Effects of Collision Induced Dissociation(CID) Voltage and Damping Gas Flow on PCDDs/PCDFs Determination by Quadrupole Ion Trap Mass Spectrometer

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Introduction

The typical method for the determination of PCDDs/PCDFs in environmental samples is high resolution mass spectrometry in combination with high resolution gas chromatography as described in US EPA Method 1613.[1]

Recently, a quadrupole ion trap(QIT) mass spectrometer sometimes has been employed to determine PCDDs/PCDFs in sewage effluents[2] and food matrices[3] because HRMS is very expensive to purchase and maintain. This method obtained by MS/MS with the QIT contains four – step process involving ionization(EI or CI), parent ion isolation, collision induced dissociation(CID) and mass analysis of the daughter ions.[4] This process can be repeated many times in order to obtain $(MS)^n$ [5].

The aim of the present study was to optimize the collision induced dissociation(CID) voltage and damping gas flow for 17 2,3,7,8-substituted-PCDDs/PCDFs by using MS-MS techniques of QIT mass spectrometer.

Methods and Materials

Standards: For this study, a commercially available and verified standard solution of native and isotopically labelled PCDDs/PCDFs was used (CS1~5:EDF9999:Cambridge Isotope Laboratories). All organic solvents used in dilution were of pesticide grade and obtained from wako chemical Co.(Japan).

Instrument: A PolarisQ ion trap mass spectrometer and a TRACE 2000 gas chromatograph(Thermo Finnigan, Austin, TX, USA) equipped with a DB-5ms(J&W Scientific, USA) capillary column(60m x 0.25mm, 0.25µm) was used. The injector temperature was 290 and 2µl was injected in a splitless mode. The ion source was set at 250 and the transfer line was set at 280. The oven temperature was programmed as follows: 120 (3min) 20.0 /min 200 (2min) 2.0 /min 260 3.0 /min 300 (10min). Helium flow was 1.2ml/min. Under these conditions, all 17 congeners of PCDDs/PCDFs were separated.(Fig. 1)

Figure 1: Total ion chromatogram of the 17 2,3,7,8-substituted congeners contained in 2ul of solution CS-3, The 17 compounds are almost completely separated, but the valley between the peaks of 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD is ca 10% of the highest peak.
1. 2,3,7,8-TCDF, **2**. ^{37}Cl-1,2,3,4-TCDD, **3**. 2,3,7,8-TCDD, **4**. 1,2,3,7,8-PeCDF, **5**. 2,3,4,7,8-PeCDF, **6**. 1,2,3,7,8-PeCDD, **7**. 1,2,3,4,7,8-HxCDF, **8**. 1,2,3,6,7,8-HxCDF, **9**. 2,3,4,6,7,8-HxCDF, **10**.1,2,3,4,7,8-HxCDD, **11**.1,2,3,6,7,8-HxCDD, **12**. 1,2,3,7,8,9-HxCDD, **13**. 1,2,3,7,8,9-HxCDF, **14**.1,2,3,4,6,7,8-HpCDF, **15.** 1,2,3,4,6,7,8-HpCDD, **16**. 1,2,3,4,7,8,9-HpCDF, **17**. 1,2,3,4,6,7,8,9-OCDD, **18**. 1,2,3,4,6,7,8,9-OCDF
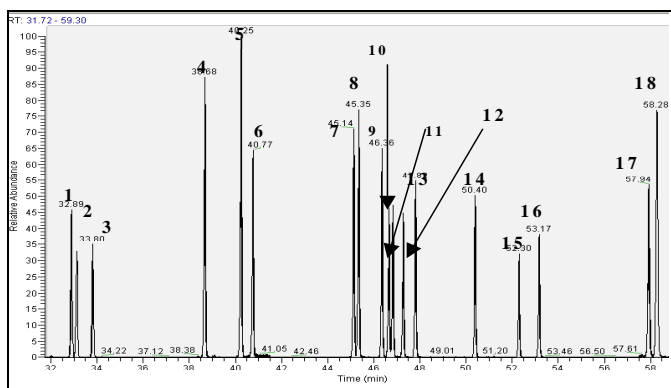

Collision Induced Dissociation(CID) voltage: The CID means that an ion/neutral process by which an ion is dissociated as a result of collisions with neutral target species(collision gas, He). The optimization of the CID voltage of each parent ion(molecule ion) was performed using multiple scan functions for each retention time window. In this study, the CID voltage was varied from 1.0V to 4.0V in 0.2V-steps.
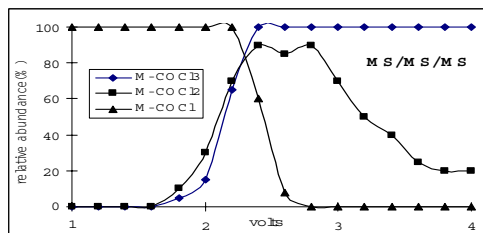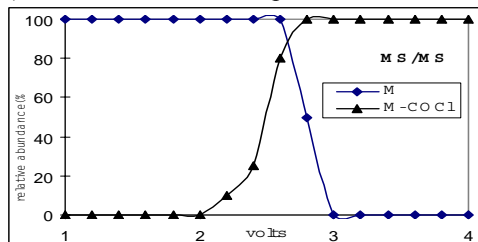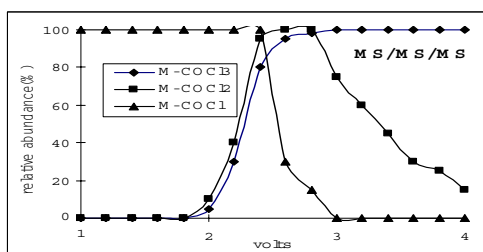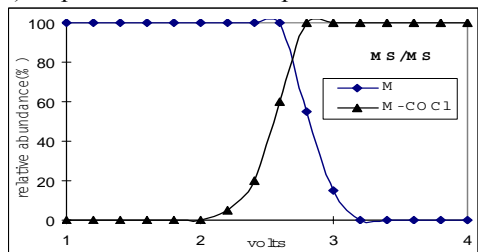
a) Tetra Chloro Dibenzo-p-Dioxin
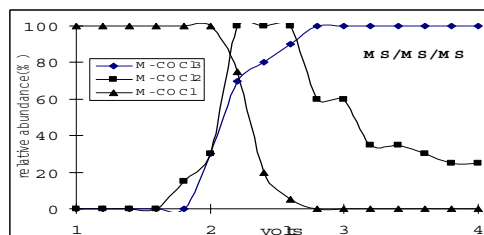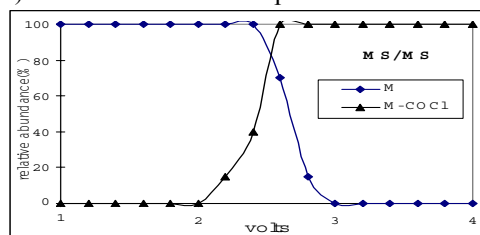
b) Penta Chloro Dibenzo-p-Dioxin
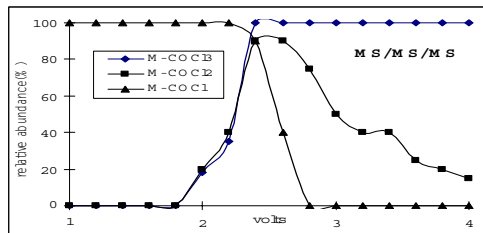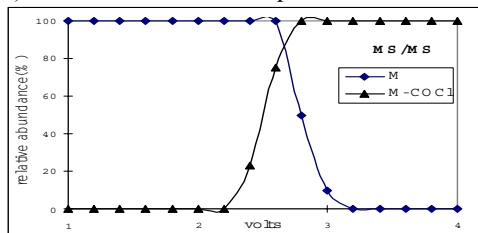
c) Hexa Chloro Dibenzo-p-Dioxin

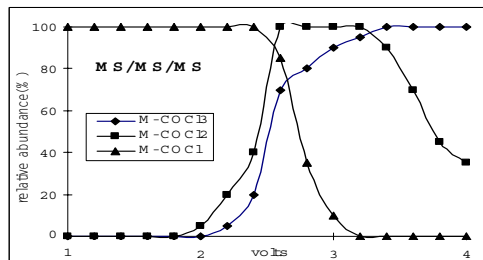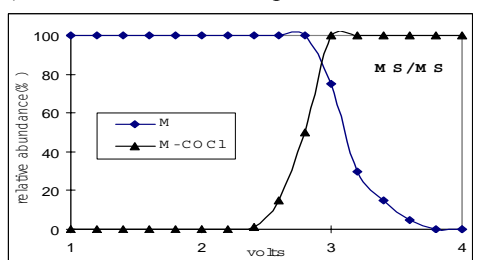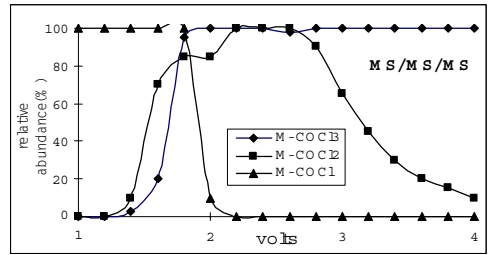d) Hepta Chloro Dibenzo-p-Dioxin
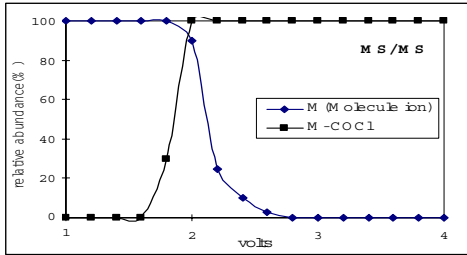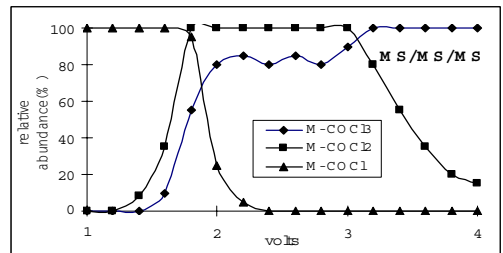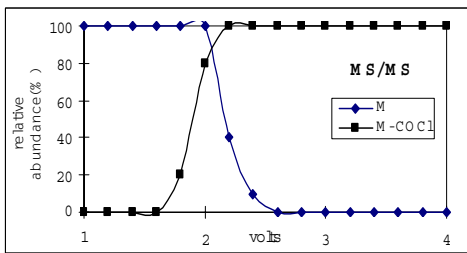

e) Octa Chloro Dibenzo-p-Dioxin

Figure 2: Effect of CID voltage on fragment ions with the MS/MS and MS/MS/MS scan function(4~8 chloro substituted dioxins)
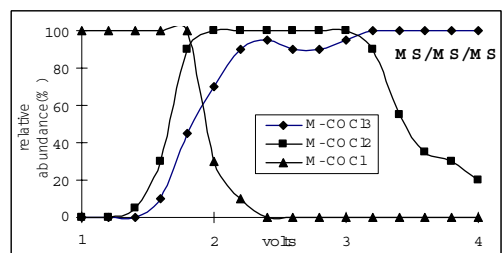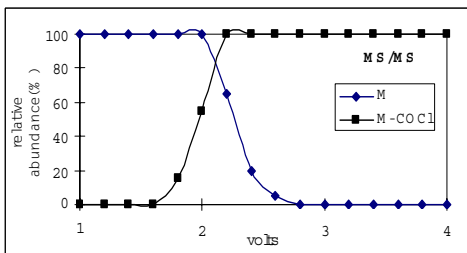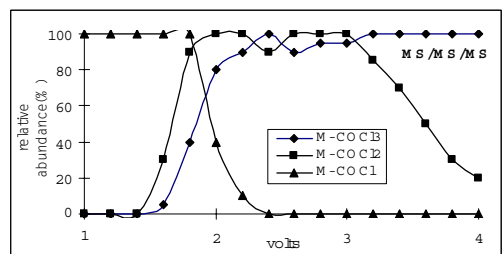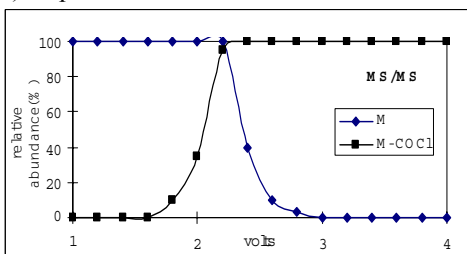
a) Tetra Chloro Dibenzofuran

b) Penta Chloro Dibenzofuran

c) Hexa Chloro Dibenzofuran

d) Hepta Chloro Dibenzofuran

e)Octa Chloro Dibenzofuran
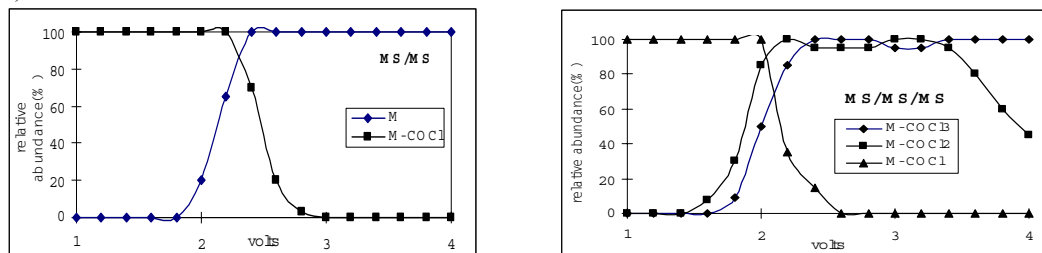

Figure 3: Effect of CID voltage on fragment ions with the a)MS/MS and b)MS/MS/MS scan function(4~8 chloro substituted furans)

Damping Gas Flow: Helium gas introduced into the ion trap mass analyzer that slows the motion of ions entering the mass analyzer so that the ions can be trapped efficiently by the electric fields. In this study, three series of 6 injections were performed at damping gas flow of 0.3, 0.6 and 1.2ml/min helium.

Results and Discussion

CID voltage: The typical behaviour of PCDDs/PCDFs in MS/MS is the fragmentation under loss of COCl, 2COCl, $COCl_2$, $COCl_3$ and $(CO)_2Cl$. For the MS/MS scan function, the optimization was performed by selecting the highest ion(parent ion) of the molecular isotopic cluster for each PCDD and PCDF, which were $[M+2]^+$ for the tetra- to hepta- compounds and $[M+4]^+$ for OCDD/OCDF. The main fragment (daughter ion) of PCDDs/PCDFs molecular ions is $[M+2-COCl]^+$ or $[M+4-COCl]^+$. Therefore the best CID voltage is to obtain the highest yield of the daughter ion by dissociation.

Figure 2 shows the effect of CID voltage on fragmentation of PCDD congeners(7 items) in MS/MS and MS/MS/MS scan function. The CID voltages were optimized 2.6-3.2V for parent ion dissociation(MS/MS) and 2.0- 2.8V for daughter ion dissociation(MS/MS/MS).

Figure 3 shows the effect of CID voltage on fragmentation of PCDF congeners(10 items) in MS/MS and MS/MS/MS scan function. The CID voltages were optimized 1.8-2.6V for parent ion dissociation(MS/MS) and 1.6-2.2V for daughter ion dissociation(MS/MS/MS).

Damping Gas Flow: Table 1 shows the effect of damping gas on area of the product ions. The result indicated that the area of total product ions was increased as damping gas flow increased with QIT in PCDD congeners, but PCDF congeners was not. The best damping gas flow was optimized to1.2ml/min for PCDD congeners (7 items) and 0.6ml/min for PCDF congeners (10 items).

Table 1: Changes in total area of fragment ions with damping gas flow.

PCDDs/PCDFs		Total area of fragment ions		
		Damping gas flow		
		0.3ml/min	0.6ml/min	1.2ml/min
PCDDs	TCDD	1228	2696	**3742**
	PeCDD	4841	10513	**14034**
	HxCDD	6803	12995	**13472**
	HpCDD	6040	11215	**17149**
	OCDD	6941	17438	**25614**
PCDFs	TCDF	1067	**2007**	953
	PeCDF	6999	**16657**	4154
	HxCDF	5946	**17157**	5171
	HpCDF	7163	**18555**	5024
	OCDF	8050	**21657**	6971

Calibration Curve: Calibration data were acquired for all of the 17 2,3,7,8-substituted congeners between 0.5 and 2000pg. Calibration curve was based on the signal areas due to $[M-COCl]^+ + [M-(CO)_2Cl]^+ + [M-2COCl]^+$ for PCDD congeners and $[M-COCl]^+ + [M-COCl_2]^+ + [M-COCl_3]^+$ for PCDF congeners with the MS/MS/MS scan function. A DL of 1.0pg/ul injected can be obtained, except for OCDD and OCDF for which the DL is 5pg/ul injected. All the correlation coefficients were ≥0.999.

References

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