

ANALYSIS OF PCBs-CONTAINING WASTES USING SCREENING SURVEYING METHODS, KOREA

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Abstract

The PCBs containing waste samples were analyzed using Chlorine contents and GC/ECD methods. Chlorine(Cl) content was analyzed using L2000DX. The L2000DX for Cl contents analysis was applied to the transformer oil, but the detection limit was reported greater than 2 ppm, and the false positive results represented greater than 25% in comparing experiments. This method can not be directly applied to the PCBs waste or not because the regulation standard is 2 ppm in Waste Management Law. So, this Cl contents method using L2000DX is used as the guidance for managing of PCBs waste or not. Also, Rapid GC/ECD method developed to save the time, cost, simple analytical method, and effective management of PCBs waste. This method was modified the original PCBs analytical method in Waste Official Test Method in Korea. As the result, the appropriate management of PCBs containing wastes using screening surveying methods to manage effectively by considering the current status in Korea was proposed.

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 1970's. 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.

PCBs were produced in the United States from 1929 and 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). During this period global production of PCBs was approximately 1.3 million tons with 625,000 tons generated in the United States and 75,000 tons exported to other countries. In Korea, about 4,000 tons of PCBs imported from Japan and USA as shown in Fig. 1. The widespread release of PCBs into the environment presents a serious problem due to their persistency and toxicity. The toxic effects are compounded by the hydrophobicity of PCBs, which causes them to bio-accumulate in the fatty tissues of animals. 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. Table 1 showed the PCBs treatment criteria and treatment technology.

In 1999, ROK the Environmental Law regarding PCBs in transformer oil limit was changed from 50 mg L⁻¹ to 2 mg L⁻¹ for liquid waste. 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.

Materials and Methods

The PCBs containing waste samples were analyzed using Chlorine contents and GC/ECD methods. Chlorine(Cl) content was analyzed using L2000DX. 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 µm) 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 1 µL 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 0.1-0.5 g of transformer oil was dissolved in hexane and pretreatment processes such as alkali treatment, acid treatment, column cleanup etc. as shown in Fig. 2.

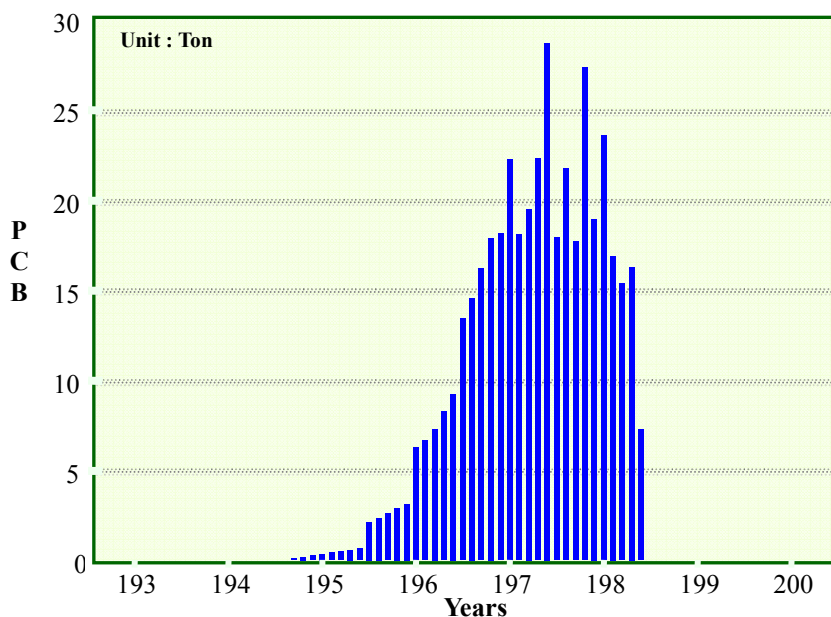


Fig. 1. The usage of Korea data from Breivik K. *et al.*, 2002.

Table 1. PCBs treatment criteria and treatment technology

Country	Regulation Conc.	Treatment Method (Final criteria)	Facilities No.	
			Incinerator (ton/yr)	Chemical
U.S.A	More than 50 ppm	HT Incineration & Chemical(2 ppm)	4	15
Canada	More than 50 ppm	HT Incineration & Chemical (2 ppm)	2(43,000)	10
U.K	More than 50 ppm	> 50 ppm : HT Incineration 10-50 ppm : Incineration or Chemical	3(9,500)	-
Germany	More than 50 ppm	HT Incineration & Chemical(50 ppm)	5(22,250)	-
France	More than 50 ppm	HT Incineration & Chemical(50 ppm)	3(35,000)	1 (2,000)
Netherlands	More than 50 ppm	HT Incineration & Chemical(5 ppm)	2(5,660)	
Australasia.	More than 50 ppm, 50g	HT Incineration & Chemical	-	7(5,400)
Japan	More than 0.5 ppm	HT Incineration & Chemical (0.5 ppm)	(5,500)	-
Korea ^{*1)}	More than 2 ppm	HT Incineration or Pyrolysis	1(200)	-

*1) Data based on UNEP(the incinerator currently stopped), HT : High Temperature.

Results and Discussion

In Korea, about more than 70% of discharged transformer oils were PCBs free oils (< 2 ppm) as shown in Fig. 3, therefore screening methods such as Cl contents measurement method and Rapid GC/ECD method were considered the current discharging status of transformer oil. The L2000DX for Cl contents analysis was applied to the transformer oil, but the detection limit was reported greater than 2 ppm, and the false positive results represented greater than 25% in comparing experiments. This method can not be directly applied to the PCBs waste or not because the regulation standard is 2 ppm in Waste Management Law. So, this Cl contents method using L2000DX is used as the guidance for managing of PCBs waste or not.

Also, Rapid GC/ECD method developed to save the time, cost, simple analytical method, and effective management of PCBs waste. This method was modified the original PCBs analytical method in Waste Official Test Method in Korea. As the result, the appropriate management of PCBs containing wastes using screening surveying methods to manage effectively by considering the current status in Korea was proposed as shown in Fig.4. As you can see this Fig. 4, the proposed analytical method was omitted the acid treatment steps, but the multi silica column cleanup introduced.

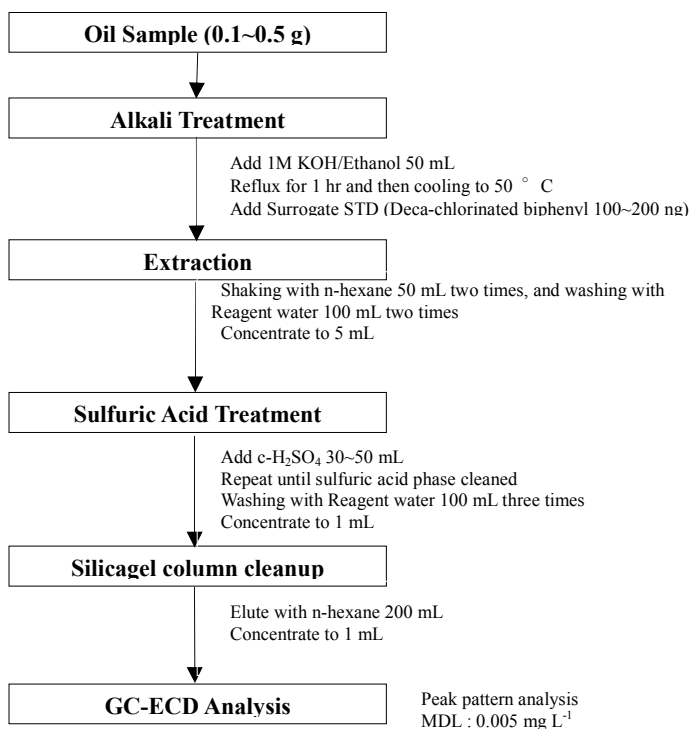


Fig. 2. Flow chart for pre-treatment procedure of PCBs in transformer

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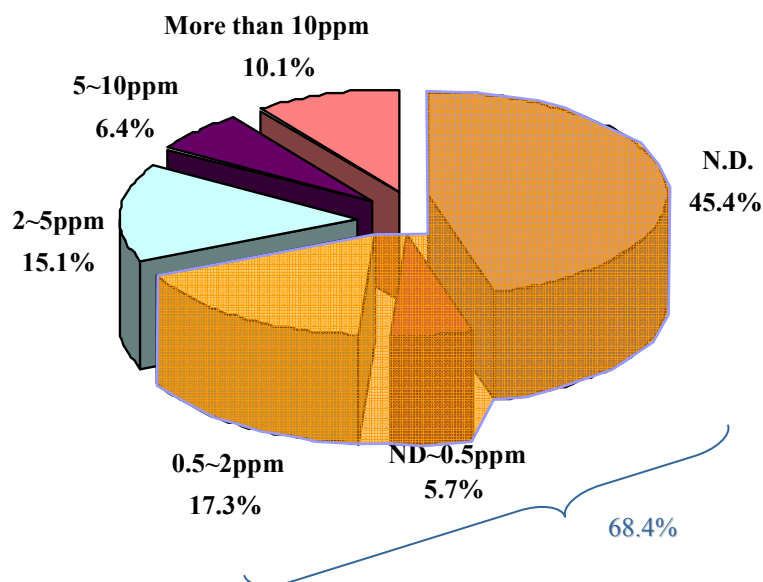


Fig. 2. Discharging Result of Transformer Oils in Korea(Exemplification)

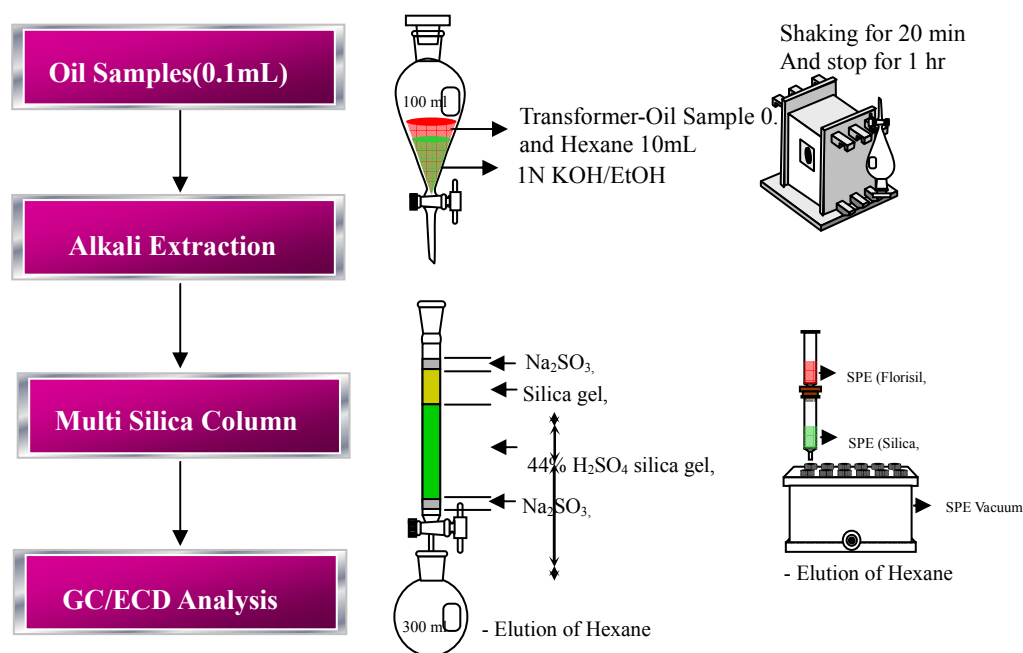


Fig. 4. Proposed Rapid GC/ECD Analytical method

References

1. Dale R. Rushnck, Andy Beliveau, Brian Fowler, Coreen Hamilton, Dale Hoover, Katharine Kaye, Marlene Berg, Terry Smith, William A. Telliard, Henry Roman, Eric Ruder, Liza Ryan, Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA Method 1668A, *Chemosphere*, 54 (2004) 79-87.
2. Dobson, S. and Van Esch, G. J., 1993. Polychlorinated Biphenyls and Terphenyls (2nd Eds), WHO, Geneva.
3. Erickson. M. D., Analytical Chemistry of PCBs, Lewis Publishers, New York, 1997.
4. Sulkowski, W., and Rosinska, A., Comparison of the efficiency of extraction methods for PCBs from environmental wastes, *Journal of Chromatography*, 845 (1999) 349-355.
5. Breivik. K., Sweetman. A., Pacyna. J. M., and Jones. K. C., Toward a global historical emission inventory for selected PCB congeners : a mass balance approach 1. Global production and consumption. *The Science of the Total Environment*. 290 (2002) 181-198.
6. De Voogt, P., Brinkman, U., 1989. In : Kimbrough, R. D., Jensen, A. A. (Eds), *Halogenated Biphenyls, Terphenyls, Naphthalene, Dibenzodioxins and Related Products*, Elsevier, Amsterdam.
7. Shin, S.K., Kim, H. J., Chung, D., Kim, J. K., Kim, K.S., Chung, Y.H., Chung, I.R., A Study on the Appropriate Management of PCBs-Containing Wastes, NIER, Republic of Korea, 2003.
8. Ismet Cok, M. Hakan Satirohlu, Polychlorinated biphenyl levels in adipose tissue of primiparous women in Turkey, *Environment International*. 30 (2004) 7-10.
9. Monosson E., Ashley J.T.F., McElroy A.E., Woltering D., Elskus A.A., PCB congener distributions in muscle, liver and gonad of *Rundulus heteroclitus* from the lower Hudson River Estuary and Newark Bay, *Chemosphere*, 52 (2003) 777-787.
10. Ministry of Environments in Korea, Management of Waste Act, 2004.
11. Ministry of Environments in Korea, Korean waste official method, 2004.
12. Basel Convention, Preparation of technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with PCBs, PCTs or PBBs, UNEP/CHW.7/8/Add.2, Geneva, 2004.
13. Shin, S.K., Kim, T. S., OH, G. J., Jeon, T. W., Yoon, J. G., Lee, J. A., Yoon, D. K., Management of PCBs-Containing Wastes using Screening Surveying Methods, NIER, Republic of Korea, 2007.