INVESTIGATION OF PCDD/DF, PXDD/DF, PBDD/DF AND NITRO-PAH DETECTED ON FLUE GAS FROM WASTE INCINERATOR

Teruyuki Nakao, Souichi Ohta, Osamu Aozasa and Hideaki Miyata

Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagaotoge-cho, Hirakata, Osaka, 573-0101, Japan

Introduction

In recent year, polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar PCBs (Co-PCBs) are researched on the various environmental fields, and real situation of environmental pollution by PCDDs, PCDFs and Co-PCBs have begun to be made clear. These days, Noren reported that polybrominated diphenyl ethers (PBDEs) were detected on high levels in human milk in Sewden[1)]. With this report, we were interested in brominated flame retardants (BFRs) such as PBDEs, polybromobiphenyls (PBBs) and tetrabromobisphenol-A (TBBPA). There is the problem of polybrominated dibenzo-*p*-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) generation as by-products in combustion process of BFRs. In addition, we expected the generation of mixed bromine/chlorine-substituted dibenzo-*p*-dioxins (PXDDs) and dibezofurans (PXDFs). Mason and Safe reported that the toxicity of PBDDs/DFs and PXDDs/DFs was examined, these molecules were extremely highly toxic[2, 3)]. Especially, it was cleared that 2-Br-3,7,8-Cl-DD and 2,3-Br-7,8-Cl-DD were 1.6 and 8.2 times higher than 2,3,7,8-TCDD with AHH induction potency in wister rat. On the other hand, we reported with nitrated polyaromatic hydrocarbons (NitroPAHs) which are strongly mutagenic in the Salmonella test and some of them are carcinogenic in the long-term test on animals, last year. NitroPAHs were released to high level from waste incinerator with low temperature burning. However, there is a little information that these compounds were researched on the environmental levels in Japan. There is the importance problem the real situation of environmental pollution by the toxic halogenated compounds are made clear. Therefore, the aim of this study was to establish and investigate to PBDDs/DFs, PXDDs/DFs and NitroPAHs.

Material and Methods

With regard to purification, mixed reference standard including Co-PCBs, PCDDs/DFs, PBDDs/DFs, PXDDs/DFs and PBDEs were prepared for development of purification method. The purified method was multi-layer silica gel (ML) column chromatography containing of Na_2SO_4 (1.0 g), 10 %(w/w) $AgNO_3$-silica (3.0 g), silica (0.6 g), 22 %(w/w) H_2SO_4-silica (3.0 g), 44 %(w/w) H_2SO_4-silica (3.0 g), silica (0.6 g), 2 %(w/w) KOH-silica (3.0 g) and silica (0.6 g), with an eluent of n-hexane and CH_2Cl_2:n-hexane (1:4). Moreover, above standards were chromatographed on active carbon-blended silica gel (AC) column with an eluent of n-hexane, CH_2Cl_2:n-hexane (1:3) and toluene.

Flue gas samples (No.1 – 6 as shown in Table 1) were sampled according to the JIS Z 8808. The burning contents were municipal solid waste (No. 1, 2), industrial waste (No. 3, 4) and sewage sludge (No. 5, 6), respectively. Each sample was extracted based on the JIS K 0311 and JIS K 0312. An aliquot of extract was spiked with 6 ^{13}C-labelled isomers (2,3,7,8-TBDD/F, 1,2,3,7,8-PeBDD, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8- HxBDD and 1,2,3,4,7,8- HxBDF) with recovery standards for PBDDs/DFs analysis. The solution was cleaned up on ML column into two fractions by successive elution with 140 ml of hexane and 140 ml of CH_2Cl_2:n-hexane (1:4). The second fraction was concentrated and then purified with AC column with an eluent of n-hexane (50 ml) and toluene (250 ml). The toluene fraction was concentrated, and then analyzed on a SGE BPX-5 capillary column (15 m * 0.25 mm, 0.25 µm) on EI-SIM mode at a resolution of 5,000 and/or 10,000 using a Hewlett Packard 6890 gas chromatograph - JEOL 700M mass spectrometer. PXDDs/DFs has been analyzed on same method with PCDDs/DFs and Co-PCBs, and $^{13}C_{12}$-1-Br- 2,3,7,8-Cl-DD was used for recovery standard.

Result and discussion

Purification of PBDEs was performed on ML column eluent with n-hexane and CH_2Cl_2: n-hexane. As a result, it was refined eluent pattern of PBDDs/DFs and PXDDs/DFs from ML and AC column. Figure 1 shows each standards eluation from ML column. In general, PCDDs/DFs were eluted to 1st fraction with n-hexane. Same as PCDDs/DFs, eluation patterns of PXDDs/DFs were observed 1st fraction with n-hexane. However, eluate ratio of 2,3-Br-7,8-Cl-DD was 70 % in 1st fraction, the remain was 30% in 2nd fraction with CH_2Cl_2:n-hexane (1:4). On the other hand, all of PBDDs/DFs were detected in 2nd fraction with CH_2Cl_2:n-hexane (1:4). In AC column (Figure 2), PBDEs were failed to retain on AC column, co-eluted to n-hexane with di-ortho Co-PCBs. Following to n-hexane, mono-ortho Co-PCBs were eluted to 2nd fraction with CH_2Cl_2:n-hexane (1:3). PCDDs/DFs, PBDDs/DFs and PXDDs/DFs were eluted to 3rd fraction with toluene and this AC column was possible to separate PBDEs which were interference on GC-MS measurement. From above-mentioned result, we developed analytical method for PCDDs/DFs, PBDDs/DFs and PXDDs/DFs. We attempted to measure 6 facilities (No.1-6). Table 1 shows concentrations of PXDDs/DFs and PCDDs/DFs detected in 6 facilities. The actual concentrations of PXDDs/DFs isomers were detected on low concentration, ranged between N.D. to 0.15 ng/m^{3}N in No. 1 facility.

The levels of 2-Br-3,7,8-Cl-DD, 2,3-Br-7,8-DD, 1-Br-2,3,7,8-Cl-DD and 3-Br-2,7,8-Cl-DF were 0.040, 0.043, 0.088 and 0.11 ng/^{3}N, respectively. We considered that toxicity of these isomers were equal to HpCDD/DF and OCDD/DF, because these isomers have highly toxic based on AHH and EROD induction potencies in wister rat. PXDDs/DFs were detected in No. 3 and 4 from industrial waste incinerator. It was considered that PXDDs/DFs as well as PCDDs/DFs generated by incomplete combustion of industrial waste including BFRs and so on. Contrary to this, the levels of No. 5 and 6 incinerators combusted sewage sludge were relatively low concentration. Total concentrations of PXDDs/DFs were ranged between N.D. to 17 ng/m^{3}N. Especially, TeXDFs is a remarkably high ratio in the total concentration. For example, the ratios of TeXDFs in No. 1, 3 and 4 were 45, 53 and 46%, respectively.

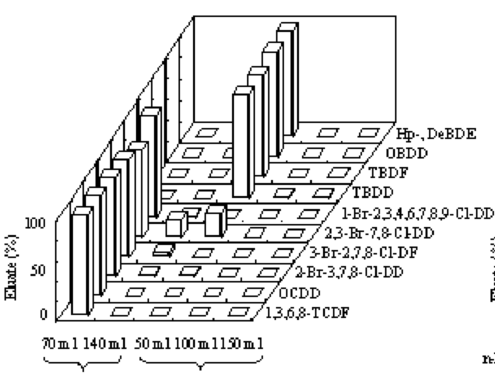

Fig. 1 Fractionation of PCDD/Fs, PXDD/Fs, PBDD/Fs and PBDEs on multi-layer silica gel column

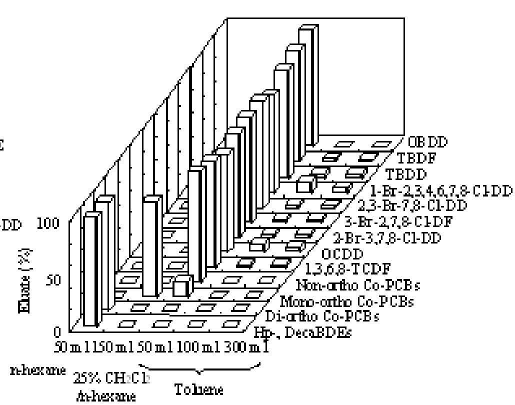

Fig. 2 Fractionation of Co-PCBs, PCDD/Fs, PXDD/Fs, PBDD/Fs and PBDEs on activated-carbon column

Table 2 and 3 shows concentrations of PCDDs/DFs, PXDDs/DFs and PBDDs/DFs, and congener ratio of these compounds of No. 1 facility. The value in parentheses is the composition ratio of each congener calculated from PCDDs/DFs congener concentration. The ratios of monobrominated /polychlorinated congener were ranged between 0.074 to 0.76 %. One of these congeners, five halogens substituted congener was the highest ratio. Secondly, that of dibrominated/dichlorinated congener was 0.71%. We suggested this indicate as to high composition ratio affect to stability such as physical and chemical properties. On the other hand, PBDDs/DFs were measured in No. 1 facility, the trace concentrations of HxBDD, TeBDF and PeBDF were 0.0019, 0.0048 and 0.0070 ng/m^{3}N, respectively. However, it is difficult to high sensitive measurement of PBDDs/DFs, the reason for rapid photolysis and higher molecular. Consequently, we referred to necessary in more detail research for PBDDs/DFs and PXDDs/DFs in the future.

References

1. Noren K. and Meironyte D., Chemosphere, Vol. 40, Nos. 9-11, pp. 1111-1123 (2000)
2. G. Mason, et al., Toxicology, Vol. 44, pp. 245-255 (1987)
3. S. Safe, et al., Toxicology and Industrial Health, Vol. 5, No. 5, pp. 757-775 (1989)

Table 1. Concentrations of PXDDs/DFs from solid waste incinerator

	Concentration (ng/m^{3}N)					
Compounds	No.1	No.2	No.3	No.4	No.5	No.6
2-Br-3,7,8-Cl-DD	0.04	N.D.	0.0086	0.0045	N.D.	N.D.
2,3-Br-7,8-Cl-DD	0.043	N.D.	0.0028	0.0032	N.D.	N.D.
TeXDDs	2.2	N.D.	0.29	0.22	N.D.	N.D.
1-Br-2,3,7,8-Cl-DD	0.088	N.D.	0.014	0.0069	N.D.	N.D.
PeXDDs	2.7	N.D.	0.42	0.24	N.D.	N.D.
2-Br-3,6,7,8,9-Cl-DD	0.0051	N.D.	N.D.	0.0013	N.D.	N.D.
HxXDDs	0.45	0.00015	0.028	0.043	N.D.	0.00030
1-Br-2,3,6,7,8,9-Cl-DD	0.15	N.D.	0.0076	0.0032	0.0009	N.D.
HpXDDs	0.64	N.D.	0.061	0.027	0.0039	N.D.
1-Br-2,3,4,6,7,8,9-Cl-DD	0.14	N.D.	0.016	0.0077	N.D.	N.D.
OcXDDs	0.21	0.022	0.016	0.0077	N.D.	N.D.
Total PXDDs	6.2	0.022	0.82	0.54	0.0039	0.00030
3-Br-2,7,8-Cl-DF	0.11	N.D.	0.016	0.0076	N.D.	N.D.
TeXDFs	7.7	N.D.	1.0	0.64	N.D.	N.D.
1-Br-2,3,7,8-Cl-DF	N.D.	N.D.	0.0070	0.0046	N.D.	N.D.
PeXDFs	2.5	N.D.	0.042	0.18	N.D.	N.D.
HxXDFs	0.14	N.D.	N.D.	N.D.	N.D.	N.D.
HpXDFs	0.39	N.D.	0.021	0.024	0.0020	N.D.
OcXDFs	0.13	N.D.	0.015	N.D.	N.D.	0.0019
Total PXDFs	11	N.D.	1.1	0.84	0.0020	0.0019
Total PXDDs/DFs	17	N.D.	1.9	1.4	0.0059	0.0022
Total PCDDs/DFs	2600	2.0	810	270	0.76	0.15

N.D.: Not Detected
PXDDs/DFs are monobromo/polychloro dibenzo-*p*-dioxins, dibenzofurans and dibromo/dichloro dibenzo-p-dioxins

Table 2. Concentrations (ng/m^3N) of PCDDs, PXDDs and PBDDs in flue gas (No. 1)

Br n	Numbers of halogen (Cl n+Br n)					
	4	5	6	7	8	Total
0	400 (100)	360 (100)	330 (100)	150 (100)	61 (100)	1300 (100)
1	1.6 (0.40)	2.7 (0.75)	0.45 (0.14)	0.64 (0.56)	0.21 (0.34)	5.6 (0.43)
2	0.59 (0.043)	-	-	-	-	0.59 (0.045)
Full	0	0	0.0019 (0.00058)	0	0	0.0019 (0.00015)

( ) : Ratio of each congener calculated from PCDDs congener, - : Not analysis

Table 3. Concentrations (ng/m^3N) of PCDFs, PXDFs and PBDFs in flue gas (No. 1)

Br n	Numbers of halogen (Cl n+Br n)					
	4	5	6	7	8	Total
0	650 (100)	330 (100)	190 (100)	100 (100)	37 (100)	1300 (100)
1	3.1 (0.48)	2.5 (0.76)	0.14 (0.074)	0.39 (0.39)	0.13 (0.35)	6.3 (0.48)
2	4.6 (0.71)	-	-	-	-	4.6 (0.35)
Full	0.0048 (0.00073)	0.0070 (0.0021)	0	0	0	0.012 (0.00092)

( ) : Ratio of each congener calculated from PCDFs congener, - : Not analysis