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Identification of acephenanthrylene and aceanthrylene in aerosol and its environmental implication

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Acephenanthrylene and aceanthrylene in aromatic fraction of aerosols were identified by means of online hydrogenation gas chromatography mass spectrometry(GCMS). Compared aerosols from various sources, acephenanthrylene and aceanthrylene were ubiquitously present in urban aerosol. High concentration of acephenanthrylene and aceanthrylene were found in agricultural biomass and coal combustion particles. However, it is difficult to detect in exhaust from gasoline and diesel engine, dustfall, waste water, soil, and sediment. Combustion emissions were considered the major source of acephenanthrylene and aceanthrylene, which can be used as a potential molecular marker for the source pollution in urban aerosols.

aerosol, source apportionment, acephenanthrylene, aceanthrylene, online hydrogenation gas chromatograph

Acephenanthrylene (AP) was first found as a reaction product of silica-catalyzed pyrolysis of methane[1]. It also was found in the carbon black extracts[2], coal[2], kerosene[2], tobacco pyrolyzate[3], baccy pyrolysis[4], combustion of lumber[5], biomass[6], and rubber[7]. Krishnan and Hites[8] had identified it by means of gas chromatograph mass spectrometry and coelution of standard acephenanthrylene. Cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) are generally considered with enhanced bioactivity (mutagenic and carcinogenic effects) compared to PAHs without the cyclopenta moiety[9]. Aceanthrylene was more mutagenic than its isomer, acephenanthrylene[10], but the epoxide of the latter exhibits direct-acting mutagenic response[11]. Acephenanthrylene can isomerize to more mutagenic fluoranthene[12].

Source identification and apportionment of polycyclic aromatic hydrocarbons on airborne particulate to calculate the contribution ratio of different pollutants can provide important resources for air pollution control. For example, the ratio of benzo[a]pyrene and benzo[ghi] pyrene can be used as an identification of different types of pollution[13]; benzonaphthothiophene (BNT) is the product of coal pyrolysis, and coronene is mainly in the car effluent gases[14]. Cheng et al.[15] reported that 1,3,5-triphenylbenzene in the aerosols can be used as an important molecular marker for chemical processing pollution. Simcik et al.[16] summarized the ratios of different compounds in PAHs from various sources pollution, and found that the ratio method can provide important information for pollutant source apportionment. However, it is still difficult to have qualitative or quantitative ratio of pollution contribution for polyaromatics, even though polyaromatics are the common pollutants.

In this report, acephenanthrylene and aceanthrylene in the polyaramatic samples from air aerosols obtained in Beijing and Chongqing area will be identified by online hydrogenation GCMS. The significance of acephenanthrylene and aceanthrylene on environmental chemistry will be discussed.

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1 Experimental

1.1 Sample collection

The aerosol sample was collected by a large volume of aerosol collection container (TH-1000, Wuhan Tianhong Automatic Instrument Company). Air flow rate range was between. 0.8 to1.2 m^3/min. The sampling procedure has been reported elsewhere[17].

1.2 Online hydrogenation gas chromatograph and mass spectrometry

Pt-catalyst was prepared by mixing molecular sieve (13X, 20g, 40—60 mesh) with chloroplatinate (1 g dissolved in 10 mL distilled water). The mixture was well-proportioned and evaporated at 120℃, and calcined at 200℃ for 4 h.

The PAH-containing fractions were analyzed by a Thermo-Finnigan Teace-DSQ GCMS. A PTV injector with a long liner was used to contain catalyst. Silica wool was inserted to the liner, at the upper capillary inlet, and a little Pt-catalyst was added to facilitate the hydrogenation reaction during the analysis. Hydrogen was used as the carrier gas.

A HP-5MS capillary column (30 m×0.25 mm×0.25 μm) was used in this work. The injector temperature was set to 230—300℃. The oven was programmed at the initial temperature of 50℃ and held for 1 min, then ramped up to a final temperature of 120℃ at 15℃/min and held for 15 min. The rate of carrier gas was 1 mL/min. The mass detector was operated in the electron impact (EI) ionization mode (70 eV) and with the mass range of 35—500 amu in 1.2 s scan period

2 Result and discussion

2.1 Identification of acephenanthrylene and aceanthrylene

Figure 1 shows the mass chromatograph of *m/z* 202 and *m/z* 204 of the aromatic fraction of aerosol from coal combustion at various hydrogenation severities. Two peaks (2 and 3) with molecule weight of 202 at high relative abundance were detected. Their characteristic gas chromatograph eluted between fluoranthene (1) and pyrene (PY)(4), and mass spectrometry characters were similar to that from fluoranthene (1) and pyrene (4).

Two peaks (shown as 5 and 6) were present on the *m/z* 204 mass chromatograms for all samples, which had similar characteristics to dihydroacephenanthrylene. It could be that 5 and 6 were derivatives of 2 and 3. The latter had a double band, the former has a single band. Aromatic fraction and its hydrogenation yield were analyzed by online hydrogenation gas chromatograph-mass spectrometry to show this deduction. Results showed that compounds 2 and 3, with high hydrogenation activity, could be partially or completely converted under mild condition, while there was no reaction taking place for the pyrene and fluoranthene. The relative intensity increase of compounds 5 and 6 (*m/z* value was 204) corresponded with the decrease of compounds 2 and 3.

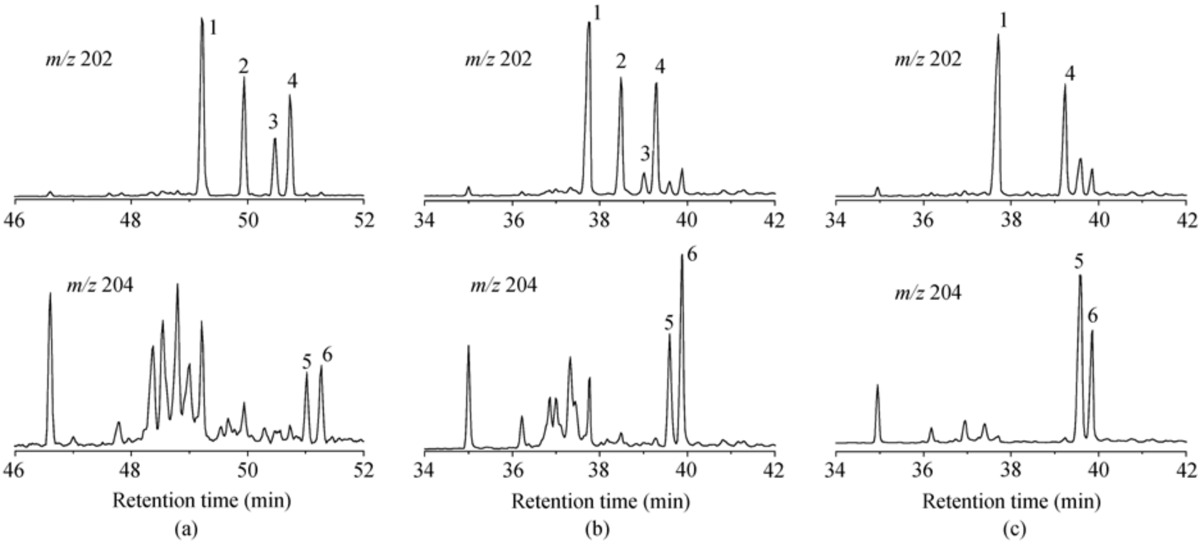

Figure 1 Mass chromatograph of aromatic fractions before and after hydrogenation. (a) Original sample; (b) after mild hydrotreatation; (c) after deep hydrogenation. Peaks labelled with 1 and 4 correspond to fluoranthene and pyrene.

Compounds 2 and 3 converted to compounds 6 and 5 respectively, and compound 2 presented a more hydrogenation activity. Figure 1(b) and (c) shows the differences between mild and deep hydrogenation products.

Compounds 2 and 3 were acephenanthrylene and aceanthrylene, resepectively, according to reference and the gas chromatograph and mass spectrometry characteristics of aromatic fraction before and after hydrogenation. Their structures are shown in Figure 2. The basis for identifying frameworks 2 and 3 as acephenanthrylene and aceanthrylene is as follows.

(1) The compounds presented in aromatic fractions.

(2) Their molecular formula was $C_{16}H_{10}$ estimated by the accurate molecular weight from a high resolution mass spectrometry with <10 ppm mass accuracy.

(3) Coelution of pure standard indicated that the unknown compounds were not diphenylbutadiyne, an isomer of acephenanthrylene and aceanthrylene. Its molecular formula is $C_{16}H_{10}$ with a similar mass spectrometry characteristic with unknown compounds.

(4) Gas chromatograph analysis showed two theoretical isomers of acephenanthrylene and aceanthrylene.

(5) High relative abundance of acenaphthene, another CP-PAHs identified in aerosol was in the samples with high concentrations of the unknown compounds.

(6) The unknown compounds could be easily hydrogenated, and produced two compounds with a molecular weight of 204, which have the same mass spectrometry characteristics of dihydroacephenanthrylene and dihydroaceanthrylene.

(7) The retention index of compound 2 approached to that of acephenanthrylene as reported in refs. [1, 4].

(8) Compound 3 was easily hydrogenated than compound 2, Since aceanthracelene, with a linear molecular structure, was more unstable thermodynamically than acephenanthrylene[1].

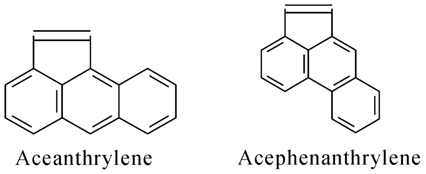

Figure 2 Structure of compounds 2 and 3.

2.2 Distribution characteristics of acephenanthrylene and aceanthrylene in aerosols from different sources

Acephenanthrylene and aceanthrylene were found in more than 200 aerosol samples collected from various cities at different seasons during 1999 to 2006. It showed that acephenanthrylene and aceanthrylene were universal compounds in aerosol. A typical total ion current (TIC) gas chromatograph of PAHs from aerosol is shown in Figure 3. The aerosol sample was collected from Beijing, in Apr. 2004. The peaks of acephenanthrylene (2) and aceanthrylene (3) as shown in the insert of Figure 3, were distinctly shown on the TIC gas chromatograph.

Peaks 1, 2, 3, and 4 shown in the insert of Figure 3, are fluoranthene, acephenanthrylene, aceanthrylene, and pyrene, respectively, which have similar mass spectrum characteristics. Table 1 lists the relative abundance of the fluoranthene, acephenanthrylene, aceanthrylene, and

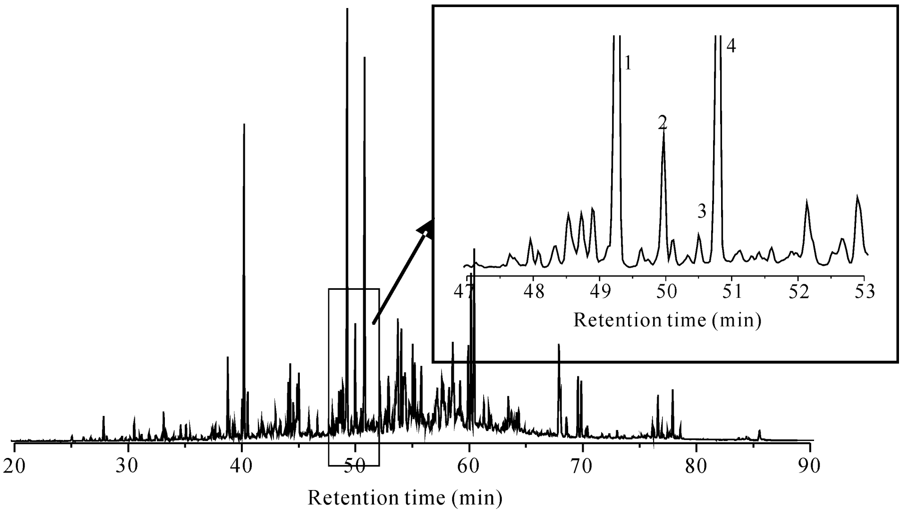

Figure 3 Total ion chromatograph of PAHs of Beijing urbon aerosol.

Table 1 Relative abundance of the 3 aromatic compounds from various sources

Sources	Ratios			Notes
	FL$^{a)}$/PY$^{b)}$	AP$^{c)}$/PY	AP/FL	
Diesel fueled vehicle exhaust	0.40	–	–	the idle speed model, 0.5 m from outlet of gas vent line
Gasoline-fueled vehicle exhaust	0.66	–	–	electronic control injection engine, the idle speed model, 0.5 m from outlet of gas vent line
Emissions of biomass combustion	1.13	0.41	0.36	dryer maize ash
Emissions of coal combustion	1.98	1.16	0.59	fix-bed combustion of anthracite coal
Emissions of carbon black combustion	0.92	0.15	0.17	meat roasting
Aerosol from urban area	1.07	0.21	0.20	Changping, Beijing
Aerosol from desert	1.49	−	−	edge region of desert in Ordos, China
Dust fall	1.00	−	−	Changping, Beijing
Sediment in the river	1.31	−	−	bottom of Shahe River, Changping, Beijing
Soil	1.22	−	−	baodi, Tianjin

a) Fluorathene; b) pyrene; c) acephenanthrylene.

pyrene from various sources. Acephenanthrylene and aceanthrylene were not found in coal or crude oil. However high concentrations of acephenanthrylene and aceanthrylene were found in aerosols from combustion sources. The car exhaust is one of key urban aerosol pollutants. However, the low concentration of acephenanthrylene and aceanthrylene in the exhaust of gasoline and diesel automobiles indicated that their pollution contribution is limited to urban aerosols. High concentration of acephenanthrylene and aceanthrylene in the gas particles from coal and biomass combustion indicated that combustion of coal and biomass is a key contribution to urban aerosol.

Extremely high concentration of aceanphrylene and acephenanthrylene was reported when the brown coal was pyrolysis at 1000℃[18]. High temperature pyrolysis is known to cause the formation of acephenanthrylene and aceanthrylene, and in the combustion process, the combustion products are subjected to pyrolysis after the combustion zone. The concentrations of acephenanthrylene and aceanthrylene and their isomers are not correlated to the combustion temperature[19], Nevertheless, the structure of the aromatic productions is related with the chemical structures of combustion materials and combustion conditions. It is postulated that CP-PAHs are produced from ethynyl-substituted aromatic radicals which was formed by the reaction of ethylene and aromatics[20].

In the polyaromatics from various sources used in experiments, the relative concentrations of acephenanthrylene and aceanthrylene varied. In the high concentration samples, their concentration is close to pyrene. As specified in the US EPA priority control polyaromatics, the abundances of 9 (out of 16) are lower than those of acephenanthrylene and aceanthrylene. High concentrations of acephenanthrylene and aceanthrylene are found in the city aerosols, however, there is no acephenanthrylene and aceanthrylene in waste water, dust and sediment. There is a correlation between city aerosols and dust, and their steady polyaromatics composition is also similar to each other. Hence, it is likely that acephenanthrylene and aceanthrylene in aerosol undergo chemical changes during the sediment process, and transform to other compounds. As well, since the decay life of acephenanthrylene and aceanthrylene is relatively short, its double bonds can be easily oxidized to cycleoxygen products[11]. There are no acephenanthrylene and aceanthrylene detected in aerosol from desert areas, indicating that chemical changes took place during the long distant immigration of acephenanthrylene and aceanthrylene. Fewer pollutants in the aerosol from desert areas also contribute to lower concentration of acephenanthrylene and aceanthrylene.

In environmental test, polyaromatics are present in aerosol from various sources. The difference of these aerosol samples is their concentration. It is difficult to appoint or exclude the pollution sources by detecting a particular molecular marker compound in previous study. However, our experimental results indicated that acephenanthrylene and aceanthrylene can be used as environmental molecular marker to distinguish the two pollution types: natural exhausted gases from automobile, oil and coal, and combustion pollution from coal and biomass. The absolute concentration of acephenanthrylene and aceanthrylene can be a potential method to investigate the pollution contribution of different pollutants. Their concentration can be an important parameter as evaluation of decay life of various pollutants when the reaction kinetics of acephenanthrylene and aceanthrylene in the aerosol are available.

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