Levels of polychlorinated biphenyls (PCBs) in transformer oils from Korea

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Abstract

Using Korean waste official method, polychlorinated biphenyls (PCBs) were analyzed from 33 transformer oils collected under National Institute of Environmental Research (NIER) in Republic of Korea (ROK) and their emission rate in Korea was estimated. Practical quantification limits analyzed by this method were in the ranges of 0.02 and 0.05 $mg\,L^{-1}$, and recovery of samples was in the ranges of 77–97%. The analytical results showed that PCBs in the transformer oils were identified as Aroclor 1242, 1254 or 1260. Twenty-nine samples were determined to contain PCBs of >0.05 $mg\,L^{-1}$ and among these samples, nine samples contained to have >2 $mg\,kg^{-1}$ which is limit of Waste Control Act (WCA) with regard to PCBs in transformer oil from Korea. The concentrations of PCBs in transformer oils were between N.D. (not detected) and 48.33 $mg\,kg^{-1}$. PCBs concentrations did not exceed 50 $mg\,kg^{-1}$ which is generally accepted limit for the definition of waste in POPs Guideline of Basel Convention.
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1. Introduction

Polychlorinated biphenyls (PCBs) are a class of 209 congeners that were widely used in a wide variety of applications, including dielectric fluid in transformers and large capacitors, heat transfer fluids, hydraulic fluids, lubricating and cutting oils, and as additives in pesticides, paints, adhesives, sealants, and plastics. Complex mixtures of PCBs were commercially produced during 1929 to early 1970s. The commercial names of PCBs are known by a variety of trade names, such as Aroclor (USA), Phenoclor (France), Kanechlor (Japan), Sovol (Russia), Chlophen (Germany), and so on [1–4].

PCBs were produced in the United States from 1929 to 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) [3,5]. During this period global production of PCBs was approximately 1.3 million tons with 625,000 t generated in the United States and 75,000 t exported to other countries [5–7]. The widespread release of PCBs into the environment presents a serious problem due to their per-

sistency and toxicity. The toxic effects are compounded by the hydrophobicity of PCBs, which causes them to bio-accumulate in the fatty tissues of animals [8,9]. 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 these senses, United States Environmental Protection Agency (USEPA) has identified remediation of PCB-contaminated soil as a high priority. Furthermore, it was reported that the recycled transformer oils were often contaminated with trace amount of PCBs (UNEP Chemicals, 1999).

In 1999, ROK the Environmental Law [10] regarding PCBs in transformer oil limit was changed from 50 to 2 $mg\,L^{-1}$ for liquid waste [7]. According to the Stockholm Convention on Persistent Organic Pollutants (POPs) entered into force on May seventeenth 2004, 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. 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 [11].

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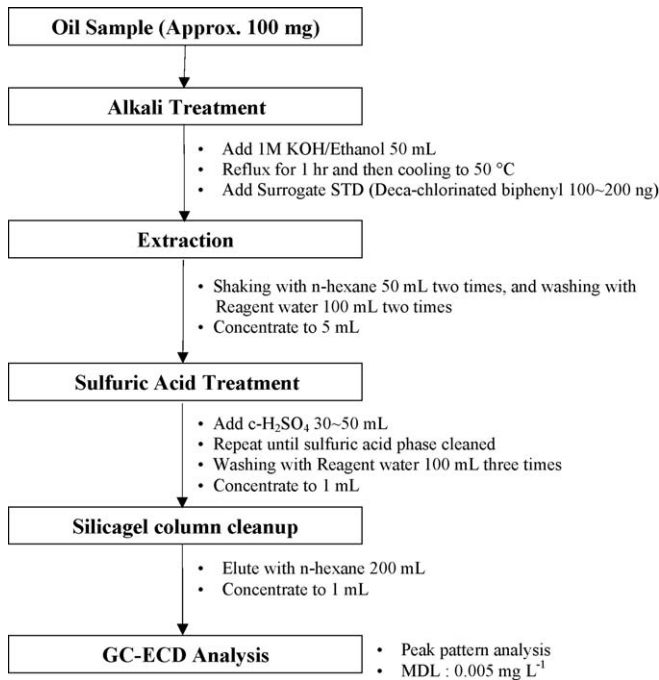 *E-mail address:* shinsun@me.go.kr (S.K. Shin).

Fig. 1. Flow chart for pre-treatment procedure of PCBs in transformer oil.

PCBs is analyzed with capillary column GC-ECD [11–13], quadrupole low-resolution GC/MS and double-focus high resolution GC/MS. All the analytical techniques have accuracy problems in PCBs detection, which are attributed to deterioration in sensitivity and baseline of chromatogram induced by interfering components from sample matrix. It is difficult to separate PCBs from the interfering components derived from the mineral oil because of their similar physical and chemical properties. Analytical techniques with high sensitivity such as high resolution GC/MS require pre-treatment which uses more advanced separation techniques such as multilayer chromatography.

In this study, PCBs analytical methods of US EPA 8082 [13], Canada [12] and Korea [7,11] were compared on quantification peaks selection, and 33 transformer oils were analyzed to determine the release patterns of PCBs based on 'Guideline for PCBs analytical method of transformer oil in Korea'.

2. Experimental method

2.1. Sample collection

Thirty-three samples of transformer oils from various regions of Power Station were collected by NIER in Republic of Korea (ROK). Sampling activities were conducted in accordance with
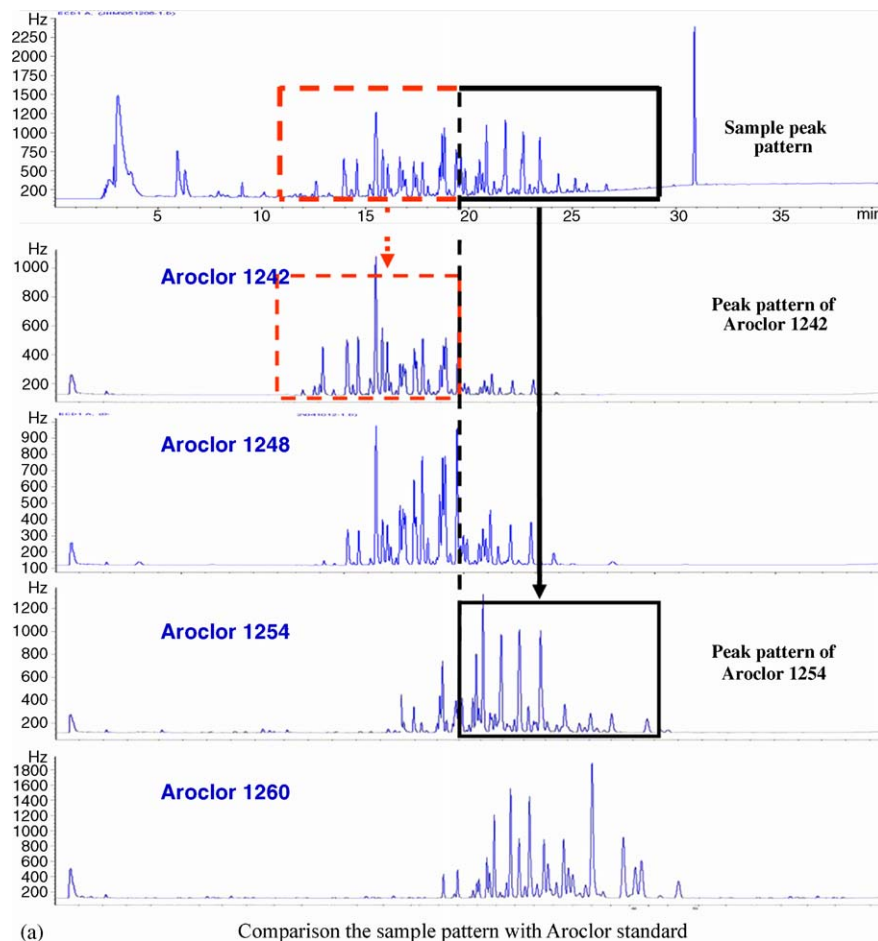

Fig. 2. Quantification method for PCBs in transformer oil: (a) comparison the sample pattern with Aroclor standard; (b) confirmation of the Aroclor mixture pattern; (c) quantification of the confirmed peaks using calibration peaks.
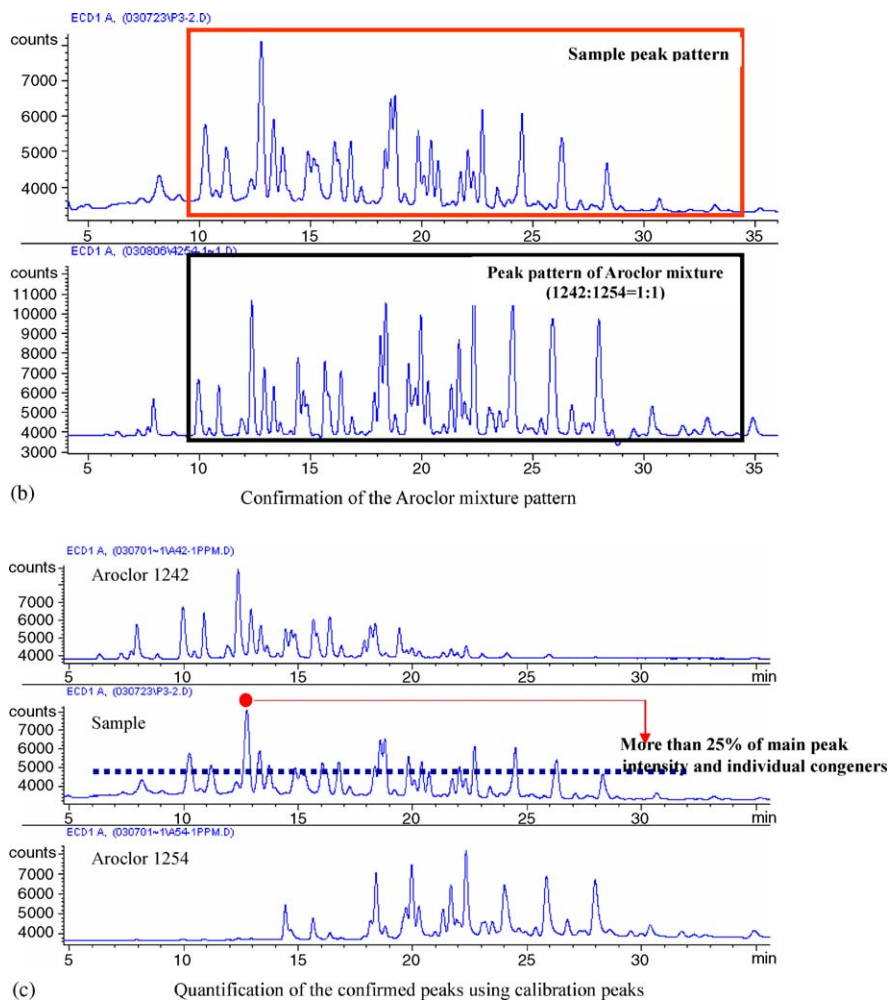
Fig. 2. (*Continued*).

procedures presented in sampling method [7,11]. Before sampling the transformer oil, the working zone with proper signs and disconnecting power by electrician were established. Also, prior to sampling, transformers were inventoried. The transformer valve opened, and collected about 40 mL of sample in amber vial with septum open top cap. When the sample container is filled above half of bottle, the transformer valve was closed carefully. Finally, 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.

2.2. PCBs analysis

Aroclor 1242, 1248, 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, which is described in Fig. 1. [11].

2.2.1. Pre-treatment procedure

Alkali treatment, liquid–liquid extraction, sulfuric acid treatment, silica gel clean-up and instrumental analysis were per-

formed. Flow chart for pre-treatment procedure of PCBs in transformer oil is shown in Fig. 1.

2.2.2. Chromatographic operating conditions

Analyses were conducted on an Agilent 6890N GC equipped with electron capture detector (ECD). An HP-five type GC column (30 m × 0.25 mm i.d., 0.25 mm) 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 280 °C (hold 10 min). A 1 μL of extract was injected in splitless mode (1 min). Injector port temperature was set at 240 °C. ECD temperature was set at 300 °C with nitrogen flow rate 1 mL min^{-1}.

2.2.3. Calibration

Five calibration standards were prepared in graduated amounts to cover the optimum performance range that is 0.2–10 mg L^{-1}. Each standard solution was injected to 1 μL under same GC conditions. 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 Aroclors as shown in Fig. 2.

2.2.4. Quality assurance

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, 1248, 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 10 oil samples. No PCBs were found above the practical quantification limits in the method blank. Laboratory control sample was spiked with 100–200 ng of Aroclor 1242, 1248, 1254, 1260 on free-PCB matrix of each batch. For recovery test, 100–200 ng of decachlorobiphenyl (IUPAC No. 209) was spiked to the every sample.

3. Results and discussion

3.1. Survey result

The transformer survey results of the electric power station, including information regarding transformer type, manufacture's name, country of manufacture and year of manufacture, are presented in Table 1.

The manufactured countries of transformers indicated that 16 of transformers were made in Korea. It was 48.5% of total transformer at Power Station. The Republic of Korea, however, did not produce the pure PCBs to use in dielectric fluid for electrical equipment and for other uses. About 2927–6412 tons of PCBs were probably imported to be used as the commercial products from USA and Japan [5,7]. Nine transformers were manufactured by America, and remaining seven transformers were manufactured by Japan. One transformer did not have information on manufactured country, company, and year.

Table 1
Transformer survey results

Year	Number	Manufacture year	Company	Nation	Sample list
1960	1	1966	FUJI	Japan	A-60S-01
	2	1966	FUJI	Japan	A-60S-02
	3	1968	General Electric	USA	A-60S-03
	4	1968	General Electric	USA	A-60S-04
	5	1968	General Electric	USA	A-60S-05
	6	1969	ASGEN	USA	A-60S-06
	7	1969	HITACHI	Japan	A-60S-07
	8	1969	TOSHIBA	Japan	A-60S-08
1970	9	1970	ASA	USA	B-70S-01
	10	1971	General Electric	USA	B-70S-02
	11	1975	ALSTHOM	USA	B-70S-03
	12	1976	General Electric	USA	B-70S-04
	13	1977	General Electric	USA	B-70S-05
	14	1978	HITACHI	Japan	B-70S-06
	15	1978	FUJI	Japan	B-70S-07
	16	1978	FUJI	Japan	B-70S-08
1980	17	1981	No record	No record	C-80S-01
	18	1981	EWHA Electric	Korea	C-80S-02
	19	1983	HYOSUNG	Korea	C-80S-03
	20	1983	HYOSUNG	Korea	C-80S-04
	21	1985	HYOSUNG	Korea	C-80S-05
	22	1985	HYOSUNG	Korea	C-80S-06
1990	23	1991	HYOSUNG	Korea	D-90S-01
	24	1991	HYUNDAI	Korea	D-90S-02
	25	1991	HYUNDAI	Korea	D-90S-03
	26	1994	Icheon Electric	Korea	D-90S-04
	27	1994	Korea Cottrell	Korea	D-90S-05
	28	1998	HYUNDAI	Korea	D-90S-06
	29	1998	HYOSUNG	Korea	D-90S-07
	30	1998	HYOSUNG	Korea	D-90S-08
	31	1998	HYOSUNG	Korea	D-90S-09
	32	1999	HYUNDAI	Korea	D-90S-10
	33	1999	EWHA Electric	Korea	D-90S-11

Manufactured year of transformers were shown as Fig. 3. These results indicated that eight (24.0%) of transformer were manufactured between 1971 and 1980. Among then, eleven (33.3%) of transformer was manufactured between 1991 and 1999.

3.2. Analytical results

The transformer oil samples were analyzed at NIER of Seoul, Korea. This project was performed to measure the release pattern of existing PCBs in transformer oil. The survey included analysis of 33 samples, six duplicate sample for quality control, and 12 quality assurance transformer oil samples from various locations.

Practical quantification limits analyzed by our method were $0.02\,mg\,L^{-1}$ for Aroclor 1242 and $0.05\,mg\,L^{-1}$ for Aroclor 1248, 1254, and 1260. The oil weighed as mass unit was converted to volume unit by measuring the density of the each transformer oil to satisfy the Korean regulation limit of $2\,mg\,L^{-1}$ (unit is not $mg\,kg^{-1}$). Quantification units in the results were recorded as $mg\,L^{-1}$. Recoveries of the sample preparation method were evaluated using an oil sample spiked with a mixture of Aroclors (1242:1248,1254 and 1260) at three different concentration
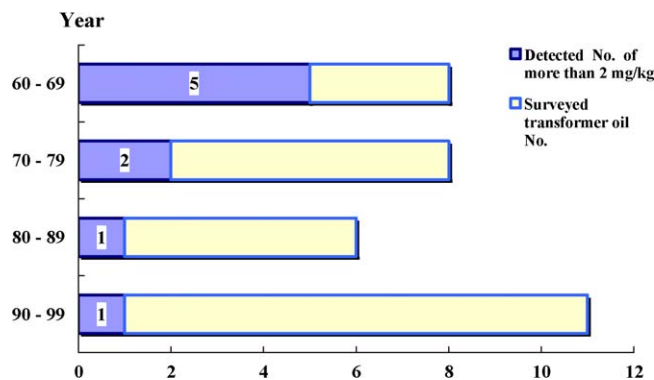

Fig. 3. Manufactured year of survey transformer.

levels. Average recoveries over 90% and relative standard deviations below 10% were achieved. In view of these results, data for real polluted samples were not corrected for recovery.

The calibration solution of Aroclor 1242, 1248, 1254 and 1260 standard, respectively, was prepared five concentrations, and the linearity of Aroclor by GC-ECD was above 0.99. Continuing calibration verification was checked with 100–200 ng of Aroclor 1242, 1248, 1254, and 1260 calibration solution before

Table 2
Analytical results of survey transformer oil

Number	Sample list	Patterns	Recovery[a] (%)	Concentration
1	A-60S-01	Arol254	81	<2 ppm
2	A-60S-02	Arol254	83	<2 ppm
3	A-60S-03	Arol254:1260 = 1:1	83	<2 ppm
4	A-60S-04	Arol254	84	>2 ppm
5	A-60S-05	Arol242	95	>2 ppm
6	A-60S-06	Arol260	80	>2 ppm
7	A-60S-07	Arol242:1254 = 1:1	85	>2 ppm
8	A-60S-08	Arol242:1260 = 3:2	87	>2 ppm
9	B-70S-01	Arol260	95	<2 ppm
10	B-70S-02	Arol254	89	>2 ppm
11	B-70S-03	Arol260	89	>2 ppm
12	B-70S-04	Arol242:1254:1260 = 1:1:1	77	<2 ppm
13	B-70S-05	N.D.	86	N.D.
14	B-70S-06	Arol260	84	<2 ppm
15	B-70S-07	Arol254	91	<2 ppm
16	B-70S-08	Arol242:1254 = 1:1	93	<2 ppm
17	C-80S-01	Arol242:1254:1260 = 1:1:1	82	<2 ppm
18	C-80S-02	Arol260	97	<2 ppm
19	C-80S-03	Aro 1242:1254 = 5:1	96	<2 ppm
20	C-80S-04	Aro 1242:1254 = 5:1	96	>2 ppm
21	C-80S-05	Aro 1242:1254 = 5:1	73	<2 ppm
22	C-80S-06	Aro 1242:1254 = 5:1	92	<2 ppm
23	D-90S-01	N.D.	92	N.D.
24	D-90S-02	N.D.	95	N.D.
25	D-90S-03	Aro1260	93	<2 ppm
26	D-90S-04	Aro1260	87	<2 ppm
27	D-90S-05	Aro1254	91	<2 ppm
28	D-90S-06	Aro 1254:1260 = 2:1	86	<2 ppm
29	D-90S-07	Aro 1242:1254 = 2:1	85	<2 ppm
30	D-90S-08	Aro1260	85	<2 ppm
31	D-90S-09	Aro 1242:1254 = 2:1	82	<2 ppm
32	D-90S-10	N.D.	85	N.D.
33	D-90S-11	Arol242:1254:1260 = 1:1:1	81	>2 ppm

[a] Average of 2–3 times duplicate analytical results.

analyzing each batch sample to ensure that the calibration has not drifted. Surrogate recovery of all samples were 77–97% and all results of quality control by our analytical method, such as laboratory control sample, matrix spike sample, sample duplicate were within these limits. These results were satisfied to the recovery ranges of 75–120% in presenting the Korean waste official method.

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. 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. Fig. 4 showed a typical chromatogram of oil extract with various peak patterns.

The results of peak pattern analysis have explained that 4 from 33 transformer oils were not contaminated with PCBs as present in Table 2. Other analyzed samples contained on the

chromatograms corresponded to the different types of PCBs mixtures. On the chromatograms of the 15 samples, the peaks corresponding to the pure Aroclor 1242, 1254 and 1260 were observed. Others contained the different commercial mixtures as shown in Figs. 4 and 5. In this study, various kinds of PCBs patterns were present in about 42.2% of analyzed samples.

The total PCBs concentration was determined by a peak pattern matching and summation the selected peaks to obtain a total amount. Among 33 transformer oil samples, 29 samples were determined to contain the PCBs above 0.05 mg L^{-1} and nine samples were greater than 2 mg kg^{-1} which is limit of ROK the Environmental Law [10] regarding PCBs in transformer oil. Fig. 6 showed the total PCBs content of transformer sample containing more than 2 mg kg^{-1} of PCBs.

The levels of PCBs in transformer oils were in between N.D. and 48.33 mg kg^{-1}. The PCBs concentrations did not exceed 50 mg kg^{-1} which is a generally accepted limit for the definition of waste in POPs Guideline of Basel Convention [14,15].
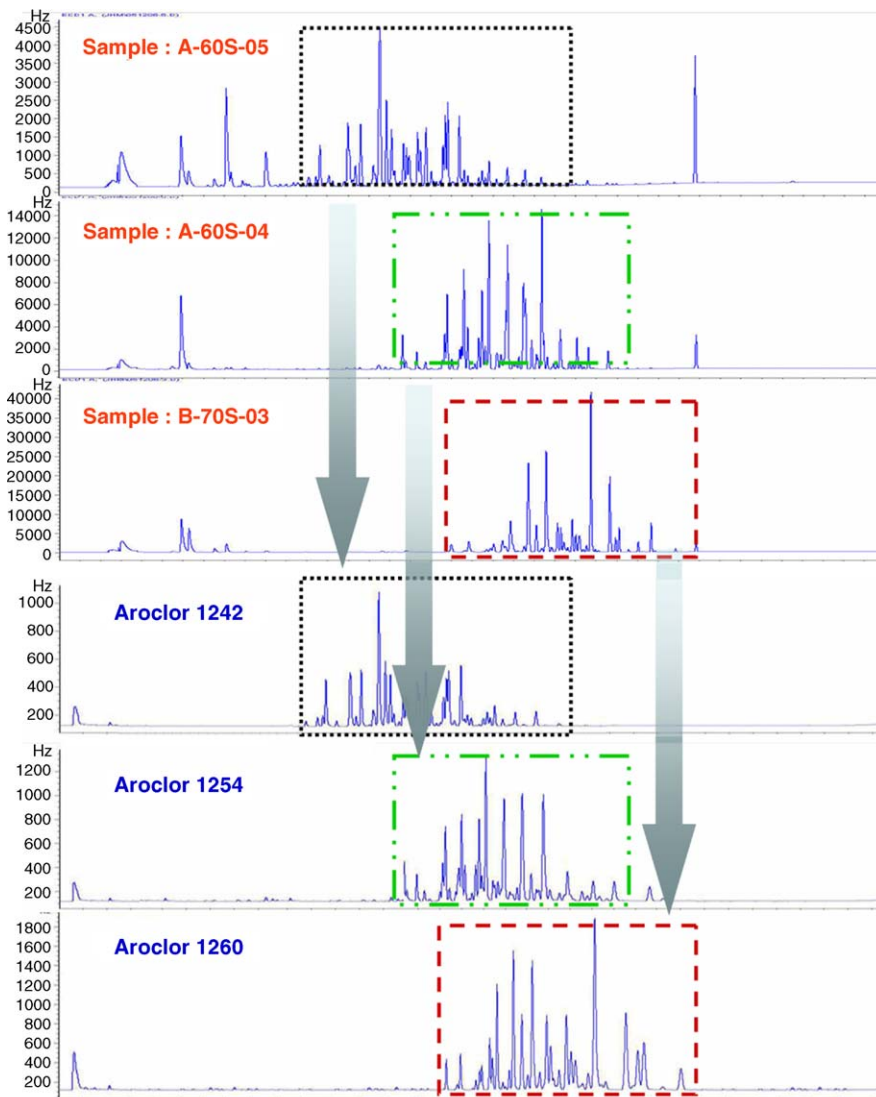

Fig. 4. Sample chromatograms of the single Aroclor commercial product contained.
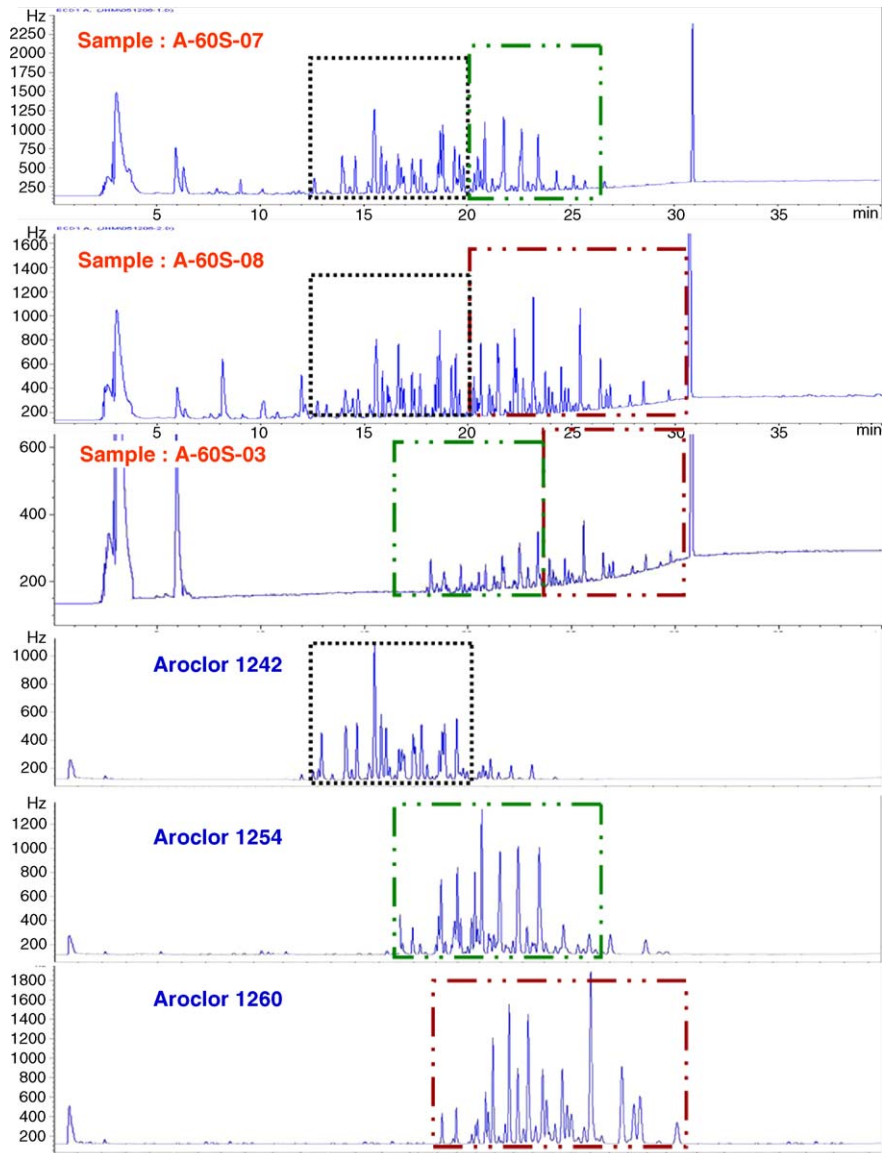
Fig. 5. Sample chromatograms of the mixed Aroclor commercial product contained.

3.3. Comparison the analytical results

The collected samples were analyzed using the quantification methods of Korean waste official methods. Also, the results were compared to the USA EPA 8082 and Canada method using different index peaks for quantification.

The quantification has been performed with three calibration standard solution. The peak height should be within the sensitivity range of the ECD. Extracts from of oil samples, prepared as described in Fig. 1, were quantified using US EPA, Canada and Korea official methods. In EPA 8082 method, three to five index peaks selected to calculate PCBs concentration, and the three to five main peaks and some minor peaks were selected in Canada method (Fig. 7). In Korean method, however, the total peaks at least 25% of the height of the largest peaks were selected.

The PCBs concentrations of two samples (B-70S-08 and D-90S-03) were compared. The analyzed sample of P-030415-12 showed a concentration range from 1.30 to 1.34 mg L^{-1}, and from 1.93 to 1.94 mg L^{-1} for P-030415-42. The each method selected the different peaks to calculate the concentration the samples. As the results by analyzing the Korean official method showed the similar results of other PCBs analytical methods.
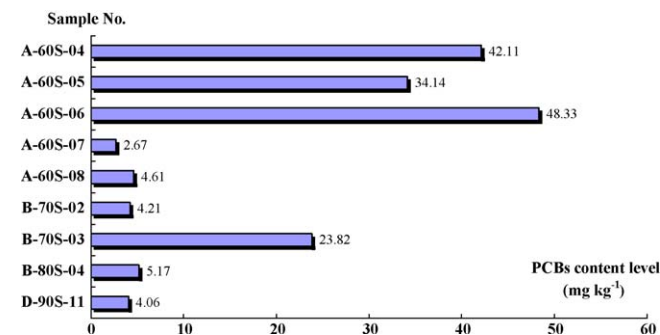

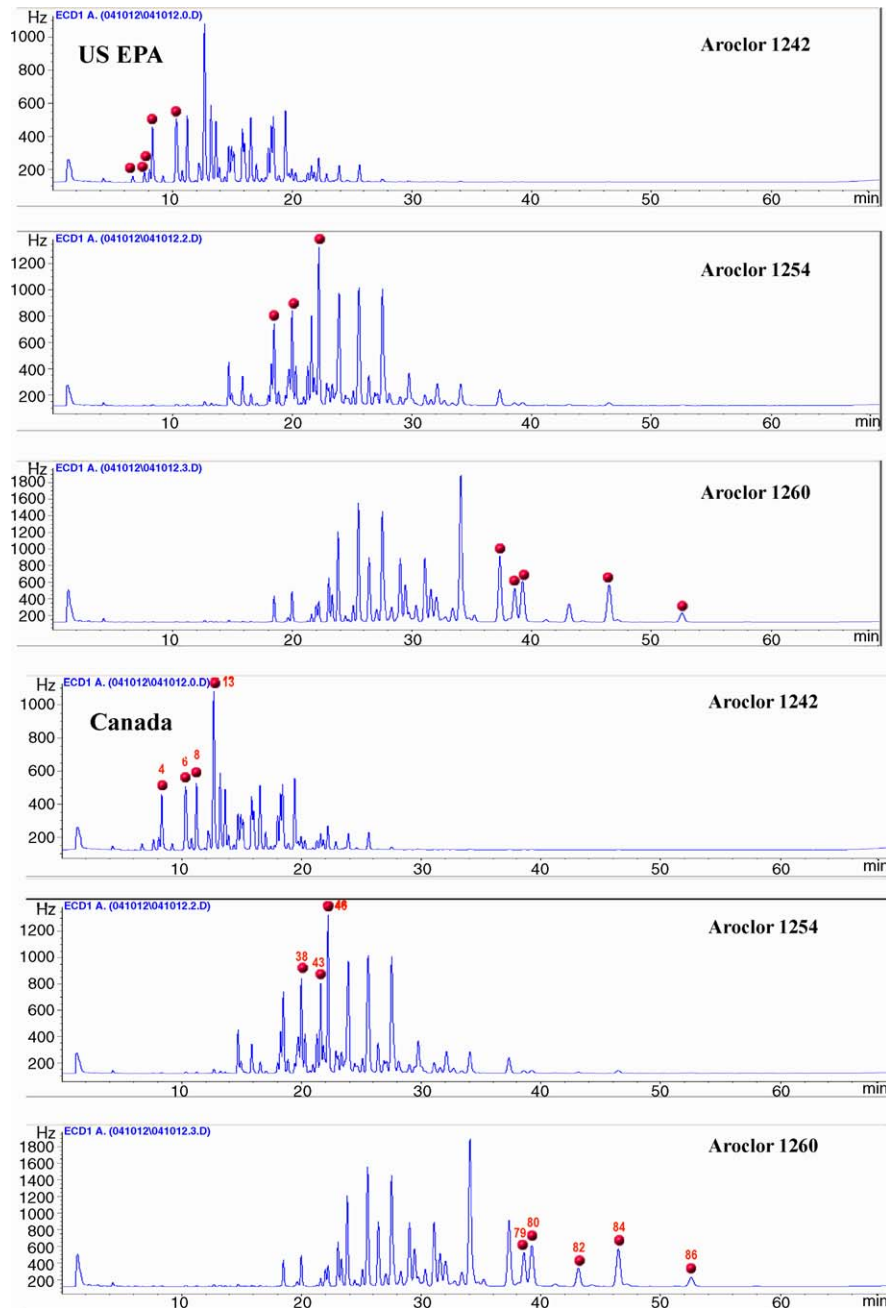Fig. 6. Total PCBs content of transformer samples exceeding the regulation value.

Fig. 7. Quantification peaks of US EPA 8082 and Canada analytical methods using in this study.

4. Conclusion

Thirty-three transformer oils were analyzed as a main source of PCBs emission into environments and collected by NIER in Republic of Korea. The method used to analyze the transformer oil samples was Korean waste official method (KWOM) of Environment Ministry for PCB analysis. Practical quantification limits analyzed by our method were 0.02–0.05 mg L^{-1}, and the recovery of all samples were 77–97%. The analysis results showed that PCB in the transformer oils was identified as Aroclor 1242, 1254 or 1260. Some of PCBs were mixture of Aroclor 1242 and 1260, 1254 and 1260, 1242 and 1254 or 1242, 1254, and 1260. On the start from chromatograms of

the 15 samples, the peaks corresponding to the pure Aroclor 1242, 1254 and 1260 were observed. In this study, different PCBs mixtures were present in about 42.2% of analyzed samples. Nine samples were greater than 2 mg kg^{-1} which is limit of the Environmental Law [10] regarding PCBs in transformer oil. The levels of PCBs in transformer oils are ranged from N.D. to 48.33 mg kg^{-1}. The PCBs concentrations did not exceed 50 mg kg^{-1} which is a generally accepted limit for the definition of waste in POPs Guideline of Basel Convention. As the results of comparing the analytical concentration using several quantification methods, the results by analyzing the Korean official method showed the similar results of other PCBs analytical methods.

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