Level of PCBs and PCDDs/Fs in transformer oil samples, Korea

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Introduction

Recently, the concern of PCBs treatment has been raised with the implementation of the Stockholm convention on persistent organic pollutants. PCBs were produced as technical mixtures with brand names such as Aroclor, Clophen, Kanechlor and Fenclor[1]. Aroclor and Kanechlor were mainly used in America and Japan, respectively and commercial PCBs products used in Korea weren't produced but all imported.

In Korea, production, importation, sale and usage of PCBs were prohibited by Toxic Chemical Control Act (1996) since usage of PCBs were restricted by Electricity Business Act (1979). By the Waste Management Act changed in 1999, the standard level of liquid waste and other wastes were 2 ppm and 0.003 ppm, respectively.

Over the past few years, a few studies have been made on level of total PCBs in transformer oil. Moreover, researches on coplanar PCBs and dioxins in transformer oils haven't been conducted in Korea. In this study, we investigated level of total PCBs and patterns of PCBs commercial products such as Aroclor 1242, 1248, 1254, 1260 and mixture in transformer oil samples using GC/ECD. In addition, we provide the congener information of coplanar PCBs and 2,3,7,8-substituted PCDDs/Fs using HRGC/HRMS.

Materials and Methods

Sample collection and Analytical method

The transformer oil samples were collected from 10 companies by Korean transformer oil sampling method[2]. The manufacturing year of transformer oils was ranged from 1968 to 1998.

The samples were digested using 1N-KOH for 1 hr and then liquid-liquid extraction was performed three times with n-hexane. The extract was divided into two samples. One was analyzed by GC/ECD after added the deca-CB congener, the other was analyzed by HRGC/HRMS after spiked ^{13}C-labeled internal standards (CIL laboratories, EC-4977), containing at least one congener for each homologue besides dioxin-like PCB congeners. After the H_2SO_4 treatment, the extract were cleaned up using a sulfuric acid-treated silica column (sulfuric acid 44% w/w) with 150ml of distilled n-hexane followed by an activated carbon (Kanto Chemical Co.) column. The detailed procedure is described in Fig. 1.

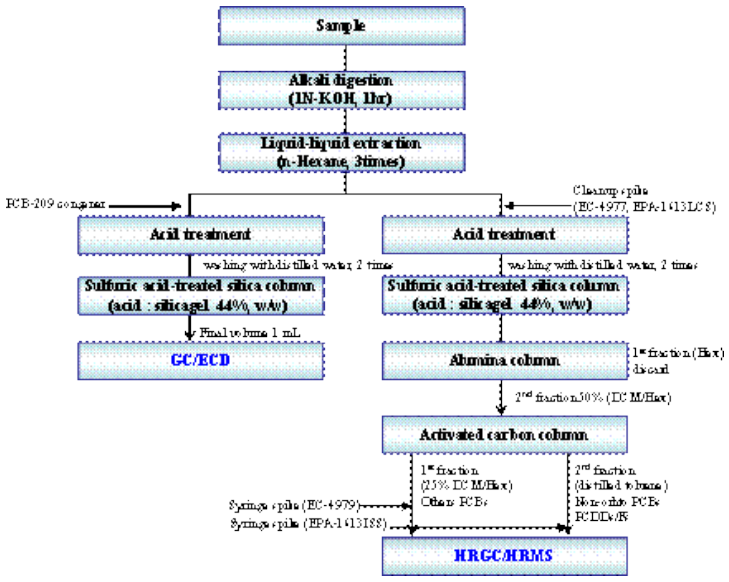

Figure 1. Cleanup procedure of transformer oil samples.

Instrumental analysis

Total PCBs was analyzed by GC/ECD (Shimadzu 2010) and Co-PCBs and 2,3,7,8-substituted PCDDs/Fs were analyzed by HRGC (HP6890)/HRMS (Finnigan MAT 95X). The DB-5 and DB-5MS columns were used. Detailed information of instrument was summarized in Table 1.

Table 1. Operating condition and parameter of GC/ECD and HRGC/HRMS for PCB analysis

Instrument	GC/ECD	HRGC/HRMS
Column	DB-5 (60m×0.25mm×0.25mm)	DB-5MS (60m×0.32mm×0.25mm)
Oven temp. program	140°C(1.5min) à 20°C/min, 200°C (0min) à 1.5°C/min, 270°C (15min) à 10°C/min, 310°C (1min)	70°C(1min) à 40°C/min, 190°C (0min) à 1°C/min, 240°C (0min) à 10°C/min, 320°C (3min)
Injector temp.	270°C	270°C
Others	Detector temp : 320°C Flow rate : 1mL/min (N_2)	Ion source temp. : 250°C Electron acceleration voltage : 35eV Ionization current : 380mA Ion acceleration voltage : 4700V

Results and Discussion

PCBs and PCDDs/Fs concentration in transformer oil samples

The total PCBs concentration were quantitatively determined by peak pattern method with GC/ECD and concentration of coplanar PCBs and PCDDs/Fs were determined by isotope dilution method with HRGC/HRMS.

The concentrations of PCBs and PCDDs/DFs in transformer oil samples are summarized Table 2. WHO-TEF was

used in calculation of TEQ. The concentration of total PCBs (calculated by GC/ECD) and TEQ values (calculated by HRGC/HRMS) were ranged from <0.05 to 77.3 ppm and from 23.3 to 600 pg-TEQ/g, respectively. The concentration of 2,3,7,8-substituted PCDDs/Fs and TEQ values calculated by HRGC/HRMS were ranged from N.D. to 2.41 ng/g and from N.D. to 128 pg-TEQ/g, respectively. In P-10 samples, higher concentration of coplanar PCBs was detected than concentration of total PCBs. It can be caused by uncertainty of GC/ECD as like no compensation of recovery. Among 10 samples, 4 samples showed higher concentration than 2 ppm (specific waste criterion of Korea).

Table 2. Concentration of PCBs and PCDDs/Fs in transformer oil samples

Sample ID	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9	P-10
Co-PCBs (mg/g)	0.245	0.192	1.596	0.528	2.486	2.300	0086	0.288	0.064	0.185
Total PCBs (ppm)	1.31	1.43	9.93	7.59	62.04	77.28	<0.05	1.99	0.47	0.17
PCDDs/Fs* (ng/g)	0.451	0.358	0.306	0.589	2.410	1.988	0.769	0.563	0.428	N.D.
Co-PCB TEQ (pg/g)	73.7	112.3	381.7	173.3	600	520	46.8	88.8	23.3	50.5
PCDDs/Fs TEQ (pg/g)	2.46	0.036	0.687	3.844	128.1	110	1.669	5.90	1.038	N.D.
Aroclor type**	42:54=1:1	42:54=1:1	42:54=2:1	42:54:60=2:1:1	60	60	-	48:54:60=2:2:1	42:54=3:1	54:60=2:1
Product-year	1978	1978	1969	1969	1975	1968	1977	1981	1998	1998

TEQ concentration was calculated using WHO-TEF, * sum of only 2,3,7,8-substituted PCDDs/Fs concentration

** 42, 48, 54 and 60 means Aroclor 1242, 1248, 1254 and 1260, respectively

Congener distribution of coplanar PCBs

Congener distribution of coplanar PCBs in Aroclor products and transformer oils was shown in Fig. 2. The congener patterns were similar with each other. In particular, the congener pattern of P-5 and P-6 sample was almost accorded with Aroclor 1260. Also, we could estimate that Aroclor 1254 was included in other samples considering PCB-156 congener. Upper result was almost same with that of peak pattern method. The highest level in Co-PCBs congeners was PCB-118 congener which contributed above 42% of the total coplanar PCB concentration, but the contribution of PCB-126 congener was highest in terms of TEQ concentration.

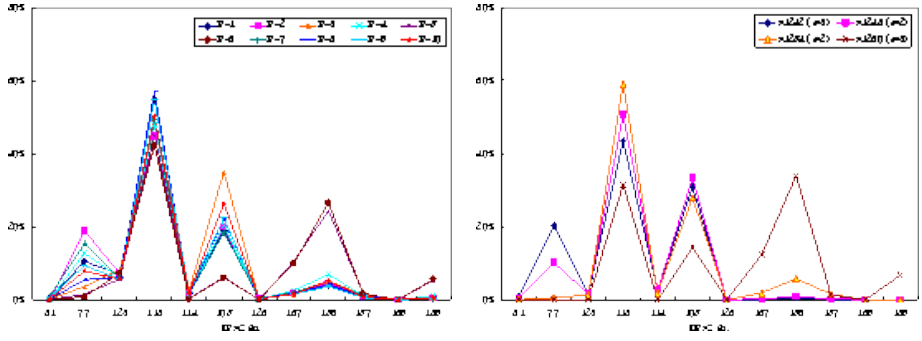

Figure 2. Congener distribution of coplanar PCBs in transformer oil and Aroclors (US EPA).

Congener distribution of PCDDs/Fs

Figure 3 shows 2,3,7,8-substituted PCDDs/Fs congener composition in transformer oils. The contribution of OCDD congener (above 53%) was higher than other congeners. The contribution of PCDDs/Fs congeners (below 12%) was

very low against total TEQ concentration.

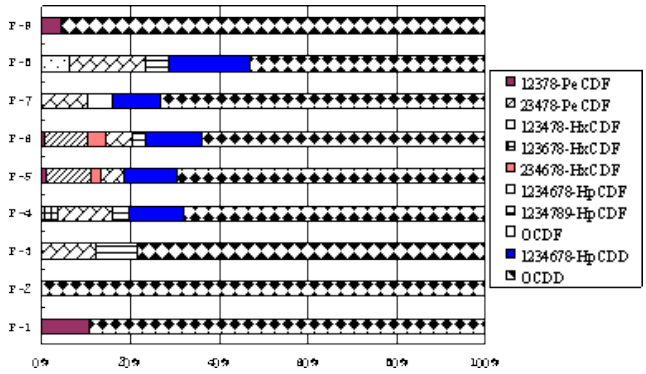

Figure 3. Congener composition of PCDDs/Fs in oils.

References

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2. Korean NIER (National Institute of Environmental Research), 2003. Korean Analytical Method for PCBs in oil.