DEVELOPMENT OF A RAPID ANALYSIS FOR DIOXINS BY USING SAMPLE PRETREATMENT DEVICE AND GC/MS MEASUREMENT SYSTEM.

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Abstract

The rapid analysis for PCDD/DFs and dioxin like-PCBs (DL-PCBs) was developed by using a sample pretreatment device (SPD) and GC/MS measurement system. The SPD is an automated cleanup procedure for dioxins analysis, and it can work to simultaneously treat two samples in 2 hrs. The volume of the treated sample is only 1.5ml of toluene, which contains approximately 90% of dioxins. In this study, the recoveries of internal standard added as cleanup spike were between 90% and 120% for all experiments using extracts, such as exhaust gases, ashes, waste waters, environmental waters, ambient airs, soils and sediments. The relative standard deviations for all isomers were below 14% in their repeated experiments (n=5). In addition, there were no drops in the lock mass monitor. Moreover, it was showed that the difference was not found in refining effect as compared with chromatograms obtained by the SPD and the conventional method. Thus, it was confirmed that the new purification by means of SPD fulfilled the requirements of Japanese Industrial Standards. Furthermore, we developed a specified measurement system for the SPD method using high-resolution GC/MS with twice injections. Our method reduced drastically working hours. The shortest analysis time from cleanup to calculation was approximately 6hrs.

Introduction

In Japan, the legal testing for dioxins uses the Japan Industrial Standard (JIS) methods and the manuals for the survey and measurement of dioxins published by Japan Environmental Agency. These methods have a common problem in that analysis cycle time is relatively long because the analytical procedures are complicated. As a result, bioassay and simplified analysis with a low- resolution GC/MS/MS have been reported as a rapid analysis for dioxins in Japan. However, we have studied sample pretreatment techniques by using high resolution GC/MS to perform rapid and more reliable analysis with accuracy and precision[1,2]. According to the results, it was found that heating multilayer silica-gel column at 60℃ was highly efficient for purification, and some concentration methods for dioxins were devised. Consequently, we developed SPD based on these techniques.

In this study, we examined the following items to confirm whether our method fulfills the requirements of JIS (JIS K0311, K0312); (1) the recovery of ^{13}C-labeled PCDD/DFs and DL-PCBs, (2) checking the monitor channel of lock mass in the chromatogram measured by high-resolution GC/MS with SIM mode, and (3) comparisons of the total ion chromatogram measured by low-resolution GC/MS between the SPD method and the conventional method.

Materials and Methods

The following experiments were performed by using a sample pretreatment device, as shown in Fig.1.

Samples

We applied the following sample media as test samples: exhaust gas, fly ash, waste water, environmental water, ambient air, soil and sediment. 5 samples were collected from different sampling point for each sample medium. All samples were extracted with toluene, and then the extracts were followed by hexane substitution. ^{13}C-labeled PCDD/DFs and DL-PCBs as cleanup spike were added into the extracts before sample pretreatment was started.

The validation test for recovery

A schematic diagram of the column flow channel of SPD is shown in Fig.2. The upper column is a multilayer silica-gel column, and the lower is 2 layers of activated carbon column. These column products were obtained from MIURA. After sample extracts were applied on the multilayer silica-gel column, followed by the setting of the column parts and starting the program sequence for automated sample pretreatment. After heating the multilayer silica-gel column at 60°C, dioxins were eluted with 85ml of hexane kept at 60°C, and then dioxins trapped in the activated carbon column were reversibly eluted with 1.5ml of toluene kept at approximately 60°C. Eluted solution was finally concentrated to 20μl by nitrogen flow after syringe spike were added, and then measured by high-resolution GC/MS (JMS-700D, JEOL). In this study, we used BPX-DXN (60m×0.25mm i.d., SGE) and RH-12ms (60m×0.25mm i.d., Invent X) as capillary columns applied for the determination with twice injections.

We performed 5 times repeated analysis for each sample in this experiment.

Fig.1 Diagram of sample pretreatment device for GC/MS.

The validation test for purification

The samples treated by SPD were prepared as described above. Reference samples were treated, basically following the conventional method. Briefly, the sample extracts were refined by multilayer silica-gel column and activated carbon dispersed silica-gel (for dioxins analysis, Kanto Chemicals) column chromatography. Dioxins were fractionated into PCDD/DFs & non-*ortho* DL-PCBs fraction and mono-*ortho* DL- PCBs fraction in the process of activated carbon dispersed silica-gel column chromatography, however these fractions were mixed as one sample in order to compare the total ion chromatogram in refining effect with the SPD method. The sample solutions were concentrated to 20μl by nitrogen flow, and then measured by low-resolution GC/MS (K9, JEOL) with scan mode in the mass range of 50-450m/z. In this experiment, we used BPX-DXN (60m×0.25mm i.d., SGE) as a capillary column.

Fig.2 Schematic diagram of the column flow channel of SPD.

Results and Discussion

The recoveries of ^{13}C-labeled PCDD/DFs and DL-PCBs

The data obtained in this experiment totaled 25 which consisted of 5 samples × 5 repeated analysis, for each sample medium. The recovery rates of spiked ^{13}C-labeled PCDD/DFs and DL-PCBs in the experiment using exhaust gas sample A were within the allowable range of 50-120%, all of them were more than 90% (Table 1). Their RSD% exhibited below 12% for all isomers, it was indicated that the reproducibility of the SPD method was highly stable. The reason for the high recovery of dioxins was that 2 layers of activated carbon column had a high efficiency of ad- and de-sorption for dioxins in the process of different solvent elution. To be concrete, it was thought that PCDD/DFs & non-*ortho* DL-PCBs were trapped in the upper layer of the carbon column, and mono-*ortho* DL-PCBs were trapped in the lower layer of the carbon column in the process of hexane elution. In addition, it was considered that the heating of the carbon column was effective for the recovery of dioxins.

Concerning chromatograms of all samples measured by high-resolution GC/MS with twice injections, there were no drops in the lock mass monitor.

The comparison of refining effect between SPD and the conventional method

The data obtained in this experiment totaled 5 for each sample medium. The total ion chromatograms obtained by the SPD method were compared with the conventional method in the experiment using exhaust gas sample A
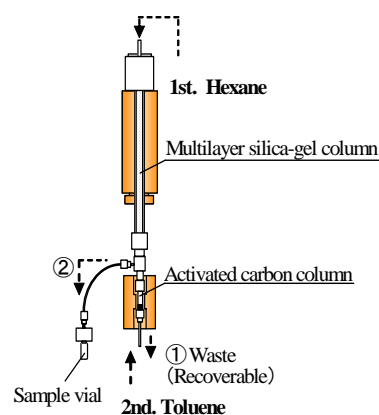
as shown in Fig.3. According to the results, each chromatogram was largely similar, although some different peaks were detected. Additionally, comparable results were obtained from the experiments using other samples and sample media. Thus, it was considered that the refining effect by means of SPD was equivalent to that of the conventional method.

The validation for the requirements of JIS

As mentioned above, it was confirmed that our method using SPD fulfilled the requirements of JIS for a new purification method. Additionally, our method allowed rapid analysis and less consumption of organic solvent. This indicates that it was possibility to achieve a reduction in the cost of dioxins analysis.

References

1) Fujita H., Hamada N., and Honda K. *Journal of Environmental Chemistry* 2005; 15:117
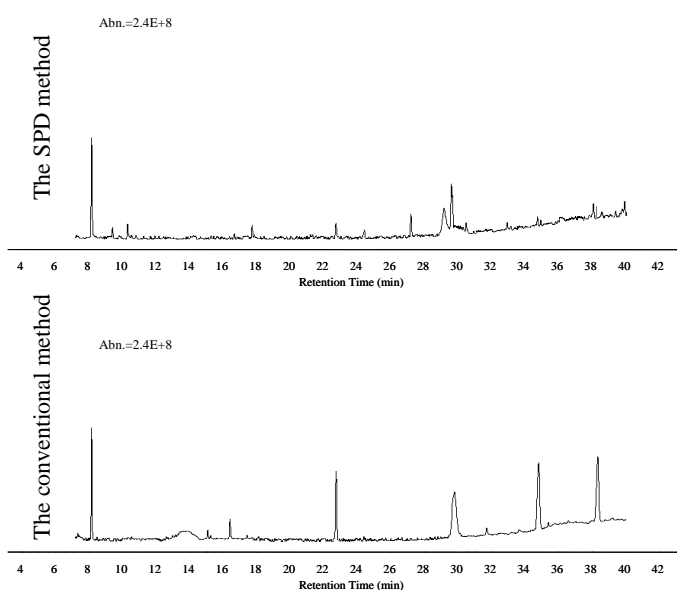2) Fujita H., Hamada N., Sawadaishi K., and Honda K. *Journal of Environmental Chemistry* 2005; 15:585

Fig.3 Comparison of total ion chromatogram between the SPD method and the conventional method.

Table 1 Recoveries of ^{13}C-labeled PCDD/DFs and DL-PCBs on the repeated analysis (n=5).

Exhaust Gas A		1	2	3	4	5	ave.	min.	−	max.	RSD%
2,3,7,8-TeCDD		106	106	104	105	105	105	104	-	106	1
1,2,3,7,8-PeCDD		106	105	100	107	102	104	100	-	107	3
1,2,3,4,7,8-HxCDD		115	111	109	90	103	106	90	-	115	9
1,2,3,6,7,8-HxCDD		117	115	111	99	103	109	99	-	117	7
1,2,3,7,8,9-HxCDD		111	108	105	91	99	103	91	-	111	8
1,2,3,4,6,7,8-HpCDD		111	113	112	95	93	105	93	-	113	10
OCDD		114	113	114	92	91	105	91	-	114	12
2,3,7,8-TeCDF		107	108	102	94	92	101	92	-	108	7
1,2,3,7,8-PeCDF		104	104	99	95	107	102	95	-	107	5
2,3,4,7,8-PeCDF		103	104	99	106	109	104	99	-	109	3
1,2,3,4,7,8-HxCDF		106	105	100	99	99	102	99	-	106	3
1,2,3,6,7,8-HxCDF		104	103	98	91	90	97	90	-	104	7
2,3,4,6,7,8-HxCDF		109	110	100	100	101	104	100	-	110	5
1,2,3,7,8,9-HxCDF		108	109	103	95	98	103	95	-	109	6
1,2,3,4,6,7,8-HpCDF		104	109	106	90	92	100	90	-	109	8
1,2,3,4,7,8,9-HpCDF		109	105	109	98	94	103	94	-	109	7
OCDF		109	111	112	90	93	103	90	-	112	10
3,4,4',5-TeCB	#81	102	109	107	94	90	100	90	-	109	8
3,3',4,4'-TeCB	#77	101	108	107	97	92	101	92	-	108	7
3,3',4,4',5-PeCB	#126	105	105	98	100	108	103	98	-	108	4
3,3',4,4',5,5'-HxCB	#169	103	107	97	106	117	106	97	-	117	7
2',3,4,4',5-PeCB	#123	97	93	92	102	94	96	92	-	102	4
2,3',4,4',5-PeCB	#118	94	94	94	96	90	93	90	-	96	3
2,3,4,4',5-PeCB	#114	96	91	93	102	98	96	91	-	102	4
2,3,3',4,4'-PeCB	#105	103	103	102	93	91	99	91	-	103	6
2,3',4,4',5,5'-HxCB	#167	96	93	92	94	104	96	92	-	104	5
2,3,3',4,4',5-HxCB	#156	97	96	92	102	111	100	92	-	111	7
2,3,3',4,4',5'-HxCB	#157	100	97	95	101	105	100	95	-	105	4
2,3,3',4,4',5,5'-HpCB	#189	95	92	93	109	103	98	92	-	109	7