Formation of Dioxin Analogues on Combustion Process with Unregulated Small Incinerator

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (Co-PCBs) are wide spread persistent contaminants, which are released into the environment from various processes. Especially, generation of these compounds in combustion processes of waste materials have been frequently studied. These compounds have extremely high toxicity, and expressed in various toxicities like carcinogenicity, reproductive toxicity, immunotoxicity and endocrine disruption. Recently, much importance has been attached to the problem of environmental pollution by PCDDs, PCDFs and Co-PCBs emitted from municipal solid waste and industrial incinerators in Japan. In 1975, the incineration amount of municipal solid waste (MSW) was 385,000 tons, equivalent to 76% of the whole MSW.

In this year, Ministry of Health Welfare established a law for controlling emission of dioxin analogues from MSW and industrial waste incineration facility with a combustion capacity of more than 50 kg/hr. However, smaller waste incinerators were not regulated until today. In addition, there are very few reports on dioxin analogues from those small incinerators. Therefore, in this study, we investigated the formation of dioxin analogues through combustion of various materials using unregulated small incinerator.

Material and Methods

As shown in Table 1, eight kinds of materials (paper, dead leaf, natural wood, plastics of nonchloric or chloric and metal) were prepared for this combustion study.

Each material was constantly threw into a small incineration with a combustion capacity of 50 kg/hr. The combustion temperature was kept 500 to 600 °C and the temperature of exhaust gas in the duct was ca. 400 °C

Figure 1 illustrates a sampling method for dioxin analogues in flue gas. Flue gas was sampled according to a modified method of JIS Z 8808 (Japanese Industrial Standard)[1]. The collected samples composed of three parts of a glass fiber filter diethylene glycol or water and XAD-2 resin. After dryness, a mixture of glass fiber filter and XAD-2 resin was extracted with 100 ml of toluene for 5 hrs. under reflux. Liquid samples were mixed and then extracted with toluene by a liquid-liquid partitioning. Each extract was concentrated, combined, and adjusted to a volume of 10 ml with n-hexane.

Table 1 Lists of combustion material for an unregulated small incinerator

Sample No.	Content of combustion material (%)	Weight
Single material		
1	Copy paper (100)	4 kg
2	Dead leaf (100)	8 kg
3	Natural wood (100)	3 kg
4	Building materials (100)	3 kg
Mix material		
5	Papers {Magazine (40), Paper dust (22.5), Newspaper (22.5) Handbills (20), Corrugated cardboard (7.5)}	4 kg
6	Papers (87.5), Fiber (3.7), Non chloric plastics (8.8)	4 kg
7	Papers (87.5), Fiber (3.7), Non chloric plastics (7.3), Chloric plastics (1.5)	4 kg
8	Papers (83), Fiber (3.5), Non chloric plastics (7.0), Chloric plastics (1.4) Electric wire (5.0)	4 kg

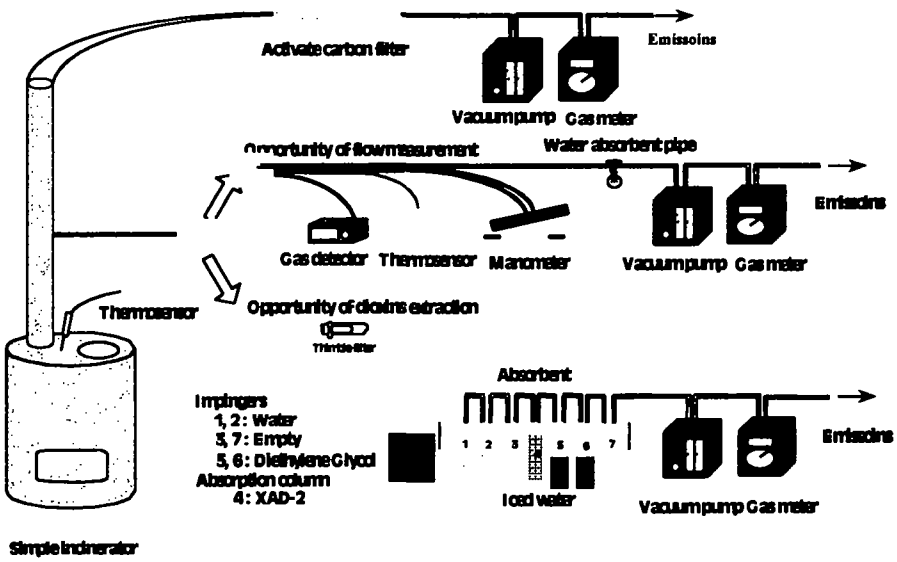

Fig. 1 Diagram of sampling method for dioxin analogues in flue gas according to a modified method of JIS Z 8808

After spiking of internal standards (seven $^{13}C_{12}$-PCDDs and ten $^{13}C_{12}$-PCDFs, each 300 pg; twelve $^{13}C_{12}$-Co-PCBs, each 300 pg), the adjusted extract was cleaned up on a multi-layer silica gel column containing of Na_2SO_4 (2.0 g), 10%(w/w) $AgNO_3$-silica (8.0 g), silica (0.8 g), 22%(w/w) H_2SO_4-silica (4.0 g), 44%(w/w) H_2SO_4-silica (4.0 g), silica (0.8 g), 2%(w/w) KOH-silica (3.0 g) and silica (0.8 g), with an eluent of n-hexane (210 ml). The eluate was concentrated and cleaned up on a neutral alumina column according to our previous method[2]. The purified extract was dissolved in 30 ł of n-decane and analyzed for PCDDs, PCDFs and Co-PCBs on EI-SIM mode at a resolution of 10000 using a Hewlett Packard 6890 gas chromatograph-JEOL 700M mass spectrometer according our report[2].

Result and discussion

Table 2 shows concentrations of dioxin analogues in flue gas collected from our small incinerator. The total Actual concentrations of dioxin analogues from copy paper (No. 1) and dead leaf (No. 2) were 116 and 42.4 ng/m^{3}N, respectively. Natural wood (No. 3) such as cedar and building materials (No. 4) gave a low level of 59.7 and 24.1 ng/m^{3}N, respectively. The TEQ concentrations of these four materials were in the range of 0.400 to 1.97 ngTEQ/m^{3}N.

Combustion of a mixture of paper materials (No. 5) such as magazine, paper dust, newspaper, handbills and corrugate showed a similar level (2.43 pgTEQ/m^{3}N) to that of copy paper (1.97 pgTEQ/m^{3}N).

On the other hand, a mixture of combustions of chloric plastic (No. 7) and electric wire (No. 8) gave a remarkably high concentration. From these results, it is clear that generation of dioxin analogues increased by a mixture of combustion with chloric plastic. Moreover, it was also revealed that the co-presence of cupper such as electric wire proceeded the formation more than 8 times greater (See sample No. 7 and No. 8). These results were well coincident with our previous data, which was obtained from the incineration of wood materials including paint, plastics concerning Hanshin Great Earthquake.

Figure 2 illustrates congener ratios of PCDDs, PCDFs and Co-PCBs. With regards to PCDDs, combustions of copy paper, papers such as magazine etc. and a mixture of papers andnonchloric plastics (Sample Nos. 1, 5 and 6) produced tetrachlorinated congener as a major occupation of about 40 to 50% in total PCDDs. However, higher chlorinated congeners such as hexa to octachlorinated ones were majors in the combustion of dead leaf (No. 2) and natural wood (No. 3). As for PCDFs, tetrachlorinated congener was produced as a major with the congener ratio of 67.8 ~ 87.4% in the combustion of copy paper, building material (No. 4), a mixture of paper, a mixture of paper, fiber and non chloric plastic (No. 6), and a mixture of papers, fiber, non-chloric plastic and chloric plastics (No. 7). However, the co-presence of Cu (No. 8) gave a noticeably different profile with majors of hexa- and heptachlorinated congeners. In addition, the co-presence of Cu changed also the profile of Co-PCBs, that is, it let to produce a decrease of tetrachlorinated congener and an increase of pentachlorinated one.

Table 2 Amounts of PCDDs, PCDFs and Co-PCBs from combustion of various materials in flue gas

Sample No. concn.*	Actual concn.* (ng/m^{3}N)				TEQ
	PCDDs	PCDFs	Co-PCBs	Total dioxins	(ngTEQ/m^{3}N)
1	7.34	86.8	21.6	116	1.97
2	5.21	35.6	1.64	42.4	0.573
3	16.8	40.9	2.09	59.7	1.07
4	7.30	16.0	0.841	24.1	0.400
5	10.5	120	4.69	135	2.43
6	4.20	68.9	4.62	77.7	1.12
7	396	2700	171	3270	67.0
8	6940	6070	121	13100	571

*concn. : concentration

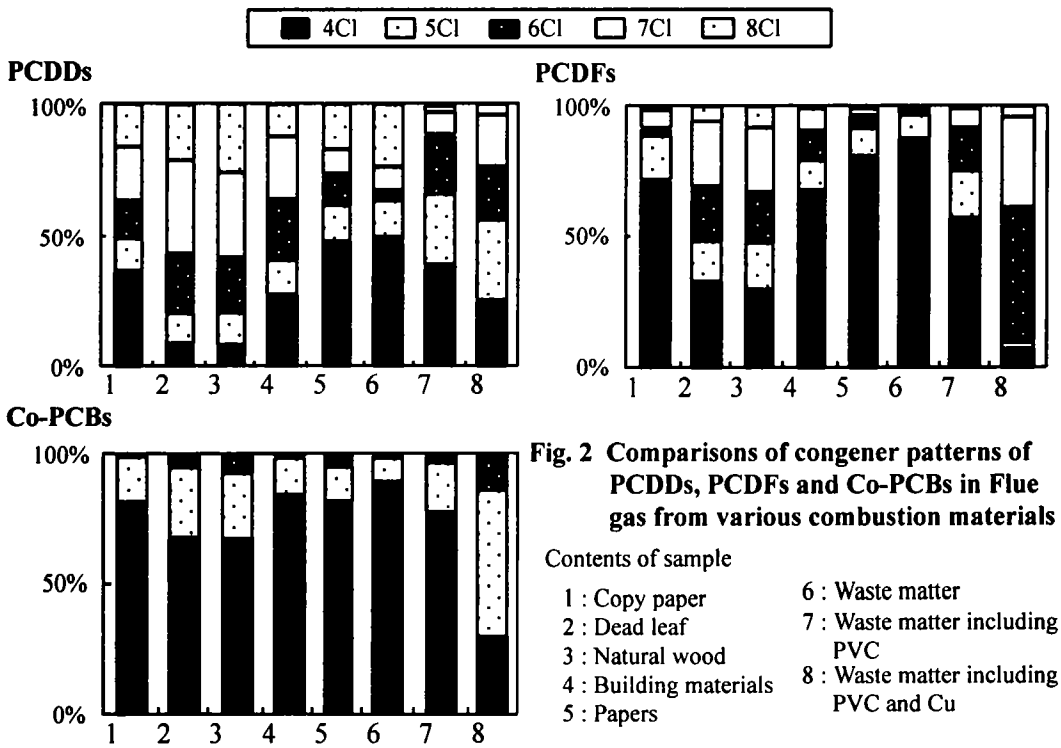

Fig. 2 Comparisons of congener patterns of PCDDs, PCDFs and Co-PCBs in Flue gas from various combustion materials

Contents of sample

1 : Copy paper
2 : Dead leaf
3 : Natural wood
4 : Building materials
5 : Papers
6 : Waste matter
7 : Waste matter including PVC
8 : Waste matter including PVC and Cu

From all results, it was revealed that the formation of dioxin analogues was produced by the co-presence of chloric plastics or catalytic activity of Cu in an unregulated small incinerator.

References

1) JAPANESE INDUSTRIAL STANDARD, JIS Z 8808, **1995**
2) T. Nakao, O. Aozasa, S. Ohta, H. Miyata, Organohalogen Compounds, **1998**, 39, 347-350.