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Chlorination for efficient identification of polycyclic aromatic hydrocarbons by liquid chromatography–mass spectrometry

Zhi-Yong Gao, Wen-Sheng Jiang, Di Sun, Ying Xie, Zhen-Liang Chen, La-Jia Yu, Su-Yuan Xie*, Rong-Bin Huang, Lan-Sun Zheng

State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, 422 Si-Ming-Nan-Lu, Xiamen 361005, China

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ABSTRACT

Utilizing liquid chromatography–mass spectrometry (LC–MS) for identification of polycyclic aromatic hydrocarbons (PAHs) has long been underrated, as the sensitivity for determination of PAHs directly by MS is very poor. In the present work a chlorination method for high-sensitive determination of PAHs by LC–MS is discussed. This method includes two steps: (1) chlorination of PAHs by the BMC method; (2) determination of the chlorinated PAHs by LC–MS. Interfaced by atmospheric pressure chemical ionization in negative ion mode, five representative perchlorinated PAHs producing from the languidly detectable parent PAHs (naphthalene $C_{10}H_8$, acenaphthene $C_{12}H_{10}$, phenanthrene $C_{14}H_{10}$, pyrene $C_{16}H_{10}$ and fluoranthene $C_{16}H_{10}$) have been LC–MS characterized in high sensitivity with determination limits in 10^{-9} g/mL level. In addition, molecular compositions and polycyclic carbon-frameworks of unknown PAHs can be identified according to the isotopic pattern of the chloro-derivatives ions in the corresponding mass spectra. Our experiments demonstrate that the proposed chlorination-involving LC–MS method is efficient for the PAHs analysis, for example, in soot and soil samples.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and persistent environmental contaminants derived mainly from anthropogenic activities such as incomplete combustion of fossil fuels and vegetation, and from the waste of chemical or other industries [1–3]. Because of their prevalence in environment, terrible effect in mutagenesis, and carcinogenesis on living body [4,5], PAHs have been considered as the priority pollutants that require scientists to design analytical method to separate and determine them with high sensitivity [6,7].

Gas chromatography coupled with mass spectrometry (GC–MS) has been classically used for the separation and identification of PAHs in complex mixtures [8–10], but this method is mainly employed for volatile molecules with thermal stability, especially for those having relatively smaller molecular weight. As for the analysis of compounds with poor thermal stability or larger molecular weight, liquid chromatography–mass spectrometry (LC–MS) is a more powerful tool.

The studies based on LC–MS are apparently less than GC–MS [11–14], largely because of the inefficient ions sources commercially available for interfacing between LC and MS. The ionization methods normally used for LC–MS analyses include electronic spray ionization (ESI), atmospheric pressure chemical ionization (APCI) or atmospheric pressure photoionization (APPI). In contrast to the electron impact (EI) that has been commonly applied in GC–MS for PAHs analyses [8–10], these LC–MS ion sources are languid to ionize PAHs [15–19].

Another limitation in the ordinary low-resolution mass spectrometry is the inability to directly establish molecular composition of PAHs. As reported in typical GC–MS experiments [20,21], unambiguous characterization of molecular composition of any PAHs has required corresponding comparable experiments with reference PAH compounds. This leads to the difficulty for MS identification of any novel molecules if lack of reference compounds as "internal standard". This problem can be solved only if the novel analyte contains elements such as chlorine or bromine that having characteristic natural abundances of isotope. For example, previous investigations have demonstrated the molecular compositions of perchlorinated PAHs could be facilely and explicitly identified by low-resolution MS even without reference compounds [22,23].

Here we report a new LC–MS method regarding chlorination derivatization and MS identification for PAHs. The proposed method not only facilitates the APCI ionization of PAHs with very low detection limits, but also is useful for characterization of molecular compositions and polycyclic carbon-frameworks of otherwise unknown PAH molecules. This chlorination-involving method has been applied for LC–MS analysis of PAHs in environmental sam-

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* Corresponding author. Tel.: +86 0592 2182 151; fax: +86 0592 2183 047.
E-mail addresses: syxie@xmu.edu.cn, syxie68@gmail.com (S.-Y. Xie).

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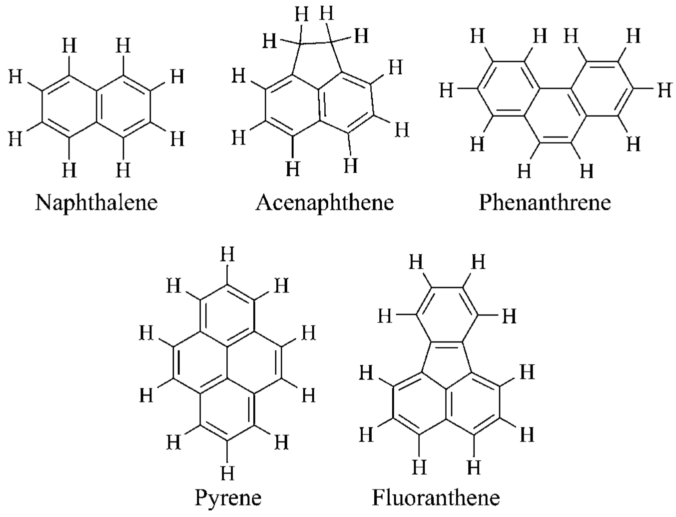

Fig. 1. The molecular structures of five reference PAHs.

ples such as the incomplete combustion of hydrocarbons and the PAH-containing soils.

2. Experimental

2.1. Chemicals and solvents

Fig. 1 shows the structures of the five reference PAHs for the present experiments. Naphthalene ($C_{10}H_8$) was purchased from Shanghai Yuanhang Reagent Corporation (Shanghai, China), acenaphthene ($C_{12}H_{10}$) was from Shanghai No.1 Reagent Corporation (Shanghai, China), phenanthrene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$) were from Flude Chemie (Buchs Switzerland), fluoranthene ($C_{16}H_{10}$) was from Acros Organics (Geel Belgium). All of them were of analytical grade.

The PAH-containing sample of soot was produced from a benzene/oxygen flame under 20 Torr pressure in our home-made setup. The PAH-containing soil was obtained by adding the reference PAHs into the soil.

Toluene used for dissolution and extraction of the combustion soot was also of analytical grade. Methanol, ethanol and cyclohexane for LC mobile phases were distilledly purified from analytical grade solvents before LC analyses.

2.2. Chlorination of the reference PAHs

The chlorination of PAHs, were conducted using a BMC reagent chlorination method [24] under relative lower temperature. For the chlorination of PAHs, each of the five reference PAHs, naphthalene, acenaphthene, phenanthrene, pyrene, and fluoranthene, was weighed separately for 0.1 g and mixed together with 2 mL sulfur monochloride (S_2Cl_2) into 25 mL newly distilled sulfuryl chloride (SO_2Cl_2). Another solution was prepared by dissolving 1.1 g anhydrous aluminum chloride ($AlCl_3$) into 75 mL newly distilled SO_2Cl_2. This $AlCl_3$ solution was heated and kept at the constant temperature close to the boiling point of sulfuryl chloride (70 °C), then adding the PAHs solution into the $AlCl_3$ solution dropwise via a constant pressure drop funnel over 20 min. The reactant mixture was stirred at this temperature for 2 h, followed by adding 30 mL SO_2Cl_2 to compensate the evaporative loss of solvent. The chlorination reaction was continued for 5 h, and the chlorinated PAHs were precipitated from the solution as most of the hydrogen atoms in PAHs were substituted by chlorine atoms. After the chlorination reaction, the mixture of products was cooled and poured into sufficient ice water, followed by basic balance with the addition of solid sodium carbonate (Na_2CO_3) or sodium bicarbonate ($NaHCO_3$). At the final stage, the solution was readjusted to the level of strong acidity with hydrochloric acid (HCl), then filtrated and washed copiously with 25% HCl and water to give perchlorinated PAHs.

2.3. Chlorination of combustion soot and soil samples

The procedure for chlorination of the PAH-containing soot is as follows: the soot (0.2 g) from incomplete combustion of a benzene/oxygen flame was extracted using toluene in supersonic bath, then filtrated by 0.45 μm filter and vapored under low pressure to afford solid samples. Procedure for the chlorination derivatization is the same with the chloro-derivatization of reference PAHs. For complete chlorination in the substitution reaction, the S_2Cl_2 and anhydrous $AlCl_3$ were added up to 1 mL and 0.6 g, respectively; these amounts are appropriately excessive for full replacement of the hydrogen in the target PAHs.

The PAH-containing soil was chlorinated using the same method with the chlorination of the soot.

2.4. Instruments

An Agilent 1200 LC System combined with a Bruker HCT Esquire 5.3 Mass Spectrometer was used for the LC–MS analyses. The ion source for mass spectrometry is APCI (Bruker, US). The softwares for the analyses are Agilent 1100 and Espuire 5.3 ChemStation Software.

2.5. Analytical conditions

The chromatographic separation was performed using a Discovery C18 column (SUPELCO 250 mm × 4.6 mm I.D., 5 μm particle size) with 20 μL injection of toluene-soluble sample at room temperature. The extracted flame soot sample, including a series of large PAHs and fullerenes, which is hard to be eluted with ordinary hydrated mobile phase, so a ternary solvent of methanol, ethanol and cyclohexane with constant flow rate (0.8 mL/min) in a gradient mode was used as the mobile phase. To increase the solubility of cyclohexane in the mobile phase, a small proportion of ethanol was mixed into methanol. In the first 40 min, the contents of the methanol and ethanol were held at 84.6% and 15.4%, respectively. In the next 40 min, cyclohexane was linearly increased from 0 to 35% while methanol and ethanol were reduced accordingly to 55% and 10%, respectively. From 80 to 100 min, the methanol, ethanol and cyclohexane were kept at 55%, 10% and 35%, respectively. The analysis of products from chlorination of PAHs, the extract of flame soot, as well as the soil samples were all performed using the same separation conditions.

The five reference PAHs were detected in positive ion mode. Because the products from the benzene/oxygen flame involve a relatively higher content of fullerenes (not shown in this work) and large PAHs (with higher molecular weights), which were possibly observed in negative ion mode, the mass spectra were recorded in negative ion mode with APCI as ion source. The setting parameters for the APCI–MS measurements were as follows: dry gas temperature, 350 °C; flow rate of dry gas, 4 L/min; nebular gas pressure, 45 PSI; vaporizer temperature, 250 °C; capillary voltage, 1000 V; detection range, 50–3000 *m*/*z*.

The detection limits (DLs) of the five perchlorinated PAHs were determined in negative ionization mode by LC–APCI–MS based on the LC and MS analytic conditions mentioned above.

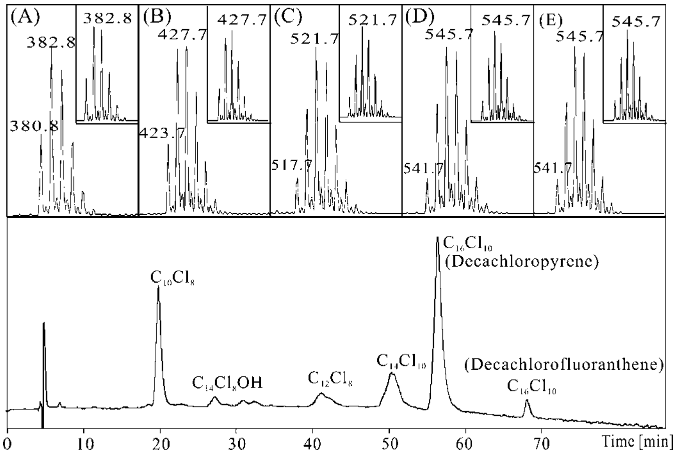

Fig. 2. UV chromatogram (330 nm) and corresponding mass spectra of the products from chlorination of the five reference PAHs, (A)–(E). The mass spectra detected and simulated (insets). (A) Octachloronaphthalene; (B) octachloroacenaphthylene; (C) decachlorophenanthrene; (D) decachloropyrene; (E) decachlorofluoranthene.

3. Results and discussion

3.1. Determination of reference PAHs by LC–MS via chlorination

In contrast to the wide application of GC–MS with EI ion source for the analysis of PAHs, investigation on LC–MS characterization of PAHs has been underrated previously [11–14]. This may attribute to the inefficient ionization of PAHs in commercially available ion sources such as ESI and APCI. Our experiments have demonstrated that, using APCI in positive ion mode, the reference PAHs may be detected only if the concentration is higher than 0.1–1 g/L level. With the APCI in negative ion mode, ineffectively, MS signals of the reference PAHs are hard to be recorded even at the concentrations as high as 5 g/L. In contrast to the pristine PAHs, however, chlorinated PAHs can be well negatively charged so as to be detected in the APCI conditions [22,23]. The identification sensitivity can thus be improved if transferring the pristine PAHs into chloro-derivatives.

Moreover, the chlorination also facilitates the identification of molecular composition. For the mass spectra of an organic compound, the MS signal intensity of each isotopic peak is the quantificational accumulation of different isotopic molecular weights. A molecule containing atoms with particular isotopic abundance would result in particular pattern of mass spectra. For example, the molecular compositions of the chlorinated species can be feasibly characterized on the basis of the recorded *m*/*z* signal pattern featured with special natural abundance distribution of chlorine isotopes (^{35}Cl:^{37}Cl = 75.77:24.23). Accordingly, the numbers of chlorine atoms, and subsequently the numbers of carbon atoms, of the corresponding perchlorinated PAH molecule can be identified accurately [23,25,26]. As shown in Fig. 2, molecular formulae of the five reference PAHs can be indirectly characterized by the *m*/*z* signal pattern of the chloro-derivatives of the five PAHs in comparison with the simulated mass spectra (insets in Fig. 2).

For APCI–MS analyses of the five perchloro-derivatives of PAHs, there are two typical styles of *m*/*z* pattern in their corresponding mass spectra. One is the *m*/*z* featured with molecular ions signals. For example, the molecular ions pattern of *m*/*z* 518 ($C_{14}Cl_{10}$) and *m*/*z* 542 ($C_{16}Cl_{10}$) are shown for the perchlorinated phenanthrene, pyrene and fluoranthene (Fig. 2). Another style of ions is the quasi-molecular ions featuring 19 less than the molecular ions. For example, instead of the *m*/*z* of 400 for $C_{10}Cl_8$, *m*/*z* 381 is detected in the perchlorinated naphthalene (Fig. 2). The evidence about the quasi-molecular ions seems to be quite ubiquitous for chlorinated PAHs in APCI–MS. The facile formation of the negative ions of the quasi-molecule is possibly due to the substitution of chlorine by oxygen from perchlorinated PAHs during the APCI process [25,26]. Indeed, the MS patterns of the quasi-molecular peaks have indicated the loss of one chlorine atom from the molecular ions. In the mass spectra of $C_{10}Cl_8$, as shown in Fig. 2, the numbers of Cl are simulated to be 7 in the quasi-molecular pattern of *m*/*z* 381.

3.2. The method for chlorination of reference PAHs

The chloro-derivatives of the five reference PAHs were produced by means of a BMC method [24]. The mass spectra (Fig. 2) having all the five full chlorinated PAHs indicate that the BMC method is an efficient way for the chlorination derivatization of PAHs. These perchlorinated PAHs correspond well with their parent PAHs.

The effect of this BMC chlorination method is better than another chlorination method with PCl_5 at higher temperature of 180–250 °C [27]. The BMC method avoids the polymerization of the produced chlorinated PAHs at high temperature, so that the chlorinated species are well consistent with their parent PAHs and the molecular composition of authentic PAHs can be identified from the chlorinated PAH products.

An exception is $C_{12}Cl_8$ (octachloroacenaphthylene) chlorinated from $C_{12}H_{10}$ (acenaphthene). The resulting chlorinated compound ($C_{12}Cl_8$) is two substituted atoms less than the expected perchlorinated PAHs ($C_{12}Cl_{10}$). Fig. 3 shows an assumed scheme for the BMC reaction starting from $C_{12}H_{10}$. The assumed intermediate $C_{12}Cl_{10}$ can be labile because of the repulsion of chlorine atoms at the structural edge of the pentagon, and turns to elimination of its two neighbor crowded chlorines to result in $C_{12}Cl_8$ in the BMC reaction process.

The perchlorination of PAHs through the BMC reagent method give yields of 77%, 75%, 70%, 81% and 76% from naphthalene, acenaphthene, phenanthrene, pyrene and fluoranthene, respectively. The formation of byproducts are likely due to incomplete chlorination. For example, in addition to the fully chlorinated product $C_{14}Cl_{10}$, a partially chlorinated $C_{14}Cl_8OH$ also produced from $C_{14}H_{10}$ (Fig. 2). The incompletely chlorinated derivatives, however, still link to their parent PAHs because they share the same original carbon frameworks.

The BMC method is able to convert ketone or hydroxy polycyclic aromatic compounds into chlorinated species as well. Taking 2,3-dihydrocyclopenta[a]naphthalen-1-one ($C_{13}H_{10}O$) and pyrenyl-methanol ($C_{17}H_{12}O$) as examples, our experiments demonstrate that $C_{13}H_{10}O$ and $C_{17}H_{12}O$ can be BMC chlorinated to $C_{13}Cl_{10}H_2$ and $C_{17}Cl_{10}H_2$, respectively. Shown in Fig. 4 is the LC

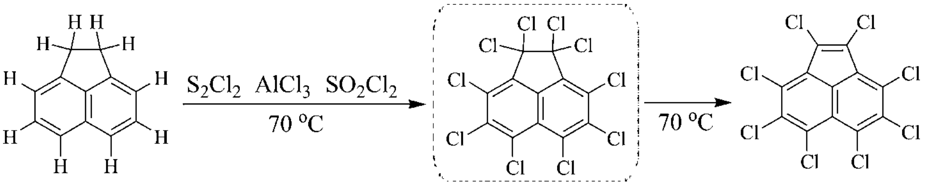

Fig. 3. The reaction scheme for the BMC chlorination of acenaphthene. The structure in dashed rectangle is an assumed intermediate.

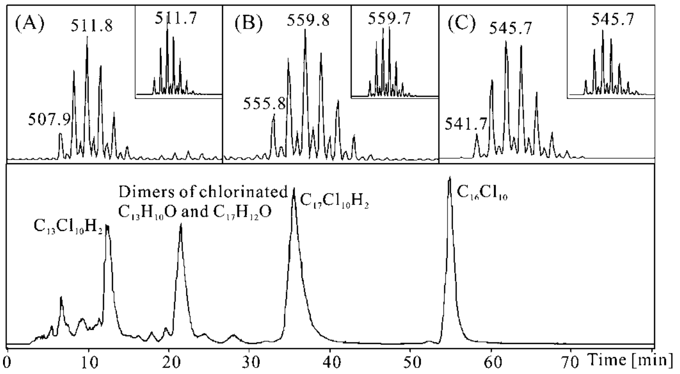

Fig. 4. LC-UV (300 nm) analysis of the chlorinated product of $C_{13}H_{10}O$ and $C_{17}H_{12}O$. (A)–(C) at the top are the mass spectra of chlorinated product $C_{13}Cl_{10}H_2$, $C_{17}Cl_{10}H_2$ and $C_{16}Cl_{10}$, insets in A–C are the simulated mass spectra.

chromatogram and corresponding MS of the mixed crude products, in which $C_{13}Cl_{10}H_2$ and $C_{17}Cl_{10}H_2$ as well as some byproducts (such as $C_{16}Cl_{10}$) are clearly identified. The $C_{16}Cl_{10}$ is likely produced because of the decomposition of $C_{17}H_{12}O$ to lose its oxymethyl group during the chlorination process. However, it is almost certainly that the byproducts share the same polycyclic carbon-skeletons with their parent ketone or hydroxy PAHs. Therefore, on the point of polycyclic carbon framework, the chlorinated byproducts such as $C_{16}Cl_{10}$ are still consistent with their parent PAHs even for ketone or hydroxy PAHs.

3.3. Determination limits (DLs) and other analytic parameters for determining the five perchloro-derivatives of PAHs

Five sets of LC–MS determinations were performed for each sample. The relationship between the detected concentration (Y) and the peak area (X) of mass spectrum for each perchlorinated PAHs is linear. The linear correlation equations and related correlation coefficient (R) are as follows:

$$Y = 1.74 \times 10^{10}X + 762.37 \ (R = 0.9947)$$

(for octachloronaphthalene)

$$Y = 3.43 \times 10^{10}X + 1252.03 \ (R = 0.9991)$$

(for octachloroacenaphthylene)

$$Y = 2.53 \times 10^{10}X - 38.5 \ (R = 0.997)$$

(for decachlorophenanthrene)

$$Y = 4.68 \times 10^{10}X - 8344.56 \ (R = 0.9997) \quad \text{(for decachloropyrene)}$$

$$Y = 1.13 \times 10^{11}X + 492.69 \ (R = 0.997)$$

(for decachlorofluoranthene).

The DLs of the chlorinated derivatives of PAHs in the mass spectrometry analysis were valuated on the basis of the intensity ratio of signal (S) to noise (N), that is defined as the concentration (C) having the value of S/N = 3 [9]. Accordingly, the DLs are calculated to be 1.57×10^{-8}, 1.85×10^{-8}, 1.80×10^{-8}, 1.16×10^{-8} and 3.08×10^{-9} g/mL for perchlorinated naphthalene, acenaphthylene, phenanthrene, pyrene and fluoranthene, respectively. Considering the formation yield of the perchlorinated species from its parent PAHs, the DLs for pristine PAHs are amended to 6.47×10^{-9}, 8.89×10^{-9}, 8.77×10^{-9}, 5.30×10^{-9}, and 1.5×10^{-9} g/mL, respectively. The DLs are within the level of the amounts in enviornmental contaminated samples, so the low amounts of some enviornmental samples can be determined by the proposed method even though the conversion of the chlorination reaction is around 70–80% as memtioned above. The RSDs of the LC–MS determinations are 15%, 19.5%, 18.9%, 18.8%, and 17.3% for octachloronaphthalene, octachloroacenaphthylene, decachlorophenanthrene, decachloropyrene, and decachlorofluoranthene in the low concentration (as low as the DLs) of 1.16×10^{-8}, 3.61×10^{-8}, 7.23×10^{-8}, 1.19×10^{-8}, and 7.95×10^{-9} g/mL, respectively.

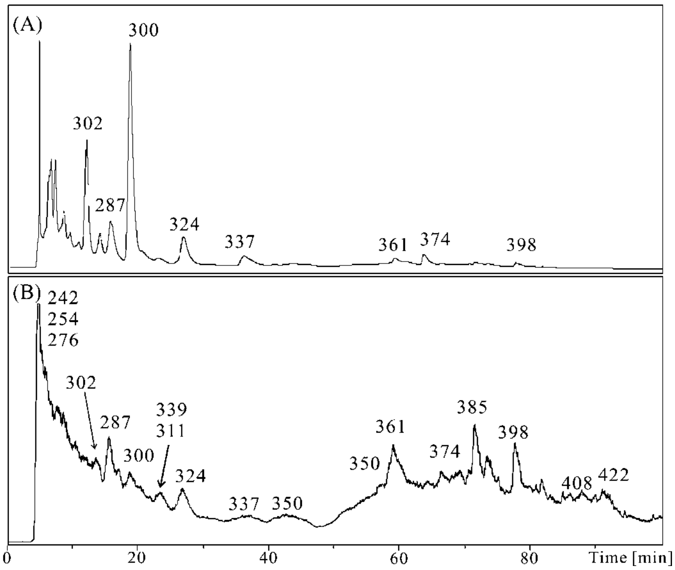

Fig. 5. LC-UV (300 nm) (A) and LC–MS chromatogram (total ion chromatogram) in negative ion mode (B) of the combustion soot. The detected m/z data are labeled in the chromatogram.

3.4. LC–MS determination of PAHs from combustion by chlorination

To validate the practical application of the proposed chlorination method, we performed an analytic experiment for a PAH-containing soot produced from incomplete combustion of benzene at low pressure. The PAHs in the soot including a series of PAHs with higher molecular weight. A series of larger PAHs in the range of m/z 240–430 are detectable in high-concentration (g/L level) toluene-extract of the soot. Fig. 5 shows the LC–APCI–MS chromatogram with labeled molecular masses. In despite of molecular weight detectable in the sample with high concentration, the molecular compositions of these detected PAHs are impossible to be characterized unless using standard reference substances. By the proposed chlorination derivatization method, however, this problem can be solved feasibly. As shown in the LC–MS chromatogram of the chlorinated soot and the representative mass spectra (Figs. 6 and 7), a wide range of PAHs with defined composition can be identified. The detected and simulated m/z data for some representative chloro-derivatives are shown in Fig. 7, in which the recorded molecular masses and isotopic distributions match very well with the simulated ones. Moreover, some of the other undetected species, such as $C_{16}Cl_{10}$ and $C_{18}Cl_{10}$, can be detected after chloro-derivatization.

The composition correlations in the determination of the PAHs before or after the chloro-derivatization are shown in Table 1. Most

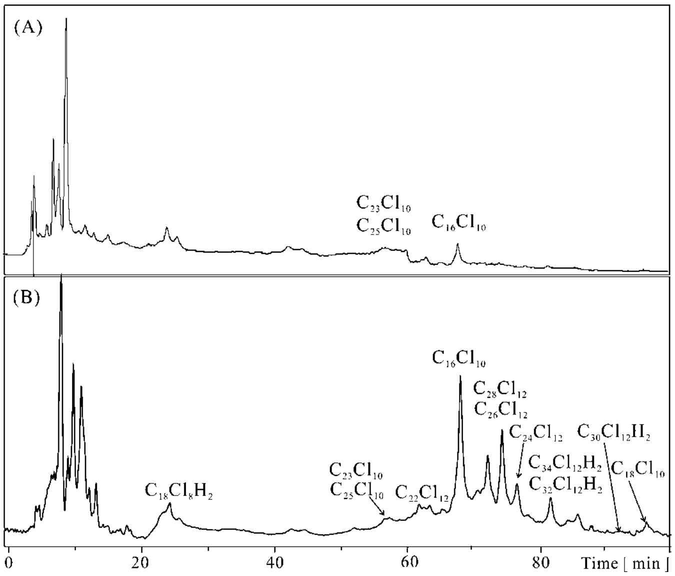

Fig. 6. LC-UV (300 nm) (A) and LC–MS chromatogram (total ion chromatogram) in negative ion mode (B) of the chlorinated soot. The molecular formulae are deduced from characteristic *m*/*z* pattern of isotopic distribution.

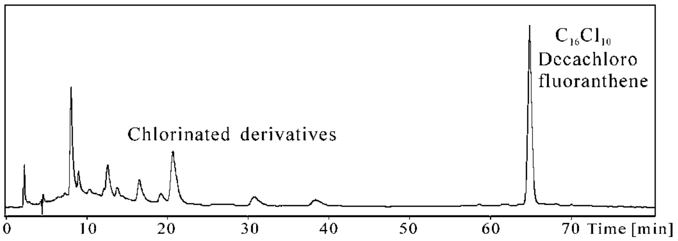

Fig. 8. LC chromatogram (300 nm) of the chlorinated fluoranthene-containing soil.

of the original parent PAHs are well corresponded with their chloro-derivatives. It should be noted that some of the parent PAHs are not fully substituted by the BMC chlorination method. For example, there are still two hydrogen atoms remained in $C_{30}Cl_{12}H_2$, $C_{32}Cl_{12}H_2$ and $C_{34}Cl_{12}H_2$ as shown in Fig. 7. However, these data about incompletely chlorinated products are still helpful for characterization of their parent molecular compositions. At least, their carbon-skeletons should be identical to those of $C_{30}H_{14}$, $C_{32}H_{14}$ and $C_{34}H_{14}$, respectively.

As the analysis of the reference $C_{12}H_{10}$ (acenaphthene) mentioned above, the molecular composition of chlorinated species ($C_{12}Cl_8$) may mismatch with authentic PAH formula ($C_{12}H_{10}$). This evidence is also shown in some other crowded PAH molecules in the soot sample. For example, the APCI–MS of the crude soot gives the *m*/*z* of 254 (tentatively assigned to $C_{20}H_{14}$) in Table 1, but the molecular formula of $C_{20}H_{12}$ was derived from the chlorinated compound $C_{20}Cl_{12}$. The mismatch is likely due to the fact that the molecule of $C_{20}Cl_{14}$ transferring from $C_{20}H_{14}$ is too crowded to be stabilized. The $C_{20}Cl_{12}$, rather than $C_{20}Cl_{14}$, is thus produced and detected, as in the case of the reference $C_{12}Cl_8$ mentioned above (Fig. 3). This rationalizes the possibility of a few resulting chloro-derivatives with one- or two-unit of substituent less than their parent PAHs as star-marked in Table 1.

3.5. LC–MS analysis of fluoranthene-containing soil via chlorination

To validate the proposed method applicable on the analysis of representative environmental sample, a fluoranthene-containing soil was quantificationally analyzed. The fluoranthene-containing soil was prepared by mixing 11 mg of fluoranthene mixed into 20 g ordinary soil. Then the 0.55 mg/g fluoranthene-containing soil was derivatized by the BMC method to afford chlorinated soil. Fig. 8 shows the LC chromatogram of the chlorinated soil containing decachlorofluoranthene. By the proposed LC–MS method, about 0.48 mg/g fluoranthene in the soil was determined and a recovery of 87.1% was quantificationally analyzed. Based on the repeated experiments for three times, the RSD for the fluoranthene analysis was valuated to be 17.2%. The quantification analysis of fluoran-

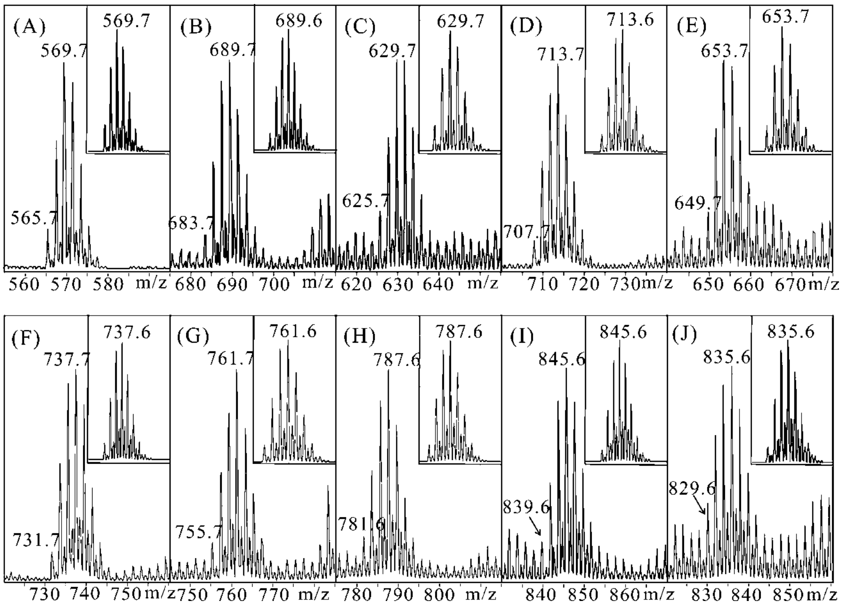

Fig. 7. The mass spectra detected (in the rectangles) and simulated (top right in each rectangle): (A) $C_{18}Cl_{10}$; (B) $C_{22}Cl_{12}$; (C) $C_{23}Cl_{10}$; (D) $C_{24}Cl_{12}$; (E) $C_{25}Cl_{10}$; (F) $C_{26}Cl_{12}$; (G) $C_{28}Cl_{12}$; (H) $C_{30}Cl_{12}H_2$; (I) $C_{32}Cl_{12}H_2$; (J) $C_{34}Cl_{12}H_2$.

Table 1
The correlation of LC–MS analysis between direct identification for the crude soot and indirect characterization for the soot after BMC chlorination derivatization.

Soot after chlorination			Original crude soot	
Retention time (min)	Detected molecular composition	Suggested molecular formula	Detected molecular mass	Calculated molecular mass[a]
8–9	$C_{17}Cl_7H_7$	$C_{17}H_{14}$	Not detected	218
	$C_{16}Cl_8H_2$	$C_{16}H_{10}$	Not detected	202
9–13	$C_{18}Cl_9H$ $C_{18}Cl_8H_2$	$C_{18}H_{10}$	Not detected	226
24–26	$C_{18}Cl_8H_2$	$C_{18}H_{10}$	Not detected	226
26–28	$C_{22}Cl_{10}H_2$	$C_{22}H_{12}$	276	276
	$C_{19}Cl_{12}H_2$	$C_{19}H_{14}$	242	242
29–31	$C_{20}Cl_{10}H_4$	$C_{20}H_{14}$	254	254
36–38	$C_{16}Cl_{10}$	$C_{16}H_{10}$	Not detected	202
38–41	$C_{18}Cl_{10}$	$C_{18}H_{10}$	Not detected	226
40–43	$C_{24}Cl_{12}$	$C_{24}H_{12}$	300	300
42–48	$C_{20}Cl_{12}$	$C_{20}H_{12}$	254[b]	252
	$C_{22}Cl_{12}$	$C_{22}H_{12}$	276	276
51–54	$C_{20}Cl_{11}H$	$C_{20}H_{12}$	254	252
57–59	$C_{23}Cl_{10}$	$C_{23}H_{10}$	287[b]	286
	$C_{25}Cl_{10}$	$C_{25}H_{10}$	311[b]	310
61–63	$C_{22}Cl_{12}$	$C_{22}H_{12}$	276	276
64–65	$C_{24}Cl_{12}$	$C_{24}H_{12}$	300	300
67–70	$C_{16}Cl_{10}$	$C_{16}H_{10}$	Not detected	202
70–72	$C_{32}Cl_{12}H_2$ $C_{32}Cl_{13}H$	$C_{32}H_{14}$	398	398
72–73	$C_{33}Cl_{12}$	$C_{33}H_{12}$	408	408
74–76	$C_{26}Cl_{12}$	$C_{26}H_{12}$	324	324
76–78	$C_{27}Cl_{12}H_2$	$C_{27}H_{14}$	339[b]	338
	$C_{28}Cl_{14}$	$C_{28}H_{14}$	350	350
78–79	$C_{34}Cl_{12}H_2$	$C_{34}H_{14}$	422	422
	$C_{34}Cl_{13}H$ $C_{24}Cl_{10}H_4$	$C_{24}H_{14}$	302	302
79–81	$C_{28}Cl_{12}H_2$	$C_{28}H_{14}$	350	350
81–83	$C_{32}Cl_{12}H_2$ $C_{32}Cl_{13}H$	$C_{32}H_{14}$	398	398
84–85	$C_{32}Cl_{14}$	$C_{32}H_{14}$	398	398
	$C_{24}Cl_{10}H_2$	$C_{24}H_{12}$	300	300
	$C_{30}Cl_{14}$	$C_{30}H_{14}$	374	374
86–87	$C_{32}Cl_{10}H_4$	$C_{32}H_{14}$	398	398
	$C_{29}Cl_{11}H$	$C_{29}H_{12}$	361[b]	360
	$C_{31}Cl_{12}$	$C_{31}H_{12}$	385[b]	384
90–91	$C_{30}Cl_{12}H_2$	$C_{30}H_{14}$	374	374
91–92	$C_{27}Cl_{12}$	$C_{27}H_{12}$	337[b]	336
96–99	$C_{18}Cl_{10}$	$C_{18}H_{10}$	Not detected	226
103–106	$C_{30}Cl_{14}$	$C_{30}H_{14}$	374	374

[a] The molecular masses are calculated from the indirectly identified parent PAHs in column 3.
[b] The molecular weight directly detected in crude soot is not in accordance with the mass deduced from chloro-derivatives.

thene in soil exemplifies the validity of the proposed chlorination method for LC–MS analysis of PAHs in practical sample.

4. Conclusions

Our experiments have demonstrated that the chlorination-involving LC–MS method is efficient for the PAHs analysis, by which the molecular composition of authentic PAHs can be indirectly identified through the isotopic distribution in the mass spectra of the resulting chloro-derivatives of PAHs. Five faintly detectable PAHs, i.e., naphthalene, acenaphthene, phenanthrene, pyrene and fluoranthene, have been well characterized via the perchlorinated species, with sensitivity in the level of 10^{-9} g/mL by LC–MS method. Even though in the case of compounds lacking of standard reference, molecular formulae of otherwise unknown PAHs can be identified by the m/z pattern of the molecular or quasi-molecular ions of their chlorinated homologies. The validity of the proposed method has been further demonstrated by the LC–MS analytic experiments with PAH-containing soil and the environmental sample produced from incomplete combustion of benzene. The present work, involving pre-derivatization of PAHs analytes through BMC chlorination and the LC–MS determination interfaced with APCI source in negative ion mode, represents a new concept and feasible method for LC–MS analysis of PAHs.

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