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Separation and identification of perchlorinated polycyclic aromatic hydrocarbons and fullerenes (C_{60}, C_{70}) by coupling high-performance liquid chromatography with ultraviolet absorption spectroscopy and atmospheric pressure chemical ionization mass spectrometry

Su-Yuan Xie, Shun-Liu Deng, La-Jia Yu, Rong-Bin Huang*, Lan-Sun Zheng*

State Key Laboratory for Physical Chemistry of Solid Surface, Department of Chemistry, Xiamen University, Xiamen 361005, China

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Abstract

Simultaneous separation and identification of perchlorinated polycyclic aromatic hydrocarbons (PCPAHs) and fullerenes is of practical interest due to the growth mechanism of fullerenes involved with PCPAHs. Non-aqueous reversed-phase high-performance liquid chromatography (HPLC), with an ODS column and a gradient mobile phase of methanol–ethanol–cyclohexane mixtures, was combined with both rapid-scan ultraviolet spectrometry (UV) and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) for the separation and identification of over 80 PCPAHs as well as fullerenes C_{60} and C_{70}, that were synthesized in the discharge reaction of chloroform. PCPAH retention was found to depend on the number of aromatic rings and the degree of non-planarity of PCPAH structure. Based on the isotopic pattern of molecular ion or/and quasi-molecular ion peaks in corresponding mass spectra, molecular compositions of the PCPAH products were unambiguously determined. The results obtained from the HPLC–UV–MS analysis not only are helpful for the understanding of the fullerenes formation mechanism, but also contribute to the analytical technique capable of separating and identifying the complicated mixture of PCPAHs and fullerenes.

Keywords: Polynuclear aromatic hydrocarbons, perchlorinated; Fullerenes

1. Introduction

Experimental data increasingly reveal that fullerenes formation in pyrolytic reaction of hydrocarbons involves polycyclic aromatic hydrocarbon (PAH) intermediates [1–3]. Investigation based on trapping PAH intermediates and focused on investigating the relationship between PAHs and fullerenes is of great interest. A few research groups [4–13] attempted to analyze aromatic by-products as well as high-molecular-mass fullerenes in flame-generated fullerene soot using high-performance liquid chromatography (HPLC) combined with ultraviolet spectrometry (UV) or atmospheric pressure chemical ionization mass spectrometry (APCI-MS). To opti-

*Corresponding authors. Tel.: +86-592-2183-807; fax: +86-592-2183-047.

E-mail addresses: rbhuang@xmu.edu.cn (R.-B. Huang), lszheng@xmu.edu.cn (L.-S. Zheng).

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mize the HPLC conditions, Anacleto and co-workers [4–8] investigated the retention of fullerenes (C_{60}, C_{70} and the higher fullerenes) and their derivatives in fullerene soot on different stationary phases, such as the commercially available reversed-phase columns Vydac 201TP52 C_{18}, Hypersil-ODS, Zorbax Rx-C18 and Cosmosil PYE. They also discussed the HPLC–UV and HPLC–APCI-MS analysis of fullerenes as well as by-products among fullerene soot using different mobile phases, and a acetonitrile–dichloromethane gradient was used in their experiments.

Recently, we have developed several synthetic methods such as liquid arc discharge [14], glow discharge [15,16], microwave discharge [17] and laser ablation [18] to produce fullerenes from chloroform. As side-products, numerous perchlorinated polycyclic aromatic hydrocarbons (PCPAHs) have also been fabricated in the reactions. These products, fullerenes and PCPAH intermediates, especially those having bowl-shaped structures, are conjectured to comply with the same growth mechanism, because they were synthesized in the same reaction starting from chloroform, a molecule containing a single carbon atom. Therefore, separation and identification of PCPAHs is of considerable practical and fundamental importance for the study of the fullerene formation mechanism. Partly due to the complexity defined by poor knowledge and chemical similarities of PCPAHs, however, chromatographic isolation of PCPAHs has rarely been reported in the literature [19–22], especially those in mixtures comprising numerous chlorocarbons with similar structures and chemical properties.

To analyze the numerous chlorocarbons from the chloroform discharge reaction, which are generally thermolabile, low-polar and non-volatile, the analytical method employing gas chromatography (GC) in combination with specific detectors is not reliable without a time-consuming derivatization step, which itself can generate interferences. Consequently, liquid chromatography should be used as fundamental method for PCPAH isolation. However it is difficult to identify numerous products from the chloroform discharge reaction simply according to their HPLC retention times and UV spectra owing to lack of standard samples. Identification of these compounds, therefore, should be obtained by coupling HPLC to mass spectrometry according to the typical isotopic distribution of PCPAHs.

Herein we report a non-aqueous reversed-phase HPLC combined with both rapid-scan UV and APCI-MS for simultaneous separation and characterization of PCPAHs and fullerenes (C_{60}, C_{70}) among the products of chloroform discharge reaction. Our successful analysis of the PCPAH mixture involves: (i) developing a trinary mixture mobile phase running in selected gradient, which can separate over 80 PCPAHs as well as fullerenes (C_{60}, C_{70}) on a conventional ODS stationary phase to provide information on molecular composition; and (ii) combining HPLC, rapid-scan UV detection and APCI-MS together, so that the retention time, UV spectrum and mass spectrum of each compound in the mixture can be simultaneously measured in a single run of the HPLC–UV–MS analysis. The study might be not only helpful for the understanding of fullerenes formation mechanism, but also contribute to the analytical technique capable of separating and identifying the complicated mixture of fullerenes and PCPAHs.

2. Experimental

2.1. Chemicals

Solvents used in the experiments were commercially available. Methanol was HPLC grade, and other solvents were analytical grade. All HPLC solvents were further distilled and degassed by vacuum filtration over a 0.45-μm membrane filter prior to use.

2.2. Sample preparation

The sample for the analyses was synthesized via the discharge reaction of chloroform. The set-up and synthesis conditions of synthetic reaction have been previously described in detail [14–17]. The mixture products, originating from liquid discharge, glow plasma and microwave plasma of chloroform, were extracted with toluene using an ultrasonic bath at room temperature, followed by filtrating for HPLC experiment. To analyze the original abundance of the products of chloroform discharge reaction, no other pre-separation procedure was taken prior to HPLC analysis.

2.3. Reference samples

As most of PCPAHs were not commercially available, some standard compounds, which have been previously isolated and structurally characterized, were prepared in the laboratory according to the methods described previously [14–17], including perchlorobenzene (C_6Cl_6), perchloronaphthalene ($C_{10}Cl_8$), perchloroacenaphthylene ($C_{12}Cl_8$), perchlorobiphenyl ($C_{12}Cl_{10}$), perchloroanthracene ($C_{14}Cl_{10}$), perchlorophenanthrene ($C_{14}Cl_{10}$), perchloropyrene ($C_{16}Cl_{10}$) and perchlorofluoranthene ($C_{16}Cl_{10}$).

2.4. Chromatography

The HPLC apparatus consists of a P200 pump and a UV3000 detector (Thermo Separation Products). The chromatographic separation was carried out at room temperature on an ODS (200×4.5 mm I.D.) column (Supelcosil). A trinary non-aqueous mobile phase of cyclohexane, methanol and ethanol was used in an optimized gradient described in Table 1. Gradient elution of the mobile phase was performed at flow-rate of 1.0 ml/min. The sample was injected by filling a 20 μl injection loop.

2.5. UV spectrometry and mass spectrometry

A rapid-scan UV3000 detector was equipped with the HPLC instrument. This detector is capable of recording UV adsorption spectra of the chromatographic elute by rapidly scanning in the detecting wavelength between 205 and 400 nm with a speed of 6.7 Hz and a spectral resolution of 5 nm. The data were processed using a PC 1000 software in an OS2 system.

The outlet of the HPLC–UV system was simply connected to the inlet of an APCI interface of a Finnigan LCQ ion-trap mass spectrometer. Negative ions mode was employed, primarily owing to the high electron affinity of PCPAHs. The operating conditions for the APCI-MS analyses were as follows: vaporization temperature: 400°C; sheath gas (N_2): 65 ml/min; aux gas (N_2): 20 ml/min; capillary temperature: 150°C; discharge current: 5.00 μA; discharge voltage: 2.52 kV; capillary voltage: −5.00 kV; scan range: 150–2000 m/z; total analysis time: 220 min.

Among all the APCI-MS analytical conditions, vaporization temperature is the most critical factor for achieving reliable results. Higher vaporization temperature could ionize PCPAHs and fullerenes more effectively, but molecular ion peaks of some compounds disappear due to serious fragmentation in the higher temperature condition.

Table 1
HPLC gradient profile

Time (min)	Cyclohexane (%)	Methanol–ethanol (5:1) (%)
0	0	100
40	5	95
220	32	68

3. Results and discussion

3.1. Extraction of PCPAHs and fullerenes

Toluene was used for extraction of PCPAHs and fullerenes (C_{60}, C_{70}) in an ultrasonic bath at room temperature. Solubility of PCPAHs in toluene was found to depend on their structural properties. The solubility decreases with increasing molecular diameters or mass of PCPAHs, and the compounds with five-membered-ring structures seem to exhibit lower solubility than those without pentagon.

3.2. Chromatographic conditions

Considering the low volatility of most PCPAHs and fullerenes from discharge reaction of chloroform, HPLC is apparently more suitable for their isolation than GC, which has been widely used for the analysis of small polychlorinated PAHs, such as polychlorinated biphenyl. Initial test showed that normal-phase liquid chromatography is not a proper choice because of its poor resolution and weak retention in the stationary phase such as silica gel. Reversed-phase HPLC on an ODS column was found to be effective in separating PCPAHs by selecting a proper mobile phase, similar to chromatographic separation of their PAH parents [23].

Selection of the mobile phase is critical for HPLC separation of PCPAHs and fullerenes. Most PCPAHs and fullerenes exhibit poor solubility in polar solvents widely used in reversed-phase HPLC, such as

methanol, acetonitrile, tetrahydrofuran and water, and they cannot elute from the ODS column when only polar solvent is applied. On the other hand, good solvents of PCPAHs and fullerenes, such as benzene, toluene, cyclohexane, dichloromethane, etc., are too strong to render enough retention on the ODS column. Hence, a mixed solvent consisting of polar and low-polar solvents might be a better choice. In addition, another requirement for the mobile phase is the transparency or low absorption in UV wavelength region (205–400 nm), so that the UV adsorption spectrum of each component can be recorded during HPLC–UV analysis. Some solvents, such as toluene and benzene, are thus excluded as component of the mobile phase due to their strong adsorption in UV wavelength region. After testing various combinations of the mixtures comprising of both polar and low-polar solvents, such as methanol, ethanol, hexane, acetonitrile, tetrahydrofuran, dichloromethane and cyclohexane, it was found that the mixed solvents of methanol–cyclohexane could be used as mobile phase for separating numerous PCPAHs and fullerenes (C_{60}, C_{70}) produced in chloroform discharge reaction. Optimum conditions were sought by varying the ratio of solvents. The capacity factor decreases and the solubility increases markedly as the concentration of cyclohexane arises, resulting in the rapid and effective separation of PCPAHs and fullerenes. Unfortunately, increasing the concentration of cyclohexane in the mobile phase is limited by its solubility in methanol, which cannot exceed 25% in volume. By adding 16.5% of ethanol in methanol, however, concentration of cyclohexane in the mobile phase could be raised up to 35%. Hence, a trinary mixture consisting of methanol–ethanol–cyclohexane was applied as mobile phase in further experiments. In practice, the methanol and ethanol were pre-mixed in a 5:1 ratio, followed by mixing gradually with cyclohexane in a gradient mode in the HPLC process. The optimized conditions are shown in Table 1.

The HPLC analytical procedure seems to be rather time-consuming. Considering there are more than 80 chlorocarbons in the sample, however, such a long eluting time is necessary for effective separation of so many PCPAHs and fullerenes among chloroform discharge reaction products. As shown in Fig. 1, the HPLC–UV chromatogram recorded at 360 nm, most components in the sample are separated under the chromatographic conditions and less room left for saving HPLC run time.

3.3. UV absorption spectroscopy

In Fig. 1, most of components in the sample are separated sufficiently to provide UV spectra. Selected UV spectra of perchloronaphthalene ($C_{10}Cl_8$), perchloroacenaphthylene ($C_{12}Cl_8$), perchlorophenanthrene ($C_{14}Cl_{10}$), perchloropyrene ($C_{16}Cl_{10}$) and perchlorofluoranthene ($C_{16}Cl_{10}$) are shown in Fig. 2. The spectra indicate that most of the products are highly fused rings, which maximum absorption wavelength normally locates in the range of 205–400 nm. UV spectra of PCPAHs are helpful in distinguishing the structural isomers that mass spectra are identical. As shown in Fig. 2, the UV spectrum of perchloropyrene ($C_{16}Cl_{10}$) is markedly different from that of perchlorofluoranthene ($C_{16}Cl_{10}$). Additionally, by comparing with available standard UV spectra and corresponding retention times, some compounds can be structurally characterized. For example, as shown in Fig. 2, the UV spectra obtained at retention times of 19.5, 33.8, 38.5, 47.0 and 69.1 min are closely identical to the standard ones of perchloronaphthalene ($C_{10}Cl_8$), perchlorophenanthrene ($C_{14}Cl_{10}$), perchloroacenaphthylene ($C_{12}Cl_8$), perchloropyrene ($C_{16}Cl_{10}$) and perchlorofluoranthene ($C_{16}Cl_{10}$), respectively. Thus their structures are characterized. In addition, their retention times also match those of standard ones. Unfortunately, only a few PCPAHs are previously identified and the available standard UV spectra are scarce. Therefore, a more powerful method, e.g., MS, is needed for structural identification of novel compounds.

3.4. Mass spectroscopy

Generally, it is difficult to determine the composition of an unknown compound simply according to its molecular mass acquired in mass spectrometry analysis. Based on isotope distributions, however, mass spectrometry is effective in the analysis of the compositions of PCPAHs and fullerenes in our experiment. As examples, Fig. 3 shows typical isotope distributions of selected PCPAHs, $C_{10}Cl_8$, $C_{16}Cl_{10}$, $C_{20}Cl_{10}$, $C_{22}Cl_{14}$, and $C_{60}Cl_8$, which were

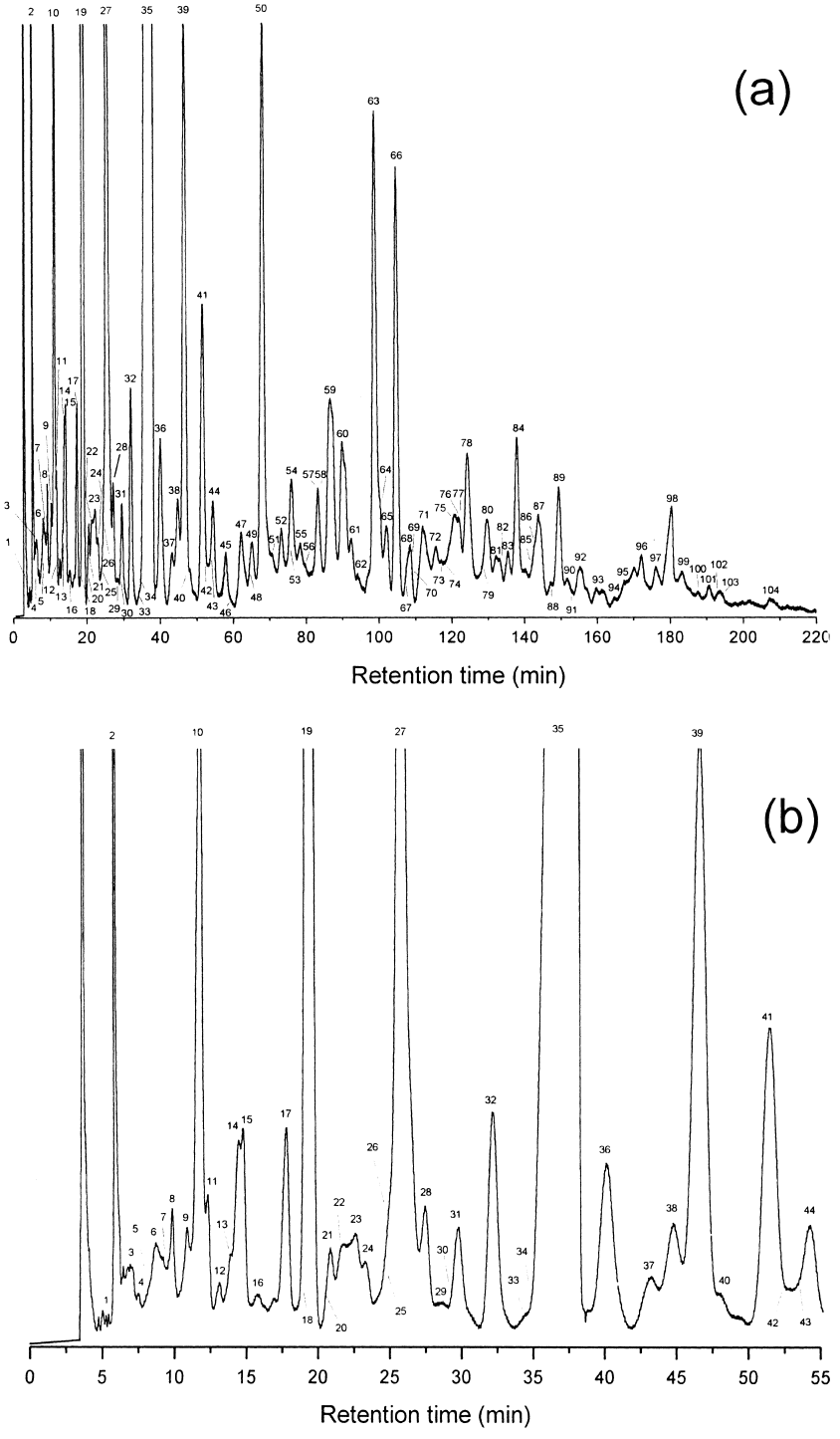

Fig. 1. HPLC chromatogram of the products from chloroform discharge reaction recorded at 360 nm wavelength (peaks are labeled by numbers and the corresponding molecular formulas as suggested from their mass spectra are shown in Table 2). (a) Retention time 0~220 min; (b) retention time 0~55 min.

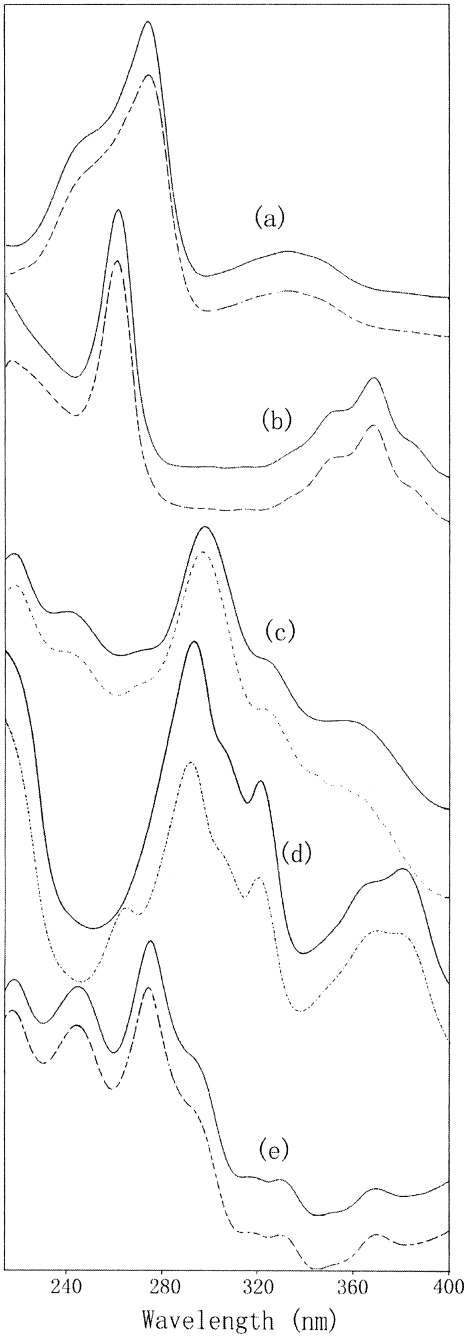

Fig. 2. UV spectra of selected PCPAHs (——: standard UV spectrum; - - -: UV spectrum acquired in the HPLC–UV experiment). (a) Perchloronaphthalene $C_{10}Cl_8$ (No. 19, acquired at 19.5 min); (b) perchloroacenaphthylene $C_{12}Cl_8$ (No. 35, acquired at 38.5 min); (c) perchlorophenanthrene $C_{14}Cl_{10}$ (No. 32, acquired at 33.8 min); (d) perchloropyrene $C_{16}Cl_{10}$ (No. 39, acquired at 47.0 min); (e) perchlorofluoranthene $C_{16}Cl_{10}$ (No. 50, acquired at 69.1 min).

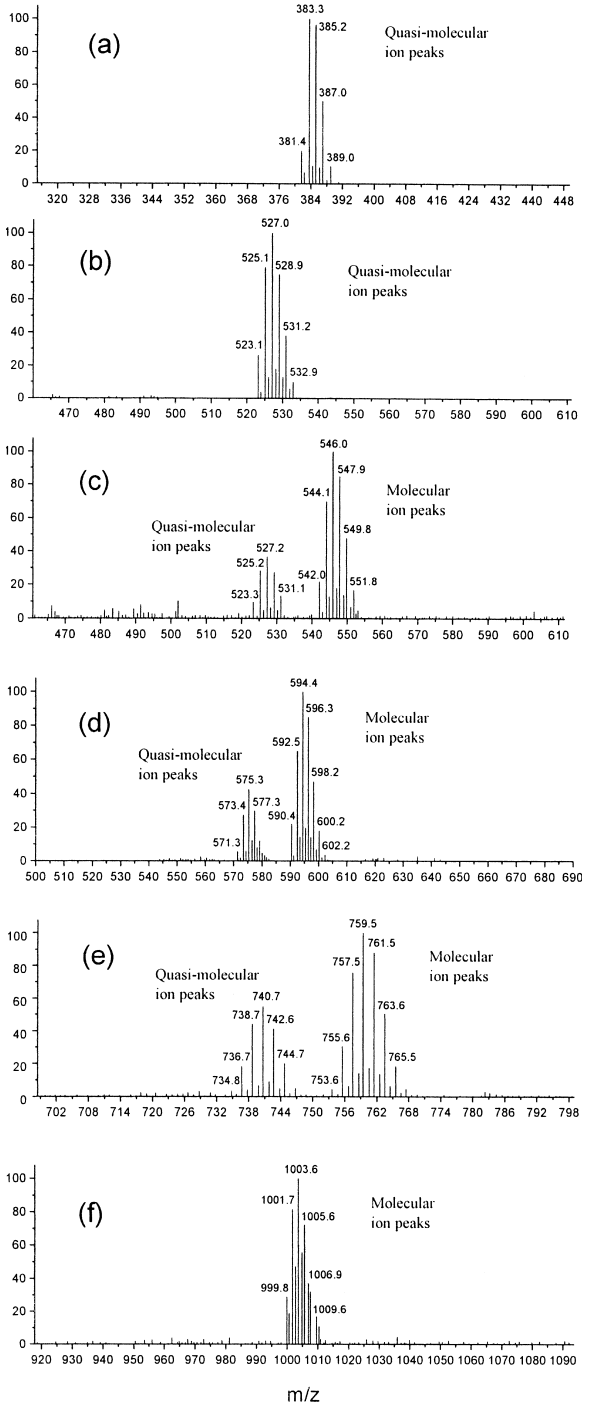

Fig. 3. Mass spectra of selected PCPAHs. (a) Perchloronaphthalene $C_{10}Cl_8$ (No. 19, acquired at 19.5 min); (b) perchloropyrene $C_{16}Cl_{10}$ (No. 39, acquired at 47.0 min); (c) perchlorofluoranthene $C_{16}Cl_{10}$ (No. 50, acquired at 69.1 min); (d) $C_{20}Cl_{10}$ (No. 100, acquired at 188.5 min), (e) $C_{22}Cl_{14}$ (No. 53, acquired at 76.1 min); (f) $C_{60}Cl_8$ (No. 76, acquired at 122.1 min).

recorded in the HPLC–MS experiment. Table 2 lists all the products molecular formulas identified by the isotopic distribution in corresponding mass spectra.

Ion peaks with masses 19 less than their molecular masses are also observed in the experiment, and we name them quasi-molecular ions herein. It was found from the isotopic distribution that quasi-molecular ions might result from losing a chlorine atom and capturing an oxygen anion during the APCI process [24]. The quasi-molecular ion peaks were always observed in APCI-MS analyses of PCPAHs. In many cases, the quasi-molecular ion peak became the sole peak in the corresponding mass spectra. According to the evidence resulting from HPLC–MS analysis of available standard compounds, occurrence of a quasi-molecular ion peak was found to depend on the structural property of PCPAHs. As shown in Fig. 3 and Table 2, the compounds with planarity structures, such as perchloronaphthalene ($C_{10}Cl_8$) [25] and perchloropyrene ($C_{16}Cl_{10}$) [26] tend to produce quasi-molecular ions peaks, while non-planar structures such as perchlorofluoranthene ($C_{16}Cl_{10}$) [15] and $C_{20}Cl_{10}$ [14] tend to produce molecular ion peaks in the APCI source. Though larger PCPAHs are not structurally identified to date, the resulting degree of non-planarity may be evaluated by their compositions [16]. Generally, the PCPAHs comprising more chlorine atoms in their carbon frame rims are very likely planar, for example, $C_{18}Cl_{14}$, $C_{20}Cl_{14}$ and $C_{22}Cl_{16}$. As shown in Table 2, these kinds of PCPAHs always exhibit stronger quasi-molecular ion peak in corresponding mass spectra.

Occasionally, some of PCPAHs or fullerenes (C_{60}, C_{70}) showed adduct peaks with mass 31 more than their molecular ion peaks in APCI mass spectra. These peaks might result from adduction of PCPAHs or fullerenes with CH_3O^- coming from the mobile phase.

3.5. Analysis and correlation of PCPAHs and fullerenes

As shown in Fig. 1, over 100 compounds in the sample were separated and characterized in a HPLC run under the chromatographic conditions mentioned above. HPLC–MS analysis of these products showed that most of them were fully chlorinated carbon clusters, though a few chlorinated hydrocarbons with certain hydrogen or oxygen atoms in their molecules were also found among the products of the chloroform discharge reaction. These perchlorinated carbon clusters were identified as aromatic conjugated double bond systems according to their strong UV absorbance within 205–400 nm. As shown in Table 2, many PCPAHs products are composed of 8, 10 and 12 chlorine atoms and an even number of carbon atoms. With regards to the limitation of chlorines in the molecular rims, it is suggested that these PCPAHs, especially larger ones, may be bowl-shaped aromatic structures consisting of both six-membered and five-membered rings [14–18]. Their carbon frameworks, considered as parts of fullerenes surface, might be the key intermediates leading to fullerenes.

The original abundance of the PCPAH and fullerene (C_{60}, C_{70}) products from the chloroform discharge reaction was maintained during the sampling procedure. Although quantitative analysis was not performed in the study, relative abundance of PCPAHs and fullerenes in the products can be evaluated approximately from the data of HPLC–UV–MS analysis and is observed to decrease with increase of their carbon number. In the reaction, all products, including fullerenes, PCPAHs and amorphous carbons, are created under the same reaction condition and from the same starting species, chloroform, a simple molecule composed of a single carbon atom. It was thus reasonable to suggest that the small carbon clusters, which were chlorinated in the reaction, might be the precursors of larger carbon species such as fullerenes and amorphous carbons. Most of the small carbon clusters, however, did not grow up in the reaction. Therefore, the experimental evidences and analysis results are valuable for revealing fullerenes formation.

In fact, the large PCPAHs are more important for the mechanistic study. Unfortunately, their yields are very low in the reaction and their analyses are time-consuming under the HPLC conditions. To analyze larger PCPAHs and fullerenes, pre-separation or clean-up procedure should be applied and the HPLC conditions need to be improved. The investigation is currently in process.

3.6. Correlation between HPLC retention and structure of PCPAHs

It is more interesting to correlate retention charac-

Table 2
APCI-MS analysis results

Labeled No.	Composition of PCPAHs and fullerenes (C_{60}, C_{70})	Retention time (min)	First mass of molecular (or quasi-molecular) ion peak
1	$C_{10}H_4Cl_6$	6.5	334
2	C_6HCl_5	6.7	229*
3	$C_{58}Cl_{12}$	6.8	1176
4	C_8Cl_8	7.5	357*
5	$C_{16}H_4Cl_{10}$	7.8	527*
6	C_6Cl_6	8.0	263*
7	C_8Cl_6	9.2	287*
8	$C_{13}H_8Cl_{10}$	9.5	514
9	$C_{19}H_8Cl_{12}$	10.1	637*
10	$C_{16}H_6Cl_8$	10.5	478
11	$C_{16}H_4Cl_{10}$	12.1	546
12	$C_{16}H_4Cl_8$	12.8	476
13	$C_{16}H_4Cl_8$	13.1	476
14	$C_{12}Cl_{10}$	13.5	494
15	$C_8H_2Cl_8$	14.4	378
16	$C_{12}H_{10}Cl_6$	15.8	345*
17	$C_{19}Cl_{14}$	17.5	699*
18	$C_{13}Cl_6$	18.3	347*
19	$C_{10}Cl_8$	19.5	381*
20	$C_{21}H_6Cl_8$	21.4	519*
21	$C_{12}Cl_8$	21.5	405*
22	$C_{17}Cl_{12}$	22.2	605*
23	$C_{14}Cl_{14}$	23.3	658
24	$C_{18}Cl_{14}$	24.1	687*
25	$C_{22}Cl_{10}O$	25.6	630
26	$C_{14}Cl_{10}$	26.1	499
27	$C_{14}Cl_8$	27.3	448
28	$C_{28}Cl_{16}$	27.9	877*
29	$C_{24}Cl_{10}$	29.5	638
30	$C_{20}Cl_{14}$	29.9	711*
31	$C_{14}Cl_{10}$	30.1	499*
32	$C_{14}Cl_{10}$	33.8	499*
33	$C_{16}Cl_{10}$	34.7	523*
34	$C_{30}Cl_{14}$	34.9	850
35	$C_{12}Cl_8$	38.5	405*
36	$C_{32}Cl_{12}$	40.7	804
37	$C_{28}Cl_{12}$	43.4	756
38	$C_{30}Cl_{12}$	45.5	780
39	$C_{16}Cl_{10}$	47.0	523*
40	$C_{22}Cl_{16}$	48.5	805*
41	$C_{18}Cl_{14}$	51.5	687*
42	$C_{36}Cl_{12}O$	52.7	849*
43	$C_{26}Cl_{14}$	53.4	783*
44	$C_{30}Cl_{14}$	54.0	850
45	$C_{14}Cl_8$	57.3	448
46	$C_{22}Cl_{12}$	59.4	665*
47	$C_{28}Cl_{12}$	63.9	756
48	$C_{28}Cl_{10}$	65.5	686
49	$C_{29}Cl_{12}$	67.7	749*
50	$C_{16}Cl_{10}$	69.1	542
51	$C_{26}Cl_{12}$	71.2	732

Table 2. Continued

Labeled No.	Composition of PCPAHs and fullerenes (C_{60}, C_{70})	Retention time (min)	First mass of molecular (or quasi-molecular) ion peak
52	$C_{58}H_8Cl_{16}$	74.3	1264
53	$C_{22}Cl_{14}$	76.1	735*
54	$C_{20}Cl_{12}$	77.1	660
55	$C_{20}Cl_{14}$	78.2	711*
56	$C_{68}Cl_{14}$	79.6	1306
57	$C_{20}Cl_{10}$	84.5	590
58	$C_{64}H_8Cl_{16}$	84.5	1336
59	$C_{75}Cl_{14}$	88.2	1371*
60	$C_{32}Cl_{12}$	90.3	804
61	$C_{20}Cl_{12}$	93.4	641*
62	$C_{18}Cl_{10}$	95.4	566
63	$C_{26}Cl_{10}$	100.8	662
64	$C_{48}Cl_8$	102.5	856
65	$C_{50}Cl_{10}$	103.1	950
66	$C_{30}Cl_{14}$	105.9	850
67	$C_{42}Cl_{14}$	108.2	994
68	$C_{22}Cl_{12}$	109.3	684
69	$C_{42}Cl_{10}$	109.5	854
70	$C_{24}Cl_{12}$	109.8	708
71	$C_{18}Cl_{10}$	112.7	566
72	$C_{60}Cl_{10}$	116.2	1070
73	$C_{24}Cl_{12}$	117.9	708
74	$C_{32}Cl_{12}$	118.5	804
75	$C_{22}Cl_{12}$	121.6	684
76	$C_{60}Cl_8$	122.1	1000
77	$C_{32}Cl_{12}$	122.2	804
78	$C_{22}Cl_{12}$	124.3	684
79	$C_{58}Cl_{10}$	129.6	1046
80	$C_{24}Cl_{12}$	130.7	689*
81	$C_{30}Cl_{10}$	132.9	710
82	$C_{24}Cl_{12}$	133.6	689*
83	$C_{36}Cl_{10}$	136.9	782
84	$C_{18}Cl_{10}$	138.7	566
85	$C_{26}Cl_{10}$	143.2	662
86	$C_{40}Cl_{10}$	143.5	830
87	$C_{28}Cl_{10}$	145.5	686
88	$C_{74}Cl_{14}$	147.5	1378
89	$C_{28}Cl_{10}$	150.1	686
90	$C_{56}Cl_{10}$	151.8	1022
91	$C_{32}Cl_{10}$	152.1	734
92	$C_{38}Cl_{10}$	153.6	806
93	$C_{60}O$	159.1	736
94	$C_{69}Cl_8$	166.7	1108
95	$C_{20}Cl_{10}$	168.6	590
96	C_{60}	171.2	720
97	$C_{56}H_8Cl_8$	175.1	960
98	$C_{32}Cl_{10}$	179.1	734
99	$C_{68}Cl_8$	182.3	1096
100	$C_{20}Cl_{10}$	188.5	590
101	$C_{28}Cl_{10}$	191.4	686
102	$C_{62}Cl_8$	193.8	1024
103	$C_{22}Cl_{10}$	194.5	614
104	C_{70}	209.0	840

*First mass of quasi-molecular ions peak with masses 19 less than its molecular masses.

teristics of each separated component versus its molecular structure. Table 3 lists the reversed-phase HPLC retention times and structures of eight available PCPAHs, perchlorobenzene (C_6Cl_6), perchloronaphthalene ($C_{10}Cl_8$), perchlorobiphenyl ($C_{12}Cl_{10}$), perchloroanthracene ($C_{14}Cl_{10}$), perchlorophenanthrene ($C_{14}Cl_{10}$), perchloroacenaphthylene ($C_{12}Cl_8$), perchloropyrene ($C_{16}Cl_{10}$) and perchlorofluoranthene ($C_{16}Cl_{10}$). The data demonstrate a dependence of the eluting sequence of the PCPAHs versus their composition: the retention time rises with increasing number of their fused rings. The correlation has also been observed in the chromatography of large PCPAHs which structures are not determined yet. As shown in Fig. 1, retention times of large PCPAHs tend to increase with the number of carbon atoms.

A variety of PCPAHs isomers are observed in the HPLC–MS analysis, but they exhibit significantly different retention times. What is the relationship between structure and retention of the isomers? Taking into account the effects of intramolecular steric strain and the resulting degree of non-planarity [27], we can deduce the correlation from comparison of two pairs of isomers (Table 3): perchlorophenanthrene (I) versus perchloroanthracene (II), and perchlorofluoranthene (III) versus perchloropyrene (IV). In this reversed-phase HPLC analysis and prior investigation [22], (I) and (III) were found to have longer retention times than those of (II) and (IV), respectively. The structures of both (II) and (IV) are lower degree of non-planarity but with stronger intramolecular steric strain due to the overcrowded chlorine atoms [26], while the structures of (I) and (III) are twisted to relieve their strain [15,27]. We thus suppose that curvature of the molecular structure contribute to the longer retention time. The

Table 3
Structures and retention of available PCPAHs

PCPAH compound	Formula	Structure	Planarity	Rings number	Retention time (min)
Perchlorobenzene	C_6Cl_6		Planarity	1	8.0
Perchlorobiphenyl	$C_{12}Cl_{10}$		Non-planarity	2	13.5
Perchloronaphthalene	$C_{10}Cl_8$		Planarity	2	19.5
Perchloroanthracene	$C_{14}Cl_{10}$		Approximate planarity	3	30.1
Perchlorophenanthrene	$C_{14}Cl_{10}$		Non-planarity	3	33.8
Perchloroacenaphthylene	$C_{12}Cl_8$		Planarity	3	38.5
Perchloropyrene	$C_{16}Cl_{10}$		Approximate planarity	4	47.0
Perchlorofluoranthene	$C_{16}Cl_{10}$		Non-planarity	4	69.1

correlation complies with the observation of retention characteristics of PAHs [28], the parent compounds of PCPAHs. Another experimental evidence supporting this hypothesis comes from the comparison of retention of PCPAHs substituted with different chlorines. As for the PCPAHs with the same carbon number, the less chlorine atoms on the rim of its carbon frames, the longer retention observed in the revered-phase HPLC. In fact, the molecule with less chlorine in the rim of carbon frame has very likely a higher degree of non-planarity, such as the curved structure incorporating the pentagons [16].

4. Conclusion

On a conventional ODS column, over 80 chlorine-substituted PAHs and fullerenes have been separated sufficiently to provide information on molecular composition by selecting a mobile phase consisting of three solvents and running in a gradient. HPLC–UV–MS combination provides retention time, UV adsorption spectrum and mass spectrum of each separated component in a single run of analysis. The reserved-phase HPLC retention of PCPAHs was found to relate to the number of aromatic rings and the degree of non-planarity in their structures. Based on isotopic pattern of the molecular ion or/and quasi-molecular ions, produced in the APCI source in negative ion mode, compositions of these fully chlorinated PAHs were identified.

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