

## Dioxin Formation During Combustion of Nonchloride Plastic, Polystyrene and Its Product

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One of the factors influencing the dioxin formation from an incinerator is the presence of chlorides in combustion materials. There are numerous reports on formation of dioxins from chloride plastics, such as polyvinyl chloride, upon combustion (Giugliano et al. 1989; Carroll et al. 2001; Yasuhara et al. 2001; Katami et al. 2002). Also, dioxin formation has been reported from flammable materials mixed with inorganic chlorides, such as NaCl, upon incineration (Yasuhara et al. 2001; Luthe et al. 1998; Katami et al. 2000; Yasuhara et al. 2002; 2003). According to a study using a fluidized-bed furnace, there was a significant correlation between chloride content of combustion materials containing inorganic chlorides or organic chlorides and dioxin formation (Hatanaka et al. 2000). On the other hand, trace amounts of dioxin formation were observed from the combustion of non-chloride plastics (Katami et al. 2002). It has been noted that formation of dioxins from combustion of flammable materials is inevitable because trace amounts of NaCl particles are present in the environmental atmosphere. For example, dioxin formation was observed from a non-chloride plastic, polystyrene, upon combustion (Yasuhara et al. 2002).

## MATERIALS AND METHODS

In order to examine influences of chloride particles in the atmosphere on dioxin formation, polystyrene, which does not contain chlorine, was combusted in a small-scale incinerator under well-controlled conditions and the exhausted gases were subsequently analyzed for dioxins (PCDDs, PCDFs, and coplanar PCBs).

Isotope-labeled PCDDs, PCDFs, and coplanar PCBs (non-ortho-PCBs and mono-PCBs) for internal standards (10 ng/mL n-nonane) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). For the solution of the sampling-spike recovery test, a 1 mL n-nonane solution containing 0.0005 ng/ $\mu$ L each of  $^{13}\text{C}_{12}$ -1,2,3,4-T<sub>4</sub>CDD; 1,2,3,4,7,8-H<sub>6</sub>CDD; and 1,2,3,4,6,7,8-H<sub>7</sub>CDF solution was prepared. For the solution of the clean-up-spike recovery test, a 100  $\mu$ L n-nonane solution containing 0.005 ng/ $\mu$ L each of  $^{13}\text{C}_{12}$ -2,3,7,8-T<sub>4</sub>CDD; 1,2,3,7,8-P<sub>5</sub>CDD; 1,2,3,6,7,8-H<sub>6</sub>CDD; 1,2,3,4,6,7,8-H<sub>7</sub>CDD; 1,2,3,4,6,7,8,9-O<sub>8</sub>CDD;  $^{13}\text{C}_{12}$ -2,3,7,8-T<sub>4</sub>CDF; 1,2,3,7,8-P<sub>5</sub>CDF; 1,2,3,4,7,8-H<sub>6</sub>CDF; 1,2,3,4,7,8,9-H<sub>7</sub>CDF; 1,2,3,4,6,7,8,9-O<sub>8</sub>CDF;  $^{13}\text{C}_{12}$ -3,3',4,4'-T<sub>4</sub>CB; 3,4,4',5-T<sub>4</sub>CB; 3,3',4,4',5-P<sub>5</sub>CB; 2',3,4,4',5-P<sub>5</sub>CB; 3,3',4,4',5,5'-H<sub>6</sub>CB; 2,3',4,4',5,5'-H<sub>6</sub>CB; and 2,3,3',4,4',5,5'-H<sub>7</sub>CB was prepared. For the solution of the internal standards, a 2  $\mu$ L n-nonane solution containing 0.25 ng/ $\mu$ L each of  $^{13}\text{C}_{12}$ -1,3,6,8-T<sub>4</sub>CDD; 1,2,3,7,8,9-H<sub>6</sub>CDD; and 2,2',3,4,4',5,5'-H<sub>7</sub>CB was prepared. n-Nonane was bought from Kanto Chemical Co., Inc. (Tokyo, Japan).

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Two plastic samples for combustion were prepared as follows: Polystyrene foam was cut into 10 cm × 10 cm × 1 cm (thickness) pieces—Sample A (Cl content, 0.025 wt%). A polystyrene plastic cover of an indoor room air-conditioner (manufactured on March, 1984) was cut into small pieces (10 cm × 10 cm) by a scissors—Sample B (Cl content, 0.036 wt%).

Samples A (450 g) and B (1,093 g) were combusted for 2 h and 22 min and 54 min, respectively, in an incinerator used previously (Yasuhara et al. 2002). The incinerator was equipped with two subsidiary combustion burners (Kato Burner Co., Ltd., Gifu, Japan)—one at the upper part of the combustion chamber and the other near the grate—with a heat supply of 30,000 kcal/h. Propane gas (97.6%), containing < 0.0005% of Cl and 0.0008% of sulfur, was used for fuel. The firebricks of the inside walls and the fire clay of the grate were changed for each experiment in order to avoid any contamination from a previous experiment. The two subsidiary burners (one placed at the upper side of the combustion chamber and the other placed at the grate) were turned on one hour prior to combustion of the samples in order to maintain a constant temperature.

Exhaust gases were collected using a method previously reported (Yasuhara et al. 2002; 2003). Gas samples were collected at the sampling port located between the combustion chamber and the cyclone. Sample preparations were conducted using methods previously reported (Katami et al. 2002). Analyses of CO, CO<sub>2</sub>, O<sub>2</sub>, PCDDs, PCDFs, and coplanar PCBs were performed by the same method previously reported (Katami et al. 2002). The chlorine content of combustion samples was measured by a total organic halogen analyzer model TOX-100 (Dia Instruments Co., Ltd., Tokyo, Japan). Combustion chamber and flame temperatures were measured by a LK-1200 thermo-couple conductor interfaced to a CT-1310 digital thermometer (Custom Co., Ltd., Tokyo, Japan).

## RESULTS AND DISCUSSION

The recovery efficiencies of standard dioxins (PCDDs, PCDFs, and co-planar PCBs) were consistent with our previous reports (Katami et al. 2002; Yasuhara et al. 2003). The recoveries of both the sampling spike and the cleanup spikes were satisfactory values of over 73%.

Table 1 shows the conditions of the incinerator during the experiments and the analytical results of exhaust gases.

The average grate temperatures were 951 °C for Sample A and 1076 °C for Sample B during combustion (both subsidiary burners were turned on). The grate temperature for Sample A was somewhat lower than that of Sample B; consequently, combustion was slightly less than complete during combustion of Sample A, and CO concentration was relatively high for Sample A (30.9 ppm).

Table 2 shows the results of dioxin analyses of the exhaust gases obtained from the combustion of plastic samples, along with the toxicity equivalency quantity (TEQ) of each sample (Van den Berg et al. 1998).

PCDFs comprised 58.8% and 86.3% of the total dioxins formed in the exhaust gases from Sample A and Sample B, respectively. The higher the number of Cl atoms, the less PCDFs were produced from Sample B. The same trend was observed from combustion of polystyrene in a previous study (Katami et al. 2002) but not in Sample A. O<sub>8</sub>CDD was found in the greatest amount (0.27 ng/g) among

**Table 1.** Analytical results of exhaust gases and combustion conditions.

Conditions and Concentrations	Combustion samples	
	Polystyrene foam (A)	Plastic cover (B)
Chlorine content (wt %)	0.025	0.036
Combustion amount (kg/h)	0.190	1.20
Grate temperature (°C)		
Range	913–991	1027–1113
Average	951	1076
Chamber temperature (°C)		
Range	648–684	800–896
Average	668	857
Ave. exhaust gas temperature (°C)	513	617
Ave. amt. of dry ext. gas (m <sup>3</sup> N/h)	274	231
Ave. oxygen concentration (%)	15.2	10.8
Ave. CO <sub>2</sub> concentration (%)	4.0	7.1
Ave. CO concentration (ppm) <sup>1</sup>	30.9	7.4
Water content in ext. gas (%)	7.1	10.0

<sup>1</sup>Relative to 12% oxygen concentration

PCDDs from combustion of polystyrene in the present study. The total dioxin formed was 5.19 ng/g from polystyrene (Sample A, grate temperature was 951 °C) and 4.10 ng/g from the plastic cover (Sample B, grate temperature was 1076 °C). The results suggest that the chloride contents of combustion materials do not influence dioxin formation at the levels (less than 1%) used in the present study. The results are consistent with a previous report (Wikström et al. 1996). A high level of dioxin formation (839 ng/g) was reported in exhaust gas collected from a high chlorine content plastic, a polyvinyl chloride sheet (chlorine content, 51.3 wt%), combusted at an average chamber temperature of 633 °C (Katami et al. 2002). On the other hand, a polyethylene sheet with a chloride content less than 0.05 wt% produced only 11.8 ng/g of dioxins when it was combusted at an average chamber temperature of 656°C (Katami et al. 2002). The reason why dioxins formed less in the present study than in a previous experiment (Katami et al. 2002) is that the grate temperature of the present study (951°C) was much higher than that of a previous experiment (749°C).

The toxic equivalent quantity per volume of exhaust gas (ng-TEQ/m<sup>3</sup>N) was less than a 0.34 ng-TEQm<sup>3</sup>N in the combustion chamber (Table 2), which was consistent with the previous report (Katami et al. 2002). An incinerator used for actual combustion of wastes is equipped with dioxin removal devices between the combustion chamber and the chimney. Therefore, 90-95% of dioxins formed are removed by these devices (Nagaŧa, 1992). Consequently, calculated values of TEQ are less than the 0.02 ng-TEQ/m<sup>3</sup>N with these devices in the present study.

The calculated amounts of total chlorine in Sample A and Sample B were 112 mg and 393 mg, respectively. The calculated amounts of chlorine in the total air used to combust Sample A and Sample B were 0.269 mg and 0.086 mg, respectively. The average amount of chlorine in the air was calculated using the value (415 ng/m<sup>3</sup>) previously reported (National Air Surveillance, 1996). The chlorine contents in the combustion samples were approximately 10 times those in the air used for combustion, suggesting that the chlorine in the combustion samples plays

**Table 2.** Analytical results of PCDDs, PCDFs, and coplanar PCBs in exhaust gases from combustion of samples (ng/g).

	Combustion samples	
	Polystyrene form (A)	Plastic cover (B)
T <sub>4</sub> CDDs	0.240	0.078
P <sub>5</sub> CDDs	0.091	0.047
H <sub>6</sub> CDDs	0.082	0.030
H <sub>7</sub> CDDs	0.240	0.020
O <sub>8</sub> CDDs	0.270	0.010
Total PCDDs	0.923	0.185
T <sub>4</sub> CDFs	1.71	2.09
P <sub>5</sub> CDFs	0.591	1.00
H <sub>6</sub> CDFs	0.158	0.362
H <sub>7</sub> CDFs	0.419	0.073
O <sub>8</sub> CDFs	0.171	0.012
Total PCDFs	3.05	3.54
Coplanar PCBs	1.22	0.37
Grand total <sup>1</sup> (ng-TEQ/m <sup>3</sup> N)	5.19	4.10
(ng-TEQ/g)	0.080	0.330
	0.079	0.072

<sup>1</sup>Grand total = total PCDDs + total PCDFs + total coplanar PCBs

an important role in dioxin formation, rather than the chlorine in the air used for combustion. The results obtained in the present study may be used as blank values for the determination of dioxins formed from combustion of materials containing inorganic and/or organic chlorides.

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