

Rapid Method for Quantification of PCB in Transformer Oil

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1. Introduction

PCB (poly chlorinated biphenyl) was used as thermal oil and transformer oil as it features remarkable chemical stability and electrical insulating properties. Production and use of PCB, however, were banned in Japan in 1972 because PCB was found to be the serious environmental contaminant and toxicity. Since then users of the PCB equipment have been required to retain it. Depending on its applications, concentration of PCB retained is widely varied. PCB used as electric condenser oil, for instance, features purity of 100%. On the other hand, used pole transformer oils are contaminated with PCB of as low as several tens parts per million.

Chemical decomposition method was approved to treat PCB contaminants in addition to the existing incineration method, setting the standard at 0.5ppm[mg/kg-oil] or below in Japan. Authors currently study BCD (base catalyzed decomposition) process, one of the chemical treatment methods of PCB[1]. Chemical decomposition of PCB gives biphenyl and trace low-chlorinated PCB. In order to grasp PCB decomposition behavior, it is necessary to monitor the PCB concentration by isomers as well as to analyze the total PCB concentration. To run PCB treatment plant, real-time PCB analysis should be necessary.

In PCB analysis, samples are generally evaluated, following clean-up, with GC-ECD, low-resolution GC/MS (LRGC/MS), or high-resolution GC/MS (HRGC/MS), depending on matrix. PCB analysis with GC-ECD, however, features low sensitivity against low chlorinated PCB such as monochlorobiphenyl and dichlorobiphenyl. In PCB analysis with HRGC/MS, thorough clean-up is required, depending on matrix, in order to sufficiently separate PCB. To measure low-level PCB in transformer oil, in particular, combination of clean-up and HRGC/MS is necessary. This clean-up, however, requires sophisticated skills and long time to complete. There are several simple methods for PCB quantification such as potentiometric titration of TOX (total organic halogen) [2] and immunoassay, but they are not applicable to 0.5 ppm or below. The conventional analytical methods are not capable of collecting sufficient information required for operation of PCB treatment plant. This paper reports a new analytical method for low-level PCB in transformer oil. This method employs SPE (solid phase extraction) and LRGC/MS, aiming at reducing analysis time and detecting low chlorinated PCB at high sensitivity.

2. Experiment

2.1 Reagents

Dimethylsulfoxide (DMSO): Wako Pure Chemical Industries, Japan

Sodium Sulfate, anhydrous : Wako Pure Chemical Industries, Japan

n-Hexane: Wako Pure Chemical Industries, Japan

PCB standards, Window defining mixture: Cambridge Isotope Laboratories, USA

M1CB:2-monochlorobiphenyl, 4-monochlorobiphenyl

D2CB:2,6-dichlorobiphenyl, 4,4'-dichlorobiphenyl

T3CB:2,2',6-trichlorobiphenyl, 3,4,4'-trichlorobiphenyl

T4CB:2,2',6,6'-tetrachlorobiphenyl, 3,3',4,4'-tetrachlorobiphenyl

P5CB:2,2',4,6,6'-pentachlorobiphenyl, 3,3',4,4',5-pentachlorobiphenyl

H6CB:2, 2',4,4',6,6'-hexachlorobiphenyl, 3,3',4,4',5,5'-hexachlorobiphenyl

H7CB:2,2',3,4,5,6,6'-heptachlorobiphenyl, 2,3,3',4,4',5,5'-heptachlorobiphenyl

O8CB:2,2',3,3',5,5',6,6'-octachlorobiphenyl, 2,3,3',4,4',5,5',6-octachlorobiphenyl

N9CB:2,2',3,3',4,4',5,5',6-nonachlorobiphenyl, 2,2',3,3',4,4',5,5',6-nonachlorobiphenyl

D10CB:2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

¹³C-PCB standards: Cambridge Isotope Laboratories, USA

¹³C₆-4-monochlorobiphenyl

¹³C₁₂-3,3',4,4'-tetrachlorobiphenyl

¹³C₁₂-2,2',3,3',5,5',6,6'-octachlorobiphenyl

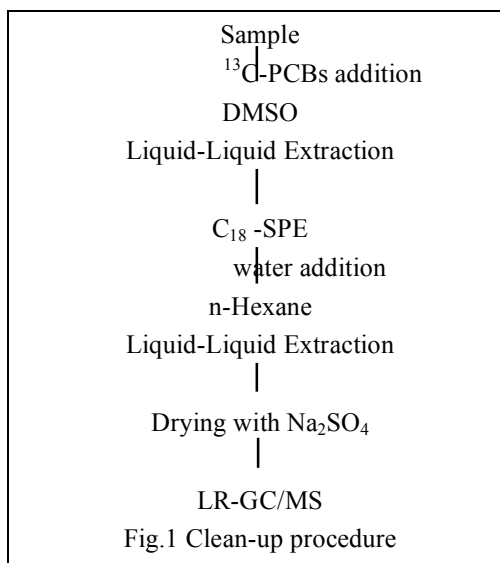
¹³C₁₂-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl

Solid phase extraction cartridge (SPE): Waters

Sep-Pak tC18:-SiC18H37

2.2 Extraction Method

Figure 1 shows procedure for clean-up. 2.5 ml of DMSO is added to 0.2g of sample to which internal standards (IS) of ¹³C-PCB is added. Then the sample solution is stood after being shaken vigorously. The upper layer is removed and 1 ml of DMSO is taken from the lower layer to be directly loaded to SPE using a glass syringe. 1 ml of deionized water is added to the solution. The solution is shaken and stood. 1 ml of n-hexane is added, and the solution is shaken vigorously. Hexane layer is collected and dried with sodium sulfate. The clean-up sample is



analyzed by mean of the LRGC/MS. The clean-up is completed with 30 minutes.

2.3 LRGC/MS Condition

Measurement conditions of GC/MS are described below.

Equipment : gas chromatograph/mass spectrometer HP6890/MSD

1) GC : HP6890

capillary column : HP-5MS (30m x 0.25mm x 0.25um)

column temperature :

50 °C (3min. hold) – 30 °C /min. – 200 °C - 8 °C /min. – 280 °C (10min. hold)

2) MS : MSD

ionization method : EI

ionization energy : 70 eV

3. Result

3.1 Extraction Pattern

Extraction pattern of PCB in the clean-up procedure using SPE was evaluated. 1 ml of DMSO was injected to SPE according to the procedure shown in Fig.1. We analyzed sample of PCB standard, and collected M1CB-P5CB of 80% or more in the first fraction. It was decided, therefore, to use fraction in the analysis.

Table1 Analytical results of PCBs using normal and rapid method				
	Sample 1		Sample 2	
	Normal method	Rapid method	Normal method	Rapid method
1-Cl	310	320	110	210
2-Cl	85	84	1200	1200
3-Cl	21	62	5100	6000
4-Cl	3.5	<10	4400	5300
5-Cl	<1	<10	6000	6800
6-Cl	<1	<10	4200	4200
7-Cl	<1	<10	1700	1100
8-Cl	<1	<10	240	110
9-Cl	<1	<10	<1	<10
10-Cl	<1	<10	<1	<10
Total PCBs	419.5	466	22950	24920
				[unit: ng/g-oil]
Normal method: multilayer silica column chromatography with HR-GC/MS				
Rapid method: SPE with LR-GC/MS				

3.2 Analytical Results

Table 1 shows analytical results of PCB in transformer oil which was treated by the chemical

decomposition method. Two samples were analyzed : transformer oil containing PCB of about 20 ppm and that treated to reduce PCB concentration to 0.5 ppm or less. Two analytical methods were compared each other : one with SPE and LRGC/MS and the other with silica gel column and HRGC/MS. Corrected with IS, the analytical results of these two methods were found in good agreement.

In the analysis of PCB with extremely low concentration (0.5 ppm), some difference was found in the quantified values of high chlorinated PCB. This is because of slightly low extraction efficiency of the high chlorinated PCB. The difference was so limited and not influenced the total amount of PCB.

When PCB concentration was 20 ppm, the high chlorinated PCB was also quantified successfully.

4. Conclusion

This analytical method was proved effective to measure PCB in transformer oil with concentration of about 0.5 ppm. This method reduced the over all analysis time to about 90 minutes : about 30 minutes for the clean-up and 60 minutes for the GC/MS analysis. Application of this method will enable the PCB treatment plant to collect the analytical data rapidly, which will enhance the efficiency of plant management.

We used the IS for the purpose of comparing this method with HRGC/MS. As operation error and equipment error induced by this method were limited to 10% or less, there should be no need to use IS in general. **It is allowed to calculate the results using the average correction factor of IS.**

This method can incorporate commercially available automation equipment as it uses the non-proprietary SPE cartridge. It is expected to evaluate several samples at a time and minimize operation errors.

- [1] Makoto Takada, Ryuji Uchida, Shin Taniguchi, Masaaki Hosomi, Chemical Decomposition of PCBs by the Base Catalyzed Decomposition Process, Dioxin'97, **1997**, Vol.31, 435-440
- [2] A. Velasco-Arjona, A. Izquierdo, M. D. Luque de Castro, Fully automated robotic method for the screening of polychlorinated biphenyls in used mineral oils, Analyst,**1998**, Vol.123, 509-512