

RAPID PRETREATMENT OF PCB-CONTAINING OIL FOR INSTRUMENTAL ANALYSIS

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Abstract

The rapid pretreatment method of polychlorinated biphenyl (PCB) in insulating oil was examined. It is possible to perform elution during purification once in this method by connecting the solid-phase partition column to the solid-phase purification column. As a result, a concentration operation using a vacuum concentration becomes unnecessary and the analysis time is shortened to within 2 h. The solid-phase purification column contains silica gel coated with sulfuric acid and silica gel coated with silver nitrate. The solid-phase partition column contains original high-performance alumina. High purification efficiency and high recovery of PCBs were obtained when three kinds of insulating oil were subject to rapid pretreatment. In addition, the applicability to various instruments such as GC-HRMS, GC-LRMS, and GC-MS/MS were examined, and the results were useful for the screening of PCBs and the quantitative determination of the concentration of PCBs in insulating oil.

Introduction

The development of a method to screen the content of polychlorinated biphenyl (PCB) in insulating oil has been expected.

In Japan, it has been declared that all PCB waste must be treated by July 2016. Among approximately 6,000,000 electric apparatuses in Japan, approximately 20%–30% were classified as having a low concentration of PCBs in oil. Although one working policy of the Ministry of the Environment is to burn oil containing a low concentration of PCBs, they cannot estimate the extent of PCB pollution caused by an electric apparatus on the basis of the details or specifications on the nameplate. Several processing periods are required to burn all polluted electric apparatuses; moreover, the processing costs and energy costs involved are very high. Therefore, screening to separate only the apparatuses containing a low concentration of PCB is necessary in order to reduce the number of electric apparatuses that will eventually be burned.

This study was carried out to develop the rapid pretreatment of oil containing PCB for instrumental analysis. Tests were conducted to determine the following: (1) the efficiency of the purification of insulating oils, (2) the efficiency of PCB recovery, and (3) application to some instrumental analysis.

Materials and Methods

PCBs

The stock solution of PCBs comprised a Kanechlor mixture solution in n-hexane (KC-MIX solution), which was prepared by mixing equal quantities of different Kanechlor formulations: KC-300, KC-400, KC-500, and KC-600. These Kanechlor standards were purchased from GL Sciences, Inc.

Measurement of PCBs concentration

PCBs concentration of samples were measured using a HP6890 gas chromatograph equipped with HRMS (JEOL JMS-700), a GC6890N gas chromatograph equipped with LRMS (Agilent 5973MSD) and a GC-MS/MS (Thermo Fisher Scientific TRACE GC Ultra-Polaris Q). Parameters of the gas chromatographs are

shown in Table 1.

	GC/HRMS	GC/LRMS	GC-MS/MS
Injection ports	Splitless : 1 μ l	Splitless : 2 μ l	Splitless with surge : 2 μ l
Column	HT8-PCB 60 m Length, 0.25 mmI.D.	DB-5MS 30 m Length, 0.25 mmI.D., 0.25 μ m Film	DB-5MS 30 m Length, 0.25 mmI.D., 0.25 μ m Film
Carrier gas	Herium	Herium	Herium
Oven	110°C, 1min - 20°C/min → 180°C - 2°C/min → 190°C - 5°Cmin → 300°C	100°C, 2min - 30°C/min → 170°C, 1min - 5°C/min → 290°C - 5°Cmin → 300°C	100°C, 1min - 20°C/min → 180°C, 5min - 5°C/min - 240°C - 20°Cmin - 300°C,

Preparation of insulating oils

Four insulating oils were prepared. Two of these oils ("Sample 1" and "Sample 4") are new insulating oils without PCBs that was added KC-MIX solution to the total concentration of 0.40 and 0.45mg/kg as Kanechlor, respectively. Sample 1 was purchased from Japan Energy Corporation (JOMO), while Sample 4 was purchased from Matsumura Oil. Another insulating oil ("Sample 2") was prepared by adding KC-MIX solution to a total concentration of 0.40 mg/kg of Kanechlor; this insulating oil did not contain any PCBs. A final sample ("Sample 3") was PCB-containing insulating oil that was taken from a used transformer.

Purification column and solid partition column

A purification column and a solid partition column are both used for rapid pretreatment, as shown in Fig.1. The purification column contains silica gel coated with sulfuric acid and silica gel coated with silver nitrate. The solid partition column is filled with high-performance alumina, which has a high adsorption ability with regard to PCBs. The alumina was improved to the alumina for dioxin analysis^{1,2)}.

Rapid analysis of PCBs in insulating oils

The procedure for rapid analysis of PCBs in insulating oil is shown in Fig.2. 0.1 g of the oil sample is added to the purification column. The purification column is heated at 80°C for 30 min. After cooling, 20 ml of n-hexane is eluted. The solid partition column is separated from the purification column and is dried using nitrogen current gas. After drying, the solid partition column is eluted with approximately 200 μ l of toluene or 20% dichloromethane/n-hexane. With the exception of monochlorobiphenyl (M₁CB) and decachlorobiphenyl (D₁₀CB), almost all PCBs are included in this eluted solvent.

Results and Discussion

Purification ability of the rapid pretreatment columns

Chromatograms of before and after rapid pretreatment of Sample 1 are shown in Fig.3. The

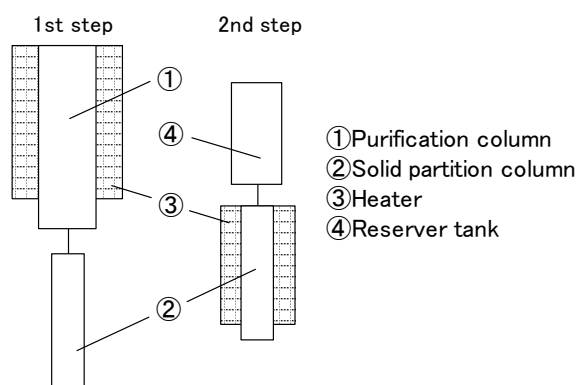


Fig.1 Columns for rapid pretreatment

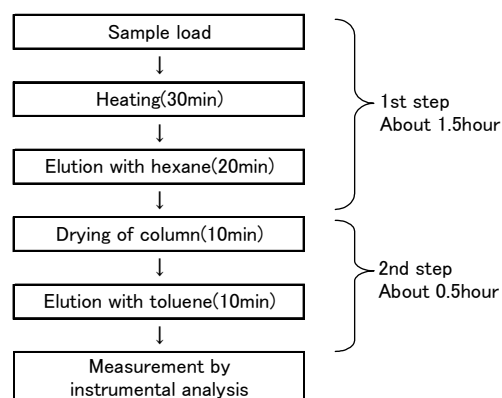


Fig.2 Procedure for rapid analysis

purification efficiency of this insulating oil sample was very high. Before rapid pretreatment, mineral oils such as saturated hydrocarbons, cyclohydrocarbons, and aromatic-hydrocarbons were present in the insulating oil sample. These compounds are shown as a hump in the chromatogram and are collectively called an unresolved complex mixture. These compounds were not detected after pretreatment; this implies that the ability of the rapid pretreatment column to purify insulating oils is very high. In this chromatogram, the peaks corresponding to the PCBs did not appear because the concentration of PCBs was very low.

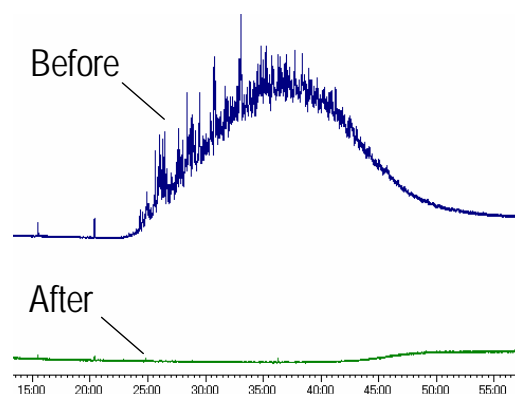


Fig.3 TIC chromatograph

Validation of quantitative capacity and recovery rate of PCBs in insulating oils

The quantitative capacity and recovery rate of the rapid pretreatment method of PCBs in insulating oils were estimated using Sample 1, Sample 2, and Sample 3. The results are shown in Table 2. The quantitative capacities of the rapid pretreatment method were evaluated on the basis of a comparison with the official method (The 192nd Ministry of Health and Welfare notification: by GC-HRMS). The recovery rates of the rapid pretreatment method were calculated at every homologue with a relative response factor with injection spikes. The GC-LRMS of Agilent was used for the PCB measurement, and satisfactory results were obtained with regard to quantitative capacity and recovery rate. In these results, the recovery rate of M₁CB and D₁₀CB was approximately 0%. It is believed that the degradation of M₁CB and elution loss of D₁₀CB in 20 ml of hexane occurred in the rapid pretreatment method. However, these low recovery rates will not affect the total concentration of PCBs because M₁CB and D₁₀CB are not usually included in real PCB-containing oil.

Table 2 Comparison of rapid analysis and official analysis methods with regard to PCB concentration and recovery

	Sample1				Sample2				Sample3			
	Rapid anal.		Official anal.		Rapid anal.		Official anal.		Rapid anal.		Official anal.	
	Conc. mg/kg	Recovery %	Conc. mg/kg	Recovery %	Conc. mg/kg	Recovery %	Conc. mg/kg	Recovery %	Conc. mg/kg	Recovery %	Conc. mg/kg	Recovery %
M1CBs	-	0	N.D.	83	-	1.7	N.D.	78	-	1.3	N.D.	79
D2CBs	0.011	90	0.0088	90	0.0079	95	0.0081	88	0.015	97	0.014	80
T3CBs	0.073	97	0.077	95	0.072	93	0.083	94	0.14	94	0.11	89
T4CBs	0.11	93	0.12	82	0.11	93	0.11	75	0.41	96	0.40	84
P5CBs	0.082	90	0.085	83	0.087	91	0.081	97	1.6	92	1.6	90
H6CBs	0.062	92	0.064	75	0.073	102	0.068	87	0.89	100	0.94	85
H7CBs	0.041	92	0.049	68	0.052	93	0.051	91	0.16	91	0.15	74
O8CBs	0.0087	86	0.0085	75	0.0077	83	0.0087	85	0.022	85	0.020	81
N9CBs	N.D.	85	N.D.	68	N.D.	83	N.D.	79	N.D.	83	N.D.	73
D10CB	-	2.4	N.D.	49	-	3.3	N.D.	55	-	3.5	N.D.	55
Total	0.39	-	0.41	-	0.41	-	0.41	-	3.2	-	3.2	-

Application to GC-HRMS, GC-LRMS, and GC-MS/MS

Applicability to three kinds of instrumental analysis (GC-HRMS, GC-LRMS, GC-MS/MS) was examined using “Sample 4”. In this case, the quantitative capacity, lower detection limit, and chromatogram shape of the PCBs were estimated. The chromatogram of T₃CB, which is particularly important with regard to insulating oil analysis, is shown in Fig.4 as an example. The measured value was in the range of 0.44–0.45mg/kg. The chromatogram shape of T₃CB was also very clear. The lower detection limit was in the following order: LRMS (0.05 mg/kg) > MS/MS (0.01 mg/kg) > HRMS (0.005 mg/kg). The lower detection limit was less than 1/10 of the Japanese regulation value (0.5 mg/kg) in all instruments. These results imply that the rapid pretreatment method of PCB-containing oil in this study can be applied to many instrumental analyses such as GC-MS. Therefore, introducing this method in environmental laboratories, which already contain analytical instruments such as GC-MS, will be beneficial with regard to running costs.

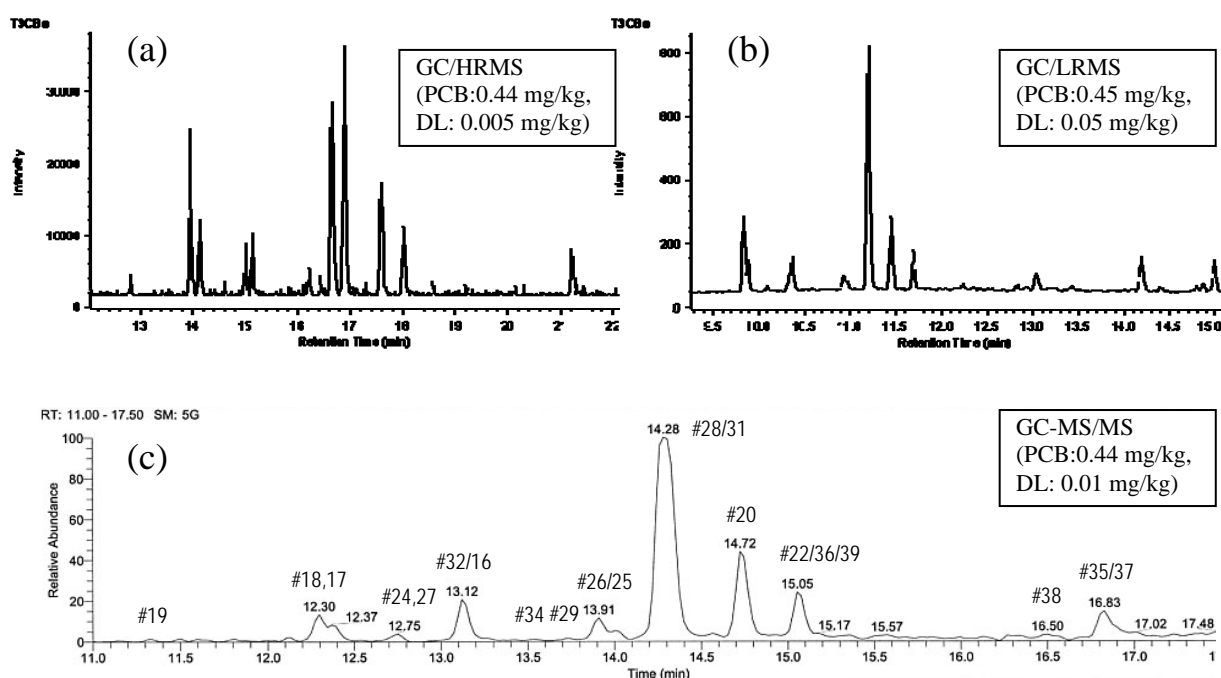


Fig.4 Result of measurement by instrumental analysis in Sample 4

Acknowledgements

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