HIGH SENSITIVITY ANALYSIS WITH SOLVENT CUT LARGE VOLUME (SCLV) INJECTION TECHNIQUE

(I) Low Femtogram level Dioxins analysis for Human Blood

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Introduction

A SCLV Injection technique system has been developed for the quantitative analysis of dioxins at levels as low as a few femto grams per microlitre. This is a two-stage chromatography system (Figure 1.), where a large inside diameter Pre-Column has been selected and operated under conditions so that a very large injection up to 15 microlitres can be carried out. The pre-separation on the Pre-Column separates the large volume of solvent from the dioxins and the solvent is vented to waste through a heart-cut valve. As the targeted dioxins from TeCDD to OCDF elute from the Pre-Column they are sent to the Analytical Column which is optimized for the separation. The dioxins are cryogenically focused with a cold trap into a narrow band at the head of the Analytical Column. Components that elute from the Pre-Column after OCDF and that are not of interest may also be vented through the heart-cut valve to waste as they are eluted from the Pre-Column.

As only targeted compounds will be introduced into the Analytical Column with this method, narrow bore capillary columns can be used. The smallest column inside diameter that can be used is determined by the minimum number of data points required for accurate quantitative results though the HRMS. For this study capillary columns with an inside diameter of 0.15mm were used for maximum resolution and speed. A column length of 30m provided similar theoretical plate numbers as a 0.25mm ID x 60m column. Following are the detailed results of determination of the systems sensitivity and quantitative results of human blood with the specifically developed BPX-Dioxin-I capillary column.

Methods and Materials

1fg/uL standard (2,3,7,8-substituted PCDDs/PCDFs mixture) is used to confirm sensitivity (S/N) and separation effectiveness. In addition human blood samples were used to evaluate quantitation compared with results from the current method which involves splitless injection and 2 microlitre injections.

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).

Results and discussion

(1) With 10uL injections of 1fg/uL 2,3,7,8-TeCDD, the system achieved to S/N 10-20 compared to S/N 5-10 for the existing method.

(2) The system gave enough separation of 2,3,7,8-substitued isomers regarding blood sample.

(3) The resulting concentrations of dioxins achieved with the system corresponded very well to the common analytical method.

(4) OCDF which tends to be at concentrations lower than the lowest detection limit using the existing method was detected within the quantitative range.

(5) Total analysis time was 55 minutes.

The system automatically reconditions the Analytical Column during the Pre-Column run and the Pre-Column during the analytical run. This is a big benefit to save analysis time. Carry-over problems often observed with programmable injection techniques do not happen with this system because the standard splitless injection technique is used.

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

	SCLV Inj. (pg/g)	Normal[1] (pg/g)
2,3,7,8-TeCDD	0.000	0.000
1,2,3,7,8-PeCDD	0.008	0.008
1,2,3,4,7,8-HxCDD	0.007	0.007
1,2,3,6,7,8-HxCDD	0.053	0.059
1,2,3,7,8,9-HxCDD	0.012	0.011
1,2,3,4,6,7,8-HpCDD	0.064	0.066
O-CDD	0.48	0.63

1 Normal : normal analysis with single-column

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

	SCLV Inj. (pg/g)	Normal[1] (pg/g)
2,3,7,8-TeCDF	0.000	0.000
1,2,3,7,8-PeCDF	0.000	0.000
2,3,4,7,8-PeCDF	0.006	0.007
1,2,3,4,7,8-HxCDF	0.008	0.008
1,2,3,6,7,8-HxCDF	0.006	0.006
2,3,4,6,7,8-HxCDF	0.000	0.000
1,2,3,7,8,9-HxCDF	0.000	0.000
1,2,3,4,6,7,8-HpCDF	0.023	0.025
1,2,3,4,7,8,9-HpCDF	0.000	0.000
O-CDF	0.000	0.000

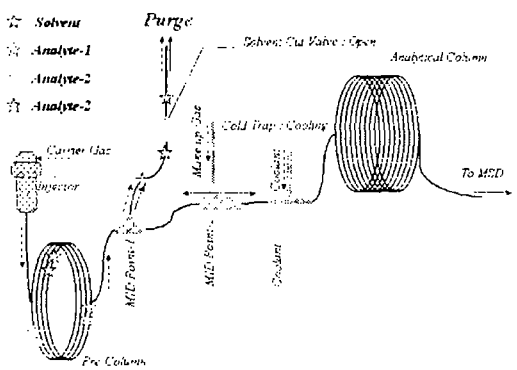

Figure 1. Schematic design of "SCLV injection system".

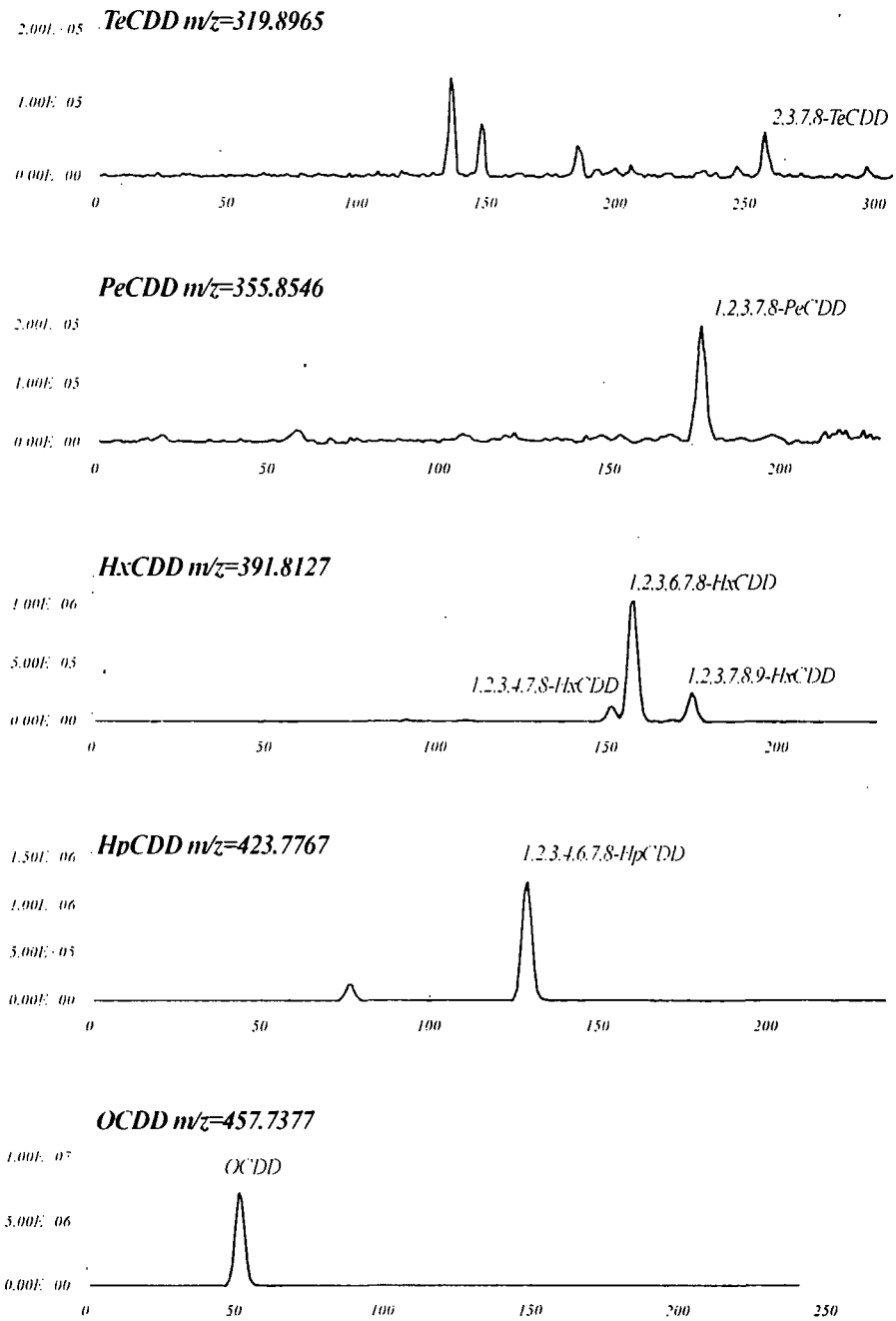

Figure 2-A. Chromatogram of blood sample (PCDDs).

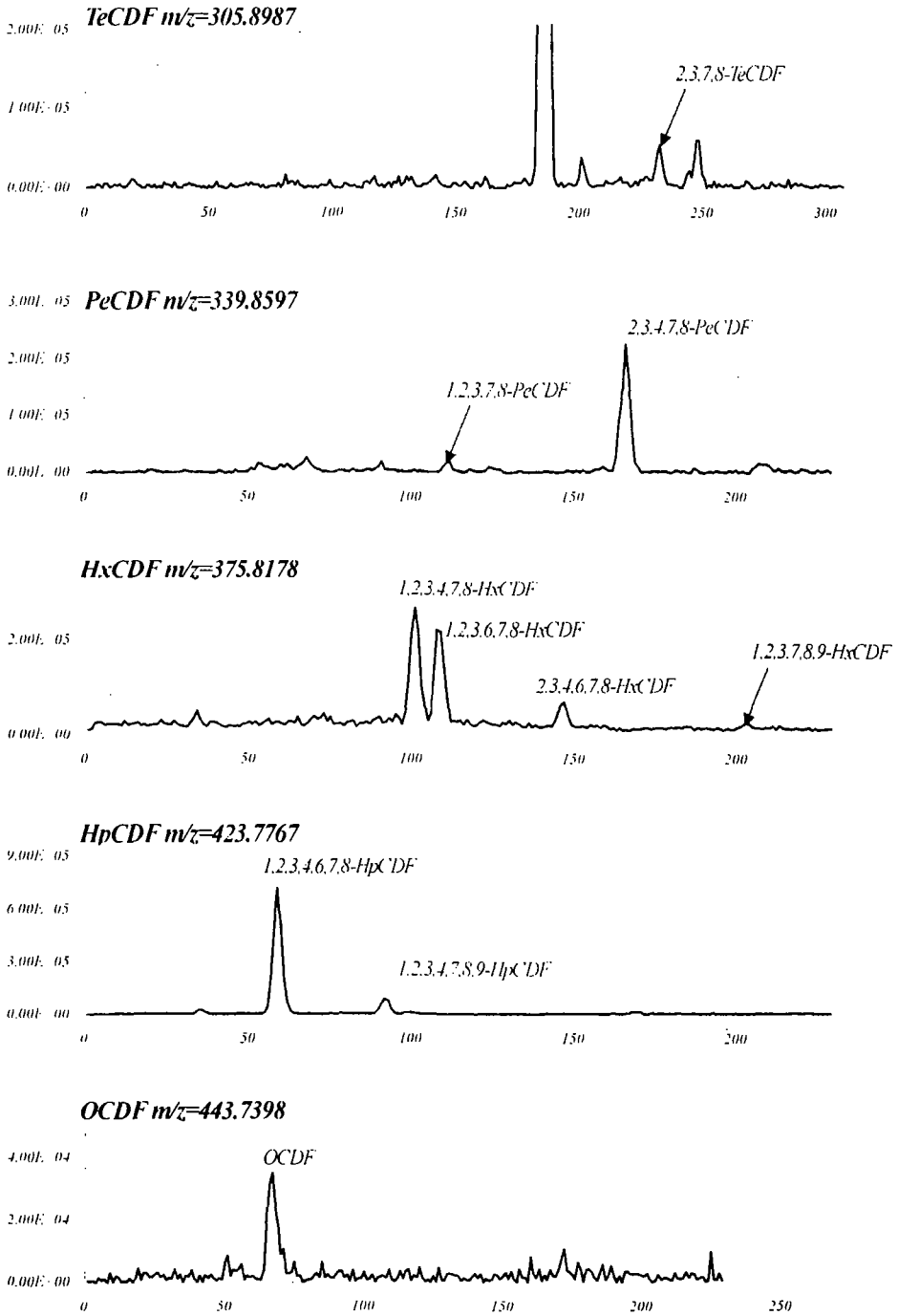

Figure 2-B. Chromatogram of blood sample (PCDFs).