

A COMPARISON STUDY ON SAMPLING DEVICE ANALYZED FOR PCDD/Fs AND CO-PCBs DURING PVC COMBUSTION USING LABORATORY SCALE INCINERATOR

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Introduction

In order to form chlorinated compounds during combustion, a chlorine source or chloride is necessary in the fuel. A chlorinated polymer such as polyvinyl chloride(PVC) release their chlorine as HCl, and may be a major source of chlorine during combustion. Recently, a number of studies are in progress about the relationship between combustion of PVC and chlorinated compounds like PCDD/Fs, PCBs or PAHs.

In that studies, most investigators have looked at very small sample size, varying from 0.002 to 2g for laboratory scale experiments and used simple sampling device. For example, M.wirts et al. used Polyurethane filter and toluene for PCDD/Fs sampling and Akio Yasuhara et al. chose only a couple of impinger with hexane.

Commonly used sampling device in laboratory scale experiments are; 1)a Filter using glasswool and followed by an adsorbent like XAD resin or PUR, 2)a filter and a adsobent and back-up solvent like toluene or hexane, 3)more complicated combinational device (filter+adsorbent+water+diethyleneglycol etc.).

In this study, some kinds of sampling device for PCDD/Fs and co-PCBs sampling is compared during PVC combustion using laboratory scale incinerator.

Methods and Materials

Combustion Experiments

PVC applied was free of additives and used as powders from Aldrich. The combustion apparatus was downstream vertical type for simplicity of sample insertion and induction of turbulence. It consisted of a quartz tube of 40 mm I.D. in a 25 cm tubular furnace. A platinum sample vessel containing the powdered PVC 0.5 g was positioned in the furnace. A high purity air(>99.99 %) was applied at a flow of 5 L/min. Temperature was adjusted to 900 °C at the vessel position and combustion experiments lasted 1hour. Thermal decomposition of PVC occurred immediately after insertion and flue gas was passed through sampling device. The concentrations of oxygen, carbon monoxide and nitrogen oxides were measured continuously.

Sampling Device

Two types of sampling device were investigated. One is a silica glass microfibre filter followed by XAD-II resin and backup solvent (Toluene 50 ml) and silicagel [Fig.2(a)], the other is filter, water 100 ml, empty, XAD-II resin, diethyleneglycol 50 ml, empty, Toluene 50ml for backup and silica gel [Fig.2(b)]. Sampling device I was separated solid (filter+XAD resin) part and Toluene and sampling device II was separated into 3 parts (filter+XAD resin, water+DEG, toluene).

Each part was pretreated and analyzed for PCDD/Fs and co-PCBs, respectively.

ANALYSIS I

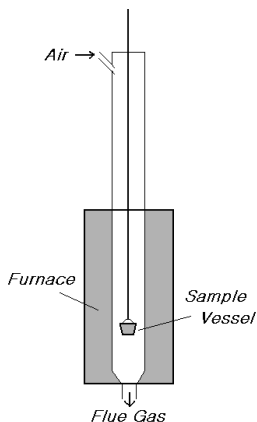
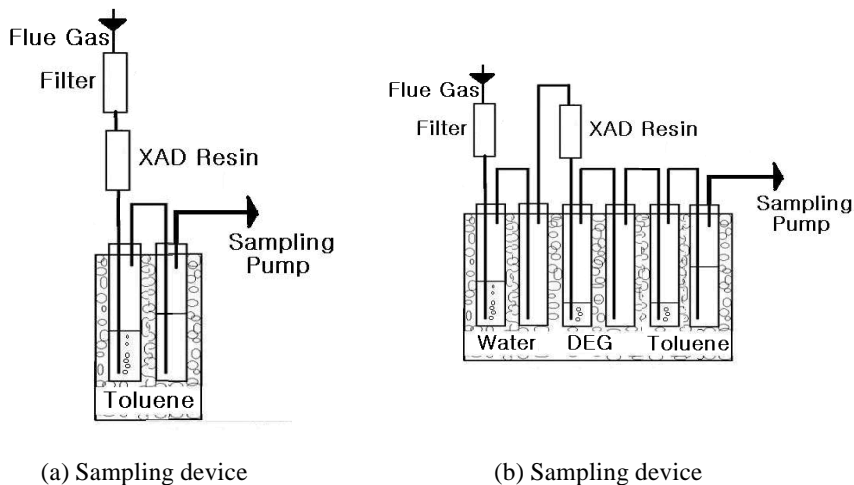


Figure 1. Combustion apparatus



(a) Sampling device

(b) Sampling device

Figure 2. Sampling device for PVC combustion experiment

Analysis

Sample extraction and clean-up were carried out in accordance with Korean Standard Method except for activated carbon clean-up. Filter and adsorbent (XAD-II resin) were soxhlet extracted with toluene for 24 hours. Before sulfuric acid treatment, 1ng of co-PCBs and PCDD/Fs ^{13}C -Labelled compounds was added to each sample. The sample clean-up procedures were composed of sulfuric acid treatment and a mixed column with differently treated multi-layered silica.

After silica column, the sample was introduced into activated carbon column. At the column, the sample was separated into two parts with elution order. 25 % methylene chloride in hexane solution was used for co-PCBs analysis and toluene used for PCDD/Fs analysis. The analysis was performed on selected ion monitoring mode with a JEOL JMS-700 high resolution mass spectrometer connected with high resolution gas chromatograph.

Results and Discussion

Some kinds of sampling device for PCDD/Fs and PCBs sampling is compared during PVC combustion using laboratory scale incinerator. The PCDD/Fs and co-PCBs concentration of each sample with units of ng/g are shown in Table 1.

Table 1. The concentrations of PCDD/Fs & co-PCBs

Sample series	PCDD/Fs concentration				co-PCBs concentration			
	ng/g	%	ng-TEQ/g	%	ng/g	%	ng-TEQ/g (WHO, 1993)	%
I-Solid-1	41.824	99.6	3.532	99.6	32.145	98.6	0.361	97.9
I-Tol-1	0.180	0.4	0.016	0.4	0.449	1.4	0.008	2.1
I-1*	42.004	100	3.548	100	32.594	100	0.368	100
I-Solid-2	212.242	96.7	8.633	98.5	23.900	97.8	0.320	97.9
I-Tol-2	7.243	3.3	0.132	1.5	0.530	2.2	0.007	2.1
I-2	219.485	100	8.765	100	24.430	100	0.327	100
II-Solid-1	147.914	94.1	5.830	92.1	12.966	82.3	0.178	85.2
II-Liquid-1	8.102	5.2	0.448	7.1	2.155	13.6	0.026	12.5
II-Tol-1	1.126	0.7	0.053	0.8	0.641	4.1	0.005	2.3
II-1	157.142	100	6.331	100	15.762	100	0.209	100
II-Solid-2	160.697	93.7	7.315	91.1	16.986	80.6	0.237	81.7
II-Liquid-2	10.445	6.1	0.689	8.6	3.383	16.0	0.042	14.6
II-Tol-2	0.341	0.2	0.027	0.3	0.717	3.4	0.011	3.7
II-2	171.484	100	8.031	100	21.086	100	0.290	100

* when I-1 was sampled, the suction of flue gas was not good because of the rapid pump pressure drop. So, the concentration of I-1 has discrepancy in some degree compared to the other samples.

The isomer pattern of PVC combustion samples was similar to it of municipal solid waste combustion sample and the concentration of PCDD/Fs versus it of co-PCBs showed positive correlation.

Using sampling device I, PCDD/Fs and co-PCBs concentrations in solid(Filter+XAD resin) part were over 96 % of whole concentration and the breakthrough of PCDD/Fs and co-PCBs concentration was below 4 %. Although this pattern is almost same in the sampling device II, the PCDD/Fs ratio of liquid parts(water+DEG) was 5.2~6.1 % but co-PCBs ratio of it was 13.6~16.0 %.

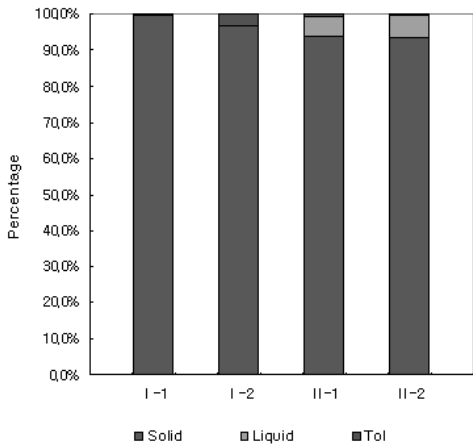
Therefore, simple sampling device like filter + XAD resin (if necessary, using toluene for backup) is sufficient for laboratory scale combustion experiments.

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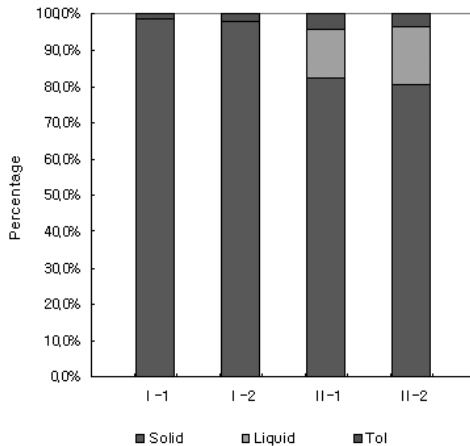
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ANALYSIS I

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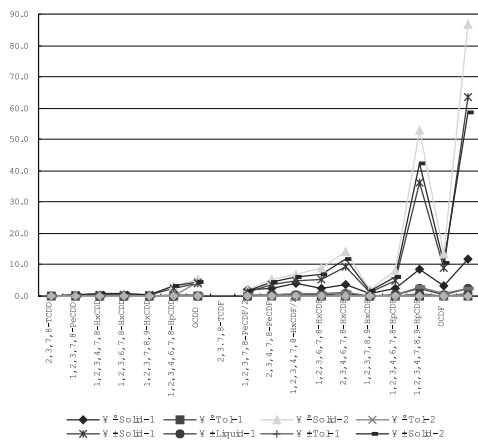


(a) PCDD/Fs

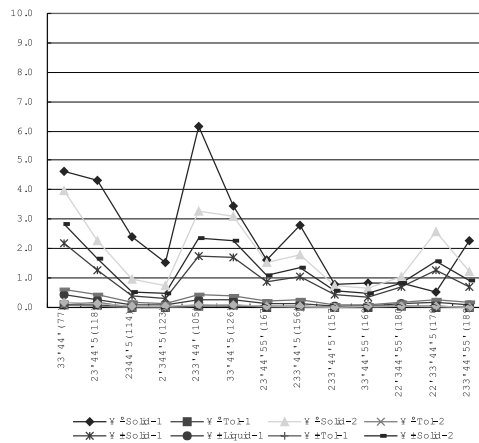


(b) co-PCBs

Figure 3. Ratio of PCDD/Fs & co-PCBs during PVC Combustion



(a) PCDD/Fs



(b) co-PCBs

Figure 4. Isomer Pattern of PCDD/Fs & co-PCBs during PVC Combustion