CHACTERSITICS OF POLYCHLORINATED BIPHENYLS (PCBs) IN TRANSFORMER OIL, KOREA

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Abstract

The main objective of this study was to investigate PCBs in end-of-life and in-used transformer oils which is based on 'Guideline for PCBs analytical method of transformer oil' and then to grasp the characteristics of PCBs release in transformer oils. The levels of total PCBs ranged from N.D (not detected) to 2062.99 mg kg-1 and differentiate over 4 order of magnitude between minimum (0.18 mg kg-1) and maximum (2062.99 mg kg-1) value. We could find the PCBs presence in transformer with single or mixed pattern as Aroclor 1242, 1254, 1260. About fifty percentage of overall were all mixture of Aroclor 1242, 1254 and 1260 (53.7% of Aroclor 1242+1254+1260, 18.9% of Aroclor 1254+1260, 16.4% of Aroclor 1254, 8.0% of Aroclor 1242+1254). Middle chlorinated compounds are relatively higher portion (H6CBs>P5CBs>H7CBs>T4CBs), however, highly biphenyls (N9CBs) and lower biphenyls (D2CBs) are very low.

Introduction

PCBs had been considered as the ideal industrial materials because of their chemical and thermal stability, low flammability and electrical insulation properties[1]. PCBs were commercially produced as technical mixture under different brand name such as Aroclor (USA), Phenoclor (France), Kanechlor(Japan) and Sovol(Russia) and so on during 1929 to early 1970s[2]. U.S.EPA concern over adverse environmental effects led to a ban on their industrial manufacture was under the Toxic Substances Control Act of 1976(TSCA).

In Republic of Korea, PCBs commercial products weren't produced and were all imported from other countries such as Japan, USA etc. however, there are no accurate statistics regarding the PCB usage in Korea. Nevertheless, many studies have been reported that PCB was detected in environmental samples such as ambient air, sediment, marine system etc. The aim of this study was to investigate PCBs in end-of-life and in-used transformer oils which is based on 'Guideline for PCBs analytical method of transformer oil[3]' and then to grasp the characteristics of PCBs release in transformer oils.

Materials and Methods

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 (Fig. 1).

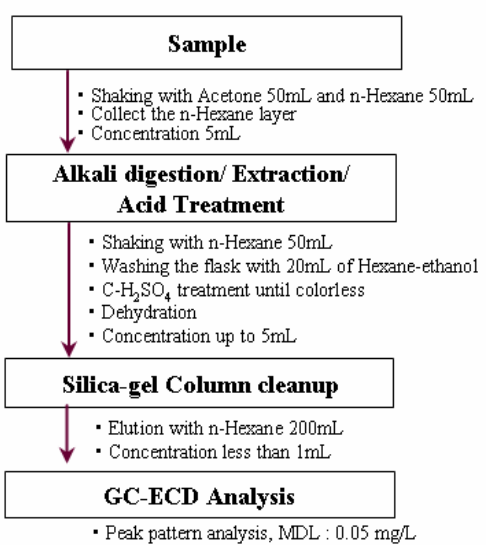

Fig. 1 Analytical procedures of PCBs

Samples (n=3,506) were collected from in-use and wasted power transformer insulating oils. Approximately 0.1g of the samples was digested using 1M-KOH/EtOH for 1 hr as alkali treatment, and then liquid-liquid extraction was performed three times with n-hexane. The aliquot was cleaned with concentrated sulfuric acid. Further cleaned extract was then passed through 20g of 44%-sulfuric silica gel packed in a glass column and eluted with 100 ml of hexane. Final elutes were concentrated to 1mL. For recovery test, 200 ng of decachlorobiphenyl (IUPAC No. 209) as surrogate material was spiked to the every sample. Total PCBs was analyzed by Shimadzu 2010 GC with equipped electron captured detector and DB-5 column (30m×0.25mm i.d.×0.25μm) was used for the analysis of oil extracts. The temperature program of the column was started at 100 °C (hold 2 min); 15 °C min−1 until 160 °C, 5 °C min−1 until 290°C (hold 10 min). A 1μL of extract was injected in splitless mode (1 min). Injector port temperature was set at 240 °C. ECD temperature was set at 310°C with nitrogen flow rate 1mL min−1.

The total PCBs concentration was determined by peak pattern-matching and summation the selected peaks to obtain a total amount. If pattern recognition of PCBs was identified as single Aroclor such as 1242, 1254, 1260, index peak was assigned at least 19.

Otherwise, if pattern was quantified as mixed Aroclor in samples, peaks with intensities higher than 25% of the largest one in each Aroclor standard mixture including IUPAC No. 18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 170, 180, 194 were also included.

Results and Discussion

Levels of PCBs in transformer oil

The levels of total PCBs ranged from N.D (not detected) to 2062.99 mg kg-1 and differentiate over 4 order of magnitude between minimum (0.18 mg kg-1) and maximum (2062.99 mg kg-1) value (Table 1). We observed that arithmetic mean of in-use groups (28.96 mg kg-1) was higher than end-of-life transformer groups (10.73 mg kg-1) and the entire data set showed positively skewed distribution.

Furthermore overall samples were not detected approximately 76 % (n=842) and PCB detection proportion (33%) of in-use group is greater than that (22%). A few of previous study reported that t-PCB was detected from N.D to 48.33 mg kg−1 (n=33) as Aroclor in transformer oils[4], 2.33~30.67 μg g-1(n=6) as Aroclor in transformer oils and 2.88~53.42 μg g-1(n=6, ∑7-indicator PCBs) as Clophen in waste motor oils[5].

Considering POPs Guideline of Basel Convention, 50 mg kg-1, excessive proportion of this value was account

for 0.8 % (n=29) in this study. However, generally speaking, highly contaminated transformer which is containing over 10 ppm of PCBs are getting remarkably decreased the latest productions (Fig 2).

Table 1. Levels of PCBs in transformer oil by manufactured year

Time-period	End-of-life (wasted)				In-use			
	Min [a)]	Max	SD	*n*	Min [a)]	Max	SD	*n*
unknown	0.64	21.26	±5.71	*44*	-	-	-	*6*[b)]
~1940					2.95	2.95	-	*1*
1946~1950					3.01	68.59	± 37.78	*7*
1951~1955					0.89	0.89	-	*1*
1971~1975	-	-	-	*1*	1.03	1.03	-	*10*[b)]
1976~1980	4.67	228.47	±50.16	*28*	1.15	11.16	± 3.41	*16*
1981~1985	4.96	58.92	± 8.01	*69*	0.43	38.35	±11.36	*21*
1986~1990	0.31	331.80	±32.03	*482*	1.86	517.92	±104.80	*75*
1991~1995	0.18	82.18	± 9.39	*1,361*	0.43	447.72	± 59.13	*214*
1996~2000	0.33	874.46	±71.46	*646*	0.26	2062.99	±294.02	*201*
2001~	1.59	12.74	± 3.28	*107*	0.40	97.62	± 17.40	*216*
total	0.18	874.46	40.52	*2,738*	0.26	2062.99	159.89	768

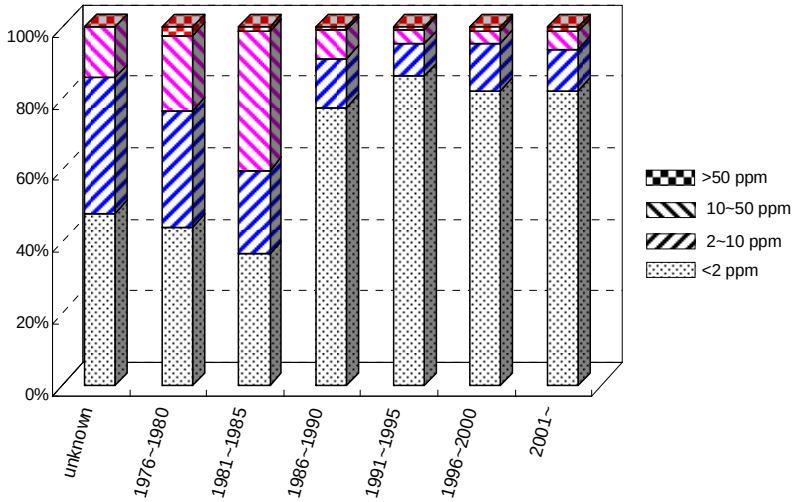

Figure 2. Distribution of PCBs concentration for time-period in analyzed samples

Homologue distribution of PCBs in transformer oil

We could find the PCBs presence in transformer with single or mixed pattern as Aroclor 1242, 1254, 1260. About fifty percentage of overall were all mixture of Aroclor 1242, 1254 and 1260 (53.7% of Aroclor 1242+1254+1260, 18.9% of Aroclor 1254+1260, 16.4% of Aroclor 1254, 8.0% of Aroclor 1242+1254). Especially Aroclor 1254 was mainly used in transformer oil as single or mixture type commercial product according to our analyzed data (approximately 97%) in this study.

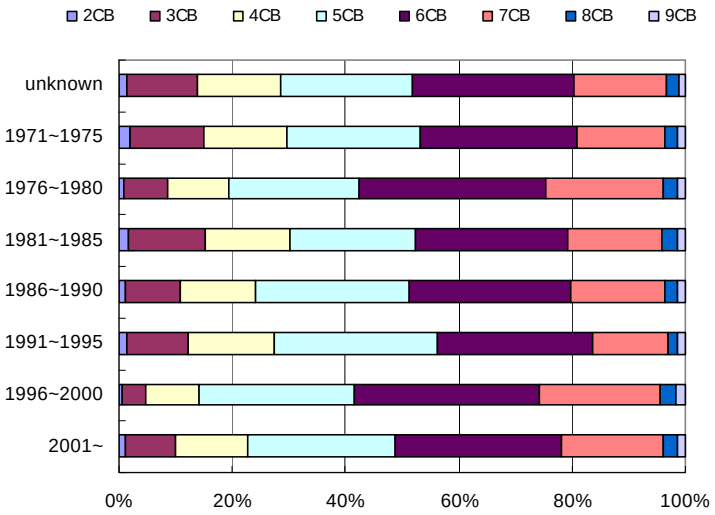

Fig. 3. Homologue distribution of PCBs

The characteristics of PCB polluted transformer oil, composition of PCBs homologue (mean) are illustrated in figure 3. Middle chlorinated compounds are relatively higher portion (H6CBs>P5CBs>H7CBs>T4CBs), however, highly biphenyls (N9CBs) and lower biphenyls (D2CBs) are very low.

Acknowledgements

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