DETECTION OF LOW FEMTO GRAM DIOXINS
- Development of Column Switching - Solvent Cut - Large Volume/Multiple Injection - Cryofocus Trap GC-HRMS -

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Introduction

Sensitivity of high-resolution mass spectrometer (double focus type) in present technology is about S/N=5-10 at 10fg for each compound of PCDDs/DFs. In order to increase sensitivity, there are two methods. One is to increase the sample size during sample preparation; the other one is to increase injection volume. The authors designed and developed "Column Switching - Solvent Cut Large Volume / Multiple Injection - Cryofocus Trap GC" and applied to PCDDs/DFs analysis connected to high resolution MS.

Methods and Materials

System Description

The schematic design of this system is shown in *Figure 1*. The Pre-Column separates "Solvent" and "PCDDs/PCDFs" and then solvent is vented out of analytical part of the GC system (A). Compounds will be eluted later than OCDF which are not targeted to this analysis are also vented. Target compounds will be trapped and focused at the head of the analytical column by "Cryogenic Trap" cooled by liquid CO_2 or liquid N_2 after the course separation between solvent and target compounds is made by Pre-Column (B). After the trapping and focusing, GC oven is cooled down to 130-150°C. Multiple injection is possible if needed (*Figure 2*). After the cycled injections, the 2nd ramp of temperature program for target compounds separation will start . Target compounds are introduced into MS after the separation with "Analytical Column (2nd Column)" is done (C).

This system has following advantages.

(1) Organic solvent will not be introduced into MS ion source.

(2) Peak shape becomes sharper because an internal volume of the column where the targets are focused is about $1/10^4$-$1/10^3$ compared with that of normal injection port liner of GC.

(3) It is possible to use narrow bore columns such as 0.15mm ID as "Analytical Column" by an effect of pressure balance.

(4) Large volume injection is possible, caused by high head pressure (Pressure of Injection Port will be about 250-450kPa).

(5) The number of cycled "Multiple Injection" will be also possible during the trapping/focusing capability is effective.

(6) Analysis time will not be so longer because of short Pre-Column is long enough to separate solvent and targets.

Hardware

6890 series GC (HP, USA) was equipped with Autospec-Ultima (Micromass, UK) or JMS-700D (JEOL, Japan). GC was controlled by the Chemstation System (HP, Japan). Pre/Analytical Columns, Heart cut valve, Cryogenic Trap, Mid Point Restrictor and all connectors related to "Column Switching System" were prepared by SGE Japan (Japan).

Results

(1) This system resulted achieved S/N=10-20 at 1fg/uL 2,3,7,8-TeCDD with 10uL single injection.

(2) Linearity for "Multiple Injection" was confirmed by contentious 3 times injections.
(3) Dual focusing/Dual analytical column system (*Figure 3*) is very potential to improve current method that requires 2-3 times injections and separation with different phases to identify the peaks. This system will split (1:1) only targeted compounds into two different columns after solvent venting then focus the targeted compounds at the head of each column. Focusing is individually controlled and then run the sample with the column one by one after the large volume injection same as the technique shown in *Figure 1*.

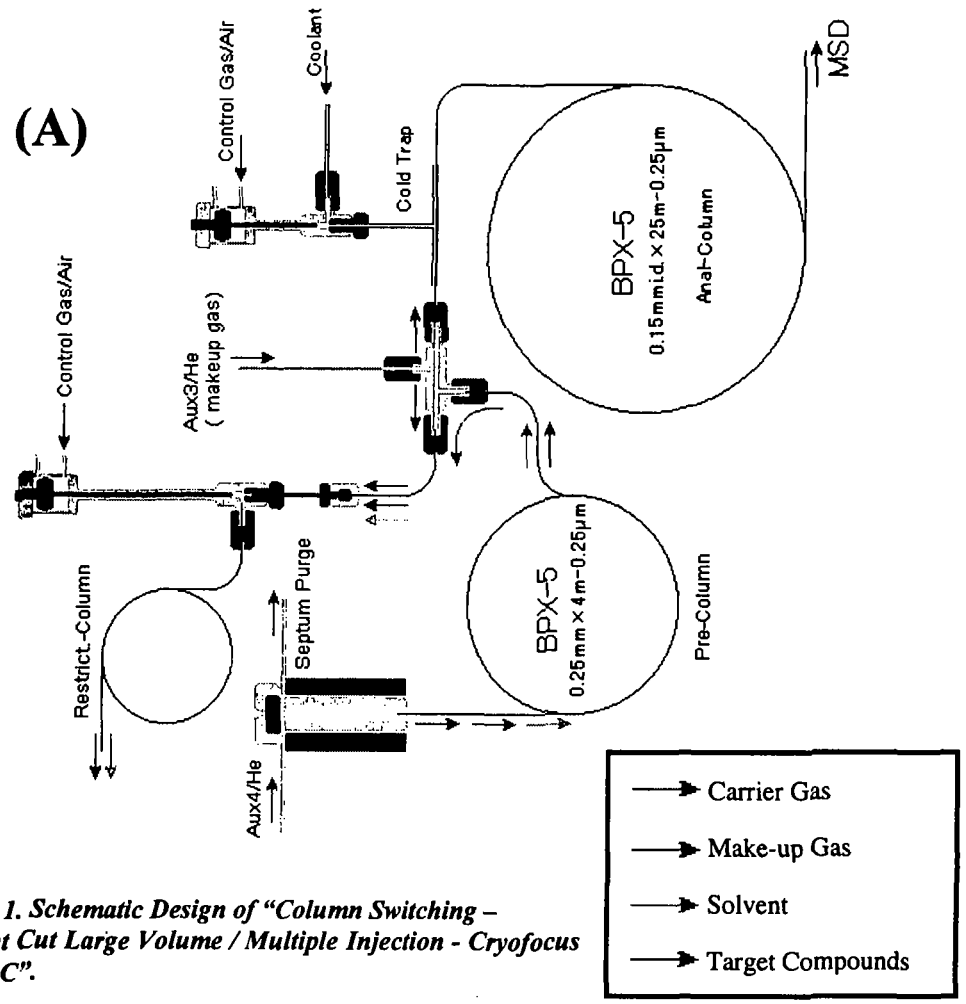

Figure 1. Schematic Design of "Column Switching – Solvent Cut Large Volume / Multiple Injection - Cryofocus Trap GC".

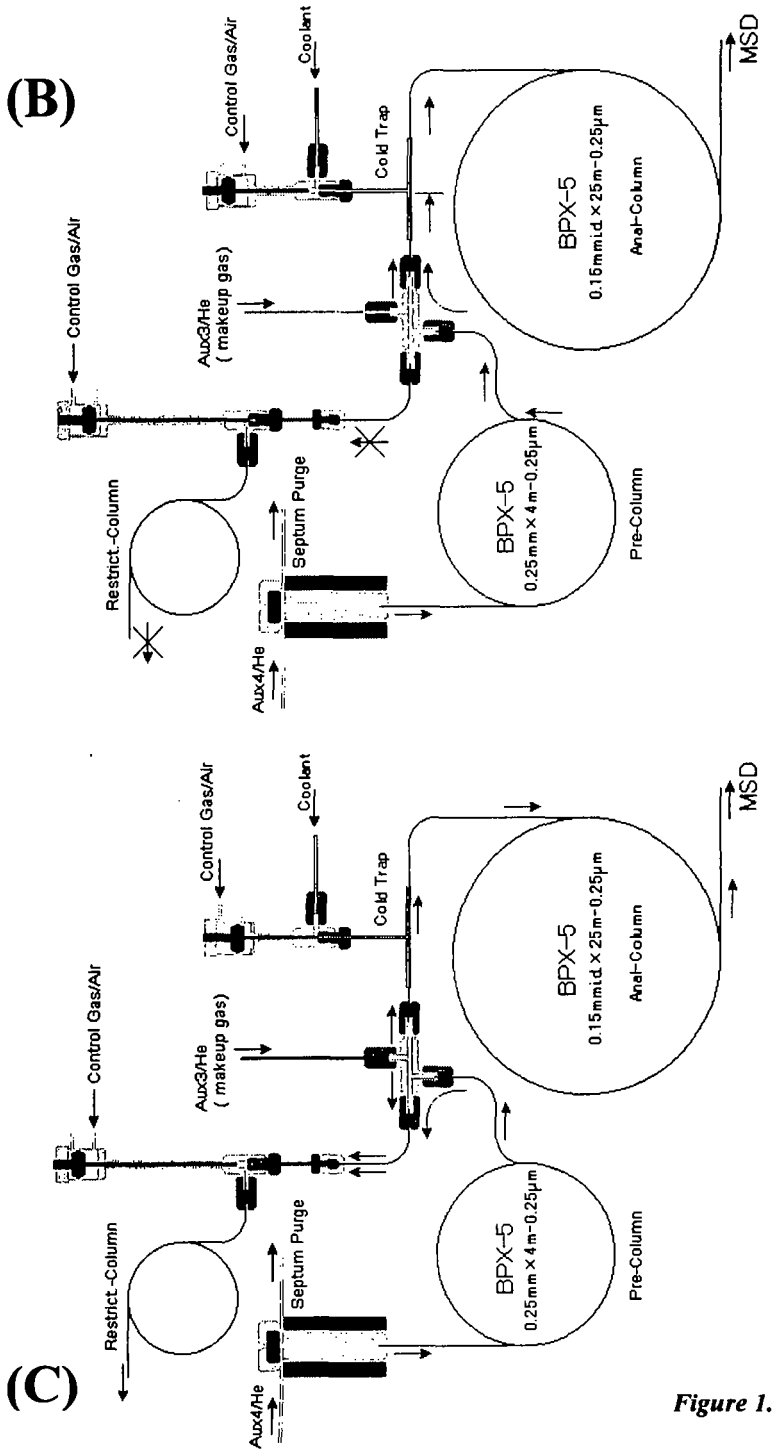

Figure 1. Continued.

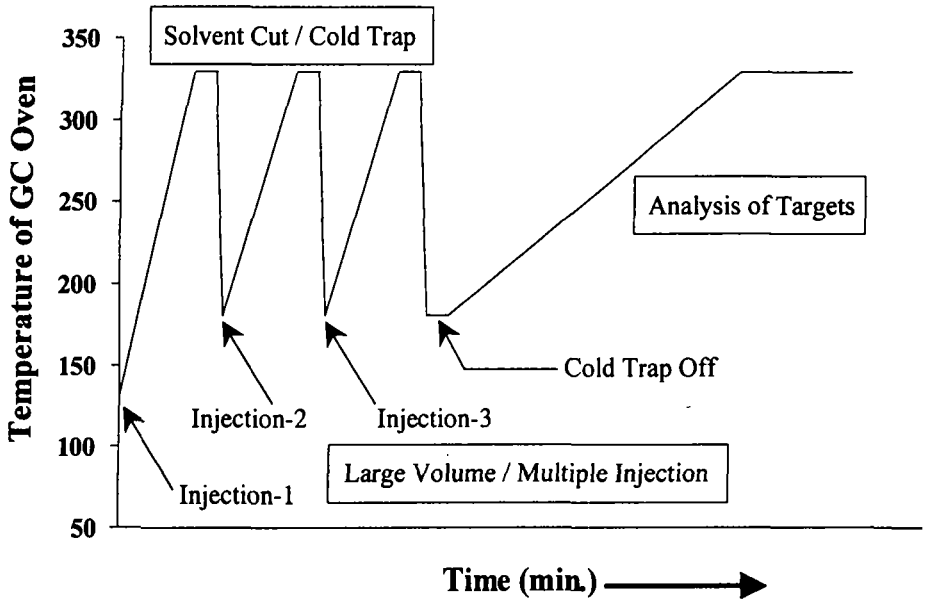

Figure 2. An Image of Ramp of Oven Temperature for Multiple Injection Sequence.

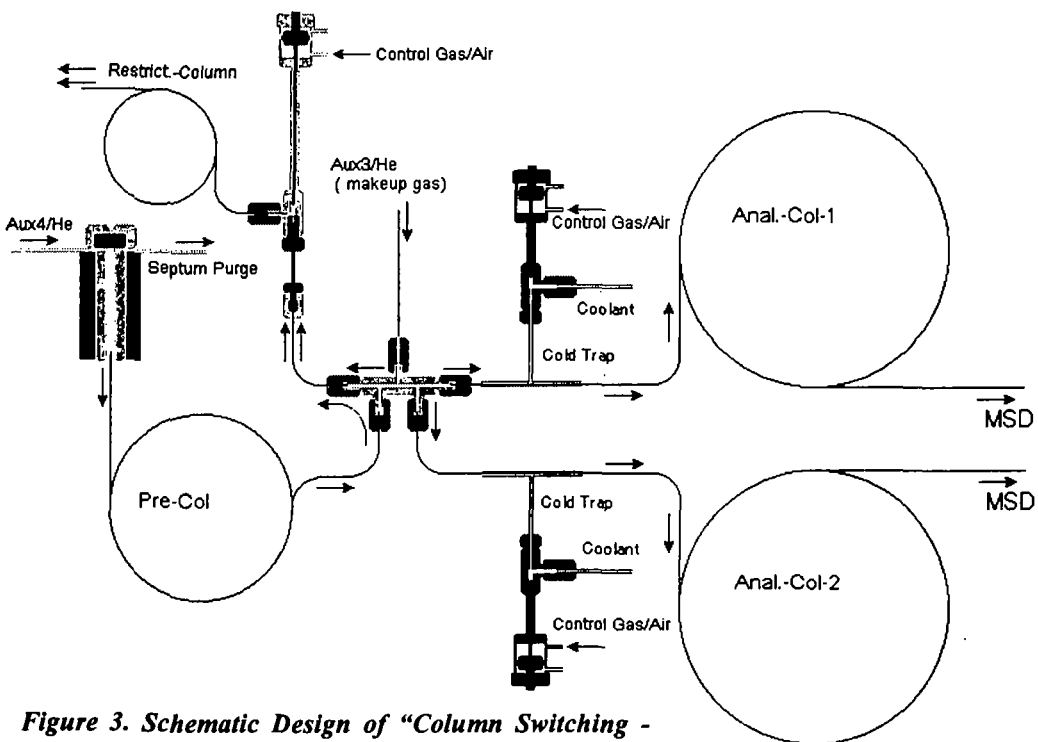

Figure 3. Schematic Design of "Column Switching - Solvent Cut Large Volume / Multiple Injection - Cryofocus Double Trap GC".