Specific Congeners Analysis of Dioxins from the Emissions of A Testing Incinerator

Ke Jiang, Lingjun Li, Yudong Chen, Jun Jin, Daihui Zhang, Chunyan Shao
Research Center for Eco-Environmental Sciences, Chinese Academy of Science, Beijing 100085, P.R.China

INTRODUCTION

About eight thousand tons of Polychlorinated Biphenyls (PCBs) were manufactured during the 1960's and 1970's in mainland of China. Most of the PCBs products were used as dielectric fluid in electric capacitors, and a small part of which were used as additives in paints. The typical models of Chinese commercial PCBs are #1PCBs (the chlorine content is 42%) and #2 PCBs (the chlorine content is 56%)[1]. Most of electric capacitors containing PCBs have become 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 exceeds 90%,the concentration of PCBs in some transformer oils attain 50%[2]. PCBs are synthetic chemicals which is 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. If the temporarily stored wastes containing high concentration of PCBs are lost to the environment, it is likely to cause serious contamination, which is harmful to the ecology and human health. The Chinese government is working on an experimental incinerator to destroy PCBs wastes of high concentration. During the experimental period, emissions from the incinerator were monitored in order to select the optimum operating conditions, resulting in high destruction efficiency and minimum formation of toxic substances.

The total content of residual PCBs and the concentration of tetra through octa PCB homologues in the emission gas, flyash, bottom ash and waste water from the incinerator have been determined under different operating conditions. The toxic dioxins congeners in the feed stock(#1 PCBs), stack ash and bottom ash have been quantified and computed as 2,3,7,8-TCDD toxic equivalents (TEQ). The components of dioxin-like PCBs in the stack ash were assayed as well.

concentration PCBs in this experimental incinerator attains 99.9999%.

The contents and their 2,3,7,8-TCDD TEQ values of dioxin-like PCBs congeners[7] in incineration raw materials #1 PCBs and the stack ash are shown in Table 1.

The residual total 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 from the raw materials #1 PCBs. The dioxins can be formed during the PCBs combustion[8]. The PCDFs was reduced greatly in the stack ash, but small amount of PCDDs have been formed (Table 2).

The TEQ value in the bottom ash is 87.9 pg/g which is diminished 2500 times compared with raw material #1 PCBs. The TEQ value of stack ash is 47.2 ng/g, whose toxicity is less than the raw material #1 PCBs. Because the TEQ values were higher than the USEPA criteria (1 ppb TEQ), it is suggested that the emissins such as stack ash from the experimental PCBs incinerator should be handled carefully.

Acknowledgement

The authors acknowledge the assistance of the River Road Environmental Technology, Environment Canada for HRGC/HRMS analysis.

References

[1] Ke Jiang, etal, Chinese Journal of Analytical Chemistry, 10,711(1982)
[2] Lingjun Li, etal, Chinese Journal of Environmental Science, 14,69(1993)
[3] USEPA, Modified Method 5 Sampling train, 560/5-83-004,1986
[4] USEPA, Method 1613, Revision A, 1990
[5] R.G.Webb, J.Chromatogr.Sci., 11,366(1973)
[6] Environment Canda, Report, EPS, 1/RM/19,1992
[7] U.G.Ahlborg, Chemosphere, 28,1049(1994)
[8] F.W.Karasek, Anal.Chem., 58,633A(1986)

The destruction efficency of high concentration PCBs in this incinerator can be higher than 99.9999%. The TEQ value of residual dioxins in a stack ash sample is 47.2ng TEQ/g. The TEQ value in a bottom ash sample is 87.9pg TEQ/g.

EXPERIMENTAL

1. Sampling

(1) Raw material for incineration: Chinese #1PCBs technical products collected from discarded capacitors manufactured by Xi'an,China.

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

(3) Stack ash, scraped from the inwall of the incinerator chimney.

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

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

2. Extraction and clean-up

USEPA 1613 Method[4] was used in extraction and clean-up.

3. Quantification

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

(2) PCB homologues.

A known amount of ^{13}C-labelled 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-labelled PCDD/Fs congeners. The spiked sample was extracted and cleaned up for HRGC/HRMS/SIM analysis. Seventeen 2,3,7,8-substituted toxic dioxins 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.

RESULTS AND DISDUSSIONS

Emission from domestic experimental PCBs incinerator were determined by reliable and accurate analytical method. The content of PCBs in the exhausted gas (and fly ash) are 3-60 ng/l, and the PCBs concentration in waste water is less than 0.3 ppb, and the residual PCBs in the bottom ash are 1-25 ppm.

It is confirmed that the destruction efficiency of high

Table 1 The Contents of Dioxin--like PCBs Congeners and their 2,3,7,8--TCDD TEQ Values in #1PCBs and Stack Ash

PCBs congeners	IUPAC No.	TEFs ('WHO/IPCS)	#1PCBs (ug/g)	stack ash (ng/g)
3,3',4,4'--T4CB	77	0.0005	2098	40
2',3,4,4',5--P5CB	123	0.0001	2.63	ND
2,3',4,4',5--P5CB	118	0.0001	ND	ND
2,3,4,4',5--P5CB	114	0.0005	ND	ND
2,3,3',4,4'--P5CB	105	0.0001	482	20
3,3',4,4',5--P5CB	126	0.1	10	ND
2,3',4,4',5,5'--H6CB	167	0.00001	ND	ND
2,3,3',4,4',5--H6CB	156	0.0005	ND	ND
3,3',4,4',5,5'--H6CB	169	0.01	ND	ND
total dioxin--like PCBs			2593	60
total TEQ			2.29	0.022

Table 2 The Contents of Seventeen Toxic Dioxins Congeners and Total TEQ Values in #1PCBs, Stack Ash and Bottom Ash

dioxins congeners	TEFs	#1PCBs(ng/g)	stack ash(ng/g)	bottom ash(ng/g)
2,3,7,8--TCDD	1	ND	0.4	0.0021
1,2,3,7,8--PeCDD	0.5	ND	1.2	0.0067
1,2,3,4,7,8--HxCDD	0.1	ND	4.2	0.0046
1,2,3,6,7,8--HxCDD	0.1	ND	3.7	0.0062
1,2,3,7,8,9--HxCDD	0.1	ND	4.5	0.0143
1,2,3,4,6,7,8--HpCDD	0.01	ND	107	0.0305
OCDD	0.001	107	624	0.052
2,3,7,8--TCDF	0.1	1376	27.1	0.171
1,2,3,7,8--PeCDF	0.05	128	38.8	0.0382
2,3,4,7,8--PeCDF	0.5	137	14.1	0.0676
1,2,3,4,7,8--HxCDF	0.1	28.3	165	0.0124
1,2,3,6,7,8--HxCDF	0.1	12.1	46.9	0.0623
2,3,4,6,7,8--HxCDF	0.1	ND	11.4	0.0598
1,2,3,7,8,9--HxCDF	0.1	ND	9.5	0.0043
1,2,3,4,6,7,8--HpCDF	0.01	10.3	336	0.143
1,2,3,4,7,8,9--HpCDF	0.01	8.3	148	0.0195
OCDF	0.001	160	3453	0.0658
TOTAL TEQ		216.99	47.21	0.0879