

CONGENER DISTRIBUTION AND PATTERN RATIO OF POLYCHLORINATED BIPHENYLS IN TRANSFORMER OIL USING GC/ECD

Kil-Hwan Hong, Eun-Ju Lim, Jae-Doo Cha, Young-Hwan Ko, Jung-Hoon Lee, Kyung-Seop Kim

Korea Testing Laboratory (KTL), 222-13 Guro3-dong, Guro-gu, Seoul, Republic of Korea

Introduction

Polychlorinated biphenyls (PCBs) are toxic and they accumulated in soil, sediment and biota when they are released into the environment. They do not readily decompose or biodegrade in the environment, which is one of the major reasons for the PCBs contamination of environment. Furthermore, it was reported that the recycled transformer oils were often contaminated with trace amount of PCBs. For different social and economic reasons, significant quantities of PCBs contaminated transformer oil are still in use or in storage¹. The actual and potential release of PCBs seriously threatens human beings and ecosystem². Decontamination of transformer oil containing PCBs has been an urgent task for decades.

Taking into account the current situation with PCBs and obligations of Korea in accordance with the Stockholm Convention on POPs, some measures on PCB management have been suggested. They are the following: the Ministry of Environment in Korea started new 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. There is a need to go on the inventory of PCBs and elaborate a plan on PCB-containing equipment replacement. It is necessary to choose environmentally sound and economically efficient technology of PCB disposal³.

This study aims to assess the character of the PCBs in transformer oil and study on congener distribution and pattern ratio of PCBs.

Materials and methods

Three hundred fifty five samples of transformer oils were collected by KTL in Republic of Korea. Sampling activities were conducted in accordance with procedures presented in sampling method⁴. The transformer valve opened, and collected about 50mL of sample in amber vial with septum open top cap. The sample container was capped tightly and labeled the sample bottle with an appropriate sample label, addressing all the categories or parameters. Samples were transported back to the laboratory and stored at 4 °C.

Aroclor 1242, 1254, and 1260 standards (Supelco Co.) were used in this study. The analytical method of this study was based on the Korean waste official method and Guideline for PCBs analytical method of transformer oil in Korea. Alkali treatment, liquid-liquid extraction, sulfuric acid treatment, silica gel clean-up and instrumental analysis were performed. An aliquot of concentrated extracts was loaded into the silica gel column and then eluted with 200 ml hexane. The elute was concentrated to about 1 ml on a nitrogen concentrator. Then, analysis by GC/ECD was performed.

To identify and quantify the PCBs, SHIMADZU 2010PLUS equipped with ECD was used, and the column was DB-5MS (30 m x 0.25 mm, 0.25 µm thickness). The injector was operated at a 5:1 split ratio and maintained at 250 °C. The oven temperature was held at 140 °C for 3 min, and then ramped to 270 °C for 2 min at a rate of 6 °C/min, to 300 °C (hold 7 min) at a rate of 10 °C/min. The carrier gas was nitrogen at a flow rate of 1 ml/min. The ECD was maintained at 320 °C with 30 ml/min of nitrogen makeup gas.

Each characteristic Aroclor peaks were used for quantitation in the initial calibration solution. For quantification of Aroclors, Peaks with intensities higher than 25% of the largest one in the chromatogram of each Aroclor standard mixture were considered for quantitative purposes and individual congeners of IUPAC No. 18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 170, 180, 194 were also included. If sample extract showed two Aroclor mixture pattern, peaks that is not overlapped with main peak of each single Aroclor was chosen for calibration.

The identification of PCBs as Aroclor was based on the agreement between the retention times of the peaks in the sample chromatogram and the retention time windows established through the analysis of the standards of the target Aroclors⁵. Calibration verification was performed in order to assess to drift of the instrument response between initial calibration and each subsequent analysis. Continuing calibration verification was conducted with 100–200 ng calibration solution of Aroclor 1242, 1254, and 1260 before analysis of each batch sample. If the drift percentage was less than 15%, then the initial calibration was considered to valid and proceeds for quantification. If the percentage drift was greater than 15%, a new calibration solution was prepared and validated. One matrix blank was included in 20 oil samples. No PCBs were found above the practical quantification limits in the method blank. Laboratory control sample was spiked with 100 ng of Aroclor 1242, 1254, 1260 on free-PCB matrix of each batch. For recovery test, 100 ng of decachlorobiphenyl (IUPAC No. 209) was spiked to the every sample. Surrogate recovery of all samples was 80-105 % and was satisfied to the recovery range in presenting the Korean waste official method.

Results and discussion

Table 1 shows the transformer survey results including manufacturer and year of manufacture. Most of transformer was manufactured in 1990's. This study included analysis of 355 transformer oil samples to analyze pattern ratio of Aroclor mixture and congener profile of PCBs.

Table 1. Detail information of Transformer manufacture and manufacture year

Manufacturer	Manufacture year			Number of Sample
	1980-1989	1990-1999	2000-	
KJ		11		11
DM		17		17
DM		11		11
DB	1	5		6
BH		5	2	7
SJG		8	1	9
SH		10		10
IC		22		22
JH		48	1	49
JW	1	160	4	165
JI		10	1	11
Others (14 manufacturers)	2	31	4	37
Total (25 manufacturers)	4	338	13	355

This study was carried out to analyze the release pattern of PCBs in transformer oil. The calibration solution of Aroclor 1242, 1254 and 1260 standard, respectively, was prepared five concentrations. Pattern identification of PCBs in transformer samples were performed by comparison of chromatograms of purified extracts with those obtained from standard solution of commercial mixtures (Aroclor). The presence of PCBs is indicated when pattern of peaks resembles that observed in standard solution chromatogram. Retention times must be agreed closely within ± 0.1 min and relative peak type must be similar. The total PCBs concentration was determined by a peak pattern matching and summation the selected peaks to obtain a total amount. The detail method to identify pattern of PCBs in transformer was well presented in previous studies⁵.

The peak pattern of transformer oil corresponding to the pure Aroclor 1242, 1254 and 1260 were observed as shown in Figure 1. The peak ratio of Aroclor mixture 2:2:1 (Aroclor 1242, 1254 and 1260) is dominant in this study. However, there is no difference of peak pattern ratio between manufacturers of transformer oil. In addition, the relationship between manufacture year and peak pattern ratio could not find out in this study. It is considered that they might manufacture transformer oil by various methods.

Various kinds of PCBs pattern were present in analyzed samples. 31% of analyzed samples shows peak ratio of Aroclor mixture 2:2:1 and 10% of analyzed samples shows peak ratio of Aroclor mixture 1:1:1 and 1:2:1, respectively. 35% of samples have various kinds of PCBs peak ratio of Aroclor mixture.

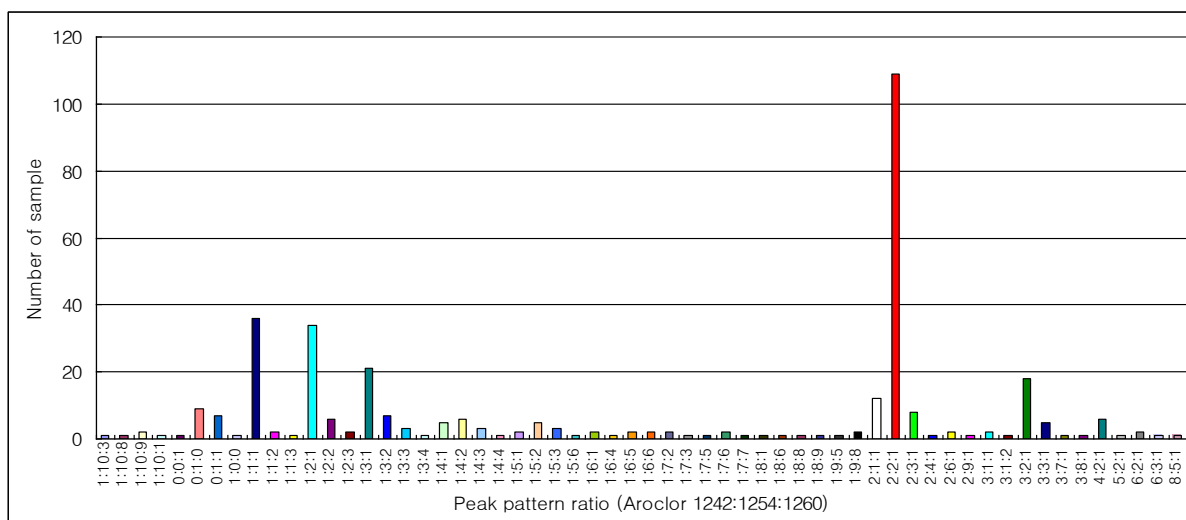


Fig. 1. Peak pattern ratio(mixture of Aroclor) of transformer oil.

Figure 2 shows the average distributions of each compound in the 355 transformer oil samples. PCB-(160/138/164), PCB-153 and PCB-(70/66/95) were the dominant isomer in case of this study. In addition, the congener distribution of transformer oil which had 2:2:1 peak pattern ratio did not show any difference with those which had other peak pattern ratio such as 1:1:1 peak pattern and so on.

They had very similar congener distribution of PCBs as shown in Figure 2 in this study in spite of various manufacturers and manufacture year.

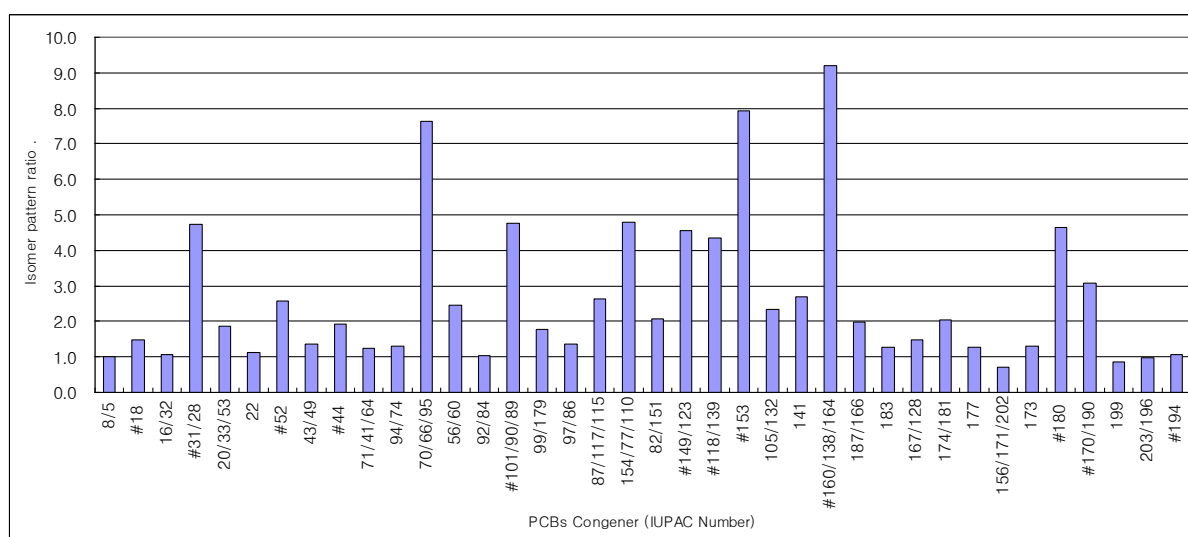


Fig. 2. The average distributions of PCBs in 355 transformer oil.

References:

1. UNEP chemicals. (2002); *United nation Environmental Programme*, Geneva, Switzerland
2. Blais, J.M., Shindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B..(1998); *Nature* 35998): 585-588
3. Tamara I. Kukharchyk, Sergey V. Kakareka. (2008); *Journal of Environmental Management* 88: 1657-1662
4. Ministry of Environments in Korea, (2004); *Korean Waste Official Method* .
5. Sun Kyoung Shin, Tae Seung Kim. (2006); *J. Hazardous Materials* B137: 1514-1522