ANALYTICAL METHOD OF POLYCHLORINATED BIPHENYLS IN TRANSFORMER OIL CONTAMINATED SOILS

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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. 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 of 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 tries to revise the Soil Official Testing Method by adding the quality control concept.[1~6]

PCBs is analyzed with an analytical equipment as capillary column GC-ECD and quadruple low-resolution GC/MS. These analytical techniques have accuracy problems in PCBs detection, which are attributed to deterioration in sensitivity and background induced by interfering components in analytical matrix. It is difficult to separate PCBs from the interfering components derived from the mineral oil because of their similar physical and chemical properties. In this study, PCBs analytical methods of ISO10382, ISO 61618, and Korean (soil & waste) compared with selecting quantification peaks, and three transformer oils contaminated soils analyzed to show the applicability based on proposed guideline for PCBs analytical method of transformer oil contaminated soils.[7~10]

2. Materials and Methods

Aroclor 1242, 1248, 1254 and 1260 standards (Supelco Co.) were used in this study. The main instrument was a HP 6890 equipped with electron capture detector. A capillary column (HP-5, 30 m × 0.32 mm, film thickness 0.25 um) was installed. The injector temperature was held at 200°C. The detector temperature set 250°C with nitrogen make-up gas at a flow rate 17 psi. The temperature program of the column of the column was started at 140°C; 2.5°C/min. until 200°C, 0.5°C/min. until 220°C and 10°C/min. until 270°C. PCB-209 was used as a surrogate standard. A 1µL 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 30-100 g of transformer oil contaminated soil was dissolved in hexane and pretreatment processes such as alkali treatment, acid treatment, column cleanup etc. as shown in Fig. 1. Four analytical methods were compared as shown Table 1 and Fig. 2. The numbers of the quantification peaks are various depending on the method
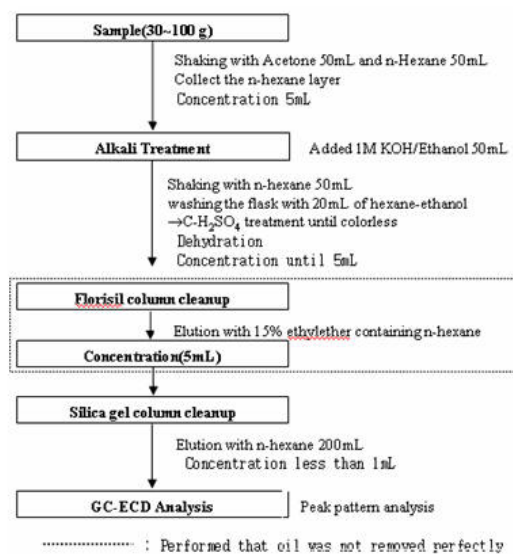

Fig. 1. Analytical procedures of PCBs

Sample preparation and analysis

Table 1. Comparison the PCBs analytical method[7~10]

|	Analytical Method	Cleanup Process	Internal Std.	Instrument	Quantification
Korea	Official Soil Test Method	- Alkali Treatment - Slicagel /Florisil column		- GC(ECD) - Capillary	- Peak pattern - Total Isomer peak
	Official Waste Test Method	- Akali Treatment - c-H_2SO_4 Treatment - Slicagel /Florisil column	- C-209	- GC(ECD) - Capillary	- Peak pattern - Index peak(13-18)
USA	EPA Method 8082	- c-H_2SO_4 Treatment - $KMnO_4$ Treatment	- C-209 - TCMX	- GC(ECD) - Capillary	- Peak pattern - Index peak(3-5)
Japan	Industrial Waste analytical method	- Alkali Treatment - Silicagel column - Florisil column		- GC(ECD) - Packed	- Coefficient comparison - Total Isomer peak
Germany	DIN EN 61619 ISO 61619	- 100:1 dilution - Acid column - Silicagel column	- C-209 - C-30	- GC(ECD) - Capillary	- Peak pattern - Index peak(13)
ISO	ISO10382	- Liquid extraction - Alumina column	- C-155 - C-143 - C-207	- GC(ECD) - Capillary	- Peak pattern - Index peak(7)
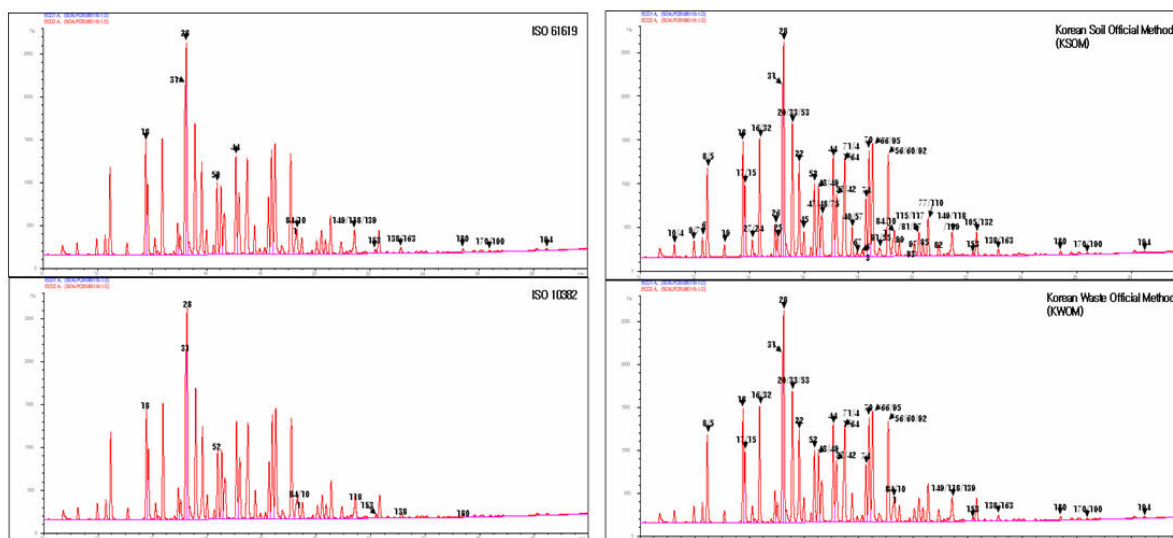
Fig. 2. Quantification peaks of each analytical method

3. Results and Discussion

3.1 Comparison of the quantification concentration

For comparison the quantification concentration, two extraction method applied to PCBs contaminated soil samples and four quantification method applied.   In soxhlet extraction, acetone:hexane (1:1, v/v) solvent was used for 16~24 hr, and alkali & liquid-liquid extraction was performed.   The detected concentration showed in Fig. 3.   The higher concentration was detected in soxhlet.

The quantification has been performed to three calibration standard solution. The peak height should lie within the linear range of the ECD detector. The quantification method of ISO and Korea were compared method as shown in Fig. 2. In ISO method, seven to thirteen index peaks selected to calculate PCBs concentration. However in Korean method the total peaks for KSOM and the least 25% of the height of the largest peaks and thirteen individual peaks (IUPAC No. 18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 170, 180, 194) were selected for KWOM.
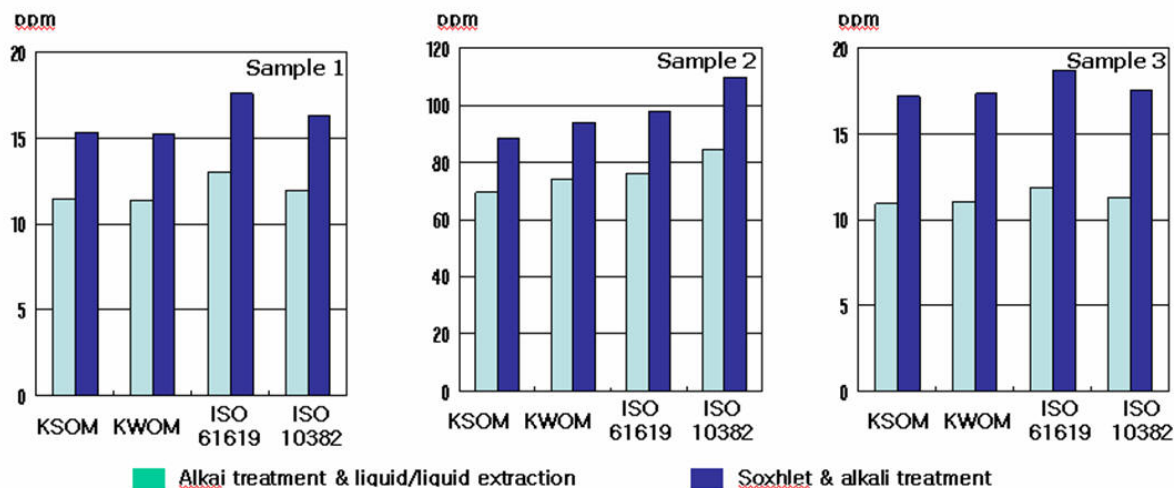
Fig. 3. Comparison of Two extraction method using PCBs oil contaminated Soils

3.2 Oil removal Treatment

To remove the oil in the samples, the alkali treatment was performed. Most of the samples can be removed the oils effectively. But, some soil samples can not remove the oil, so the extract was applied to the florisil column. After that the extract can be also removed, too. In this case, the DMSO treatment applied to separate the PCBs peaks as shown in Fig. 4.

3.3 Column chromatography clean-up

Sample extract clean-up was carried out by packed silica column chromatography. The use of multi-layer silica column in combination with basic and acidified silica for clean-up resulted in cleaner extracts than silica or Florisil. To optimize the volume of column elution, fraction test of multilayer silica and florisil column were studied. The elution amount of multilayer silica and florisil column were determined with 200 mL and 140 mL of hexane, respectively. In this study, the collected fraction fractions extended from 300 mL to 200 mL of elutes for PCBs in multilayer silica column cleanup. The collected fractions were evaporated to incipient dryness by gentle stream nitrogen at 40 ^{o}C.

Fig. 4. DMSO treatment sample chromatogram

3.4 Sample analytical results

Three contaminated oil samples were analyzed. Practical quantification limits analyzed by our method were 0.0005 mg kg^{-1} for Aroclor 1242, 1248, 1254 and 1260. Quantification units in the results were recorded as mg L^{-1}. The cleanup procedure used in the present study has been tested with Aroclor 1242:1248:1254:1260 mixture
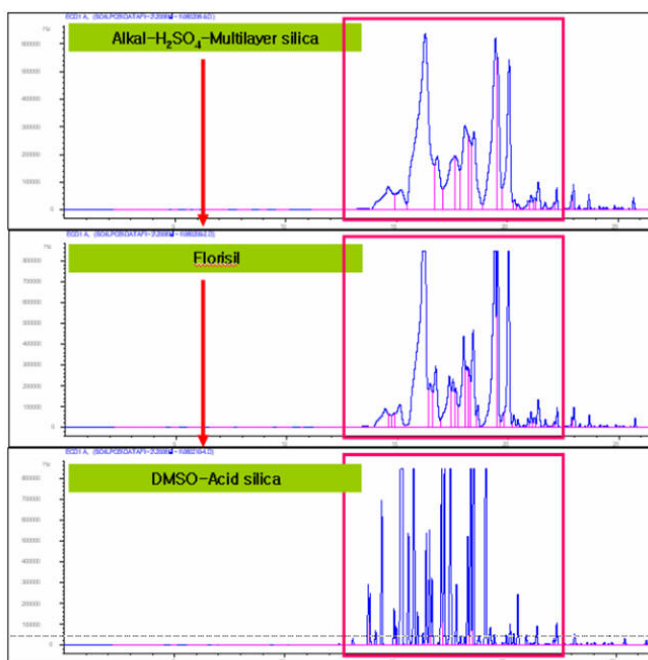
solution with containing transformer oil spiked with three different levels.

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 analyzing each batch sample to ensure that the calibration has not drifted. The criteria of laboratory control sample, matrix spike sample, sample duplicate and surrogate recovery of all samples were 64~95% and all results of quality control by our analytical method were within these limits. These results were satisfied to the recovery ranges of 60~120% in proposed Korean soil 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. 5 showed a typical chromatogram of oil extract with various peak patterns. The results of peak pattern analysis showed in Fig. 4. The analyzed samples contained on the chromatograms corresponded to the different types of PCBs mixtures.
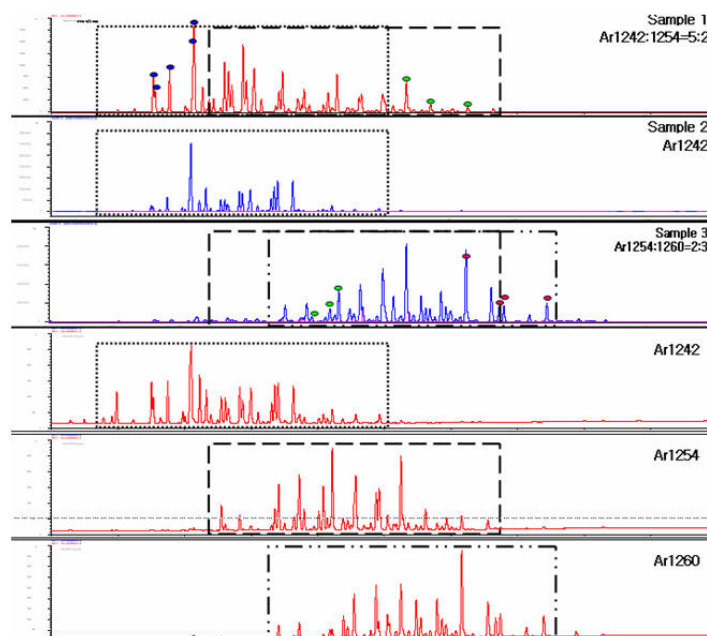

Fig. 5. Sample chromatograms

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