Study on HRGC/HRMS method of PBDDs/DFs by SCLV injection system

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Introduction

It has been suggested that monitoring studies on polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) are required to understand the contamination and distribution in the environment by the Japanese government.

It is pointed out that PBDDs/DFs have toxic consequences equivalent of polychlororinated dibenzo-p-dioxins and polychlorinated dibenzofurans[1)]. In general the analysis of PBDDs/DFs has many problems which makes it difficult to reduce detection limits.[2)]

For the analysis of PBDDs/DFs we conducted examinations on the application of a solvent cut large volume (SCLV) injection system which has already been put to practical use in the supersensitive analysis of PCDDs/DFs.

Material and Methods

PBDDs/PBDFs have large molecular weights, therefore retention times are late using HRGC-HRMS instrumentation. The principles of SCLV injection systems render it unavoidable to reach a high temperature in the GC oven to elute the analytes from the pre-column onto an analytical column.

It has been reported that highly brominated compounds decompose during measurement and therefore it is necessary to elute the analytes as rapidly as possible using a short column.[3)] We set up the GC operation programs based on established programs for splitless injection.

HRGC-HRMS analysis was conducted on a 6890 series GC (Agilent Technology, USA) equipped with Autospec Ultima (Micromass, UK). The SCLV injection system (SGE, Australia) was equipped with a EMV5-MS (Kanto Chemical, Japan) capillary column with a deactivated stationary phase [4)] as a precolumn and a DB5-HT (Agilent Technology, USA) capillary column as an analytical column for TeBDD/DF, PeBDD/DFs and HxBDDs/DF.

For HpBDD/DF and OctaBDD/DF the system was equipped with an EMV-5MS as a pre-column and BP1(SGE, Australia), with a deactivated stationnary phase as well as EMV-5MS[4)], as analytical column.

The analytical conditions are shown in Table 1 and 2.

The 5-point calibration standard solutions were controlled by spiking each of the EDF-5070 PBDDs/DFs calibration standard mixtures (Cambridge Isotope Laboratories, USA) diluted 50 times, with 1,2,3,4,7,8-HxBDF.

The calibration standard contained TeBDD/DF spanning the concentration range 0.01 to 2 pg/µL, PeBDD/DFs and HxBDDs/DF spanning the concentration range 0.05 to 10 pg/µL, $^{13}C_{12}$-labeled analytes at concentration of 2 pg/µL. The calibration solutions were injected 3 times each for 5, 10, 15 and 20 µL.

Table 1 Analytical Conditions for the SCLV injection system	
Pre-column	EMV-5MS(Kanto Chemical) 0.25㎜×3m 0.25μm film thickness
Analytical column	DB5-HT(Agilent Technologies) 0.25㎜×30m 0.1μm film thickness
Injector temperature	260°C
Oven temperature	160°C(1.5min)→ 15°C/min→ 250°C(8min)→ -30°C/min
	→ 220°C(2min)→ 3°C/min→ 280°C(9.5min)
Injector pressure	265 kPa(1.5min)→ 370kPa/min→ 450kPa(13.5min)
	→ -370kPa/min→ 265kPa(32min)
Auxiliary #3 pressure	270kPa(1.5min)→ 320kPa/min→ 430kPa(13.5min)
	→ -320kPa/min→ 270kPa(32min)
Auxiliary #5 pressure	240kPa(1.5min)→ 360kPa/min→ 420kPa(13.5min)
	→ -360kPa/min→ 240kPa(32min)
Solvent cut volve	0 min(off)→ 1.5min(on)→ 15.5min(off)
Cold trap volve	0 min(off)→ 1.0min(on)→ 18.5min(off)
MS Resolution	>12,000
Accelerating voltage	8,000V
Trap current	500μA
Chanel	1st function(Tetra):10, 2nd function(Penta):10, 3rd function(Hexa):10
Cycle time	1st function:970ms, 2nd function:970ms, 3rd function:970ms
Analysis time	48min

Table 2 Analytical Conditions for the SCLV injection system	
Pre-column	EMV-5MS(Kanto Chemical) 0.25㎜×3m 0.25μm film thickness
Analytical column	BP1(Kanto Chemical) 0.25㎜×30m 0.1μm film thickness
Injector temperature	260°C
Oven temperature	160°C(1.5min)→ 15°C/min→ 280°C(20min)→ 30°C/min
	→ 220°C(2min)→ 5°C/min→ 280°C(9min)
Injector pressure	170kPa(1.5min)→ 280kPa/min→ 310kPa(31.5min)→ -280kPa/min
	→ 170kPa(20.5min)
Auxiliary #3 pressure	178kPa(1.5min)→ 200kPa/min→ 278kPa(31.5min)→ -200kPa/min
	→ 178kPa(20.5min)
Auxiliary #5 pressure	158kPa(1.5min)→ 200kPa/min→ 258kPa(31.5min)→ -200kPa/min
	→ 158kPa(20.5min)
Solvent cut volve	0 min(off)→ 1.5min(on)→ 29.5min(off)
Cold trap volve	0 min(off)→ 1.0min(on)→ 33.5min(off)
MS Resolution	>12,000
Accelerating voltage	8,000V
Trap current	500μA
Chanel	1st function(^{13}C$_{12}$-Penta, ^{13}C$_{12}$-Hexa)6,
	2nd function(Hepta)6, 3rd function(Octa)8
Cycle time	1st function:980ms, 2nd function:990ms, 3rd function:990ms
Analysis time	54.5min

We had trouble resolving matters of concern for OBDD/DF using a splitless injection. We had to confirm whether the analyte decomposed during measurement on the SCLV injection system. We injected 5μL each of the 5-point calibration standard solutions which contained only OBDD/DF, spanning the concentration range 0.05 to 0.5 pg/μL to confirm whether we detected HpBDD/DF as resolved.

Results and Discussion

TeBDD/DF, PeBDD/DFs and HxBDDs/DF

In Table 3 it is shown that all calibration curves had good linearity for 5, 10, 15 and 20 μL injections. All variations for relative sensitivity coefficient on calibration curves and relative standard deviation for various injection volume were within plus or minus 10 %. Figure 1 shows that relative peak area ratio for each injection volume.

Table 3 Relative sensitivity coefficient and coefficient of variance for various injection volume

Injection volume(μl)	5		10		15		20		RSD%*
2,3,7,8-TeBDD	0.973	(4.5)	1.006	(4.9)	1.038	(3.1)	0.995	(2.0)	1.67
1,2,3,7,8-PeBDD	1.087	(4.4)	1.087	(3.8)	1.124	(2.5)	1.088	(2.2)	0.05
1,2,3,4,7,8/1,2,3,6,7,8-HxBDD	1.331	(7.2)	1.251	(5.8)	1.299	(6.4)	1.256	(3.3)	3.47
1,2,3,7,8,9-HxBDD	1.033	(4.7)	1.079	(7.4)	1.101	(4.3)	1.072	(4.9)	2.34
2,3,7,8-TeBDF	1.099	(2.9)	1.106	(2.3)	1.135	(3.0)	1.098	(4.0)	0.34
1,2,3,7,8-PeBDF	0.949	(3.2)	0.956	(2.5)	1.007	(3.6)	0.961	(3.9)	0.61
2,3,4,7,8-PeBDF	1.022	(5.8)	0.994	(3.0)	1.028	(3.0)	0.987	(3.9)	1.83
1,2,3,4,7,8-HxBDF	1.098	(5.6)	1.065	(5.7)	1.114	(4.1)	1.063	(4.1)	1.82
[$^{13}C_{12}$]-2,3,7,8-TeBDD **	1.542	(2.6)	1.463	(5.0)	1.38	(3.7)	1.446	(4.6)	3.40
[$^{13}C_{12}$]-1,2,3,7,8-PeBDD **	0.77	(3.9)	0.792	(2.5)	0.775	(2.9)	0.798	(2.6)	1.87
[$^{13}C_{12}$]-1,2,3,7,8,9-HxBDD **	0.279	(6.8)	0.309	(6.6)	0.3	(5.8)	0.307	(4.5)	5.71
[$^{13}C_{12}$]-2,3,7,8-TeBDF **	2.08	(3.6)	1.977	(6.6)	1.728	(5.4)	1.971	(6.9)	3.02
[$^{13}C_{12}$]-2,3,4,7,8-PeBDF **	1.111	(3.6)	1.099	(3.0)	1.065	(3.2)	1.085	(2.4)	1.12
[$^{13}C_{12}$]-1,2,3,4,7,8-HxBDF **	0.458	(7.6)	0.495	(4.7)	0.464	(5.9)	0.478	(4.5)	3.78

* Relative standard deviation among calibration curves

** Relative sensitivity coefficient based on [$^{13}C_{12}$]-1,2,3,7,8-PeBDF

Coefficient of variance for relative sensitivity of calibration curve is shown in parentheses.

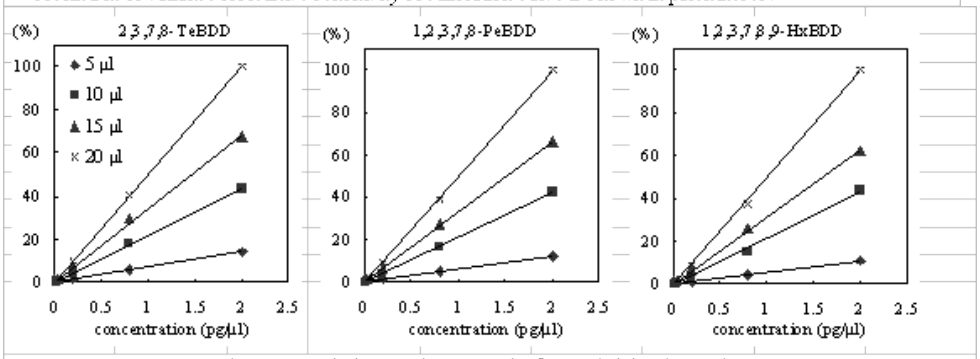

Figure 1 Relative peak area ratio for each injection volume

HpBDDs/DFs, HpBDDs/DFs, OBDD/DF

For the injections of only OBDD/DF, HpBDDs/DFs were detected. Furthermore HpBDDs/DFs increased with increasing concentration of OBDD/DF. It was considered that OBDD/DF decomposed during measurement on this system.

In this study it was established that the SCLV injection system was applicable to the measurment of TeBDDs/DFs, PeBDDs/DFs and HxBDDs/DFs. For the SCLV method, we set the initial pressure in injection port higher, and confirmed that the measurement of low brominated compounds were not influenced by decomposition of the higher brominated compounds.Utilizing the characteristics of SCLV, trapping TeBDDs/DFs, PeBDDs/DFs and HxBDDs/DFs, then eliminating higher brominated compounds before getting onto the analytical column, we expected to prevent the deterioration of solution layer by decomposition of high brominated compounds in the interior of the column and reduced response to consecutive injections.

We could not however establish the conditions for the measurement of OBDD/DF. On this system, analytes are exposed to high temperatures in the pre-column. We therefore have to find the conditions to elute the analytes from the pre-column without much decomposition. Also, it is necessary to eliminate any possibilities of decomposition and adsorption of PBDDs and PBDFs during the experimental procedure.

We intend to continue this study for prompt establishment of optimal conditions for this system.

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References

1. Polybrominated Dibenzo-p-dioxins and Dibenzofurans, Environmental Health Criteria No.205(1998) WHO

2. Miyazaki T., Takasuga T., Watanabe I. and Yoneda K. (2001) 10th Symposium on Environmental Chemistry Program and Abstracts, 108.

3. Takasuga T., Miyazaki T., Watanabe I. and Yoneda K. (2001) 10th Symposium on Environmental Chemistry Program and Abstracts, 110.

4 Kataoka T., Akiba M., Kudo S. and Ezaki T. (2004) 13th Symposium on Environmental Chemistry Program and Abstracts, 24.