Bull Environ Contam Toxicol (2009) 82:189–193
DOI 10.1007/s00128-008-9597-0

Determination of Alkyl Polycyclic Aromatic Hydrocarbons in Dustfall by Supercritical Fluid Extraction Followed by Gas Chromatography/Mass Spectrum

**Jin-Jun Lian · Chun-Lei Li · Yu Ren ·
Tian-Tao Cheng · Jian-Min Chen**

Received: 20 March 2008 / Accepted: 9 October 2008 / Published online: 31 October 2008

Abstract A method of supercritical fluid extraction (SFE) followed by gas chromatography/mass spectrum was developed for the determination of alkyl polycyclic aromatic hydrocarbons (APAHs) in dustfall. Extraction parameters including pressure, temperature and time were optimized by orthogonal experimental design. Recovery fell into the range of 73.6%–105.0%, and was prior to the efficiency of ultrasonic extraction. Forty-one 2–4-ring APAHs homologues were detected from dustfall samples. The concentrations of total APAHs were about 2 $\mu g\ g^{-1}$. The ratios of APAHs/TPAHs (PAHs + APAHs) altered from 19.8% to 24.8%. Source analysis indicated that APAHs originated from combustion.

Keywords Alkyl PAHs · Dustfall · SFE · Orthogonal experimental design

APAHs are a class of persistent organic pollutants widely found in the environment. They result largely from the release of crude oil or the combustion of fuels at low to moderate temperature (Youngblood and Blumer 1975; Requejo et al. 1996). APAHs are especially important in the case of an accidental release of crude oil, in which 90% PAHs are alkylated. APAHs consist of many homologues due to the various parent rings and alkyl substituents. For instance, more than 100 homologues were found in surface sediments from Bransfield Strait, Antarctica (Lu et al. 1999). Due to their mutagenic and carcinogenic properties, they pose a high risk to the health of human beings and wildlife.

The determination of APAHs associated with atmospheric particulates like dustfall was complicated by two factors. First, dustfall is a complex matrix that contains various organic compounds such as alkanes, fatty acids, PAHs and polychlorinated biphenyls, etc. Second, concentrations of APAHs in aerosol are of so low levels that a method with high sensitivity and selectivity is needed.

In the present decade, SFE has been widely used as a viable approach to environmental sample analysis with several distinct advantages over traditional solvent extraction. Supercritical fluid CO_2 (SF-CO_2) with zero toxicity is suitable for the analysis of nonpolar organic compounds, and the clean-up treatment could be avoided due to high selectivity (Colmsjo 1998). SFE was used to investigate PAHs in aerosol, sediments, soils, etc. (Ali and Cole 1998; Hawthorne and Grabanski 2000; Jonker et al. 2005). However, little work has been reported on the determination of APAHs in dustfall and aerosol.

Our previous works were concentrated on the determination of PAHs in both indoor and outdoor dustfall by SFE in the meanwhile the extraction parameters were discussed (Ren et al. 2006a, b). It was found that recovery of APAHs was in a low level under the extraction condition of PAHs due to the existence of alkyl substituents. The purpose of this study is to develop an optimized method by which APAHs in dustfall could be identified and quantified. The optimized SFE procedures were applied to analyze APAHs in dustfall collected from the campus of Fudan University in order to gain knowledge of APAHs in atmospheric environment.

J.-J. Lian · C.-L. Li · Y. Ren · T.-T. Cheng · J.-M. Chen (✉)
Department of Environmental Science and Engineering,
Center for Atmospheric Chemistry Study, Fudan University,
220 Handan Road, Shanghai 200433, China
e-mail: jmchen@fudan.edu.cn; 051047003@fudan.edu.cn

Materials and Methods

1-Methyl-naphthalene (1MN, 98.2%), 2-methyl-naphthalene (2MN, 99.5%), 2,6-dimethyl-naphthalene (26DMN, 99.9%), 1,3-dimethyl-naphthalene (13DMN, 96.2%), 2,3,5-trimethyl-naphthalene (235TMN, 99.0%), 1-methyl-phenanthrene (1MP, 99.1%), 2-methyl-phenanthrene (2MP, 100%), 1-methyl-anthracene (1MA, 100%), 2-methyl-anthracene (2MA, 99.7%), 2-methyl-fluoranthene (2MF, 98.2%), 1-methyl-pyrene (1MPy, 97.9%), 6-methyl-chrysene (6MC, 99.0%) were used and mixed into APAHs standard solutions. Naphthalene-d_8 (100%) and phenanthrene-d_{10} (99.3%) were internal standards. Pyrene-d_{10} (P-d_{10}, 98.8%) was added to all samples prior to extraction as a surrogate. All compounds were purchased from Accu-Standard (USA). Residual-grade dichloromethane was purchased from Sigma-Aldrich Lab (Milwaukee, WI, USA).

Sets of stainless steel trays (area 60 × 40 cm^2, height 5 cm, flat bottom) for collecting bulk deposition were placed in a variety of sites on the campus of Fudan University in Shanghai. The height of all sampling sites form the ground was about 1 m. Five dustfall samples (D1–D5) were collected for 1 month. The collected samples were dried in a desiccator for 24 h, and then sieved (200 and 500 meshes). The samples were stored in dark in a refrigerator at −18°C. PM_{10} and $PM_{2.5}$ samples were collected using a high-volume cascade impactor (Andersen Instruments Inc.). Particulate-associated APAHs were trapped on quartz fiber filters. 20.3 × 25.4 cm quartz fiber filters (Whatman Company, Maidstone, UK) were treated at 400°C for 5 h before use. The filters were balanced under controlled temperature and moisture conditions (25°C and 50% RH) for 24 h before and after sampling. Sampling was conducted with an air flow of 1.13 $m^3\ min^{-1}$ for 24 h. The sampling site was on the top of a 20-m high-rise on the campus. Samples were stored in dark in a refrigerator at −18°C until analysis, after balanced under the same conditions and weighted on a microbalance (Sartorius Model BP210D) with an accuracy of 0.01 mg.

SFE was performed with a SFX^{TM} 220 Supercritical Fluid Extraction System (Isco, Inc. USA) using SFE-grade CO_2. Each aerosol sample was extracted in a 10 mL extraction cell. Collection of the extracted analytes was carried out in a test tube filled with 10 mL dichloromethane. Different parameters were selected for certain purposes. USE was performed with an Ultrasonic Disrupter (Fisher Scientific, Germany). Each sample was extracted twice with 15 mL mixture of 1:1 dichloromethane and acetone using sonication at 110 W for 15 min. After extraction, all solutions were evaporated by N_2 (99.999%) and concentrated to 500 μL in dichloromethane.

The analysis was performed on GC/MS spectrometer (Agilent, USA). A VF-5MS (Varian USA), 30 m × 0.25 mm I.D., FactorFour^{TM} capillary column of 0.25 μm film thickness was used. The carrier gas was high purity helium (99.999%, 1.0 mL min^{-1}). The temperature program was: initial 60°C, hold 4 min, to 300°C at 10°C min^{-1}, hold 5 min. The injector temperature was set at 250°C and 1 μL analyte was injected in splitless mode. The mass spectrometer was operated in the electron ionization (EI) mode at the electron energy of 70 eV. The transfer line and ion source temperatures were set at 280 and 230°C, respectively. The qualitative analysis was performed in full scan mode in the range of 40–350 and the quantitative analysis in SIM mode, in which selected ions are their molecular weights.

Quantitation was done using the internal calibration method (five-point standard curves). The standard solutions of 12 APAHs were analyzed by GC/MS, and relative data of calibration curves were listed in Table 1. As seen from the table, the retention time (R.T.) indicated that 12 APAHs could be separated sufficiently. The calibration curves showed good linear behavior ($r^2 > 0.99$). The detection limits (D.L.) obtained for the relationship signal-to-noise (S/N) of 3 was 0.33–3.05 pg. The relative standard deviation (RSD) of the whole method was in the range of 4.12%–18.03%. A few APAHs were available as pure standard solutions, so their concentrations could be measured and others would be estimated according to their response values and the calibration of their homologues in many cases. During analyses, method blanks were routinely performed once a day from cleaned dustfall samples spiked with the same internal standards as were used for the aerosol samples. The recovery of surrogate was in the range of 85.8%–99.8% and indicated the whole process was valid.

Table 1 Target compounds, rings, retention time (R.T.), relative coefficient (r^2), detection limits (D.L.) and RSD (n = 6)

No.	APAHs	Ring number	R.T. (min)	r^2	D.L. (pg)	RSD (%)
1	1MN	2	7.00	0.999	1.00	8.55
2	2MN	2	7.15	0.999	0.81	6.42
3	26DMN	2	8.04	0.999	0.85	7.71
4	13DMN	2	8.21	0.995	0.88	8.33
5	235TMN	2	9.91	0.998	1.38	4.28
6	1MP	3	14.88	0.997	0.79	6.93
7	2MP	3	15.04	0.997	1.21	6.11
8	1MA	3	15.21	0.996	3.05	6.64
9	2MA	3	15.25	0.999	2.97	12.03
10	P-d_{10}	–	18.06	0.999	–	4.12
11	2MF	4	19.02	0.995	0.42	6.64
12	1MPy	4	20.26	0.996	0.33	10.50
13	6MC	4	24.62	0.995	2.86	18.03

Results and Discussion

Temperature and pressure are the primary variable parameters in SFE (Ali and Cole 1998; Hawthorne and Grabanski 2000). In addition, it is helpful to prolong time to improve the extraction efficiency (Jonker et al. 2005). On the basis of our previous work (Ren et al. 2006a, b), orthogonal experimental design $L_9(3^4)$ was employed to optimize experimental parameters, and temperatures (80–120°C), pressures (5000–7000 psi) and times (30–60 min) were selected as the extracted conditions of spiked dustfall samples. The total concentrations of 12 APAHs in the different conditions are showed in Table 2.

Table 2 shows obviously that the total concentrations of 12 APAHs increased with temperature, and the top value appeared at 120°C. Increasing SFE temperature provides adsorbed molecules more thermal energy to overcome the desorption barrier and prevent target analytes once solvated in SF-CO_2 from reabsorbing. At the same time, it was easy to find that the concentrations also increased with pressures and were close to each other. As described in previous studies (Reindl and Hoefler 1994; Reimer and Suarez 1995), an increase of pressure caused the increase of viscosity of the supercritical fluid, which resulted in an increase of solvating power of SF-CO_2. As for the time condition experiments, the maximum appeared at 40 min because some volatile APAHs, such as alkyl naphthalenes, vaporized with CO_2. It was obvious that the increase of pressure, temperature and time could enhance the extraction efficiency. Moreover, both *Range* and $SS_{Deviation}$ indicated that the ascended temperature was more effective to improve the extraction efficiencies than the prolonged time, and the effect of pressure was weakest. And the $F_{0.05}$ value signified that the three parameters had no statistical relation. So, 120°C, 6000 psi, and 40 min were selected as the final extraction conditions. Compared to PAHs (Ren et al. 2006a, b), higher pressure and temperature were required for APAHs extraction.

The recovery of the spiked sample in the optimized condition was ranged from 73.6% to 105.0%. In order to compare with the efficiency of SFE, USE was used for the extraction of spiked samples. The efficiency of different methods is showed in a histogram. As seen in Fig. 1, recovery of SFE for 2–3-ring APAHs was about 2.7%–18.8% higher than that of USE, and the opposite was true for 4-ring part. Because 2–3-ring compounds dominated in the real-world samples, SFE was more suitable for the analysis of APAHs in dustfall than USE.

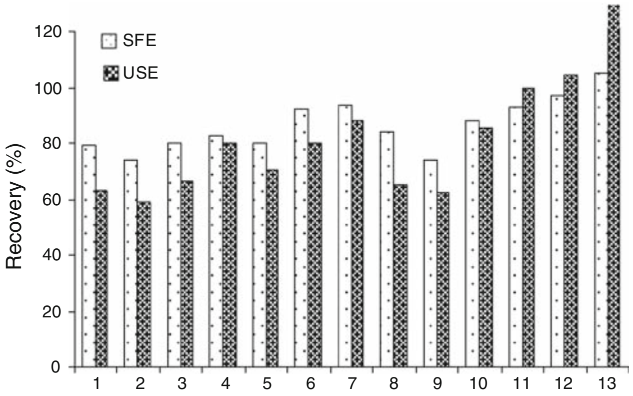

Fig. 1 Extraction efficiency of SFE and USE (1–13 represented the compounds listed in Table 1)

With the established sample-processing method, the contents of APAHs in dustfall samples were identified by GC/MS. Figure 2 is the representative chromatogram of APAHs in a dustfall sample and shows that all APAHs were satisfactorily separated. Forty-one APAHs were found altogether in all samples and identified by ion chromatogram. Due to the lack of standard solution, APAHs homologues were hardly differed from each other. All APAHs were 2–4-ring compounds and none of 5–7-ring APAHs was detected in any samples, and there was no high-molecular-weight APAHs in sediment pore water and crude oil either (Hawthorne et al. 2005; Requejo et al. 1996). All APAHs were categorized according to the number of parent rings and the carbon number of alkyl substituents. Alkyl naphthalene (ANa) had the most homologues with C1–C3 substituents. 3-Ring APAHs including alkyl phenanthrene (APh) and alkyl anthracene

Table 2 Results of orthogonal experimental design

Experiment no.	1	2	3	4	5	6	7	8	9
Concentration ($\mu g\ g^{-1}$)	4.26	6.07	5.7	6.29	5.93	7.24	7.65	7.01	6.53
	Temperature (°C)			Pressure (psi)			Time (min)		
	80	100	120	5000	6000	7000	30	40	60
Mean ($\mu g\ g^{-1}$)	5.34	6.49	7.06	6.07	6.34	6.49	5.57	6.99	6.33
Range		1.72			0.42			1.41	
$SS_{Deviation}$		4.60			0.28			3.00	
$F_{0.05}$		2.31			0.14			1.51	

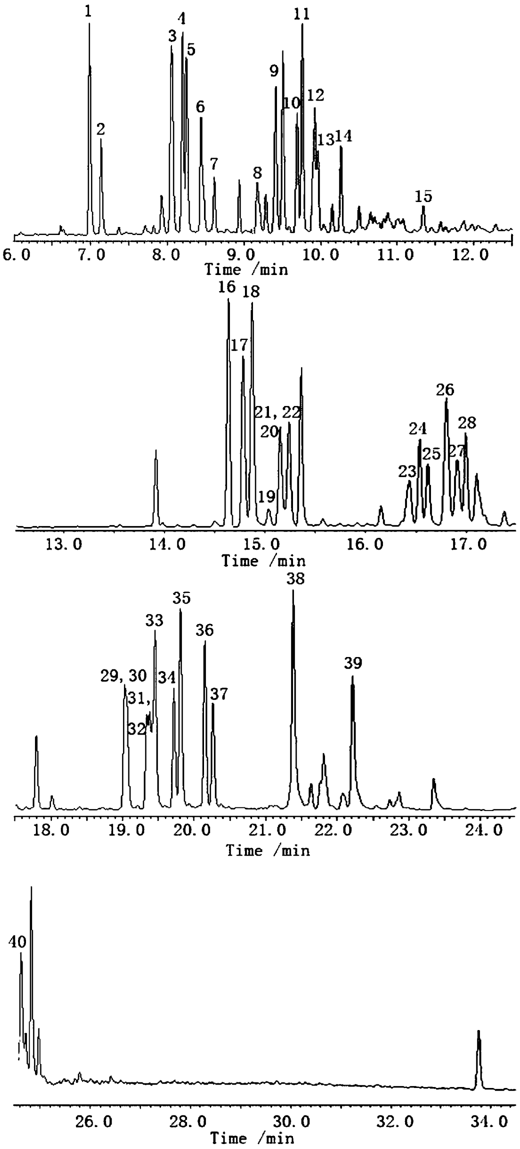

Fig. 2 The representative chromatograph of APAHs. **a–d** Formed a whole chromatograph with the absence of an ANa homologue. 1 and 2, methyl-naphthalene; 3–7, dimethyl-naphthalene; 8–15, trimethyl-naphthalene; 16–22, methyl-phenanthrene/anthracene; 23–28, dimethyl-phenanthrene/anthracene; 29–37 methyl-pyrene/fluorathene; 38 and 39, dimethyl-pyrene/fluorathene; 40, methyl-chrysene

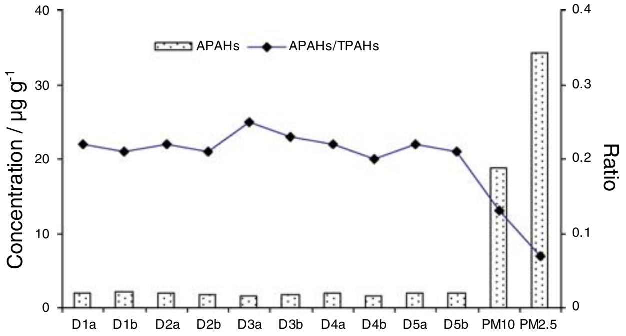

Fig. 3 Concentrations and ratios of APAHs in dustfall and aerosol samples. *a* and *b* represented the sample sieved by a 500-mesh sieve and a 200-mesh one, respectively)

(AAn) had homologues with C1–C2 substituents. And 4-ring homologues including alkyl fluoranthene (AFl), alkyl pyrene (APy) and alkyl chrysene (ACh) only had homologues with C1 substituents. 2–4-Ring APAHs with C1–C4 substituents had been detected in crude oil and sediment pore water (Hawthorne et al. 2005; Requejo et al. 1996). There are two possible reasons why 3–4-ring APAHs with C2–C4 substituents lost in aerosol. One could be that the volatility of APAHs from oil to aerosol decreased with the increase of carbon-number of substituents if the APAHs originated from oil. Another was suggested that there were no 3–4-ring APAHs with C2–C4 substituents if they were produced by combustion. Anyhow, future research is required.

In comparison with the content of APAHs, the concentrations of 16 priority PAHs in each sample were obtained according to our former reports (Ren et al. 2006a, b). Both the concentrations of total APAHs and the alkylation proportion in dustfall samples are showed in Fig. 3. It was obviously found that the concentrations of total APAHs in dustfall were around 2.0 μg g^{-1}, and the values of series a were same as those of series b. It reflected that the particle size of dustfall had little impact on the concentration distribution of APAHs. PM_{10} and $PM_{2.5}$ samples were collected and analyzed to compare with dustfall samples. The concentrations of APAHs in PM_{10} and $PM_{2.5}$ samples were 18.84 and 34.24 μg g^{-1}, respectively, and 10–18 times higher than those of dustfall. The concentrations of PAHs were also determined to investigate the alkylation proportion. The ratios of APAHs to TPAHs (the sum of APAHs and PAHs) were around 20% in dustfall, and decreased to 13.2% in PM_{10} and 7.3% in $PM_{2.5}$, suggesting the more alkylation appeared in dustfall.

The ratio of APAHs to PAHs was used to identify the source due to abundant APAHs in oil and a deficiency in combusted mass. For example, the ratios in oil were 3.7–7.3 (Youngblood and Blumer 1975; Gregory et al. 2005). The values were ranged narrowly from 0.25 to 0.33 and 0.08 to 0.15 in dustfall and inhalable particles, respectively. It indicated that APAHs in atmospheric particles had the same source which was different from oil. The ratio of methyl-phenanthrene to phenanthrene (MP/P) was also employed in discriminating between the sources. The ratio <1 was found in combustion mixture, and the values fell over the range of 2–6 in fossil oils (Youngblood and Blumer 1975; Zakaria et al. 2002). In this study, the ratios of 0.28–0.56 in all aerosol samples indicated that the aerosol APAHs derived mainly from combustion, which was coincident with Ren et al. (2006a, b).

Acknowledgements This work has been supported by the National Natural Science Foundation of China (Key Project Grant No. 40533017, Grant No. 20377008) and Special Fund for Ph.D. Studies of Ministry of Education of China (Grant No. 20030246029).

References

Ali MY, Cole RB (1998) SFE plus C_{18} lipid cleanup method for selective extraction and GC/MS quantitation of polycyclic aromatic hydrocarbons in biological tissues. Anal Chem 70: 3242–3248. doi:10.1021/ac980201+

Colmsjo A (1998) Handbook of environmental chemistry. Springer, Berlin

Gregory ST, Shea D, Nichols EG (2005) Impact of vegetation on sedimentary organic matter composition and polycyclic aromatic hydrocarbon attenuation. Environ Sci Technol 39:5285–5292. doi:10.1021/es048028o

Hawthorne SB, Grabanski CB (2000) Correlating selective supercritical fluid extraction with bioremediation behavior of PAHs in a field treatment plot. Environ Sci Technol 34:4103–4110. doi: 10.1021/es001178o

Hawthorne SB, Grabanski CB, Miller DJ, Kreitinger JP (2005) Solid-phase microextraction measurement of parent and alkyl polycyclic aromatic hydrocarbons in milliliter sediment pore water samples and determination of K_{DOC} values. Environ Sci Technol 39:2795–2803. doi:10.1021/es0405171

Jonker MTO, Hawthorne SB, Koelmans AA (2005) Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot-like materials: evidence by supercritical fluid extraction. Environ Environ Sci Technol 39:7889–7895. doi:10.1021/es0505191

Lu B, Tang YQ, Sui LR, Li SH (1999) Alkyl aromatic compounds in surface sediments from Bransfield Strait, Antarctica. Acta Oceanol Sin 21(2):124–133

Reimer G, Suarez A (1995) Comparison of supercritical fluid extraction and soxhlet extraction for the analysis of native polycyclic aromatic hydrocarbons in soils. J Chromatogr A 699: 253–263. doi:10.1016/0021-9673(95)00063-S

Reindl S, Hoefler F (1994) Optimization of the parameters in supercritical fluid extraction of polynuclear aromatic hydrocarbons from soil samples. Anal Chem 66(11):1808–1816. doi: 10.1021/ac00083a006

Ren Y, Lian JJ, Xue HX, Chen JM, Cheng TT (2006a) Analysis of polycyclic aromatic hydrocarbons (PAHs) in dust by supercritical fluid extraction (SFE) and gas chromatography/mass detector (GC/MS). Annali di Chimica 96:669–680. doi:10.1002/adic.200690069

Ren Y, Zhang QJ, Chen JM (2006b) Distribution and source of polycyclic aromatic hydrocarbons of dust collected in Shanghai, China. Bull Environ Contam Toxicol 76:442–450. doi:10.1007/s00128-006-0941-y

Requejo AG, Sassen R, Mcdonald T, Denoux G, Kennicutt MC, Brooks JM (1996) Polyneclear aromatic hydrocarbons as indicators of the source and maturity of marine crude oils. Org Geochem 24:1017–1033. doi:10.1016/S0146-6380(96)00079-4

Youngblood WW, Blumer M (1975) Polycyclic aromatic hydrocarbons in the environment: homologous series in soils and recent marine sediments. Geochim Cosmochim Acta 39:1303–1314. doi:10.1016/0016-7037(75)90137-4

Zakaria MP, Takada H, Tsutsumi S, Ohno K, Yamada J, Kouno E, Kumata H (2002) Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in malaysia: a widespread input of petrogenic PAHs. Environ Sci Technol 36:1907–1918. doi:10.1021/es011278+