

Fast and Direct Analysis of Trace Amount PCB in Waste Coating Film Generated from Steel Structures Such as Road Bridges Using GC/MS/MS

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Introduction

It is known that PCBs have been used in some of the coatings for structures such as road bridges manufactured and used in the 1960s and early 1970s. In November 2018, the Ministry of the Environment notified that the relevant facilities and equipment to be surveyed on time.¹⁾ Given this background, need for PCB analysis in waste coating is increasing because whether it is PCB waste or ordinary industrial waste makes a big difference in waste processing costs. The Ministry of the Environment published a "Measuring method for low concentration PCB-containing waste", which also showed the analysis method of PCB in the waste coating film.²⁾ However, this measurement method is for determining high concentration of more than 5000 mg/kg and low concentration of less than 5000 mg/kg, and it cannot be used to judge if it is PCB waste of more than 0.5 mg/kg. In addition, since this method assumes the isomer composition of PCB product such as Kanechlor, it cannot cope with the specific PCB composition derived from pigment. Therefore, we examined the measurement method using GC/MS/MS which can determine whether it is PCB waste or not and can cope with the specific PCB composition derived from pigment. For PCB analysis, GC/ECD and GC/HRMS methods are also often used. However, since the waste coating film has a large amount of matrix, even if the cleanup is performed, the interference components cannot be sufficiently removed, and the analysis may be difficult in the GC/ECD method. On the other hand, the GC/HRMS method requires high cost for maintenance of the instrument and requires skilled techniques for operation. From this, we selected GC/MS/MS method, which is relatively easy to operate and high selectivity. As analytical equipment, Agilent 7890B GC/7010B triple quadrupole MS equipped with a function capable of performing measurement while cleaning the MS ion source by flowing hydrogen gas of about 0.13 to 0.53 mL/min was used. For data acquisition, in addition to quantitative analysis by MRM, scan measurement for qualitative analysis of sample matrix was performed. As the GC column, VF Rapid-MS PCB screen column for fast analysis of PCB, which can analyze PCB in 15 minutes cycle per sample, was used. We also examined the simplified direct analysis using thermal desorption method that we have reported in the past.³⁾ In this method, the analysis can be performed only by setting the waste coating film directly to the inlet of the GC, so the total analysis time including the sample prep can be shortened.

Materials and methods

Evaluation of quantitative values calculated by our examined GC/MS/MS method was performed by comparing the quantitative values calculated by GC/HRMS method according to "Simplified Manual for Measurement of Trace PCBs in Insulating Oil 2.2.1" for three types of waste coating film.⁴⁾ The extraction operation was performed according to "Measuring method for low concentration PCB-containing waste 8".²⁾ After 5 g of the crushed waste coating film was subjected to ultrasonic extraction with 50 mL dichloromethane twice, the residue was dispersed in hexane and then dissolved in sulfuric acid, and liquid-liquid extraction with 20 mL of hexane was performed twice. The liquid-liquid extract and the filtrate were combined, concentrated, and then adjusted to 5 mL. The cleanup operation was performed according to the "Simplified Manual for Measurement of Trace PCBs in Insulating Oil Manual 2.3.1".⁴⁾ 0.2 mL is collected from 5 mL of the extracted solution, 2 ng of clean up spike (MBP-MXP manufactured by Wellington) is added, heated multilayer silica gel column clean-up and heated alumina column clean-up are performed, 2 ng of syringe spike (RS-STK manufactured by Wellington) is added, concentrated, and final 400 µL of a test solution was obtained. Table 1

shows the GC/MS/MS run conditions. As a column, VF Rapid-MS PCB screen column was used, and the condition of GC oven program was used where 209 PCB isomers have been identified on the VF Rapid-MS PCB screen column. In addition, the column flow rate was determined by adjusting PCB # 209 to 0.5733 min. This makes it possible to use a retention time database of 209 PCB isomers, and to address specific composition patterns that are not compositions of PCB products. For data acquisition, the transitions of MRM analysis were set according to the manual, and the range of scan was set to m/z 29 - 550. In order to obtain stable sensitivity, measurement was performed by flowing hydrogen at 0.53 mL/min to the ion source of MS. The calibration curve was prepared by the RRF method using the results of three times measuring each of 0.5, 1, 2, 5, 10 ng/mL standard solution (BP-MXP manufactured by Wellington) including ^{13}C -labeled PCBs. In addition, in the simplified direct analysis, about 2 mg of the crushed waste coating film was set to GC inlet using Thermal Separation Probe (TSP) manufactured by Agilent, and direct analysis by thermal desorption was performed for sample A and C. For the condition of thermal desorption, the flow was set to about 20 mL/min, injection split ratio of 10:1, with the temperature of 260 ° C from the examination result of our past report.³⁾ The calibration curve was prepared by ESTD method with two points of 20pg and 100pg for MoCB and DiCB, 10pg and 50pg for from TrCB to DeCB.

Table 1 GC/MS/MS run condition

GC condition	
Instrument	Agilent 7890B Gas Chromatograph
Column	VF Rapid-MS PCB screen column (0.1mm × 0.6m + 0.53mm × 10m × 0.25μm)
Injection mode	Pulsed Splitless, 1 μL (pulse pressure 25psi, pulse time 1min)
Inlet temperature	300°C
Oven program	85°C(1min)-40°C/min-305°C(3min)
Carrier gas	Helium, inlet pressure: about 13-15 psi (adjust the pressure to elute #209 in 5.733min)
MS condition	
Instrument	Agilent 7010 Triple Quadrupole
Acquisition parameter	El mode; multiple reaction monitoring(MRM)
Collision gas	Nitrogen 1.5mL/min
Quench gas	Helim 2.25mL/min
MS temperature	Source 320°C, Qudrupole 150°C
JetClean	Hydrogen 0.53mL/min

Results and discussion

The calculation of IQL (Instrument Quantification Limit) was performed by seven repeated analysis of 5 KC-mix standard solution of 5 ng/mL, sample conversion concentration of 0.01 mg/kg. The standard deviation (σ) was calculated to 0.220, and the IQL was calculated to 2.2 ng/mL by the following equation: $IQL = 10 \times \sigma$. Since this value is 0.0044 mg/kg in terms of sample conversion concentration, sufficient sensitivity was obtained in a trace PCB analysis to determine 0.5 mg/kg. Table 3 shows the average values of RRF and % RSD of each of the prepared calibration curves. The %RSD of RRF was within 11% for all calibration curves, meeting the standard of the manual. The MRM chromatograms obtained by measuring the three types of coating film, samples A, B and C, were approximately the Kanechlor PCB isomer pattern. However, as shown in Fig. 1, in all samples, # 11 which is not included in Kanechlor was detected with an intensity that cannot be ignored in the quantitative value. In the sample B, the composition ratio was particularly high. It is known that this isomer is unintentionally produced in the process of producing a diazo pigment.⁵⁾ In sample C, # 206 and 209 were detected as shown in Fig. 2. These isomers are known to be produced unintentionally in the process of producing phthalocyanine pigments.⁵⁾ Thus, it was shown that this GC/MS/MS method can quantify PCB isomers which are not included in Kanechlor products. Table 4 shows the total PCB concentration of each sample calculated by GC/MS/MS method and direct analysis using thermal desorption together with the

value of GC/HRMS method. Fig. 3 shows the relative value when the quantitative value of GC/HRMS method is 100%. In sample A of low concentration, the quantitative value of GC/MS/MS method was 235% of the GC/HRMS method. However, it was 133% for sample B and 80% for sample C, and at concentrations around 0.5 ppm, which is criterion for trace PCB, the quantitative values of GC/MS/MS agreed well with GC/HRMS. For direct analysis by thermal desorption, sample A was calculated to be 1.0 mg/kg, which was higher quantitative value than the GC/HRMS method and the normal GC/MS/MS method. This is considered to be one factor that sample A contain a high matrix and causes a positive matrix effect, as can be understood from the total ion chromatogram (TIC) of direct analysis of sample A shown in Fig. 4. Likewise, in the MRM chromatogram, the baseline fluctuation was large, and many interference peaks were also observed. The quantitative value of sample C was 85%, and it was in good agreement with the value of the GC/HRMS method. As can be seen from the TIC of the direct analysis of sample C shown in Fig. 5, it can be seen that the number of interference components is smaller than sample A and the intensity is also lower. These results indicate the possibility that direct analysis by thermal desorption can be used to quantify samples that were confirmed to be less affected by interference peaks. As conclusion of this report, it was shown that the fast GC/MS/MS method and the direct analysis by thermal desorption could be applied to efficiently analyze the trace amount PCB in waste coating film quantitatively.

Table 2 Reproducibility of repeated analysis of 5 ng/mL KC-mix, unit: ng/mL

1	2	3	4	5	6	7	Mean	σ	RSD
6.16	5.89	6.12	5.73	6.24	5.78	6.24	6.02	0.220	3.7

Table 3 RRF average and %RSD of each calibration curve

	1Cl	2Cl	3Cl	4Cl	5Cl	5Cl	6Cl	6Cl	7Cl	8Cl	9Cl	10Cl
Congener	#3	#8	#28	#52	#101	#118	#153	#138	#180	#194	#206	#209
RRF Mean	0.977	0.993	1.03	1.13	1.11	1.03	1.02	0.979	0.923	0.986	0.885	1.13
RRF RSD	1.9	2.3	2.5	5.3	5.6	3.0	6.8	6.2	11	7.7	6.8	4.6

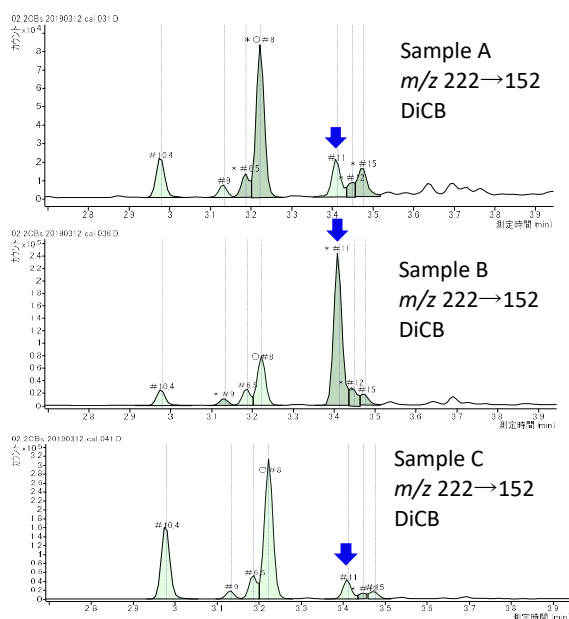


Fig. 1 MRM chromatograms for DiCB of sample A, B, and C (The arrow points to #11.)

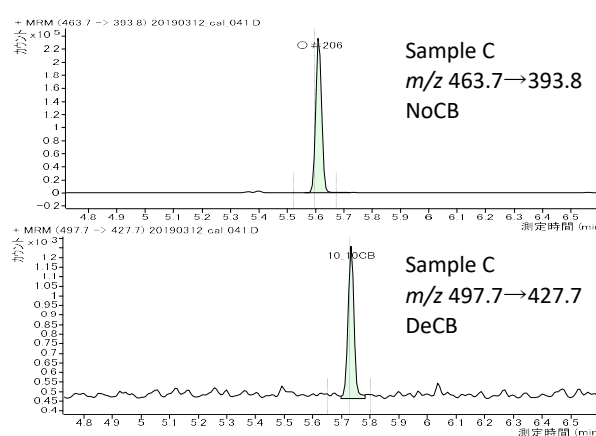
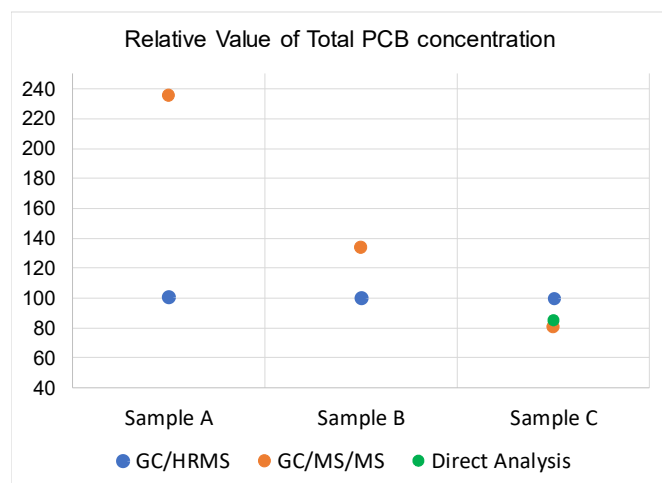
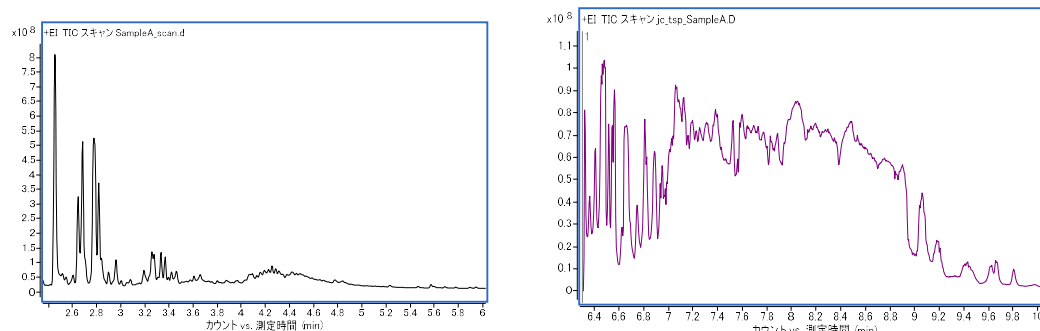
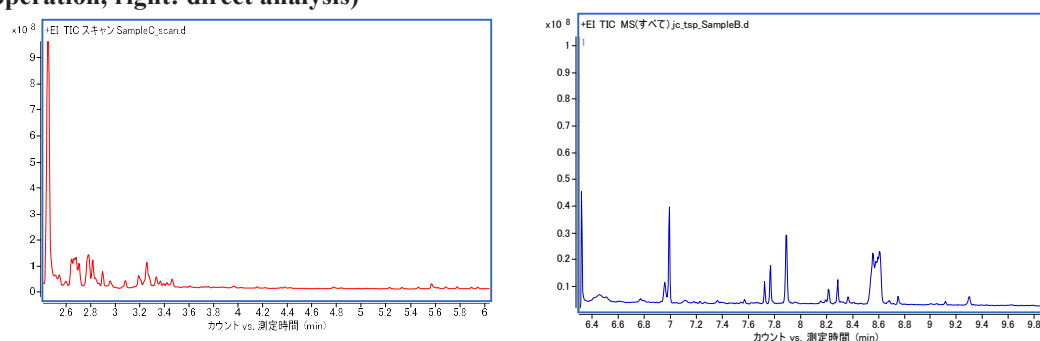


Fig. 2 MRM chromatograms for NoCB and DeCB of sample C

Table 4 Total PCB concentration of sample A, B, and C by each analysis method (unit: mg/kg)

	Sample A	Sample B	Sample C
GC/HRMS	0.02	0.09	0.6
GC/MS/MS	0.047	0.12	0.48
Direct Analysis	1.0	-	0.51

**Fig. 3 The relative value of the total PCB concentration by GC/MS/MS analysis and direct analysis when the value by GC / HRMS method is 100****Fig. 4 Total ion chromatograms of sample A by scan mode (left: liquid injection after cleanup operation, right: direct analysis)****Fig. 5 Total ion chromatograms of sample C by scan mode (left: liquid injection after cleanup operation, right: direct analysis)**

Reference

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