CHARACTERISTICS OF HIGH-TEMPERATURE-INDUCED DESTRUCTION OF SHORT-CHAIN CHLORINATED PARAFFINS IN WAX

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Introduction

Short-chain chlorinated paraffins (SCCPs), which are alkanes containing 10–13 carbons and several chlorines, have been manufactured extensively and are used as preservatives. Recently, they have been used for other applications, including as plasticizers in the plastic industry, flame retardants in the rubber industry, curing agents in the paint industry, fat-liquoring agents in the leather industry, and adhesives. In 2001, Japan manufactured 502 tons of SCCPs¹. In 2017, at the 8th annual conference of the Stockholm Convention in Geneva regarding persistent organic pollutants, SCCPs were included in Annex A (elimination), resulting in the complete ban of both the production and usage of SCCPs. Therefore, the destruction of SCCPs present in products or waste is important for reducing their harmful effects on the environment. In the case of Poly-Chlorinated Biphenyls (PCBs), also listed in Annex A, the Ministry of Environment in Japan proposed the use of incineration (temperature: 850° C, resident time: > 2 s) to destroy PCBs². Considering the similarities between PCBs and SCCPs, these incineration conditions may be effective for the destruction of SCCPs as well. However, the by-products of incineration need to be considered.

In municipal waste incineration, chlorinated organic compounds such as dioxins are produced in the furnace during the incineration process (primary generation) and during the cooling process of exhaust gas (secondary generation). In primary generation, chlorinated dioxins are produced by the incomplete combustion of aromatic and aliphatic products, such as chlorobenzene and chlorophenol, at temperatures of 300–500 °C. Preventing the formation of these compounds can be achieved by careful control of the incineration conditions (3T: turbulence, time, temperature). Secondary generation tends to occur in exhaust flues or dust collectors. Unburned carbons, chlorinated products, and heavy metals present in dust at 300–500 °C can lead to formation of dioxins (de novo formation)^{3,4}. SCCPs present in flame retardants decompose when temperatures exceed 400 °C; SCCPs were not detected in either the residual or gas phase. As expected, chlorinated aromatic hydrocarbons were detected in the gas phase⁵. In the presence of hydrocarbons at temperatures of 200–400 °C, the most likely fate for SCCPs is cyclization and aromatization⁶.

It is apparent that combustion of SCCPs likely generates chlorinated organic compounds. Due to the harmful effects they have on the environment, it is imperative that further research is conducted on SCCPs and their unintentional combustion by-products. In this study, we focused our efforts on materials containing SCCPs and their decomposition rates in heating tests.

Materials and methods

Samples: The wax sample evaluated in the sample was generated at Shandong Yousuo Chemical Technology Co., Ltd. (52#).

Heating conditions: Based on the conditions outlined by the Ministry of Environment in Japan for the destruction of low-concentration PCB waste and dioxins, we designed our own heating conditions, listed in **Table 1**.

Methods: Figure 1 outlines the heating system employed in this study. SCCP samples were placed on a quartz boat, which was set into a quartz tube, and the sample was heated. Glass wool was used to plug the end of the quartz tube to prevent particulate matter from entering the toluene traps. Once heating was finished, particulate

matter on the inner wall of the tube was carefully removed using a Kimwipe perfused in toluene. The particulate matter present on the experimental pulp sheet and glass wool is considered fly ash. The underside of the quartz boat was wiped using an experimental pulp sheet, and the collected particulate matter is considered bottom ash. The toluene trap is referred to as exhaust gas. SCCPs, medium-chain chlorinated paraffins (MCCPs), and unintentional products obtained from the experimental pulp sheets and glass wool were extracted by Soxhlet extraction. The extraction and toluene trap samples were further purified by column chromatography (silica gel, acid

Table 1. Heating conditions				
sample weight	: 1 g			
heating temperature	: 850°C			
gas	: Air (200 mL/min)			
heating time	: 1 hour			
residence time in heating temp	: 7.9 sec			



Figure 1. Heating system

Analysis of SCCPs and MCCPs: SCCPs and MCCPs in the wax sample were quantified precisely using GC (Agilent 7200) coupled to a time-of-flight MS (TOFMS) (Agilent Q-TOF GC-MS) or using GC (Thermo Trace 1310) coupled to an Orbitrap MS (Thermo Q Exactive GC). SCCPs in heated samples, such as bottom ash, fly ash, and exhausted gas, were quantified by GC (Agilent 7890) coupled to qMS (JEOL JMS-Q1500GC).



Figure 2. Flow chart illustrating the method used

Analysis of unintentional products: Analysis of polychlorinated dibenzo-p-dioxins/furans (PCDD/PCDF) and dioxin-like polychlorinated biphenyls (DL-PCBs) was performed using GC (Agilent HP-6890) coupled to a high-resolution MS (HRMS) (JEOL JMS-700 MStation).

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Results and discussion:

Determination of SCCP and MCCP concentrations: Due to the limited SCCP internal standards available and the large number of SCCP isomers, exact determination of the SCCP concentration (Σ SCCP) was troublesome. To overcome this, the chromatograms of the diluted wax sample (standard chromatogram) and heated sample were compared. The standard chromatogram possessed a larger area than the chromatogram of the heated sample, indicating that the Σ SCCP was lower in the heated sample. A representative chromatogram for SCCPs ($C_{13}H_{18}Cl_{9}$) is presented in **Figure 3**. The area of the wax sample corresponded to 15.4 ppm, representing the greatest SCCP amount among all chromatograms.





Figure 3. C₁₃H₁₈Cl₉ chromatogram

Determination of the destruction rate: We calculated the rate of destruction of the SCCPs in the heated sample compared with the original wax sample. Initially, we defined the total amount of SCCPs (comprising 10–13 carbons and 5–9 chlorines) as the Σ SCCP determined from the GC/TOFMS and GC/OrbitrapMS results. The original wax sample was diluted by 5 ppm to yield a Σ SCCP of 2.9 ppm. The sample was analyzed, and the resulting chromatogram was defined as the standard chromatogram. The standard chromatogram and chromatogram from the heated sample were compared, and the Σ SCCP in the heated sample was determined. Next, we calculated the destruction rate by comparing the Σ SCCP between the original wax sample and heated sample.

SCCPs, MCCPs , and impurities in the wax sample: We determined the Σ SCCP and MCCP concentration in 1 g of the original wax sample using GC/TOFMS (**Table 2**). The Σ SCCP accounted for 77% of the original wax sample. However, the total mass of both SCCPs and MCCPs was 1.23 g per 1 g of the original wax sample; therefore, it is likely the analysis overestimated the amount of SCCPs and MCCPs. SCCPs are composed of various isomers that differ in both the number and positions of chlorines. Thus, isomers with different numbers of carbon atoms will likely still have the same mass because of the varying numbers of chlorine atoms among isomers. This complex isomer pattern likely influences ionization in MS. To overcome this limitation, we used GC/OrbitrapMS analysis (**Table 3**). The amount of SCCPs with 10–13 carbons and 6–9 chlorines determined by GC/OrbitrapMS analysis was less than that determined by GC/TOFMS analysis. As GC/TOFMS overestimated the amount of SCCPs in the sample, it was concluded that the GC/OrbitrapMS results were more accurate. Quantification of the Σ SCCP in the original wax sample, via combination of the GC/TOFMS (C₁₀₋₁₃, Cl₅) and GC/OrbitrapMS (C₁₀₋₁₃, Cl₆₋₉) results, revealed that 58% of the original wax sample comprised SCCPs, with a total SCCP and MCCP

(µg/g)	C10	C11	C12	C13	C14	C15	C16	C17
CB	<10000	<20000	<10000	<10000				
C14	13000	31000	18000	<10000				
C15	26000	100000	56000	25000	2000	700		
C16	24000	85000	78000	58000	20000	10000	4000	
C17	11000	59000	73000	66000	50000	26000	13000	5000
C18	4200	16000	28000	50000	40000	39000	30000	10000
C19	<1000	1500	5400	10000	20000	30000	30000	20000
C110		200	540	1700			20000	17000

Table 2. SCCP and MCCP levels in the original wax sample determined by GC/TOFMS

Table 3. SCCP levels in the original wax sample determined by GC/OrbitrapMS

(µg/g)	C10	C11	C12	C13
Cl6	18000	46000	49000	25000
Cl7	7700	37000	59000	40000
Cl8	2500	11000	26000	31000
C19	<1000	1600	4200	9700

In addition to SCCPs and MCCPs, impurities in the original wax sample were also assessed and identified as DL-PCBs, PCDDs, and PCDFs (**Table 4**). Regarding DL-PCBs, the mass of non-ortho and mono-ortho PCBs was 1.4 ng/g, which is defined as a low POP content (LPC) according to the limit defined at the Basel Convention (<50 μ g/g)⁷. The TEQ concentration in total PCDDs/PCDFs was 0.13 ng/g and satisfied the LPC limit of <15 ng/g⁷. Analysis of the estimated amounts of unintentional products made by high-temperature heating is likely important.

Table 4. Impurities in the original wax sample

-	-		-	-	
pg/g	PCDDs	PCDEc	DL-PCBs	DL-PCBs	
(pg-TEQ/g)	TCDDs	TCDIS	(non-ortho)	(mono-ortho)	
Cl4	N.D.	4900	440	-	
C15	N.D.	2400	220	500	
Cl6	350	1500	50	140	
Cl7	340	880	-	60	
Cl8	340	350	-	-	
total	1000(7.1)	10000(120)	710(24)	700(0.021)	

Destruction characteristics of SCCPs: We heated the original wax sample and then measured SCCPs, MCCPs, and unintentional products. The chromatograms for SCCPs in the bottom ash, fly ash, and exhaust gas samples were smaller than the respective standard chromatograms. The Σ SCCP values in the bottom ash, fly ash, and exhaust gas samples were <1.74, <348, and <17.4 ppm, indicating that >99.9997%, >99.94%, and >99.997% of SCCPs were destroyed, respectively. These results suggest that >99.999% of SCCPs in bottom ash can be removed by the high-temperature heating method. However, we could not achieve a SCCP removal rate of >99.999% from

the original fly ash or exhaust gas samples. Increasing the amount of sample and/or decreasing the dilution factor may help increase SCCP removal, until a rate of >99.999% can be achieved. As defined at the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal, the destruction efficiency (DE) is the total amount of target pollutants in a heated solid, liquid, or gas sample divided by that in the original sample. Additionally, the destruction and removal efficiency (DRE) is defined as the total amount of target pollutants in a heated gas sample divided by that in the original sample. In our study, the DE was >99.94% and the DRE was >99.997%.



Figure 4. SCCP destruction rate in the heated sample

The unintentional products (PCBs, PCDDs and PCDFs) in the heated sample were also analyzed (**Table 5**). The amounts of DL-PCBs in all heated samples met the LPC limit set at the Basel Convention ($<50 \mu g/g$)⁷; interestingly, that in the fly ash sample was highest (0.101 $\mu g/g$). The amounts of both PCDD and PCDFs in all heated samples, excluding the fly ash sample, met the LPC limit (15 ng TEQ/g)⁷. The fly ash sample was kept at a relatively low temperature (~850 °C), which together with the presence of unburned particulate matter may account for the high concentrations of PCDD/PCDFs and PCBs in fly ash. High-temperature heating of SCCPs tends to produce unintentional products (PCBs and PCDbs/PCDFs) under low temperatures. In addition, the results suggest that aliphatic chlorinated pollutants are likely transformed into aromatic chlorinated pollutants.

pg/g (pg-TEQ/g)		PCDDs	PCDFs	DL-PCBs (non-ortho)	DL-PCBs (mono-ortho)
	Cl4	3.6	29.1	15.6	-
	Cl5	2.9	9.6	5.4	61.0
bottom	Cl6	6.0	8.5	1.4	7.0
ash	Cl7	6.5	6.4	-	1.8
	Cl8	11.6	6.0	-	-
	total	29(0.0504)	60(0.128)	18.6(0.271)	68(0.00181)
	Cl4	3330	380000	32200	-
	Cl5	5270	208000	9600	29400
fly	Cl6	7500	134000	2900	16250
ash	Cl7	7200	83000	-	9700
	Cl8	3540	32000	-	-
	total	27300(2260)	840000(19200)	45000(1050)	56000(1.66)
	Cl4	10	434	92	-
	Cl5	5	223	17	83
exhaust	Cl6	45	191	6	24
gas	Cl7	34	180	-	10
U	Cl8	38	104	-	-
	total	127(0.38)	1120(29,2)	114(1.89)	123(0.00348)

Table 5. Intentional products in the heated sample

Conclusions

In this study, we determined the Σ SCCP to be 58% in the original wax sample. The DE and DRE in the heated samples were accurately determined to be >99.94 and >99.997%, respectively. However, these values do not meet the limits set at the Basel Convention (DE <99.999% and DRE <99.9999%). This shortfall is not due to inefficient combustion of the SCCPs but more to a limitation of the analysis method. To satisfy the limits set by the Basal Convention, other analytical methods of SCCP combustion need to be employed to evaluate the lower determination limits. Unintentional products, such as PCDDs/PCDFs and DL-PCBs, are present within the original wax sample but are more prevalent as combustion products of SCCP destruction. Fly ash samples, kept at ~850 °C, were found to exceed the levels of allowed PCDDs/PDCFs set at the Basel Convention (<15 ng TEQ/g). To prevent further release of PCDDs/PDCFs into the atmosphere, treatment of fly ash, in both the industrial and academic fields, should be carried out prior to combustion.

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