Quantitation method of PCDDs/DFs and Dioxin-like PCBs with High Sensitivity and Complete Separation by SCLV

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Introduction

In the ordinary analytical methods for the determination of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and Dioxin-like PCBs (DL-PCBs), these compounds have been analyzed by using two or more kinds of capillary columns and some of these compounds have not be able to separate from other co-existing isomers or congeners in the prepared solution[1,2,3,4,5,6].

Because of the analytical method has been required extremely high sensitivity for the determination of PCDDs, PCDFs and DL-PCBs in environmental water samples, the water samples have had to be collected more than 100L.

In this study, more than ten times higher sensitive analytical method for these compounds than ordinary standard methods and operating conditions for the complete separations of these compounds were established by optimizing solvent-cut large volume injection (SCLV) technique.

Materials and Methods

All high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) analyses were conducted on a 6890N GC (Agilent Technology, USA) equipped with AutoSpec-Ultima NT (Micromass, UK). The SCLV injection system (SGE, Australia) was equipped with BPX Dioxin-I and BPX Dioxin-II (SGE, 30m length, 0.15mmID) capillary columns as the analytical columns, and BPX-5 (SGE, 6m length, 0.25mmID, film thickness 0.25μm) or ENV-5MS (Kanto Chemical, 0.25mmID, film thickness 0.25mm) as a pre-concentration column.

DB-17 (J&W, 30m length, 0.32mmID, film thickness 0.25mm) was used for the comparison of decomposition extent to present condition.

Perfluorokerosene (PFK) was used for the lock-mass standard gas.

The analytical conditions for the SCLV injection system are shown in Table 1.

All native and ^{13}C labeled standard solutions of PCDDs, PCDFs and DL-PCBs were purchased from Wellington Laboratories.

The fly ash sample solution for the optimization of analytical conditions was prepared according to

JIS K0311 and separated to Fraction 1 (containing PCDDs, PCDFs and non-ortho DL-PCBs) and Fraction 2 (containing PCBs except non-ortho DL-PCBs). Both fractions were dissolved in decane.

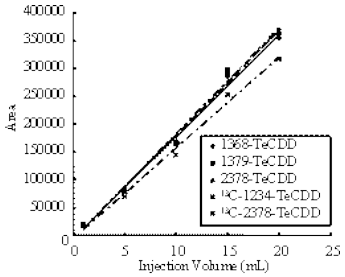

Figure 1. Linearity between peak area and injection volume

Results and Discussion

Linearity according to the change of injection volume: Injection volume applicable to SCLV was evaluated. Linearity of peak area against injection volume during the range of 1mL to 20mL for TetraCDDs/CDFs are shown in Figure 1. Good relationship between peak area and injection volume were observed, and varying of injection volume according to sample amount or concentration was available.

Reducing of Octachloro-congeners decomposition during the focusing process: In the ordinary SCLV conditions, 6m of BPX-5 capillary column was used for the pre-concentration column, and the oven temperature was raised to 300 degC to elute all of PCDDs, PCDFs and DL-PCBs to the

cold trap. In this process, more than 5% of OctaCDDs and octaCDFs have been known to decompose and produce 1,2,3,4,6,7,8-HeptaCDD/DF and 1,2,3,4,7,8,9-HeptaCDF in the pre-concentration column. Then, the shorter and more inert capillary column, ENV-5MS, was used and the eluting temperature was set up to 260 degC to evaluate the reducing this decomposition of OCDD and OCDF during the focusing process. The example of the comparison of the measured Conentrations of 1,2,3,4,6,7,8-heptaCDD between ordinary DB-17 capillary column and present condition was shown in Figure 2.

The reduction of decomposition of OCDDs and OCDFs was observed by use of shorter and more inert column and lower eluting temperature.

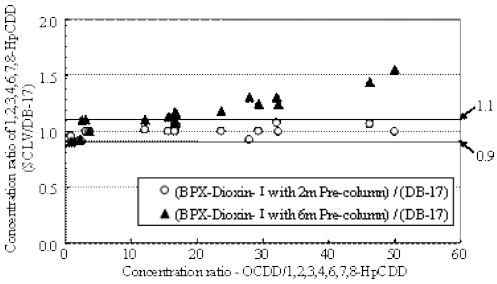

Figure 2. Effect of decomposition reduction by present condition

Optimization of oventemperature for the separation analysis: The oven temperature could be set arbitrarily, since the solvent has already been eliminated at the start point of analysis. The optimization of this initial and raising rate of oven temperature let optimize the separation behavior of target analytes. Initial temperatures were changed to 200 degC, 220 degC and 240 degC for BPX Dioxin-I and 220 degC, 240 degC and 260 degC for BPX Dioxin-II capillary column. In ordinary analytical conditions, 2,3,7,8-TetraCDF and 2,3,4,6,7,8-HexaCDF were difficult to obtain isolated peaks. The separation behavior according to changing initial oven temperature were shown in Figure 3 for 2,3,7,8-TetraCDF on BPX Dioxin-I and Figure 4 for 2,3,4,6,7,8- HexaCDF on BPX Dioxin-II.

The optimal initial temperatures was defined as 200degC for BPX Dioxin-I and 260degC for BPX Dioxin-II.

Obtained optimized analytical conditions for PCDDs, PCDFs and DL-PCBs were shown in Table 1.

Table 1. Optimized analytical conditions for SCLV-HRGC

Condition-1 for the analysis of tetra through octaCDDs/CDFs except penta and hexaCDFs using BPX Dioxin-I	
Column	BPX Dioxin-I, 0.15mmID, 30m length
Oven temp.	at injection: 160 degC
Injection port	solvent elimination: 20 degC/min to 260 degC, keep 10 min.
Carrier gas	cool down to: 200 degC (initial temperature)
	analysis: 3 degC/min to 265 degC, then 10 degC/min to 300 degC
	temperature: 300 degC
	injection mode: SCLV
	Helium
Condition-2 for the analysis of penta through hexaCDFs and DL-PCBs using BPX Dioxin-II	
Column	BPX Dioxin-II, 0.15mmID, 30m length
Oven temp.	at injection: 160 degC
Injection port	solvent elimination: 20 degC/min to 260 degC, keep 10 min.
Carrier gas	cool down to: 260 degC (initial temperature)
	analysis: 2 degC/min to 300 degC
	temperature: 300 degC
	injection mode: SCLV
	Helium

In these operating conditions, almost complete separation of all peaks of 2,3,7,8-position chlorine substituted PCDDs and PCDFs, and DL-PCB were observed.

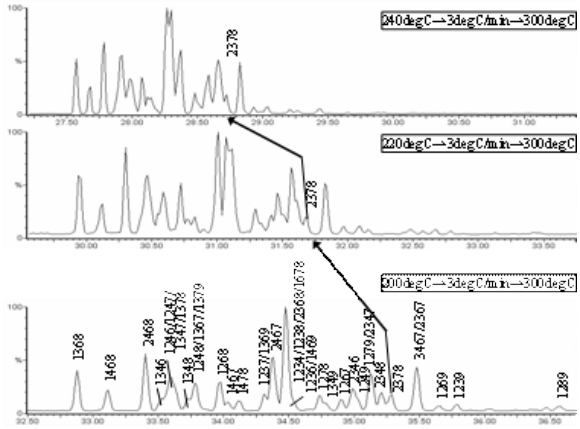

Figure 3. Separation behavior of 2,3,7,8-TetraCDF according to the change of initial temperature

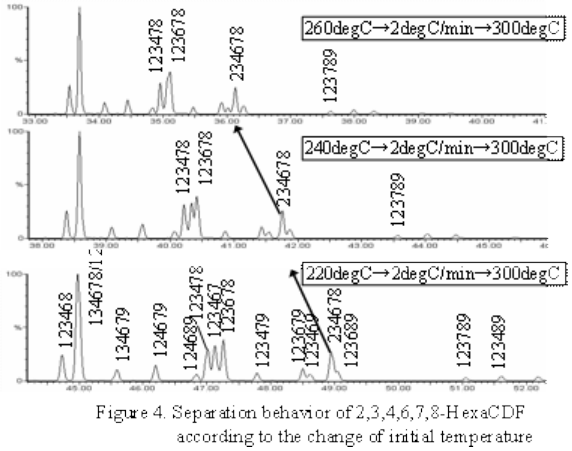

Figure 4. Separation behavior of 2,3,4,6,7,8-HexaCDF according to the change of initial temperature

Conclusion

Some of pentaCDF and hexaCDF isomers have not been able to separate from other co-existing PCDDs, PCDFs or DL-PCBs isomers or congeners by ordinary analytical conditions, and the more sensitive analyses of these compounds have not been achieved by ordinary method using splitless or on-column injection.

Even using the large volume injection techniques, such as programmed temperature vaporizing method (PTV) or SCLV, octaCDD and octaCDF were well known to decompose to heptachlorinated isomers.

In this study, high sensitive and easily applicable high volume injection method for the PCDDs, PCDFs and DL-PCBs analysis with reducing decomposition of these highly chlorinated isomers and almost complete separations of these compounds was established.

References

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