DECHLORINATION OF PCBs CONTAINING WASTES APPLYING CHEMICAL TREATMENT TECHNOLOGY IN KOREA

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Abstract

The sample treated by dechlorination to destruct the PCBs from the PCBs containing transformer oil wastes. The sample analyzed to verify the by-products before treatment and after treatment. In the after treatment samples, PCBs were not detected by comparing the peak patterns using Aroclor 1242, 1254 and 1260. On the other hand, PCBs isomers were detected by analyzing the HRGC/MS. Most of the PCBs congeners in waste were decomposed to monochlorinated biphenyls. However, the PCBs concentration after dechlorination is satisfied the Korea regulation criteria. Also, the hazardous compounds such as dioxin were not observed.

Introduction

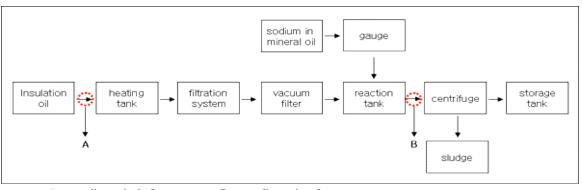
PCBs were produced in the United States from 1929 and 1977, when concern over adverse environmental effects led to a ban on their industrial manufacture was under the Toxic Substances Control Act of 1976 (TSCA). During this period global production of PCBs was approximately 1.3 million. In Korea, about 4,000 tons of PCBs imported from Japan and USA. The widespread release of PCBs into the environment presents a serious problem due to their persistency and toxicity. The toxic effects are compounded by the hydrophobicity of PCBs, which causes them to bio-accumulate in the fatty tissues of animals. Actually, PCBs do not readily decompose or biodegrade in the environment, which is one of the major reasons for the PCBs contamination of environment.

In 1999, ROK the Environmental Law regarding PCBs in transformer oil limit was revised from 50 mg L⁻¹ to 2 mg L⁻¹ for liquid waste. According to the Stockholm Convention on Persistent Organic Pollutants (POPs) entered into force on May seventeenth 2004, the Ministry of Environment in Korea started the survey on PCBs concentration existing transformers at Power Station, and launched an initiative to set up a project on environmental sound management of end-of-life transformer oils with regard to the elimination of the use of PCBs in equipment by 2015. In response to new regulation, the Ministry of Environment revised the Waste Official Testing Method (WOTM) by adding the quality control concept to regulate the waste management. Also, the chemical PCBs treatment technologies were introduced to remove the PCBs safely.

Therefore, in this study, the dechlorination method of PCBs using metal sodium was considered to check the efficiency and environmental affects.

Materials and Methods

The chemical treatment scheme and sampling points were showed in Fig. 1. The PCBs and PCDDs/PCDFs were analyzed using GC/ECD and HRGC/MS as shown in Table 1.



A : sampling point before treatment, B : sampling point after treatment Fig. 1. Scheme of PCBs dechlorination system and sampling points.

PCB-209 was used as a surrogate standard. A 1 μ L of extract was injected under splitless condition. An initial multi-point calibration was constructed up to 10 ppm. Daily calibration of GC was performed using a minimum of two standards of 0.5 and 1 ppm. About 0.1-0.5 g of transformer oil was dissolved in hexane and pretreatment processes such as alkali treatment, acid treatment, column cleanup etc. as shown in Fig. 2.

Condition					
GC/ECD	Column	DB-5 (30m, 0.25mm I.D., 0.25 µm film thickness)			
	Carrier Gas	99.999% N ₂			
	Detector	μECD			
	Total Flow	60mL/min			
	Injector Temp.	250°C			
	Oven Temp.	100°C→ 160°Q15°C/min)→300°Q5°C/min)			
	Detector Temp.	320°C			
HRGC	Column	DB-5MS (60m, 0.32mm I.D., 0.25 µm film thickness)			
	Carrier Gas	99.9999% He			
	Column flow	1mL/min			
	Injector Temp.	270°C			
	Injection mode	splitless			
	Oven Temp.	75°C(1min, 40°C/min)→190°Q(1°C/min)→240°Q(10°C/min)→320°Q(2min)			
HRMS	Ionization volt	36.0eV			
	Ionization mode	EI			
	Ion current	0.38mA			

Table 1. Analytical conditions of GC/ECD and HRGC/HRMS for determination of PCBs

Results and Discussion

The sample analyzed using GC/ECD and HRGC/MS to verify the byproducts before treatment and after treatment. In the after treatment samples, PCBs were not detected by comparing the peak patterns using Aroclor 1242, 1254 and 1260.

On the other hand, PCBs isomers were detected by analyzing the HRGC/MS. Most of the PCBs congeners in waste were decomposed to monochlorinated biphenyls. PCBs individual isomer was decomposed low chlorinated biphenyls and produced (3-chlorobiphenyls). The sample represented the Aroclor 1254 pattern before-treatment, but the peak patter disappeared after-treatment as shown in Fig. 3. However, the PCBs concentration after dechlorination is satisfied the Korea regulation criteria. Also, the hazardous compounds such as dioxin were not observed.

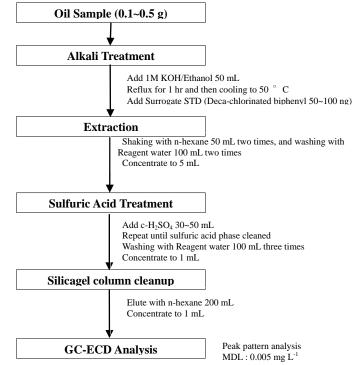


Fig. 2. Analysis Flow chart of PCBs in transformer oil

The additional hazardous component (individual PCBs isomers and PCDDs/PCDFs) analyzed using HRGC/MS. In the future study, we performed to analyze the more hazardous compounds such as Polyaromatic hydrocarbons (PAHs) and so on.

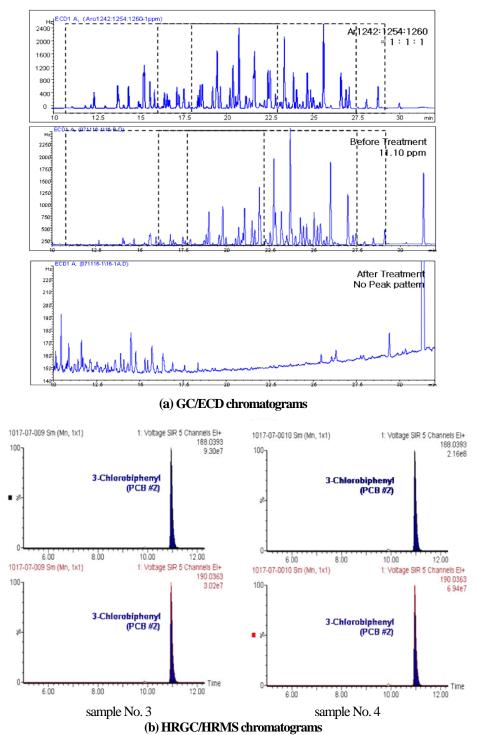


Fig. 3. HRGC/HRMS chromatograms of transformer insulation oil before and after physical treatment.

sample	Before treatment	After treatment	description	
	GC/ECD	HRGC/HRMS	description	
1	7.04	0.64/0.10		
2	11.10	0.18/0.14	The PCBs patterns were destroyed after treatment; therefore the analytical results of PCBs after treatment obtained "Non	
3	55.28	1.44/8.39	Detectable" using GC/ECD.	
4	371.18	0.43/0.16		

Table 2. PCBs concentration (mg/L) of transformer insulation oil before and after treatment

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