DETERMINATION OF PCDD/Fs AND DIOXIN-LIKE PCBs IN CHINESE COMMERCIAL PCBs AND EMISSIONS FROM A TESTING PCB INCINERATOR

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ABSTRACT

Large amounts of polychlorinated biphenyls (PCBs) had been produced in China. In order to dispose of them appropriately, a set of experimental PCB incinerators have been manufactured in China. The 2,3,7,8-substituted toxic polychlorinated dibenzodioxins and furans (PCDD/Fs) congeners in stack ash and bottom ash samples from the incinerator and technical products #1PCB and #2PCB (for the reason of comparison) were measured. In addition, the levels of these toxic congeners were converted to 2,3,7,8-TCDD TEQ. Moreover, levels of dioxin-like PCB congeners and 2,3,7,8-TCDD TEQ values in two types of commercial PCBs products and stack ash were determined.

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are synthetic chemicals which are resistant to degradation in nature. Their long-time persistence and high bioaccumulation potential through the food chain resulted in the contamination of PCBs in every component of the global ecosystem. Approximately eight thousand tons of PCBs were produced in China during the 1960's and 1970's. The typical models of Chinese commercial PCBs are #1 PCB (the chlorine content is 42%, which is similar to Aroclor 1242) and #2PCB (the chlorine content is 56%, which is similar to Aroclor 1254).^[1] Most of these PCBs products were used as dielectric fluid in electronic capacitors, and a small part of which were used as additives in paints.

Many electronic capacitors containing PCBs have been considered as solid wastes since the 1980's. According to our investigation, a large number of the capacitors are domestic. There are also some imported capacitors and transformers. The content of PCBs in capacitor soaker fluid exceeds 90%. The concentration of PCBs in some transformer oils attains 50%.^[2] If the temporarily stored wastes containing high concentration of PCBs are released into the environment, it is likely to cause serious contamination, which is harmful to the eco-environment and human health. An experimental incinerator is designed and manufactured to destroy wastes of high PCBs concentration. During the experimental period, emissions from the incinerator were monitored in order to select the optimal operating conditions, resulting in high destruction efficiency and minimum formation of toxic substances.

The total contents of residual PCBs and the concentration of tetra through octa PCB homologues in the emissions from different parts of the incinerator have been determined under different operating conditions. Considering the fact that the toxicity of PCBs congeners is related to the substitution pattern of chlorine atoms, it was found that non-ortho substituted or only one or two chlorine atoms in ortho position show a dioxin-like toxicity. The evaluation of PCBs environmental toxicity depends mostly on the analysis of dioxin-like PCBs. In this paper, the levels of dioxin-like PCB congeners and their 2,3,7,8-TCDD toxic equivalents (TEQ) values in two types of commercial PCBs products and stack ash samples were provided. In addition, the 2,3,7,8-substituted toxic polychlorinated dibenzodioxins and furans (PCDD/Fs) congeners in the technical products #1PCB and #2PCB (for the reason of comparison), stack ash and bottom ash samples have been quantified and reported as 2,3,7,8-TCDD TEQ.

The destruction efficiency of high concentration PCBs in this incinerator can be higher than 99.9999%. With the TEQ value of 217 ng TEQ/g in the technical product #1PCB, the TEQ value of residual dioxins in a stack ash sample and a bottom ash sample are reduced to 47.2 ng TEQ/g and 87.9 pg TEQ/g, respectively. The determination results of dioxin-like PCBs in the stack ash sample from PCBs incinerators showed that the content and toxicity of dioxin-like PCBs diminished 20000 and 50000 times respectively after incineration.

EXPERIMENTAL

1. Information of the incinerator:

Type: The first chamber: fixed bed combustor;

The second chamber: gas purified combustor.

Total volume: 1 m³

Temperature: the first chamber: 700-1100 °C;

the second chamber: 1200-1400 °C.

Feeding: semi-continuous type for solid waste 30-60 kg/h; continuous type for liquid waste: 15 kg/h.

Flue gas treatment: cooling and removing HCl by introducing alkali aqueous solution.

Chimney height: 15 m

The quantity of stack gas: 300-600 Nm³/h, 1200-1300 Nm³/h (after injection and adding gas)

The content of O₂ in flue gas: 5-10% (v/v)

Gas retention time: about 2 seconds

The quantity of emission water: 2.5 tons/h

2. Sampling

(1) Raw material for incineration: Chinese technical PCBs products collected from discarded capacitors manufactured in Xi'an Chemical Factory, China. #1 PCB contains 42% chlorine, which is similar to Aroclor 1242, #2 PCB contains 53% chlorine, which is similar to Aroclor 1254.

(2) Bottom ash was obtained from the chamber of the incinerator.

(3) Stack ash was scraped from the in wall of the incinerator chimney.

(4) Modified gas sampling method 5 of USEPA^[3] were used to collect fly ash and stack gas samples.

(5) Waste water had been used to wash exhaust gas of the incinerator.

3. Extraction and clean up

USEPA Method 1613^[4] was modified to treat the PCBs technical products and stack ash samples from PCBs incinerator before HRGC/HRMS analysis. The stack ash sample was digested with 3 M HCl, followed by Soxhlet extraction with toluene. For the analysis of PCDD/Fs, nine ¹³C-PCDD/Fs standards were used to spike the sample before extraction. The extracted sample solution was applied onto the acid/base silica column and basic alumina column. 3% CH₂Cl₂/hexane solution was used to elute the sample from the acid/base silica column. 2% CH₂Cl₂/ hexane and 50% CH₂Cl₂/ hexane were used to elute the basic alumina column. PCDD/Fs and dioxin-like PCBs were collected in the last fraction of elution (50% CH₂Cl₂/ hexane mixed solvent).

4. Quantification

(1) Total contents of PCBs were determined by GC/ECD and GC/MS, and calculated by Webb method.^[5]

(2) PCB homologue.

A known amount of ¹³C-labeled tri- through deca- chlorobiphenyls surrogates were spiked into the sample, and the sample was extracted and cleaned up by the above methods for HRGC/MS analysis.

(3) PCDD/Fs analysis.

According to the reference method by Environment Canada,^[6] the sample was spiked with a surrogate standard mixture of ^{13}C -labeled PCDD/Fs congeners. The spiked sample was extracted and cleaned up for HRGC/HRMS/SIM analysis. 30 m x 0.32 mm (i.d.) DB-5 capillary column was used. 1 ng ^{13}C -1,2,3,4-TCDD and ^{13}C -1,2,3,7,8,9-HxCDD were added right before HRGC/HRMS analysis to determine internal standard recovery. Seventeen 2,3,7,8-substituted PCDD/PCDF congeners were quantified.

(4) Dioxin-like PCBs.

The same sample pretreatment method was used for the extraction of dioxin-like PCBs congeners. The sample extract was analyzed by HRGC/MS and quantified using the external standard method. Coplanar PCB congener standards PCB77, PCB123, PCB118, PCB114, PCB105, PCB126, PCB167, PCB156 and PCB169 were provided by Environment Canada.

RESULTS AND DISCUSSIONS

The content of PCBs in the stack gas (and fly ash) from domestic experimental PCBs incinerators was 3-60 ng/l, the PCBs concentration in waste water was less than 0.3 ppb, and the level of the residual PCBs in the bottom ash ranged from 1 to 25 ppm. It is confirmed that the destruction efficiency of high concentration PCBs in this experimental incinerator attains 99.9999%. The total amount of residual PCBs in the stack ash is 51 ppm. It can be concluded that the toxicity from PCBs in stack ash was diminished about 100,000 times compared to the technical product #1 PCB.

Since most of the PCBs' environmental toxicity is contributed by the dioxin-like PCBs congeners,^[7] the study of destruction of dioxin-like PCBs after incineration treatment is of special interest. The levels of nine dioxin-like PCB congeners in #1PCB, #2PCB and stack ash samples are provided in Table 1. Their toxicity is reported as 2,3,7,8-TCDD TEQ value. From the data in Table 1, the major toxicity of the incineration material #1PCB is due to the significantly high level of PCB77 and PCB105, the total TEQ value is 2.097ug/g. With slightly higher TEQ value, more kinds of dioxin-like PCBs congeners are presented in #2PCB. With similar congener patterns in stack ash samples as in technical product #1PCB, both of the total content of dioxin-like PCBs and total TEQ value decreased dramatically after incineration. According to our calculation, the content of dioxin-like PCBs and the toxicity in stack ash is diminished 20000 and 50000 times, respectively.

Table 1. The contents of dioxin-like PCBs congeners and their 2,3,7,8-TCDD TEQ values in #1 PCB, #2 PCB and stack ash					
PCB congeners	IUPAC No.	TEFs	#1 PCB (ug/g)	#2 PCB (ug/g)	stack ash (ng/g)
3,3',4,4'-TCB	77	0.0005	2098	149	40
2',3,4,4',5--PeCB	123	0.0001	2.63	59.7	ND
2,3',4,4',5--PeCB	118	0.0001	ND	ND	ND
2,3,4,4',5--PeCB	114	0.0005	ND	ND	ND
2,3,3',4,4'--PeCB	105	0.0001	482	6529	20
3,3',4,4',5--PeCB	126	0.1	10	20.9	ND
2,3',4,4',5,5'--HxCB	167	0.00001	ND	ND	ND
2,3,3',4,4',5--HxCB	156	0.0005	ND	11.8	ND
3,3',4,4',5,5'--HxCB	169	0.01	ND	ND	ND
total dioxin-like PCBs			2593	6761	60
total TEQ			2.097	2.829	0.022

Figure 1 through Figure 5 are the high resolution mass chromatogram for tetra- through octa-CDD/Fs. For all the sample analyses, ^{13}C -labeled internal standards were added to confirm the existence of the specific congener and ensure the accurate quantification.

Figure 1. The high resolution mass chromatogram for TCDD/Fs in stack ash.

Figure 2. The high resolution mass chromatogram for P_5CDD/Fs in stack ash.

Figure 3. The high resolution mass chromatogram for H_6CDD/Fs in stack ash.

Figure 4. The high resolution mass chromatogram for H₇CDD/Fs in stack ash.

Figure 5. The high resolution mass chromatogram for OCDD/Fs in stack ash.

Table 2 presents congener-specific PCDD/F analytical results and calculated 2,3,7,8-TCDD TEQ values for raw materials Chinese commercial #1PCB, stack ash and bottom ash samples from the incinerator. Data of #2PCB is also provided for comparison.

dioxins congeners	TEFs	#1 PCB(ng/g)		#2PCB(ng/g)		stackash(ng/g)		bottom ash(pg/g)	
		content	TEQ	content	TEQ	content	TEQ	content	TEQ
2,3,7,8-TCDD	1	ND	ND	ND	ND	0.4	0.4	2.1	2.1
1,2,3,7,8-PeCDD	0.5	ND	ND	ND	ND	1.2	0.6	6.7	3.35
1,2,3,4,7,8-HxCDD	0.1	ND	ND	ND	ND	4.2	0.42	4.6	0.46
1,2,3,6,7,8-HxCDD	0.1	ND	ND	ND	ND	3.7	0.37	6.2	0.62
1,2,3,7,8,9-HxCDD	0.1	ND	ND	ND	ND	4.5	0.45	14.3	1.43
1,2,3,4,6,7,8-HpCDD	0.01	ND	ND	ND	ND	107	1.07	30.5	0.31
OCDD	0.001	107	0.11	ND	ND	624	0.62	52	0.05
2,3,7,8-TCDF	0.1	1376	137.6	1082	108.2	27.1	2.71	171	17.1
1,2,3,7,8-PeCDF	0.05	128	6.4	74	3.7	38.8	1.94	38.2	1.91
2,3,4,7,8-PeCDF	0.5	137	68.5	503	251.5	14.1	7.05	67.6	33.8
1,2,3,4,7,8-HxCDF	0.1	28.3	2.83	430	43	165	16.5	124	12.4
1,2,3,6,7,8-HxCDF	0.1	12.1	1.21	75.4	7.54	46.9	4.69	62.3	6.23
2,3,4,6,7,8-HxCDF	0.1	ND	ND	25.4	2.54	11.4	1.14	59.8	5.98
1,2,3,7,8,9-HxCDF	0.1	ND	ND	ND	ND	9.5	0.95	4.3	0.43
1,2,3,4,6,7,8-HpCDF	0.01	10.3	0.1	28.8	0.29	336	3.36	143	1.43
1,2,3,4,7,8,9-HpCDF	0.01	8.3	0.08	10.8	0.11	148	1.48	19.5	0.2
OCDF	0.001	160	0.16	36.9	0.04	3453	3.45	65.8	0.07
total PCDDs		124	0.11	<4	ND	745	3.93	116	8.32
total PCDFs		6180	216.88	7863	416.91	4250	43.28	756	79.54
total PCDD/Fs		6304	216.99	7863	416.91	4995	47.21	872	87.86

Based on Table 2, most of the TEQ toxicity of PCBs samples is contributed by the elevated levels of PCDFs. Only very low level of OCDD was detected in #1PCB, whereas the high level of PCDFs resulted in TEQ value of 217 ng/g. No dioxins were detected in #2PCB, but elevated levels of PCDFs congeners generated 417 ng TEQ/g. Both stack ash and bottom ash samples contained small amount of dioxins, which were formed during incineration. However, the more toxic PCDF congeners such as 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF reduced significantly.

Figure 6 illustrated the homologue profile of PCDD/Fs in Chinese technical product #1PCB and stack ash samples. This profile is quite different from municipal waste incineration. For municipal incineration emission, generally the furan level is high for tetra and penta homologues and decreases progressively toward OCDF. Stack ashes from PCB incineration, however, normally have low level of dioxins but higher level of furans that increase with the increment of substituted chlorine atoms from tetra to octa homologue.

Figure 6. Homologues Distribution of PCDD/Fs for Stack ash and Chinese # 1PCBs

2,3,7,8-substituted congener-specific PCDD/Fs pattern of #1PCB, stack ash and bottom ash samples are shown in Figure 7. Significant high levels of TCDF through HxCDF congeners, contribute to most of the TEQ value of #1PCB. After the incineration, all seventeen 2,3,7,8-substituted PCDD/Fs congeners were detected in the stack ash and bottom ash samples. However, the TEQ values reduced greatly in the ash samples. Quantitative results are provided in Table 2.

Compared with technical product #1PCB, the TEQ value of 87.9 pg/g in the bottom ash is 2500 times lower, which demonstrates the effectiveness of the PCB incinerator. The TEQ value of stack ash is 47.2 ng/g, whose toxicity is less than that of technical product #1 PCB. Because this TEQ value is higher than the USEPA criterion (1ppb TEQ), it is suggested that the emissions such as stack ash from the

experimental PCBs incinerator should be handled more carefully. Further study to optimize the operating conditions of the PCB incinerator is necessary.

Figure 7. PCDD/Fs profile of #1PCB, stack ash and bottom ash samples

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