



# Analysis and structure prediction of chlorinated polycyclic aromatic hydrocarbons released from combustion of polyvinylchloride

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## Abstract

Chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) released from combustion of polyvinylchloride (PVC) at different furnace temperatures were investigated. A laboratory-scale tube-type furnace with electric heating was utilized to control combustion conditions. Glass fabric filters and adsorbents were used to collect the combustion emissions. Following Soxhlet extraction, concentration and column chromatography purification, isomers separation, selective detection and identification of Cl-PAHs were performed on GC/MS system on the basis of retention data and mass spectra. Their quantification was accomplished by using external standard calibration technique. About 18 Cl-PAHs were determined, most of which were monochlorinated derivatives of naphthalene, biphenyl, fluorene, phenanthrene, anthracene, fluoranthene and pyrene. Only two dichlorophenanthrenes or anthracenes were identified. The possible positions of chlorine atoms attached to the aromatic rings are predicted by quantitative structure–property relationship. The levels of these compounds were in the range of 0.30–29.08  $\mu\text{g/g}$  PVC. The relationship between the formation of Cl-PAHs and PAHs was discussed.

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**Keywords:** Polyvinylchloride; Combustion; Cl-PAHs; Structure prediction

## 1. Introduction

During recent decades, a lot of interest has been focused on the detection of chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) in environmental samples. Apart from polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs), polychlorinated naph-

thalenes (PCNs) and other halogenated polycyclic aromatic hydrocarbons (Cl-PAHs and Br-PAHs) with three or more fused aromatic rings have been detected in samples of various origins. Shiraishi et al. (1985) demonstrated their presence in chlorinated tap waters. Rappe et al. (1982) reported the formation of polychlorinated pyrenes during PCB fires. Occurrence of a large number of Cl-PAHs was reported in automobile exhausts, snow, urban air and wastewater of pulp and paper mills (Haglund et al., 1987; Nilsson and Östman, 1993; Brodskv et al., 1999). Tausch and Stehlik (1985) detected Cl-PAHs, ranging from four to seven aromatic rings, in fly ash from an incineration plant for radioactive wastes. Polychlorinated PAHs were detected in emissions from coal combustion and municipal waste incineration by Eklund and Strömberg (1983) and by

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Oehme et al. (1987). According to Sovocool et al. (1989), chlorobromo-substituted PAHs were also shown to occur in fly ash from a municipal waste incinerator. Recently more detailed data on congeners of PCNs that accumulated in wildlife and abiotic environmental matrices become available (Falandysz, 1998).

Interest has been focused on Cl-PAHs since some of them have also been shown to have stronger toxicity and mutagenic properties than their corresponding PAHs in test systems for biological activity (Table 1). For instance, it was found by Colmsjö et al. (1984, 1988) and Rannug et al. (1986) that some Cl-PAHs showed significant mutagenic effects in the presence of a metabolizing system. Löfroth et al. (1985) found that 7-chlorobenzo[*a*]anthracene, 9-chloroanthracene, and 6-chlorochrysene showed strong direct mutagenic effects. The latter compound has also been shown to have a high affinity to the tetrachlorodibenzo-*p*-dioxin (TCDD) receptor (Töftgård et al., 1985) and to be a potent aryl

hydrocarbon hydroxylase (AHH) inducer (Franzen et al., 1988). Some of the 75 possible PCN congeners exhibit toxic effects similar to those of 2,3,7,8-TCDD (Table 1).

The chlorine in the emissions from municipal waste incinerators most likely originates from chlorine-containing waste materials like PVC. It has been confirmed that PVC can lead to the formation of PCDD/Fs during incineration of wastes (Elomaa et al., 1997). The formation of polychlorinated benzene has also been determined during combustion of PVC (Ahling et al., 1978). However, to the best of our knowledge, no extensive analysis and identification of Cl-PAHs released from PVC combustion has been reported previously except for PCDD/Fs. The aim of the present work was mainly to determine Cl-PAHs in emissions from PVC combustion and to investigate their formation mechanism in the combustion process, as well as the relationship between their formation and the furnace operation

Table 1

Toxicity data of Cl-PAHs cited from previous publications (Registry of Toxic Effects of Chemical Substances, 1998; Kannan et al., 1998)

| Compounds                                     | Toxicity  |
|---|---|
| 2-Chloronaphthalene                           | TWA 0.2 mg/m <sup>3</sup> ; STEL 0.6 mg/m <sup>3</sup> ; LD <sub>50</sub> = 2078 mg/kg (mouse); LD <sub>50</sub> = 886 mg/kg (rat)  |
| 1-Chloronaphthalene                           | TWA 0.2 mg/m <sup>3</sup> ; STEL 0.6 mg/m <sup>3</sup> ; LD <sub>50</sub> = 1540 mg/kg (mouse); LD <sub>50</sub> = 1091 mg/kg (rat) |
| Trichloronaphthalene                          | TWA 5 mg/m <sup>3</sup>   |
| Tetrachloronaphthalene                        | TWA 2 mg/m <sup>3</sup>   |
| 2,3,6,7-Tetrachloronaphthalene                | Oral administration guinea pig<br>LD <sub>50</sub> > 3 mg/kg  |
| 1,2,6,8-Tetrachloronaphthalene                | TEF 1.65E-05  |
| Pentachloronaphthalene                        | TWA 0.5 mg/m <sup>3</sup>   |
| 1,2,3,6,7-Pentachloronaphthalene              | TEF 1.7E-04   |
| Hexachloronaphthalene                         | TWA 0.2 mg/m <sup>3</sup>   |
| 1,2,3,4,5,6-Hexachloronaphthalene             | TEF 2E-03   |
| 1,2,3,5,6,8-Hexachloronaphthalene             | TEF 1.5E-04   |
| 1,2,3,4,6,7-1,2,3,5,6,7-Hexachloronaphthalene | TEF 2.27E-03  |
| 1,2,3,5,7,8-Hexachloronaphthalene             | TEF 2E-03   |
| 1,2,3,6,7,8-Hexachloronaphthalene             | TEF 5.9E-04   |
| 1,2,3,4,5,6,7-Heptachloronaphthalene          | TEF 3.45E-03  |
| Octachloronaphthalene                         | TWA 0.1 mg/m <sup>3</sup> ; STEL 0.3 mg/m <sup>3</sup>  |
| 9-Chlorofluorene                              | Intravenous injection mouse<br>LD <sub>50</sub> = 56 mg/kg  |
| 2-Chloroanthracene                            | SAT 100 µg/plate, 0.4702 µmol/plate   |
| 9-Chlorophenanthrene                          | SAT 10 µg/plate, 0.0470 µmol/plate  |
| 9-Chloroanthracene                            | SAT 20 µg/plate, 0.0940 µmol/plate  |
| 6-Chlorochrysene                              | SAT 20 µg/plate, 0.07612 µmol/plate   |
| 1-Chloropyrene                                | SAT 10 µmol/plate   |
| 1,3-Dichloropyrene                            | SAT 3330 µmol/plate   |
| 1,6-Dichloropyrene                            | SAT 3330 µmol/plate   |
| 1,8-Dichloropyrene                            | SAT 3330 µmol/plate   |
| 6-Chlorobenzo[ <i>a</i> ]pyrene               | Tumourity-mouse TDLo 80 mg/kg/8D-I  |

Note: TWA—time weighted average; STEL—short term expose limit; LD<sub>50</sub>—lethal dose 50 percent kill; TEF—toxic equivalent factor; SAT—testing for mutagenicity on *Salmonella typhimurium* TA98 and TA100; TDLo—lowest published toxic concentration.

parameters. The possible positions of chlorine atoms attached to some of Cl-PAHs are predicted by quantitative structure–property relationship (QSPR).

## 2. Experimental method

### 2.1. Materials

PVC, in powder form, free of additives, was the product of Beijing Second Chemical Factory. 1-Chloronaphthalene, 2-chloronaphthalene, 9-chlorophenanthrene, 9-chloroanthracene and PCB14 were purchased from Fluka (Sweden), AccuStandard Inc., Acros, Aldrich Chem. Co. (Germany) and Chem Service, respectively. Standard solutions of Cl-PAHs were prepared using *n*-hexane as the solvent. The silica gel in particle size from 100 to 200 mesh was activated in 130 °C for 13 h. Subsequent deactivation was performed by adding 3% (w/w) distilled water. Analytical grade solvents were used after distillation in an all-glass apparatus.

### 2.2. Combustion procedure

The combustion tests were performed in a tube-type furnace shown in Fig. 1 as described previously (Piao et al., 1999). At the beginning of a test, the tube furnace was first heated up to the test temperature (600–900 °C), then air was introduced into the quartz tube at a 2 l/min flow rate. The quartz boat containing about 1 g of PVC was pushed into the combustion zone of the furnace. The emissions were collected with glass wool, glass fiber filter (pore diameter 0.2 μm), and an adsorption cartridge filled with 7 g of XAD-2.

### 2.3. Extraction and purification

After cooling, the sample boat, glass wool, glass fiber filter and XAD-2 adsorbents were collected and extracted with dichloromethane in Soxhlet apparatus for 18 h. The extracts were concentrated to a volume of 4 ml by K–D apparatus and a gentle stream of nitrogen. 0.5 ml of extract was cleaned up by a glass column (10 mm i.d.) filled with 10 g of silica gel (deactivated by 3% H<sub>2</sub>O), which was eluted with 80 ml of *n*-hexane, and 50 ml of a mixture of *n*-hexane and dichloromethane (6:4, v/v). The first fraction, which contained Cl-PAHs, was concentrated to 1 ml for GC/MS analysis.

### 2.4. Gas chromatography and mass spectrometry

Analysis of Cl-PAHs was performed on a HP 6890 GC/5973 MSD system fitted with a 30 m HP-5ms column (0.25 mm i.d., 0.25 μm film). The oven temperature of the gas chromatograph was programmed from 50 °C (2 min) to 290 °C at a rate of 4 °C/min, and the temperature held on for 10 min. The temperature of the injector was maintained at 290 °C. The temperature of ion source of mass spectrometry was 280 °C, ionizing voltage 70 eV, and scan range *m/z* 50–550 amu.

Extraction ion chromatograph peaks of Cl-PAHs were determined by selecting molecular ion ( $M^+$ ), its isotopic ion ( $M+2)^+$  and fragment ion ( $M^+-Cl$ ). Cl-PAHs were identified by comparing their GC retention data and mass spectra with those of authentic compounds. In cases when the authentic standards were not available, identification was performed by checking reported relative retention data (Shiraishi et al., 1985) and library mass spectra against an isotopic ratio within

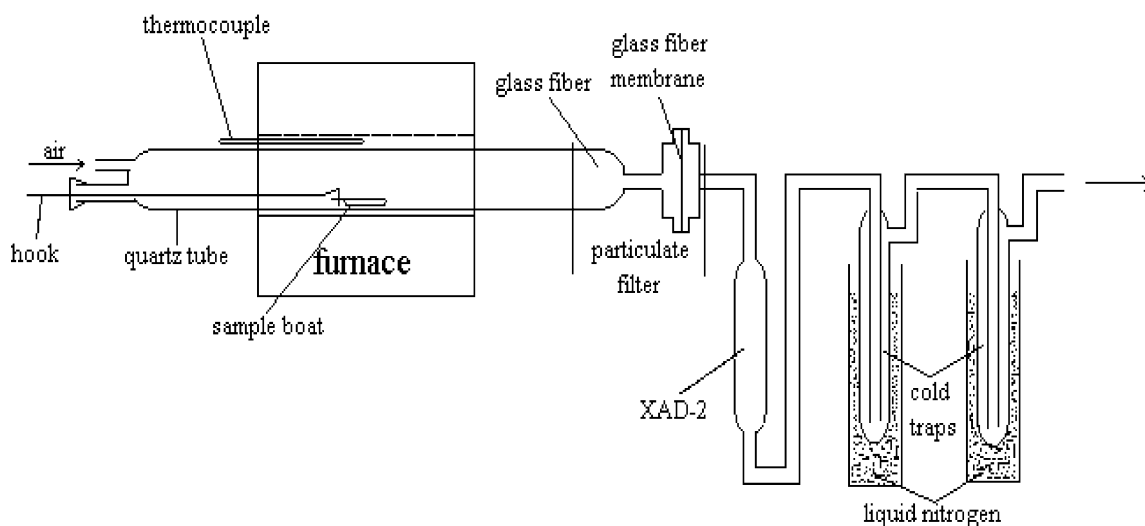


Fig. 1. A schematic diagram of the experimental apparatus for PVC combustion.

$\pm 10\%$  of the theoretical value. The possible positions of chlorine atoms attached to the aromatic rings were predicted by QSPR.

Cl-PAHs were quantified from the peak area of mass chromatograms using an external standard technique. Monochlorobiphenyl was determined against PCB14, of which relative response factor was estimated to be 1.638 (Ericksson, 1992). Semiquantitative estimation of Cl-PAHs of which authentic samples were not available was tentatively performed according to 9-chlorophenanthrene.

Quality assurance criteria for Cl-PAHs analysis were based on the first measure of a blank sample covering the complete analytical procedure. The limit of detection (LOD) for chlorinated naphthalene and chlorinated phenanthrene were estimated to be 0.061 and 0.072  $\mu\text{g/g}$  PVC respectively using a signal-to-noise ratio of 3:1. Recovery tests were carried out by spiking standard solution containing Cl-PAHs into glass fabric filter, which was then sequentially subjected to the entire sample preparation process. The recoveries of Cl-PAHs were within the range of 83–113%. Reproducibility for the determination of Cl-PAHs by external standard technique was within 12%.

### 3. Results and discussion

The extraction ion chromatograms of Cl-PAHs released from PVC combustion at 900 °C are shown in Fig. 2. At least 18 chlorinated compounds can be seen on the chromatogram. Fig. 3 shows the typical mass spectra of these compounds.

The mass spectrum of Peak 1 (RT 22.95 min) in Fig. 2 is shown in Fig. 3A. The molecular ion ( $M^+$ ) of the peak occurs at  $m/z$  162, indicating one chlorine atom, and a fragment ion occurs at  $m/z$  127, which arises out of the loss of one chlorine atom from the molecular ion. The mass spectrum and retention time of this compound was in agreement with those of 2-chloronaphthalene. Peak 2 (RT 23.17 min) in Fig. 2 gave a similar molecular ion and a similar fragment ion. This compound was identified as 1-chloronaphthalene on the basis of comparing its retention time and mass spectrum with those of authentic compounds.

Fig. 3B shows the mass spectrum of Peak 4 (RT 29.00 min) in Fig. 2. The molecular ion ( $M^+$ ) of the peak occurs at  $m/z$  188, and a fragment ion occurs at  $m/z$  152, indicating that this compound contains one chlorine atom. Peak 3 (RT 26.82 min) and Peak 5 (RT 29.22 min) have similar mass spectra to that of Peak 4. Compounds corresponding to these peaks were identified as monochlorobiphenyl from the mass spectra of each peak.

Fig. 3C shows the typical mass spectrum of Peak 6 (RT 34.40 min) and 7 (RT 35.32 min). The molecular

ion ( $M^+$ ) of the two peaks occurs at  $m/z$  200, and a fragment ion occurs at  $m/z$  165, indicating that a chlorine atom is attached to fluorene molecule. The compound corresponding to Peak 6 was identified as monochlorofluorene on the basis of mass spectrum. The compound corresponding to Peak 7 was tentatively identified as 2-chlorofluorene from the mass spectrum and relative retention time.

Fig. 3D shows the typical mass spectra of Peak 8, 9, 10, 11, 12, eluting at RT 39.73, 39.89, 40.12, 40.30, 40.55 min, respectively, as shown in Fig. 2. The molecular ion ( $M^+$ ) of these peaks occurs at  $m/z$  212, and a fragment ion occurs at  $m/z$  176. Compounds corresponding to these peaks were tentatively identified as monochlorophenanthrene or monochloroanthracene. The mass spectra and retention times of the compounds corresponding to Peak 10 and 12 were in agreement with those of 9-chlorophenanthrene and 9-chloroanthracene, respectively.

The compounds corresponding to Peak 13 (RT 44.81 min) in Fig. 2 gave a molecular ion at  $m/z$  246 (Fig. 3E), indicating two chlorine atoms, and two fragment ions at  $m/z$  212 ( $M^+ - \text{Cl}$ ) and 176 ( $M^+ - \text{Cl} - \text{HCl}$ ). Peak 14 (RT 45.06 min) in Fig. 2 gave a similar fragmentation pattern, with two chlorine atoms, to that of Peak 13. The compound corresponding to this peak was tentatively identified as 9,10-dichlorophenanthrene on the basis of relative retention time (Shiraishi et al., 1985) (Table 2). The molecular ion and its fragmentation pattern indicate the occurrence of dichloroanthracene or dichlorophenanthrene during combustion of PVC.

Fig. 3F shows the typical mass spectra of Peak 15, 16, 17, 18, eluting at RT 46.33, 46.54, 46.97, 47.82 min, respectively. The molecular ion ( $M^+$ ) of these peaks occurs at  $m/z$  236, indicating one chlorine atom, and a fragment ion occurs at  $m/z$  200, which arises from the loss of one chlorine atom from the molecular ion. Compounds corresponding to these peaks were tentatively identified as monochloropyrene and monochlorofluoranthene on the basis of mass spectra.

For the compounds, in which positions of chlorine atoms attached to the aromatic rings cannot be determined, QSPR was used to predict the possible structures. Eight parameters obtained by MNDO quantum chemical computations were used as molecular descriptors, including total energy (TENG), heat of formation (HF), ionization potential (IP), dipole moment (DM), molecular surface area (MSA), LUMO, surface area of Cl atoms (CISA) and net atomic charge of Cl (CINC). For Cl-PAHs substituted by two chlorine atoms, the larger absolute value is adopted. A better regression model is obtained:

$$\text{RRT} = -2.0459 - 0.000906\text{TENG} - 8.7340\text{CINC} \\ + 0.06175\text{DM}$$

$$R^2 = 0.9937 \quad F = 735.458 (> F_{0.0001})$$

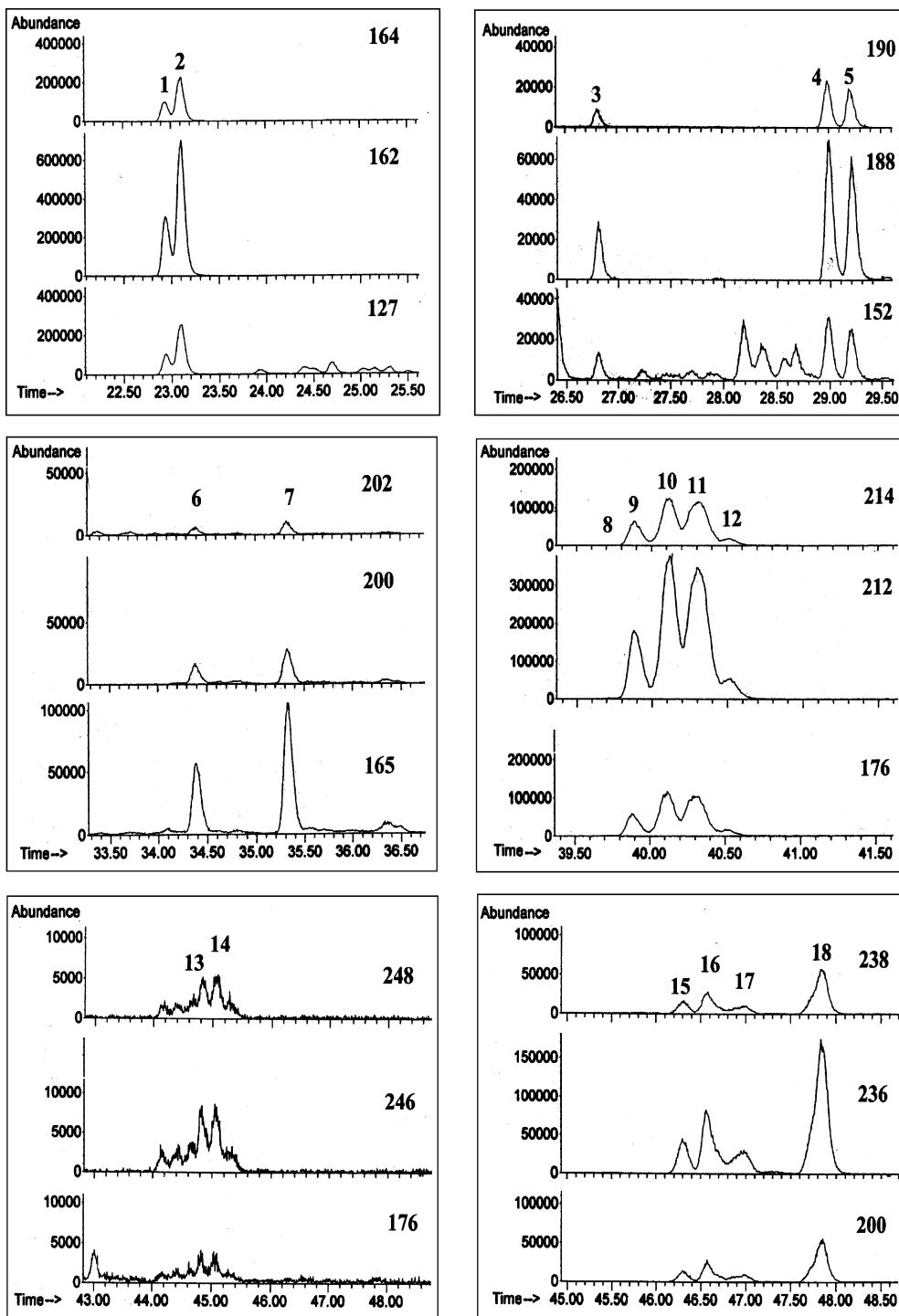


Fig. 2. Extraction ion chromatograms of Cl-PAHs from PVC combustion at the furnace temperature of 900 °C.

$$T_0 = -16.732, \quad T_1 = -46.850, \quad T_2 = 10.482,$$

$$T_3 = 6.240 \quad (|T_{0,1,2,3}| > |T|_{0.0001})$$

A summary of Cl-PAHs identified and predicted is presented in Table 2. About 18 Cl-PAHs were determined, among which most were monochlorinated

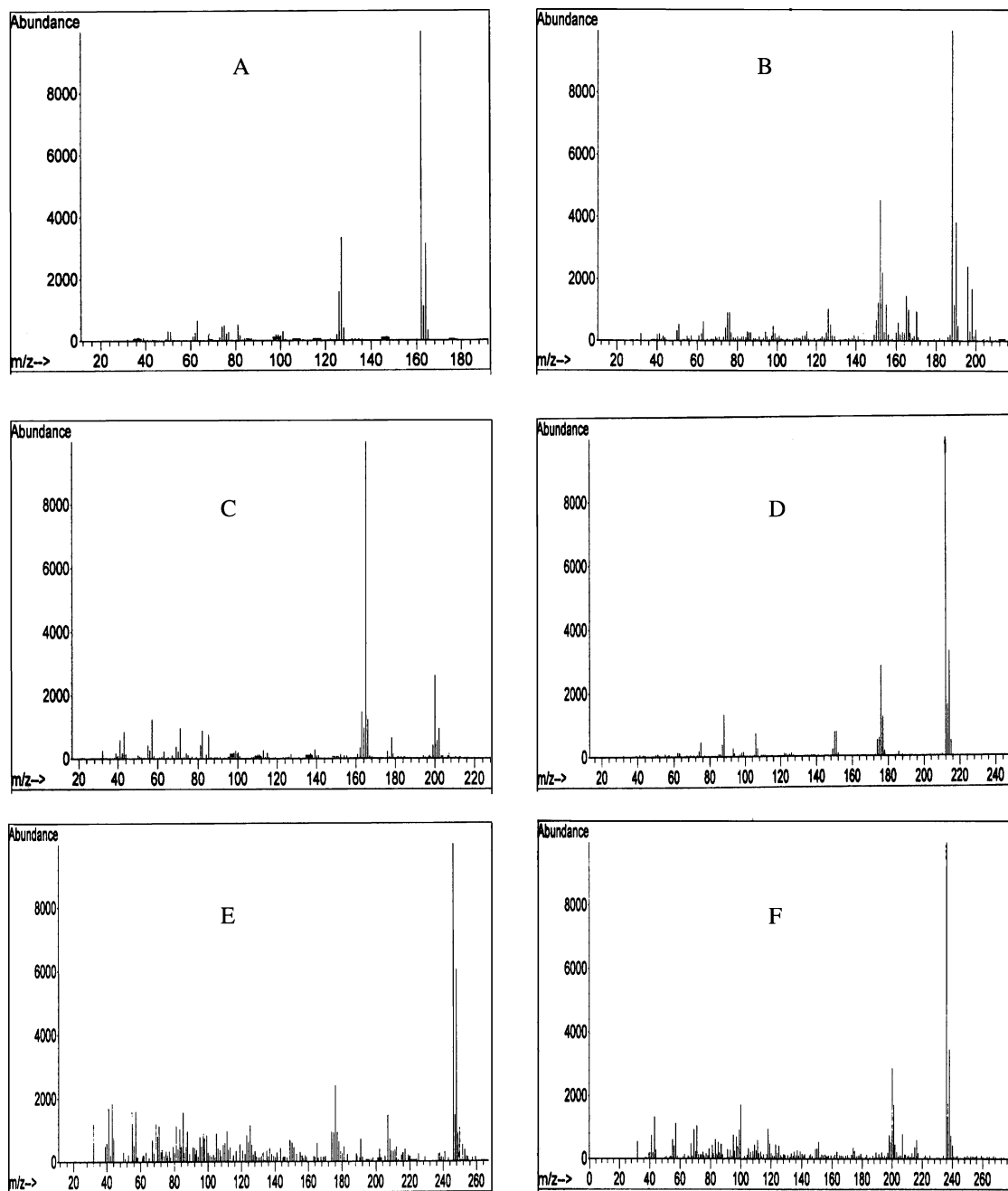


Fig. 3. Representative mass spectra of some chromatographic peaks in Fig. 2.

PAHs, and only two dichlorophenanthrenes or anthracenes were identified.

The types and the yields of Cl-PAHs released from PVC combustion at different furnace temperature are listed in Table 3. The result shows that the species and the levels of these Cl-PAHs increased with increasing furnace temperatures within the experimental range of 600–

900 °C. Dichlorinated phenanthrene or anthracene in particular was detected only at 800 and 900 °C. The total amount of these Cl-PAHs also gradually increased from 13.58 µg/g PVC at 600 °C to 101.95 µg/g PVC at 900 °C.

This tendency of increasing formation of Cl-PAHs with increasing furnace temperature was also observed in PAHs formation in the emissions during combustion

Table 2  
 Cl-PAHs identified by GC retention time, mass spectra and QSPR prediction in the emissions from PVC combustion

| No. | Compounds                                   | RRT <sup>a</sup> (Obs.) | Compounds                              | RRT (Pred.) | Ions selected |
|-----|---|-------------------------|--|-------------|---------------|
| 1   | 2-Chloronaphthalene <sup>b</sup>            | 0.658                   | 2-Chloronaphthalene <sup>b</sup>       | 0.6293      | 164, 162, 127 |
| 2   | 1-Chloronaphthalene <sup>b</sup>            | 0.663                   | 1-Chloronaphthalene <sup>b</sup>       | 0.6557      | 164, 162, 127 |
| 3   | Monochlorobiphenyl                          | 0.770                   | 4-Chlorobiphenyl                       | 0.8270      | 190, 188, 152 |
| 4   | Monochlorobiphenyl                          | 0.832                   | 3-Chlorobiphenyl                       | 0.8383      | 190, 188, 152 |
| 5   | Monochlorobiphenyl                          | 0.838                   | 1-Chlorobiphenyl                       | 0.8424      | 190, 188, 152 |
| 6   | Monochlorofluorene                          | 0.987                   | 1-Chlorofluorene                       | 0.9764      | 202, 200, 165 |
|     | Phenanthrene                                | 1.000                   | Phenanthrene                           | 1.0000      |               |
| 7   | 2-Chlorofluorene <sup>c</sup>               | 1.014                   | 2-Chlorofluorene <sup>c</sup>          | 1.0133      | 202, 200, 165 |
| 8   | Monochlorophenanthrene/monochloroanthracene | 1.140                   | 2-Chloroanthracene                     | 1.1262      | 214, 212, 176 |
| 9   | Monochlorophenanthrene/monochloroanthracene | 1.145                   | 1-Chloroanthracene                     | 1.1471      | 214, 212, 176 |
| 10  | 9-Chlorophenanthrene <sup>b,c</sup>         | 1.152                   | 9-Chlorophenanthrene <sup>b,c</sup>    | 1.1527      | 214, 212, 176 |
| 11  | Monochlorophenanthrene/monochloroanthracene | 1.157                   | 1-Chlorophenanthrene                   | 1.1539      | 214, 212, 176 |
| 12  | 9-Chloroanthracene <sup>b,c</sup>           | 1.163                   | 9-Chloroanthracene <sup>b,c</sup>      | 1.1689      | 214, 212, 176 |
| 13  | Dichlorophenanthrene/dichloroanthracene     | 1.286                   | 9,10-Dichloroanthracene                | 1.2813      | 248, 246, 176 |
| 14  | 9,10-Dichlorophenanthrene <sup>c</sup>      | 1.293                   | 9,10-Dichlorophenanthrene <sup>c</sup> | 1.2922      | 248, 246, 176 |
| 15  | 3-Chlorofluoranthene <sup>c</sup>           | 1.329                   | 3-Chlorofluoranthene <sup>c</sup>      | 1.3117      | 238, 236, 200 |
| 16  | Monochloropyrene                            | 1.337                   | 2-Chloropyrene                         | 1.3124      | 238, 236, 200 |
| 17  | Monochloropyrene                            | 1.349                   | 1-Chloropyrene                         | 1.3595      | 238, 236, 200 |
| 18  | Monochloropyrene                            | 1.373                   | 4-Chloropyrene                         | 1.3977      | 238, 236, 200 |

<sup>a</sup> Relative retention time calculated against phenanthrene.

<sup>b</sup> Comparison with authentic standard.

<sup>c</sup> Comparison with reference retention data (Shiraishi et al., 1985).

Table 3  
 Types and yields of Cl-PAHs in the emissions from PVC combustion at the temperature range of 600–900 °C

| Compounds                 | Yields (µg/g PVC) |        |        |        |
|---------------------------|-------------------|--------|--------|--------|
|                           | 600 °C            | 700 °C | 800 °C | 900 °C |
| 2-Chloronaphthalene       | 1.76              | 3.90   | 10.71  | 11.50  |
| 1-Chloronaphthalene       | 2.68              | 7.56   | 22.86  | 29.08  |
| 4-Chlorobiphenyl          | 0.59              | 0.99   | 1.36   | 1.32   |
| 3-Chlorobiphenyl          | 1.19              | 2.48   | 4.06   | 3.86   |
| 1-Chlorobiphenyl          | 1.02              | 0.22   | 3.47   | 3.38   |
| 1-Chlorofluorene          | nd                | 0.27   | 0.41   | 0.50   |
| 2-Chlorofluorene          | 0.73              | 0.70   | 0.74   | 0.96   |
| 2-Chloroanthracene        | 0.074             | 0.47   | 0.14   | 0.062  |
| 1-Chloroanthracene        | 0.78              | 2.92   | 4.39   | 5.83   |
| 9-Chlorophenanthrene      | 1.55              | 6.63   | 9.64   | 14.01  |
| 1-Chlorophenanthrene      | 1.39              | 7.06   | 11.90  | 16.68  |
| 9-Chloroanthracene        | 0.36              | 1.18   | 0.70   | 1.80   |
| 9,10-Dichloroanthracene   | nd                | nd     | 0.49   | 0.36   |
| 9,10-Dichlorophenanthrene | nd                | nd     | 0.68   | 0.43   |
| 3-Chlorofluoranthene      | 0.30              | 1.03   | 0.96   | 1.25   |
| 2-Chloropyrene            | 0.41              | 2.03   | 1.98   | 2.91   |
| 1-Chloropyrene            | nd                | 1.39   | 1.14   | 1.40   |
| 4-Chloropyrene            | 0.75              | 3.66   | 4.49   | 6.62   |
| Total                     | 13.58             | 42.49  | 80.12  | 101.95 |

“nd” refers to lower than detection limit.

of PVC by other researchers. Hawley-Fedder et al. (1984) found that under simulated incinerator condi-

tions, the total amounts of PAHs produced from PVC combustion are greatest at 950 °C within the furnace

temperature range of 800–950 °C. This suggested that polychlorinated PAHs and their parent PAHs are easily formed at higher furnace temperature, i.e. 800 and 900 °C. The possible reasons are as follows: These compounds contain aromatic rings which are stable at higher temperatures, and more favored cyclisation reaction can occur by different gaseous hydrocarbons intermediates released from incomplete combustion of PVC. Thus increasing furnace temperature can enhance these PAHs formation. Cl-PAHs detected in these tests are mainly derivatives of naphthalene, phenanthrene, anthracene, biphenyl, fluorene and pyrene. These chlorinated derivatives might be formed mainly by chlorination reaction of the PAHs with chlorine released from PVC combustion, because direct scission of PVC chains to form chlorine-containing compounds is a very minor decomposition pathway (Lattimer and Kroenke, 1980).

Furnace temperature, airflow, the burning time and the combustion duration have an effect on the levels of Cl-PAHs in the emissions from PVC combustion. During combustion under high temperature, HCl is first released from PVC, and then PAHs are produced in the cooler zone of the furnace by cyclisation reaction of gaseous hydrocarbon fragments formed by incomplete combustion. But the PVC burning with a flame, which can be observed, started approximately at 4 s (900 °C) and 45 s (600 °C) after the boat containing PVC plastics was positioned in the oven. Due to this delay of PVC burning with decreasing furnace temperature, most of HCl may leave along with the airflow, and a temperature dependent equilibrium between HCl and Cl<sub>2</sub>:  $2\text{HCl (g)} + 1/2 \text{O}_2 \xrightarrow{\Delta} \text{Cl}_2 \text{(g)} + \text{H}_2\text{O (g)}$  can shift to the reverse reaction, thus reduce the opportunity of PAHs exposure to Cl<sub>2</sub>. So less Cl-PAHs formation was found at lower furnace temperature of 600 °C. On the contrary, with increasing furnace temperature, PAHs released from PVC combustion have increasing chances of exposure to Cl<sub>2</sub>, thus promoting the Cl-PAHs formation.

However, it should be noted that this experimental system was but a simulated incinerator, in which abatement of Cl-PAHs formation cannot be anticipated only by changing the furnace temperature. In fact in a combustion system, complicated factors have an effect on Cl-PAHs formation. Further works on this subject will be performed.

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