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Separation of PAHs in aerosol by thin layer chromatography for compound-specific stable carbon isotope analysis

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Abstract

A method using a thin layer chromatography (TLC) for compound-specific stable carbon isotope analysis of polycyclic aromatic hydrocarbons (PAHs) with four to seven rings was developed in this study. Five aerosol samples were used as test samples. Two stationary phases and eight developing systems were tested. The results indicated: (1) silica gel is superior to aluminum oxide and the silica gel precoated plate developed with hexane:chloroform (45:5, v/v) can give the best separation effect; (2) individual PAHs associated with aerosols can be effectively separated from unresolved complex mixture (UCM) by this procedure. The carbon isotope composition of PAHs can be measured with a standard deviation (S.D.) < 0.5‰, $n = 4$. No significant isotopic fractionation was observed during the TLC procedure. And this technique can be used as a potential tool for source identification of PAHs in the aerosols.

Keywords: Separation; PAHs; Aerosol; Thin layer chromatography; Carbon isotope

1. Introduction

There has been a worldwide increase in interest to polycyclic aromatic hydrocarbons (PAHs). This is due to their known carcinogenic and mutagenic properties. These highly toxic compounds have been detected throughout the environment (i.e., aerosol, soil, water, sludge and sediment) [1–5]. PAHs are thought to be the results of incomplete combustion. Emissions are generally from many sources such as diesel and gasoline engine exhausts, coal-fired, electronic generating power plants, environmental tobacco smoke, residential wood or coal combustion and the other area sources. The source apportionment of PAHs may help to understand the fate and transformation pathway of PAHs in the environment. To identify sources of PAHs, though various techniques have been performed, such as molecular marker approaches and mathematical modeling [6–10], development of new methods for source apportionment of PAHs is still an ongoing concern.

The stable isotopic composition of individual organic compound can be indicative of its history. The compound-specific carbon isotope analysis (CSIA) of individual hydrocarbons measured with gas chromatography–combustion–isotope ratio mass spectrometry (GC–C–IRMS) has been used in different fields such as oil source identification and paleoenvironment reconstruction [11–15]. O'Malley firstly demonstrated the potential of GC–C–IRMS for PAHs source apportionment [16]. Further, many researchers applied it for different environmental samples such as aerosol, sediment, coal combustion particles [17–24]. All these studies suggested that CSIA was a very useful tool for PAHs' source identification. However, lighter PAHs (less than four rings) can be easily biodegraded and photodegraded in the environment [16,25,26], and the $\delta^{13}C$ value of these PAHs might not reflect exactly their sources. Okuda reported that the $\delta^{13}C$ value of lighter PAHs in the gas phase (sampled by PUF) shows discrepancies with the $\delta^{13}C$ value

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of the same compounds extracted from the particle phase [27]. At the same time, PAHs with more than three rings have higher toxic equivalence factors (TEF) [28]. Therefore, it is more important to identify the origin of such compounds.

Aerosol is a complex matrix that contains many kinds of organic compounds. The PAHs fraction separated from the extracts of aerosol usually shows a ''hump'' in the GC chromatogram, named as the unresolved complex mixture (UCM) [27]. Because individual compound is converted to CO_2 before the detection of its $\delta^{13}C$ value, the isotopic composition of a specific compound can be measured accurately only if this compound of interest has no interference from coelution. In order to ensure the high accuracy and precision of the stable carbon isotope data of individual PAHs, separation and purification of PAHs fraction is often very important and necessary before GC–C–IRMS measurement. Different kinds of methods were applied to separate PAHs in environmental samples for stable carbon isotope measurements such as column chromatography, solid phase extraction and liquid chromatography in the previous studies [16,18,19,23,29], but nearly none of these methods can provide good separation for individual PAHs with more than three rings. thin layer chromatography (TLC) is useful in analysis of trace amounts of organic compounds, and classical TLC remains a popular and inexpensive technique for the separation of complex mixtures. There are many previous studies that have used TLC to isolate PAHs from many kinds of environmental samples and showed the satisfying results [29–32]. This paper presents a method for separation and purification of individual PAHs containing more than three rings in aerosol samples by TLC without altering PAHs isotopic composition for GC–C–IRMS measurement.

2. Experimental

2.1. Chemicals and materials

(a) *Reagents*: dichloromethane (DCM), *n*-hexane (HPLC grade), and ethyl acetate (pesticide grade) were purchased from Dima Technology Inc., USA; benzene (AB Solve) was acquired from Tedia Company, Inc., USA; toluene and chloroform (AR, distilled before use) were purchased from Shangtou Xilong Chemical Factory, Guangdong, PR China; carbon tetrachloride (AR, distilled before use) came from Guangzhou Chemical Reagent Factory, PR China; 3-aminopropyl bonded silica gel was acquired from SIGMA Chemical Co., St. Louise, MO, USA. PAHs standard compounds include: phenanthrene, benzo[*a*]pyrene, pyrene, coronene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*g*,*h*,*i*]perylene. Phenanthrene used in this experiment was acquired from a Japanese chemical company, and the others were purchased from Aldrich Chem. Co. (Milw., USA), the purity of every compound is above 97%.

(b) *Silica gel and aluminum oxide used for column chromatography*: silica gel (80–100 mesh, Qingdao Oceanic Chemical Factory, PR China) and neutral aluminum oxide (100–200 mesh, Shanghai Wusi Chemical Reagent Company, PR China) were Soxhlet extracted for 72 h in DCM. The silica gel was heated at 160 °C for 12 h, cooled to approximately 70–80 °C, then deactivated with 3% (w/w) distilled water and finally preserved in *n*-hexane. Aluminum oxide was heated for 12 h at 250 °C, cooled to about 70–80 °C, deactivated with 3% (w/w) distilled water and suspended in *n*-hexane.

(c) *Preparation of TLC plates*: 20 cm × 20 cm glass plates were respectively coated with 0.25 mm layers of silica gel 60G or 0.25 mm layers of neutral aluminum oxide 60G (Merck, Merck KGaA, Darmstadt Germany). The plates were washed with ethyl acetate before being used for TLC analysis. The plates coated with silica gel were activated at 110 °C for 1 h before use, and the ones coated with aluminum oxide were activated for 30 min at the same temperature.

2.2. Methodology

The procedure used for the experimental work was outlined in Fig. 1. Steps were described in details below.

2.2.1. Preparation and pretreatment of PAH fraction in aerosol sample

Aerosol samples were collected on a quartz fiber filter (heated at 450 °C for 4 h before use) by a high-volume air sampler with a flow rate of 1.05 $m^3 h^{-1}$ for 72 h. The sampling was conducted at four outdoor sites: (1) a bus station where the ventilation is bad, (2) the South China Botany Garden (SCBG), (3) China Petroleum & Chemical Corporation Guangzhou Company (GPC), (4) on the roof of a commercial restaurant directly downwind at the kitchen chimney (KR). Additionally environmental tobacco smoke (ETS) samples were collected in smoking areas indoors.

The loaded filter was cut into small pieces and extracted ultrasonically with 30 ml DCM for 15 min. This operation was repeated four times and the extracts were combined. The solution was concentrated by a rotary evaporator until it is dry and re-dissolved with *n*-hexane to approximately 1 ml.

The organic extract was transferred to a column (1.0 cm i.d. × 25 cm) composed of 12 cm silica gel (lower) and 6 cm aluminum oxide (upper), and 1–2 cm anhydrous Na_2SO_4 at the top to dehydrate the sample. The column was eluted by 40 ml of *n*-hexane followed by 50 ml of *n*-hexane/DCM (1:1, v:v) [33]. The second eluate (PAHs fraction) was submitted to the further separation by TLC.

2.2.2. Thin layer chromatography

TLC was performed on 20 cm × 20 cm glass plates coated with a 0.25 mm layer of silica gel or a 0.25 mm layer of aluminum oxide. A standard solution containing five PAHs was prepared in DCM, and approximately 5 μl standard solution

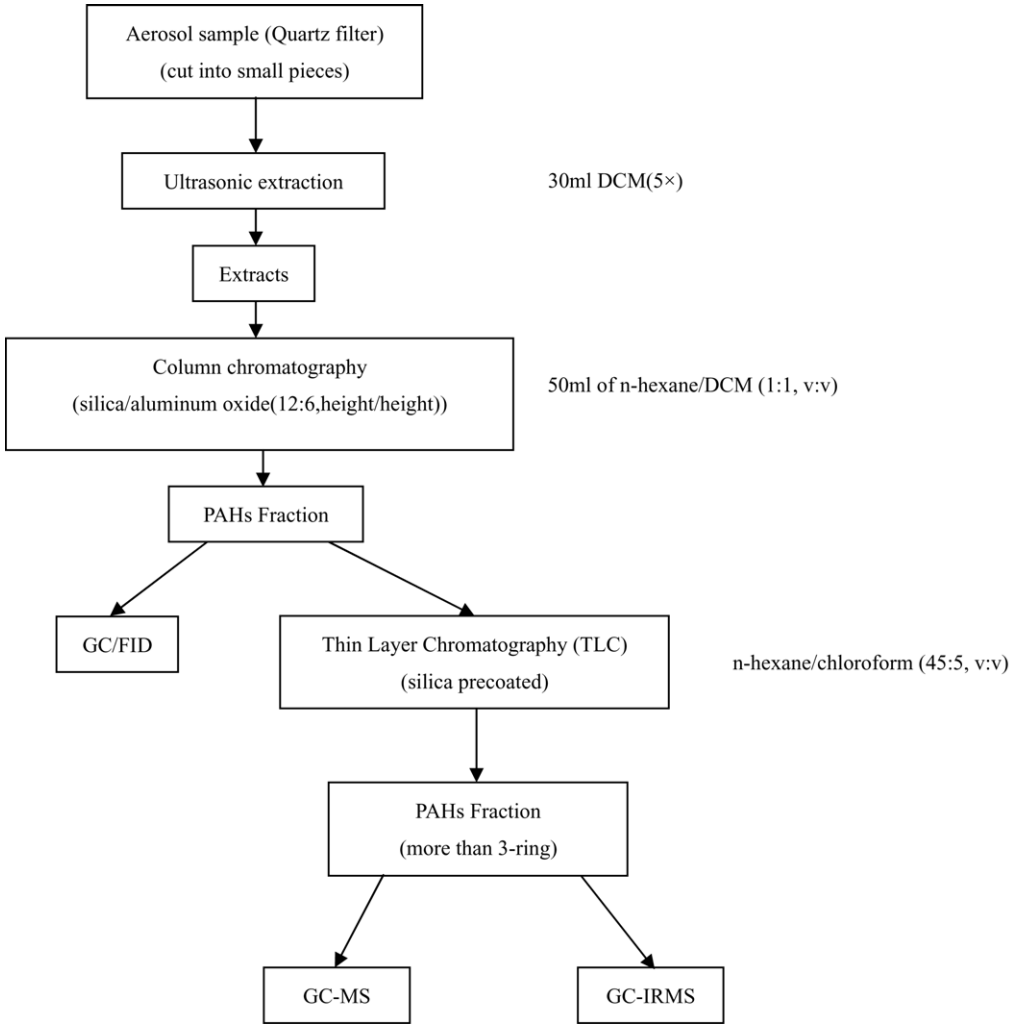

Fig. 1. Extraction and purification procedure of PAHs in aerosol samples for GC–IRMS.

was spotted onto the left part of the plates (the breadth of this part is approximately 5 cm) for reference. The PAHs fraction for TLC separation were spotted onto the other part of the same plate; the two parts of the plate were absolutely isolated to avoid interaction. All plates were developed to a distance of 16 cm in saturated tanks.

There were eight mixtures used for development, including benzene/DCM (10:90, v:v); benzene/DCM (6:94, v:v); *n*-hexane/toluene/chloroform (45:5:5, v:v:v); *n*-hexane/DCM (50:50, v:v); *n*-hexane/toluene/carbon tetrachloride (45:5:5, v:v:v); *n*-hexane/chloroform (45:5, v:v); *n*-hexane/carbon tetrachloride (50:5, v:v); *n*-hexane/toluene (45:5, v:v). The plates were dried in air and observed under UV illumination ($\lambda = 254$ nm) after the development. The color cingulum at the sample side, which was paralleled with the reference color cingulum, was collected and eluted by DCM. The eluate was concentrated to dryness with DCM and re-dissolved in *n*-hexane. The solution was reduced to 30 μl under a gentle stream of N_2, and was analyzed by GC. The same procedure was repeated three times to test the reproducibility of the experiment.

2.2.3. Qualitative analysis and isotope analysis

Qualitative analysis was performed by Hewlett-Packard 5890 chromatograph equipped with a FID detector and Hewlett-Packard 6890A chromatograph equipped with a Micromass mass spectrometer (Finnigan MAT, Bremen, Germany). The Hewlett-Packard 5890 chromatograph was fitted with a HP-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness), and the GC–MS was fitted with a HP-5 capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature was programmed from 60 to 290 °C at 3 °C min^{-1}, and then held for 30 min at 290 °C. Helium was employed as the carrier gas at a flow rate of 1.5 ml min^{-1}.

Stable carbon isotope measurements of individual PAHs were carried out by HP6890 gas chromatograph equipped with a split/splitless injector interfaced via a combustion furnace and a hydroscopic membrane to a Delta^{plus} XL isotopic mass spectrometer (Finnigan MAT, Bremen, Germany). The combustion interface contained Cu, Ni and Pt wires which were doped with oxygen (CuO, NiO) and maintained at a temperature of 960 °C; the operation of the combustion interface has been described by Merritt et al. [34]. Sample was

injected with splitless mode. The temperature of injector was maintained at 290 °C. The carrier gas was helium at a constant flow rate of 1.0 ml min^{-1}. The separation of compounds was performed on a HP-5 capillary column (60 m × 0.25 mm i.d., 0.25 μm film thickness). The temperature program for analysis was from 50 to 180 °C at 20 °C min^{-1}, held 1 min at 180 °C, then from 180 to 280 °C at 2 °C min^{-1}, and held 1 min at 280 °C, and then from 280 to 290 °C at 20 °C min^{-1}, and then held for 10 min at 290 °C.

For calculation purpose, CO_2 reference gas was automatically introduced into the isotopic ratio mass spectrometer in a series of pulses at the beginning and at the end of each analysis, and the data were reported in per mil (‰) relative to the V-PDB (Vienna Pee Dee Belemnite) standard. In addition, a standard mixture containing 10 *n*-alkanes with known isotopic composition (provided by University of Indiana, Bloomington, USA) was injected two to three times per day during the measuring period in order to check the precision and reproducibility of the instrument [14].

Only the PAHs peaks with values higher than 0.5 V (volt) were approbated to guarantee the accuracy of the results.

3. Results and discussion

3.1. Selection of stationary phase and developing system

The samples were developed by the procedure described in Section 2.2.2. The plates coated with layer of 0.25 mm of silica gel or layer of 0.25 mm aluminum oxide were spotted by samples and separately developed with the different mixtures. Fig. 2 gives an example for these developing mixtures, and the separate effect of solid phase extraction method, in which the 3-aminopropyl bonded silica gel was used as the adsorber [27], is also presented. Comparing the GC chromatograms of PAH fraction among these developments, it can be seen that the plates coated with silica gel developed with a mixture of *n*-hexane/chloroform (45:5, v:v) presented the best results and consequently this system was chosen to separate the aerosol organic extracts for GC–C–IRMS.

The effect of the developing system *n*-hexane/chloroform (45:5; v:v) over the separation of the PAHs extracted from aerosol is presented in Fig. 3. The results showed that the ''hump'' of UCM has nearly completely disappeared, and the peaks of the PAHs with more than three rings were resolved. No coelution of the PAHs was observed in the chromatogram.

3.2. Precision and accuracy of $\delta^{13}C$ measure

Four standard PAHs' $\delta^{13}C$ values were respectively measured by conventional GC–C–IRMS and elements analysis (EA) method in order to evaluate the performance of the GC–C–IRMS system. The EA measurements were performed by a Flash EA (1112 series, Thermo Quest) instrument, of which the operation has been described by O'Malley et al. [16]. The results are shown in Table 1. The standard deviation (S.D.) of the conventional IRMS method were between 0.13 and 0.3 for six time measurements and the S.D. range of the EA method was from 0.13 to 0.24 for 15 time measurements.

The $\delta^{13}C$ values of the standard PAHs produced by two methods agreed well within 0.25%. The consistency of the two methods suggested that the GC–C–IRMS technique is applicable to measure the $\delta^{13}C$ value of individual PAHs with high confidence.

3.3. Effect of TLC on $\delta^{13}C$ values of individual PAHs

Any separation method used for sample origin identification must insure that no significant isotopic fractionation occurred for the compounds of interest during the TLC procedure. The $\delta^{13}C$ values of a mixture containing four PAHs standards before and after TLC procedure were determined to test if significant isotopic fractionation occurred. Table 2 shows the results. The difference of $\delta^{13}C$ values of each compound was less than 0.17%, and the S.D. ranged from 0.06 to 0.31%. It is obvious that no significant isotope fractionation occurred.

3.4. $\delta^{13}C$ values measured for individual PAHs in aerosol samples

The organic extracts of the aerosol samples were cleaned up by column chromatography using silica gel/aluminum oxide followed by TLC, and the fraction of PAHs was concentrated to about 30 μl. 0.6–1.5 μl samples were injected

Table 1
$\delta^{13}C$ values of standard PAHs measured by different methods

Compound name	Method for measure				
	EA		GC–IRMS (mixture)		$\Delta\delta^{13}C$ (‰)[c]
	$\delta^{13}C$(‰)	S.D.[a]	$\delta^{13}C$ (‰)	S.D.[b]	
Phenanthrene	−23.52	0.17	−23.52	0.28	0
Pyrene	−24.97	0.13	−25.05	0.14	−0.08
Benzo[*a*]pyrene	−25.23	0.15	−25.48	0.30	−0.25
Benzo[*g*,*h*,*i*]perylene	−26.26	0.24	−26.20	0.13	0.06

[a] Number of runs = 15.
[b] Number of runs = 6.
[c] $\Delta\delta^{13}C$ (‰) = $\delta^{13}C$ (‰)$_{by\ EA}$ − $\delta^{13}C$ (‰)$_{by\ GC–IRMS}$.

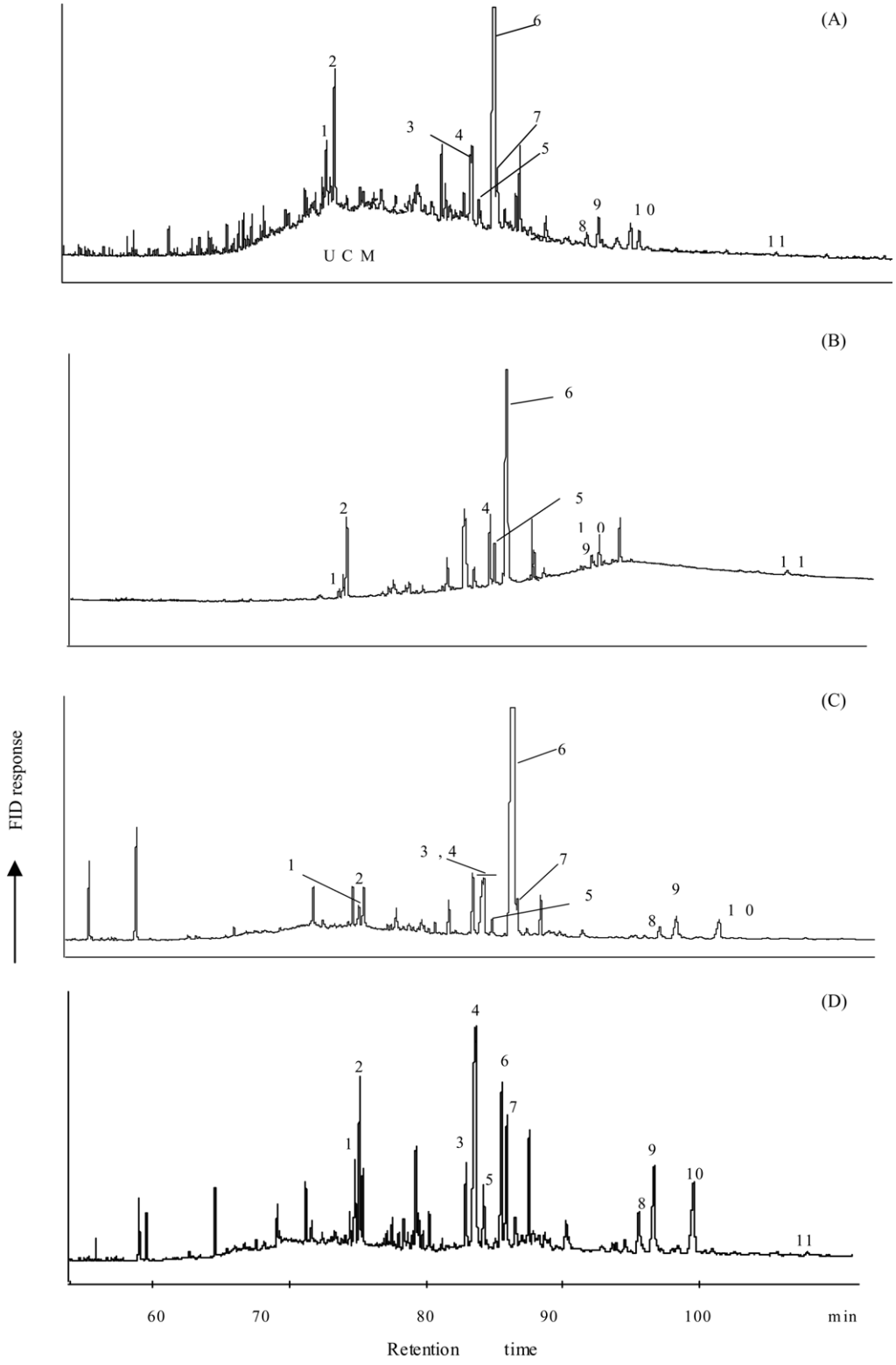

Fig. 2. Chromatograms obtained by GC–FID from (A) the sample purified only by column chromatography; (B) purified by 3-aminopropyl bonded silica gel; (C) developed by *n*-hexane/toluene (45:5, v:v); (D) developed by *n*-hexane/chloroform (45:5, v:v). The stationary phase was silica gel. (1) benzo[*a*]anthracene, (2) chrysene, (3) benzo[*b*]fluoranthene + benzo[*k*]fluoranthene, (4) benzo[*a*]fluoranthene, (5) benzo[*e*]pyrene, (6) benzo[*a*]pyrene, (7) perylene, (8) indeno[*c*,*d*,*e*,*f*]chrysene, (9) indeno[1,2,3-*c*,*d*]pyrene, (10) benzo[*g*,*h*,*i*]perylene, (11) coronene.

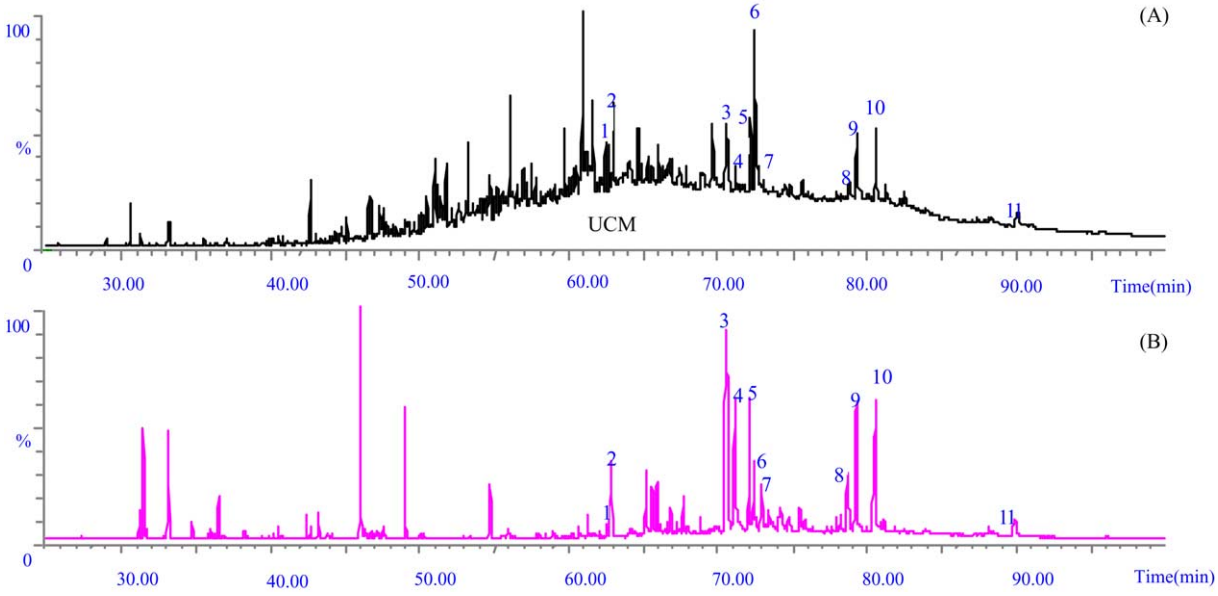

Fig. 3. Total ion chromatograms (gained by GC–MS), (A) PAHs fraction of aerosol collected in a bus station just cleaned up by column chromatography and (B) PAHs fractions purified by TLC (*n*-hexane/chloroform (45:5, v:v)). (1) benzo[*a*]anthracene, (2) chrysene, (3) benzo[*b*]fluoranthene + benzo[*k*]fluoranthene, (4) benzo[*a*]fluoranthene, (5) benzo[*e*]pyrene, (6) benzo[*a*]pyrene, (7) perylene, (8) indeno[*c,d,e,f*]chrysene, (9) indeno[1,2,3-*c,d*]pyrene, (10) benzo[*g,h,i*]perylene, (11) coronene.

Table 2
δ^{13}C values of standard PAHs mixture before and after TLC procedure

Compound name	Procedure				
	Before TLC		After TLC		$\Delta\delta^{13}$C (‰)[b]
	δ^{13}C (‰)	S.D.[a]	δ^{13}C (‰)	S.D.[a]	
Phenanthrene	−23.56	0.08	−23.57	0.10	−0.01
Pyrene	−25.22	0.06	−25.05	0.21	0.17
Benzo[*b*] fluoranthene	−26.52	0.16	−26.59	0.29	−0.07
Benzo[*g,h,i*]perylene	−25.66	0.22	−25.60	0.31	0.06

[a] Number of runs = 4.
[b] $\Delta\delta^{13}$C (‰) = δ^{13}C (‰)$_{\text{after TLC}}$ − δ^{13}C (‰)$_{\text{before TLC}}$.

Table 3
δ^{13}C values of individual PAHs in aerosol samples

Compound name	Sampling site									
	Bus station		SCBG[a]		GPC[b]		KR[c]		ETS[d]	
	δ^{13}C (‰)	S.D.*	δ^{13}C (‰)	S.D.*	δ^{13}C (‰)	S.D.*	δ^{13}C (‰)	S.D.*	δ^{13}C (‰)	S.D.*
Benzo[*a*]anthracene	−25.36	0.60	–	–	–	–	–	–	–27.36	0.38
Chrysene	−26.84	0.24	−28.80	0.25	−28.16	0.25	−26.53	0.22	−27.24	0.10
Benzo[*b* + *k*]fluoranthene	−26.72	0.28	−27.42	0.18	−26.84	0.15	−26.20	0.18	−28.40	0.27
Benzo[*a*]fluoranthene	−28.99	0.11	–	–	–	–	–	–	−29.79	0.56
Benzo[*e*]pyrene	−26.36	0.43	−25.46	0.48	−27.00	0.09	−23.64	0.11	–	–
Benzo[*a*]pyrene	−26.32	0.02	−27.04	0.21	−27.00	0.25	–	–	−27.83	0.03
Indeno[*c,d,e,f*]chrysene	−25.82	0.11	−26.48	0.27	−26.59	0.28	–	–	–	–
Indeno[*c,d*]pyrene	−27.26	0.21	−27.13	0.25	−26.87	0.03	−25.59	0.23	−26.85	0.23
Benzo[*g,h,i*]perylene	−26.86	0.16	−27.29	0.17	−27.02	0.15	−23.71	0.09	−28.61	0.20

Symbol (−) means the concentration of the particular compound is too low to get the accurate stable carbon isotopic value.
* Number of runs = 4.
[a] South China Botany Garden (SCBG).
[b] China Petroleum & Chemical Corporation Guangzhou Company (GPC).
[c] Roof of a commercial restaurant directly downwind at the kitchen chimney (KR).
[d] Environment tobacco smoke (ETS).

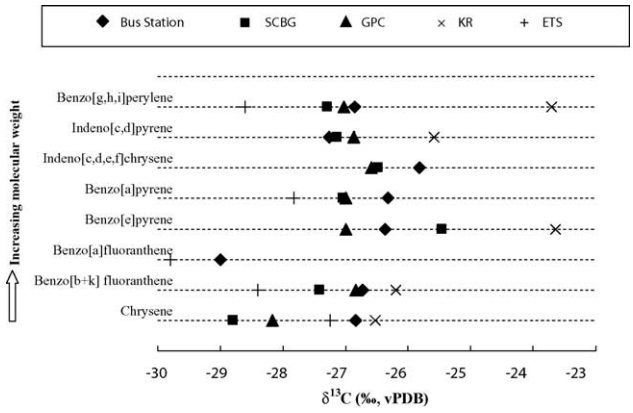

Fig. 4. Results of δ ^{13}C of PAHs in different aerosol samples.

to the GC–C–IRMS system for δ ^{13}C analysis. The results are presented in Table 3 and Fig. 4. Four-time measurements showed that the S.D. of the detected PAHs were less than 0.5‰, except for Benzo[*a*]anthrance in the bus station (S.D. = 0.6‰) and Benzo[*a*]fluoranthene in the ETS (S.D. = 0.56‰).

The δ ^{13}C values of PAHs extracted from the ETS varied from −26.8 to −29.8‰, which was similar to those of PAHs obtained from the wood burning smoke [22]. PAHs; δ ^{13}C values were similar for bus station (−25.3 to −29.0‰), SCBG (−25.4 to −28.8‰) and GPC (−26.5 to −28.2‰), while heavier PAH δ ^{13}C values (−23.6 to −26.6‰) were observed in KR and more depleted in δ ^{13}C (−26.8 to −29.8‰)were found in ETS. *t*-Test indicated that the differences were statistically significant ($p < 0.05$). As shown in Fig. 4, five samples can be classified into three groups, ''Bus Station + SCBG + GPC'', ''KR'' and ''ETS'' based on the PAHs δ ^{13}C values.

The major source of PAHs from bus station is automotive exhausts. The similarity of δ ^{13}C values between SCBG, GPC and the bus station indicated that the atmosphere in Guangzhou City was significantly affected by the automotive exhausts. The same conclusion was obtained by molecular signature studies [33,35]. ETS and woodburning smoke showed the similar PAHs δ ^{13}C values, which may result from that both of them came from the combustion of biomass. In addition, the source of the PAHs from KR is cooking and the δ ^{13}C values were quite different from the other samples. The results suggested that PAHs from the same source have the similar δ ^{13}C values, and the difference of the δ ^{13}C values may reflect the different sources.

4. Conclusion

A TLC method was developed for the measurement of δ ^{13}C values of the individual PAHs in this study. When the samples were spotted onto a plate coated with 0.25 mm layers of silica gel and developed in hexane/chloroform (45.5, v:v), the UCM of the PAH fractions was wiped off. There were some advantages for this method: (1) parallel separation and direct comparison between standards and sample components can be performed efficiently at low-cost; (2) this method was highly selective to the PAHs with more than three rings and (3) the precision of the method presented S.D. < 0.5‰. It can be concluded that the application of this method to determine the δ ^{13}C values of individual PAHs in environmental samples is advantageous and credible. And this technique can be successfully used to judge if PAHs in aerosol come from the same source.

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