSFC-PDA method can be easily transferred to UHPSFC-MS method to obtain a higher sensitivity. A series of 13 PAH-derivatives with different concentrations were used to evaluate the linearity of the method and the calibration curves were created by plotting response area versus the concentration of each analyte. All individual PAH-derivatives showed excellent linearity over 2 orders of magnitude as shown in Table 1.

### 3.6. Determination of PAH-derivatives in soil samples

The soil samples with three different spiking concentrations of 13 PAH-derivatives (low, moderate and high level of 12, 50 and  $200 \text{ ng g}^{-1}$ , respectively), were analyzed using the proposed method. The soil samples were firstly enriched by SFE with CNTs as solid collection trap in 15 min, followed by UHPSFC-PDA quantitative analysis. The complexity of oil contamination was remarkably reduced by the CNTs-SFE step. Quantitative recoveries of PAH-derivatives are comparable to those detected by GC-MS in our previous works (Han et al., 2015), but the running time was reduced from 65.0 min to 4.1 min, saving about 15 times the running time.

## 4. Conclusions

In summary, we have developed a fast and environment-friendly method for quantitative analysis of trace-level PAH-derivatives in soil samples by combining SFE-CNTs pretreatment with UHPSFC-PDA analysis. The whole set of this method including enrichment, separation and detection just takes about 20.0 min and consumes less than 2.0 mL organic solvent. It works well for soil sample analysis with good sensitivity and repeatability. The robustness and reliability of the proposed method makes it promising for screening or high-throughput analysis of oil-contaminated soils, before which matrix interference and method accuracy need further investigation.

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