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IMPROVEMENT OF SOLVENT CUT LARGE VOLUME (SCLV) INJECTION SYSTEM USING NARROW-BORE COLUMN IN DIOXINS ANALYSIS BY HRGC-HRMS

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Introduction

An SCLV injection system has been developed as a quantitative technique on the scale of a few femtograms per microlitre[1,2]. It is advantageous in that it allows a large volume injection without GC injector modification, and it can be carried out under high vacuum because of its narrow-bore column. This system should therefore contribute to improving column noise level and resolution. There has been a few information regarding different types of capillary columns. We presented comparison of the SCLV injection system with the conventional technique for analyzing dioxins by HRGC-HRMS using cyanopropyl phase capillary columns.[3,4] The aim of this study is to improve SCLV injection system using narrower bore column.

Methods and Materials

All 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 BPX-Dioxin-II (3m×0.15mm) capillary column (SGE, Australia) as the pre-column and an EQUITY-5 (15m×0.1mm×0.1µm) capillary column (Supelco, USA) as the analytical column. Four microlitre of standard (0.1ng/mL, 2,3,7,8-substituted PCDDs and PCDFs mixture) in nonane was injected. For the conventional SCLV injection system, a BPX-5 (6m×0.25mm×0.25µm) capillary column (SGE, Australia) as the pre-column and a BPX-5 (30m×0.15mm×0.15µm) capillary column (SGE, Australia) as the analytical column were used. The analytical conditions for the SCLV injection system are shown in Table 1.

Results and Discussion

Chromatograms of the dioxin standard were compared between the 15m×0.1mm column system and the 30m×0.15mm column system. The chromatograms of TeCDD, HxCDD, and HxCDF are presented in Figures 1-3, respectively; (A) stands for the use of the 15m×0.1mm column system, and (B) for the use of the 30m×0.15mm column system. These comparisons demonstrate excellent agreement between the two systems. The resolution of the chromatograms obtained using 15m×0.1mm column system was slightly lower than that of the 30m×0.15mm column system. The peak width of 2,3,7,8-TeCDD in the chromatogram for the 15m×0.1mm column system was about 4 seconds, while that for the 30m×0.15mm column system was about 8 seconds. It is considered that the cycle time per scan must be set shorter in the 15m×0.1mm column system than in the 30m×0.15mm column system.

Table 2 summarizes the ratios of native peak area to $^{13}C_{12}$-labeled internal standard peak area. The data between the two techniques agreed by 95-118%. All PCDD/F analytes were eluted within about

28 minutes with the 15m×0.1mm column system, whereas elution took about 49 minutes with the 30m×0.15mm column system. When a standard was injected using the 15m×0.1mm column system, 0.4pg of 2,3,7,8-TeCDD was detected with S/N=398. This indicates that the 15m×0.1mm column system has the same sensitivity as the 30m×0.15mm column system, with which 0.4pg of 2,3,7,8-TeCDD was detected with S/N=381. From these results, it is concluded that the 15m×0.1mm column system is effective for determining low-level dioxins.

Table 1: Analytical conditions for the SCLV injection system

Column specifications	(A) 15m×0.1mm×0.1µm EQUITY-5 (non polar)	(B) 30m×0.15mm×0.15µm BPX-5 (non polar)
Purge on time	5 min	
Injector temperature	300ºC	
Oven temperature	160ºC(4min)→20ºC/min→ 300ºC(4.5min)→60ºC/min→ 210ºC (0.5min)→10ºC/min→ 300ºC (1.5min)	160ºC(3min)→20ºC/min→ 300ºC(8min)→60ºC/min→ 210ºC (0.5min)→3ºC/min→ 300ºC (1min)
Injector pressure	688kPa (4min)→2kPa/min→ 689kPa (11min)→265kPa/min→ 424kPa (1min)→8kPa/min→ 496kPa (1.5min)	469kPa (3min)→418kPa/min→ 678kPa (14.5min)→338kPa/min→ 340kPa (1min)→3.4kPa/min→ 442kPa (1min)
Cold trap	3.5-17.5min cooling	2.5-20min cooling
Solvent cut	4-15.5min solvent cut: off	3-18min solvent cut: off
MS Resolution	>10000	
Channels	8-11	
Cycle time	210-220 ms	510-690 ms

Table 2: Comparisons of retention time and peak-area ratios

	(A) 15m×0.1mm×0.1µm		(B) 30m×0.15mm×0.15µm	
	Retention time	peak-area ratios	Retention time	peak-area ratios
2378-TeCDD	22.43	1.08	32.71	1.10
2378-TeCDF	22.26	1.11	32.33	0.94
12378-PeCDD	23.68	0.99	36.51	0.94
12378-PeCDF	23.33	0.97	35.38	0.95
123478-HxCDD	24.88	0.90	40.23	0.87
123478-HxCDF	24.58	1.02	39.28	1.03
1234678-HpCDD	26.23	1.14	44.36	1.07
1234678-HpCDF	25.81	1.05	42.93	0.97
OCDD	27.56	1.15	48.25	1.04
OCDF	27.63	1.04	48.50	0.92

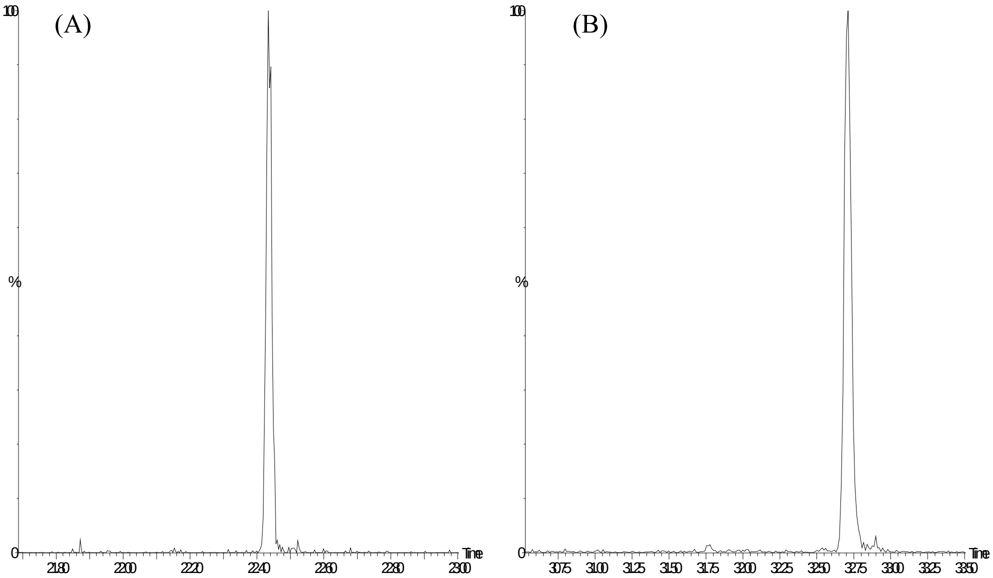

Figure 1: Chromatograms of TeCDD
(A) 15m×0.1mm column system, (B) 30m×0.15mm column system

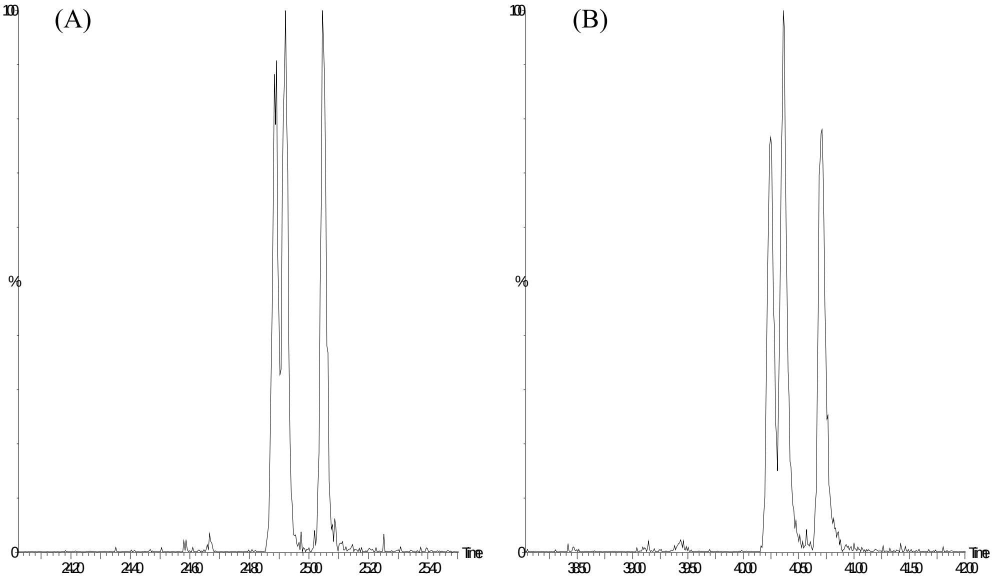

Figure 2: Chromatograms of HxCDD
(A) 15m×0.1mm column system, (B) 30m×0.15mm column system

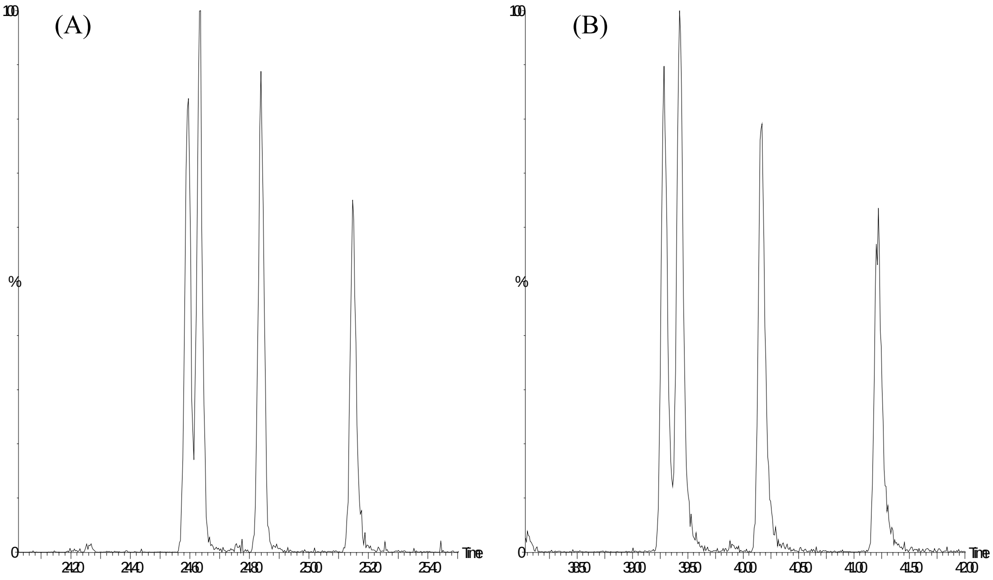

Figure 3: Chromatograms of HxCDF
(A) 15m×0.1mm column system, (B) 30m×0.15mm column system

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