DEVELOPMENT OF SOLVENT CUT LARGE VOLUME (SCLV) INJECTION TECHNIQUE WITH DUAL COLUMN CONFIGURATION FOR RAPID AND HIGH SENSITIVE GC-HRMS ANALYSIS

- (I) Narrow Bore Capillary Column Applied to Low Femto Gram Dioxins-

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Introduction

Current necessity of Dioxin analysis are ; how to shorten the time, how to achieve accurate lower lowest detection limit for quantitative analysis. Then we have developed SCLV Injection Technique. The SCLV Injection Technique will allow a large volume injection currently up to 15 micro liters without GC injector modification for some GC models and we applied this technique to dual narrow bore capillary column configuration to separate specific isomers of PCBs, PCDDs and PCDFs have different TEF value to get accurate TEQ value at the end. Scientists are realizing a limitation of current single column analysis with the columns such as BPX5, SP-2331. Analyst must take time for ion source stabilization when change over their column to run the same sample with different columns. We tried this technique to reduce these GC/MS work with 0.15mmID BPX-Dioxin-I and BPX-Dioxin-II configuring dual column system. Then this technique simplified the important isomer separation and resulted high sensitive analysis. The details of SCLV Injection Technique with dual column configuration and some results are shown in below.

Methods and Materials

- System Description

The schematic design of the technique is shown in Figure 1. The Pre-Column separates the sample into three portions as (1) Solvent (A: Solvent Cut process) , (2) Others includes target compounds such as PCDDs and PCDFs (B: Focusing process) and (3) Contaminants and matrices elute later than OCDF(A : Solvent Cut process). Two portions of (1) and (3) will be vented through MID Point-1 and heart cut valve (valve is opened) and the only portion (2) will be introduced into analytical columns (valve is closed) with split ratio at 50/50 through MID Point-1 and MID Point-2. The portion includes all targets introduced into both column at same amount will firstly be trapped at a head of each columns and focused with Liq-CO_2 to minimize the injection band to obtain excellent peak shape. Then finish focusing (Trap-1) and start run with analytical column BPX-Dioxin-I (C: Analysis process with Column-1), Trap-2 is on duration of the analysis with Column-1. Finish Trap-2 and start run with analytical column BPX-Dioxin-II(D: Analysis process with Column-2) after completing analysis with column-1.

- Advantages

The technique has advantages described as below

(1) The system will allow two columns (different polarity) to run one after the other upon one large volume injection without column change over (80-90 min total analysis time for PCDDs and

PCDFs).

(2) Organic solvent and high boilers elute later than OCDF will not be introduced into analytical column.

(3) Low fg Dioxins analyses can be performed with low bleed 0.15mmID capillary columns. The total carrier gas flow rate 0.72ml/min (0.36ml/min each) will maintain MS ion source stable.

(4) Cryogenic Cold Trap maintains excellent peak shape and height to improve S/N though it is large volume injection.

(5) No GC injector modification to perform large volume injection up to 15 micro liters.

Hardware

SCLV Injection System with Dual Columns Configuration (SGE Japan Inc.,Japan).
6890 series GC (Agilent Technology, USA) was equipped with Autospec-Ultima (Micromass, UK).
GC was controlled by the Chemistation system (Japanease Ver. /Agilent Technology, Japan).

Results and Discussion

S/N 240-245 was resulted from both columns with 10μL injection of 50fg/μL 2,3,7,8-TeCDD in Decane standard. It is equal to introduce 10fg of absolute quantity into each analytical column and calculated S/N will be 10.

Also we determined 2,3,7,8-PCDDs and 2,3,7,8-PCDFs in clean water as one of difficult sample. The quantitative result from both columns was compared with the one obtained from current standard method and these are corresponding with each other. It is clear evidence for this technique to be used for quantitative analysis.

References

1. Tohru Matsumura, Yuko Masuzaki, Tatsuya Ezaki, Makoto Ohashi, Masatoshi Morita. (2000) Organohalogen compd. **45**, 25-28.

Table 1. Comparison with Quantity Results 2,3,7,8-CDDs

	SCLV injection[1]		Normal[2]
	I[4]	II[4]	(pg/L)
2,3,7,8-Tc	0.01	0.01	0.01
1,2,3,7,8-	0.02	0.03	0.03
1,2,3,4,7,	0.03	0.02	0.02
1,2,3,6,7,	0.05	0.05	0.05
1,2,3,7,8,	0.06	0.04	0.04
1,2,3,4,6,	0.71	0.67	0.74
O-CDD	12	12	13

1. SCLV Injection Technique with Dual Column Configuration
2. Normal : normal analysis with single-column
3. It is a mistake to set SIM Grouping time.
4. I : BPX-Dioxin-I, II : BPX-Dioxin-II

Table 2. Comparison with Quantity Results/2,3,7,8-CDFs

	SCLV injection[1]		Normal[2]
	I	II	(pg/L)
2,3,7,8-Tc	0.04	overlap	0.04
1,2,3,7,8-	0.04	0.03	0.04
2,3,4,7,8-	0.05	0.04	0.05
1,2,3,4,7,	0.05	overlap	0.06
1,2,3,6,7,	0.06	overlap	0.06
2,3,4,6,7,	0.11	0.10	0.10
1,2,3,7,8,	overlap	0.01	0.01
1,2,3,4,6,	0.29	miss[3]	0.32
1,2,3,4,7,	0.04	0.05	0.04
O-CDF	0.49	0.47	0.49

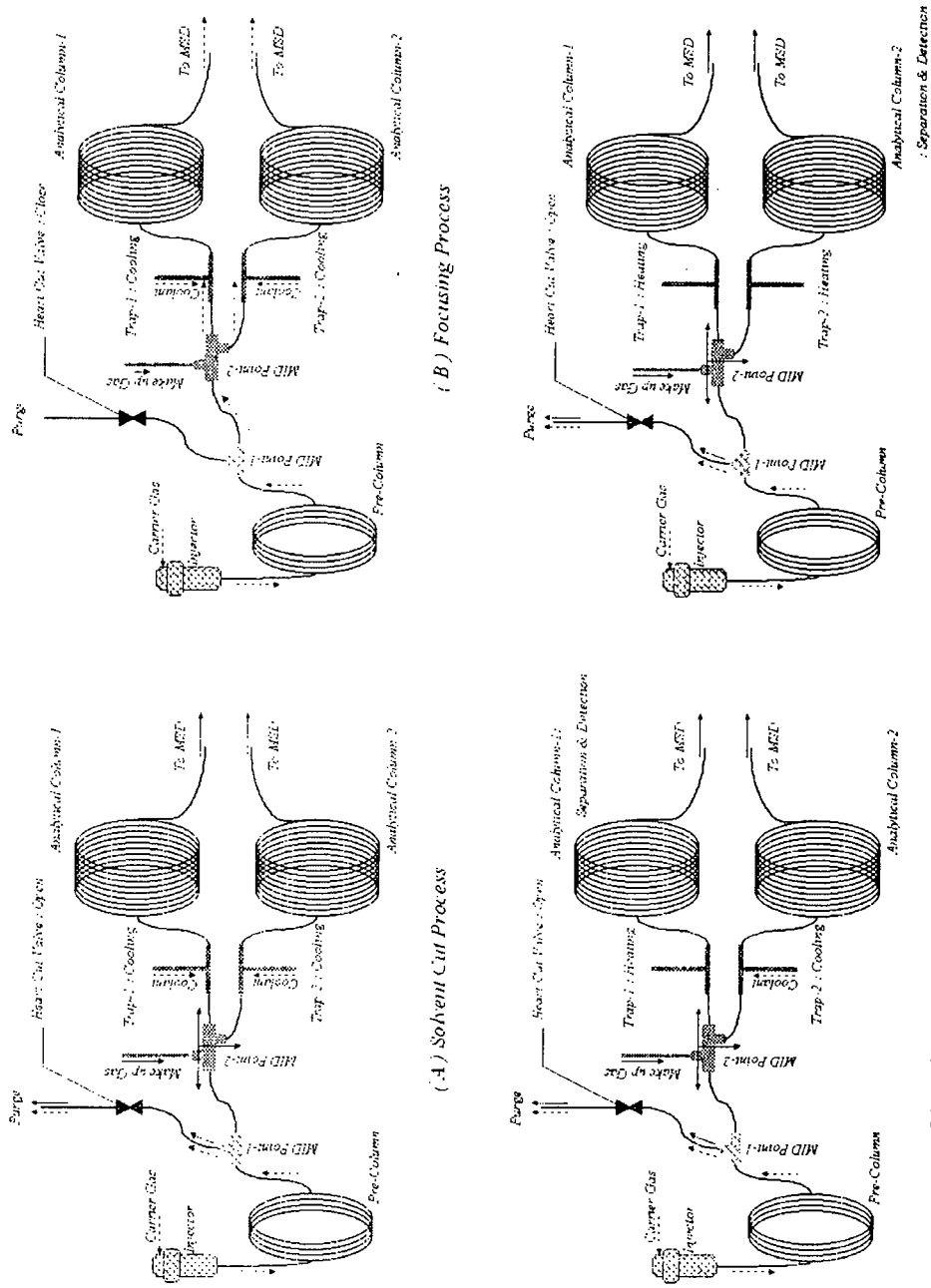
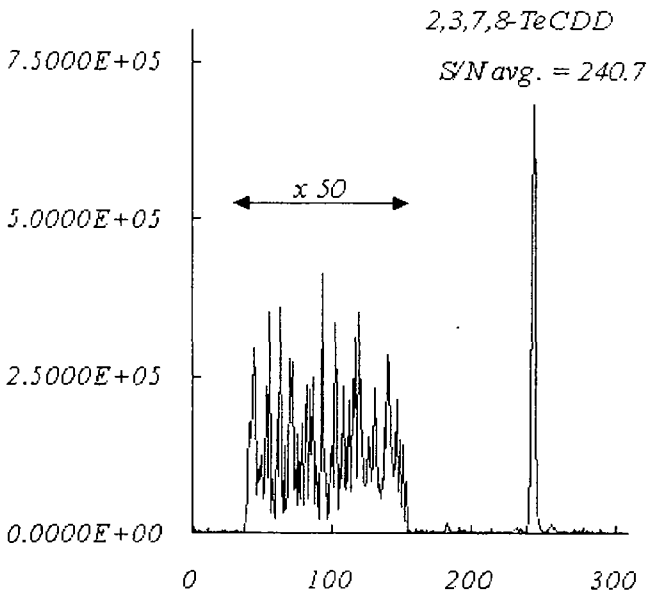
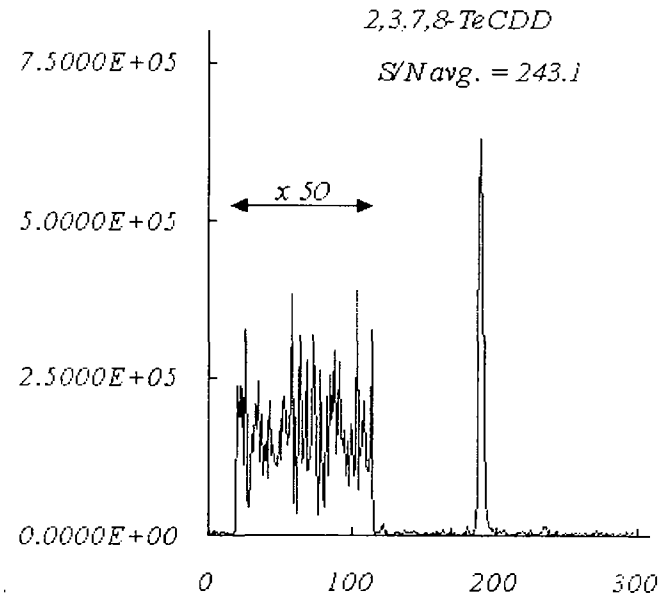


Figure 1.Schematic Design of SCLV Injection Technique with Dual Column Configuration



(E) Chromatogram of 2,3,7,8-TeCDD on BPX-Dioxin-I



(F) Chromatogram of 2,3,7,8-TeCDD on BPX-Dioxin-II

Figure 2.Chromatogram injected 50fg/μL 2,3,7,8-TeCDD decane solution 10μL.