

Formation of Dioxins from Sodium Chloride-Impregnated Newspapers by Combustion

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Dioxins, in particular, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), are the most potent man-made carcinogen. Their contamination in the environment has received much attention from the public because they form during the combustion of waste materials as well as from many other high-temperature processes commonly used in industrial settings (Lustenhower and Hutzinger, 1980; Tuppurainen et al., 1998). It is important to determine the formation conditions of dioxins in high-temperature processes in order to reduce their role in environmental contamination. Therefore, intensive efforts have been made to reduce dioxin formation during the above processes.

Many hypotheses about dioxin formation in combustion systems have been advanced, but the chemical reactions involved are extremely complex and heterogeneous (Huang and Buekens, 1995). In particular, the source of chloride has been one of the major concerns in studies of dioxin formation in incinerators. Organic chlorine (tetrachloroethylene) with a catalyst such as iron (III), tin (II), and copper (II) promoted the formation of particle-bound dioxins in combustion experiments. On the other hand, inorganic chlorine (sodium chloride) promoted the formation of dioxins more effectively in the gas phase than in the particle phase (Halonen et al., 1995). It appears that both organic and inorganic chlorides can be a precursor of dioxins in incinerators. However, there are still many unknown mechanisms of dioxins formation in high-temperature processes. More experiments and theoretical studies to elucidate the details of dioxin formation in a combustion is needed.

In the present study, newspaper impregnated with sodium chloride was combusted in an incinerator and the dioxins formed were analyzed by GUMS.

MATERIALS AND METHODS

A newspaper (top circulation in Japan) purchased from a local store was soaked in a 3% sodium chloride solution for 20 min. The newspaper was dried prior to use in the experiment. The percentage of impregnated chlorine was 3.1 (w/w).

Four different samples were combusted in an incinerator diagramed in Figure 1. 1). Blank: Heavy oil A containing < 0.005% (w/w) chloride, 0.25% (w/w) sulfur, and 0.02% nitrogen (w/w) was combusted for 4 h at the rate of 15 L/h. 2). Five kilograms each of newspaper was combusted with heavy oil A (15 L/h) at 25 min intervals for 4 h (total 55 kg). 3). Five kilograms each of sodium chloride

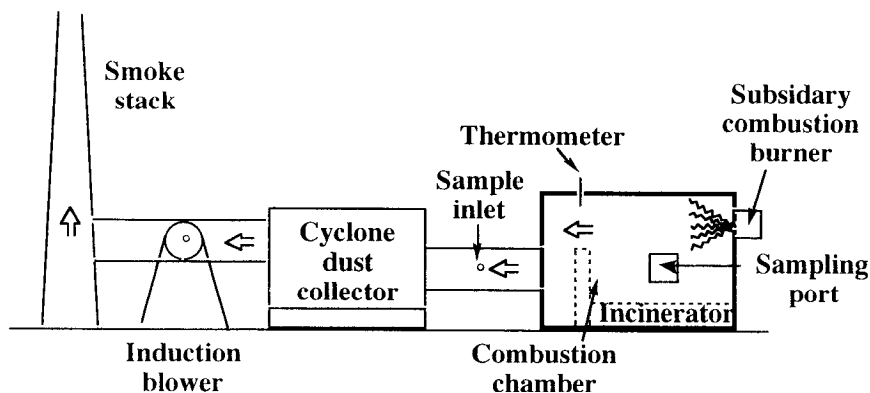


Figure 1. Incinerator used for combustion of newspaper samples.

impregnated-newspaper was cornbusted with heavy oil A (15 L/h) at 25 min intervals for 3 h and 55 min (total 50 kg). 4). Three kilograms each of newspaper was cornbusted with 0.5 kilograms each of polyvinyl chloride (PVC) (40 x 28 cm and 0.2 mm thickness, soft PVC sheet) and heavy oil A (15 L/h) at 25 min intervals for 3 h and 20 min (total 28 kg). Chloride content in the PVC was 35.7% (w/w).

Exhaust gas samples for dioxin analyses were collected at the sampling port located between the combustion chamber and cyclone (Figure 1). The overall sample collection apparatus used is diagramed in Figure 2. Analysis of dioxins in the collected exhaust gas was conducted according to the official method of the Japan Ministry of Health and Welfare (JMHW, 1997).

Dust in the exhaust gas was trapped in an in-line silica-fiber thimble filter. The exhaust gas was next drawn into two 1 L-impingers each containing 150 mL of water (washed with hexane prior to use) and an empty impinger connected in series. The empty impinger was further connected to a column packed with 40 g of XAD-2 resin which was interfaced to a 1 L-impinger containing 250 mL diethylene glycol and an empty impinger connected in series. The impingers were kept at 5 °C during sample collections in an ice-cooled water bath. The exhaust gas was drawn using a diaphragm vacuum pump with the flow rate as same as that of exhaust gas in the duct (21 - 23 L/min).

The dust trapped in the silica-fiber thimble filter (apx., 1 g) was washed with 2 mol/L hydrochloric acid solution (20 mL), and combined with the XAD-2 resin. The resin was extracted with toluene (200 mL) using a Soxhlet extractor for 16 h. The water (500 mL) and diethylene glycol (250 mL) in the impingers, as well as the water trapped (trace) in the empty impingers, were combined and extracted with toluene (500 mL). After extraction, each extract was condensed by distillation using a rotary flash evaporator, and the combined samples were cleaned with multilayer silicagel chromatography (JMHW, 1997). The sample was further cleaned using alumina column chromatography with a 120 mL hexane/dichloromethane (1/1) solution. The internal standards (0.5 ng each), $^{13}\text{C}_{12}$ -2,3,7,8- T_4CDD , 1,2,3,7,8- P_5CDD , 1,2,3,6,7- H_6CDD , 1,2,3,4,6,7,8- H_7CDD , 1,2,3,4,6,7,8,9- O_8CDD , $^{13}\text{C}_{12}$ -2,3,7,8- T_4CDF , 1,2,3,7,8- P_5CDF , 1,2,3,4,7,8- H_6CDF , 1,2,3,4,6,7,8- H_7CDF , and 1,2,3,4,6,7,8,9- O_8CDF were used to spike the sample.

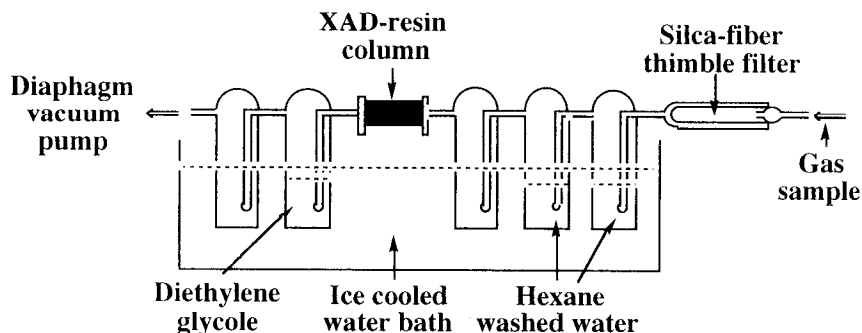


Figure 2. Apparatus used for collection of exhaust gas from combustion of newspaper samples.

After each sample was condensed using a rotary flash evaporator, the condensed sample was dissolved into a minimum amount of *n*-nonane and then the volume of the sample was adjusted to exactly 50 mL with *n*-nonane. The samples were analyzed by gas chromatography/mass spectrometry (GC/MS) for dioxins.

A Hewlett-Packard (HP) model 5890 gas chromatograph (GC) interfaced to Micromass double focus MS (Auto Spec ULTIMA, England) and equipped with a 60 m x 0.25 mm i.d. ($d_i = 0.2 \mu\text{m}$) SP-2331 bonded-phase fused-silica capillary column (Supelco, Bellefonte, PA) for $\text{Cl}_{4,6}$ dioxines or a 30 m x 0.25 mm i.d. ($d_i = 0.25 \mu\text{m}$) DB-5 bonded-phase fused-silica capillary column (J & W Scientific, Folsom, CA) for Cl_1 , dioxins was used. Gas chromatographic oven temperatures were programmed from 130°C to 190°C at 20°C/min and then to 250°C at 2 °C/min for the SP-2331 column, and programmed from 130°C to 280°C at 10°C/min for the DB-5 column. The linear velocity of helium carrier gas was 30 cm/set. The injector temperatures were 250°C for the SP 2331 column and 280°C for the DB-5 column. MS ion source temperatures were 250°C for the SP-2331 column and 289°C for the DB-5 column. MS ionization voltage was 35 eV.

RESULTS AND DISCUSSION

Because a subsidiary combustion burner (Figure 1) was used, the temperature of the combustion chamber was kept above 350°C during the combustion. The average temperatures in the combustion chamber during combustion of the four samples ranged from 460 to 650°C. The recovery efficiencies of spiked standard dioxins were 91% for $^{13}\text{C}_{12}$ -2,3,7,8- T_4CDD , 94% for 1,2,3,7,8- P_5CDD , 103% for 1,2,3,6,7,8- H_6CDD , 82% for 1,2,3,4,6,7,8- H_7CDD , 99% for 1,2,3,4,6,7,8,9- O_8CDD , 80% for $^{13}\text{C}_{12}$ -2,3,7,8- T_4CDF , 97% for 1,2,3,7,8- P_5CDF , 110% for 1,2,3,4,7,8- H_6CDF , 79% for 1,2,3,4,6,7,8- H_7CDF , and 76% for 1,2,3,4,6,7,8,9- O_8CDF in the present study. Values are the average of two experiments.

Table 1 shows the results of analysis of the exhaust gas samples. The amount of dioxins formed according to the number of chlorides in isomers was $\text{Cl}_3 > \text{Cl}_4 > \text{Cl}_6 > \text{Cl}_7 > \text{Cl}_8$. In the case of benzofurans, the higher the number of chloride, the less production of dioxin was observed. The calculated contents of chloride in the samples were less than 0.005% for heavy oil A, 0.0064% for the blank

newspaper. 3.1% for NaCl-impregnated newspaper, and 5.1% for newspaper with PVC. It is obvious that the samples with a higher chloride content produced more dioxins.

Table 1. Results of dioxin analysis in combusted newspaper samples.

Dioxins	Amount of dioxins (ng/g)			
	Heavy oil A	Newspaper	Newspaper with NaCl	Newspaper with PVC
PCDDs				
T ₄ CDDs	0.015	0.037	6.5	8.8
P ₅ CDDs	0.017	0.035	7.5	11
H ₆ CDDs	0.012	0.035	5.9	6.4
H ₇ CDDs	0.020	0.025	3.9	3.1
O ₈ CDD	0.021	0.017	1.4	0.7
Total	0.085	0.149	25.2	30.0
PCDFs				
T ₄ CDFs	0.47	0.53	34	42
P ₅ CDFs	0.13	0.15	23	37
H ₆ CDFs	0.044	0.055	15	26
H ₇ CDFs	0.016	0.030	5.0	9.1
O ₈ CDF	-	0.007	1.1	1.7
Total	0.66	0.772	78.1	115.8
Grand total of dioxins	0.75	0.92	100	150

Samples with inorganic chloride (NaCl) or with organic chloride (PVC) produced significantly higher amounts of dioxins as compared with the blank newspaper. There have been different reports on the promotion of dioxin formation by PVC. In fires in public and industrial buildings where PVC materials were involved, significantly higher levels of dioxins were found (Theisen et al., 1989; Marklund et al., 1989). On the other hand, some investigators have reported that no appreciable amounts of dioxins were formed from combustion of materials with PVC (Karasec et al., 1983; De Fre, 1986). When PVC and PVC-cable sheathings were combusted, ppm levels of dioxins were formed (Christmann et al., 1989). However, addition of PVC to urban wastes up to 10% did not produce detectable concentrations of dioxins upon combustion (Giugliano et al., 1989).

There have been only a few reports on the possible formation of dioxins from a reaction of inorganic chloride such as sodium chloride with waste materials during combustion. Some feed material generated dioxins when they were combusted with sodium chloride in a pilot scale incinerator (Pandompam et al., 1995). In the present study, both organic and inorganic chloride was shown to be a source of chloride for dioxin formation. It is hypothesized that HCl is formed at first by high temperature from sodium chloride or PVC and

subsequently dioxins are produced (Takasuga et al., 1998). However, details of the actual formation mechanisms are not yet well understood. Further investigation of the formation mechanisms of dioxins from waste materials upon combustion are in order to discover ways to reduce their formation in incinerators.

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