Application of Isomer Specific LC-50 GC Capillary Column for Fast Analysis of 2,3,7,8-Substituted Chlorinated Dibenzo-p-dioxins

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Introduction:

Isomeric organic compounds have wide differences in their toxicity and assessment of environmental samples for their toxicity varies depending upon the amount of the toxic isomers present in a particular sample. For the true assessment of toxicity of an environmental sample, it is essential to quantify the most toxic isomers/compounds accurately. Generally, GC-MS in the electron impact selected ion monitoring (EISIM) mode is used for analysis of polychlorinated dibenzo-p-dioxins (PCDD). Recent trend is to use comprehensive two-dimensional gas chromatography (GCxGC) technique to achieve better selectivity for separation of isomeric compounds.[1-6] It is also possible to use simple detector as μECD for monitoring purpose rather than expensive and relatively complicated mass spectrometer detection technique, provided GC column can separate compounds of interest [1] .The separation of close boiling isomeric compounds using conventional capillary columns is very difficult. However, the separation of isomeric compounds can be achieved using capillary columns with liquid crystal polymer (LCP) stationary phases [7-9]. For the use of LCP as stationary phases in capillary columns, they need to exhibit high thermal stability, broad liquid crystalline range and high upper transition temperatures. The structure of mesogenic group, degree of polymerisation, packing of the side chains and the procedure of making the columns with LCP are important factors for the optimum performance of liquid crystal columns. To make a column for routine trace analysis, the stationary phase needs to be highly stable, which can increase the life of a column and decrease the column bleed. In the current investigation two isomer specific columns have been evaluated for the separation of 2,3,7,8-substituted polychlorinated dibenzo-p-dioxins from the other isomer.

Materials and Methods:

The columns evaluated in this study were prepared from naphthalene moiety containing side chain liquid crystal polysiloxane stationary phases.[7] Two columns, 10m in length with 0.15 mm and 0.10 mm internal diameters were prepared using static column coating procedures. Both columns were conditioned for 6 hours at their maximum operating temperature. Both were evaluated for the separation and analysis of chlorinated dioxins. A mixture of PCDD synthesised in our laboratory and individual standards of 2,3,7,8-substituted PCDD isomers available from commercial sources were used to determine the selectivity of LC-50 column. The ions monitored for the tetra- to octa-chlorinated dibenzo-p-dioxins and dibenzofurans were M, M+2, M+4 or M+2, M+4, M+6 for each congener group. An Agilent 6890 GC equipped with MSD (EI/PCI/NCI), FID and μECD, split/splitless EPC injectors was used to evaluate the performance of the columns. LC-50 columns were used in analysis of fish and sludge extracts for chlorinated dioxins.

Results and Discussions:

The separation of polychlorinated dibenzo-p-dioxins (PCDD) from other interfering compounds can be achieved using HRGC-HRMS and HRGC-MS/MS techniques. However these techniques are not useful for the separation of isomers in each congener group. Especially, the separation of 2,3,7,8-substituted PCDD from other isomers is very important to determine the toxicity of a particular sample. The analytical methodology can be simplified if a gas chromatographic column can separate the interfering compounds as well as the isomers in all congener groups of dioxins. The separation achieved using LC-50 column and GC-MS selected ion monitoring (SIM) technique for a synthetic mixture containing mono- to octachlorodibenzo-p-dioxin isomers is shown in **Figure 1.** It is important to notice that all dioxins are eluted in less than 27 minutes and can be quantified as total dioxins. The complete

separation of 2,3,7,8-substituted PCDD from all other isomers using LC-50 column was achieved**.** The separation and retention time of 2,3,7,8-PCDD were confirmed from the retention time of the 2,4,7,8,-substituted PCDD standard injected under identical conditions. It can be seen from Figure 1 that 2,3,7,8-TCDD is completely separated from all other tetra-CDD isomers. The selectivity of the LC-50 column can be explained based on the mechanism of separation on liquid crystal stationary phases. Among the isomers with similar volatilities, the linear and symmetrical isomers will be retained longer than the bulkier isomers because the linear and symmetrical isomers favour the geometry of the liquid crystal stationary phase. The 2,3,7,8-substituted PCDD are the most symmetrical and linear of all corresponding isomers of similar volatilities and hence retains longer.

There are important advantages of LC-50 column for analysis of environmental samples. It can be used for the analysis of the total PCDD in addition to 2,3,7,8-substituted PCDD in environmental and other samples. In a single GC-MS run of less than 27 minutes, the separation of 2,3,7,8-substituted PCDD from other isomers, and analyses of all mono- to octa-chlorinated dibenzo-p-dioxins is shown.

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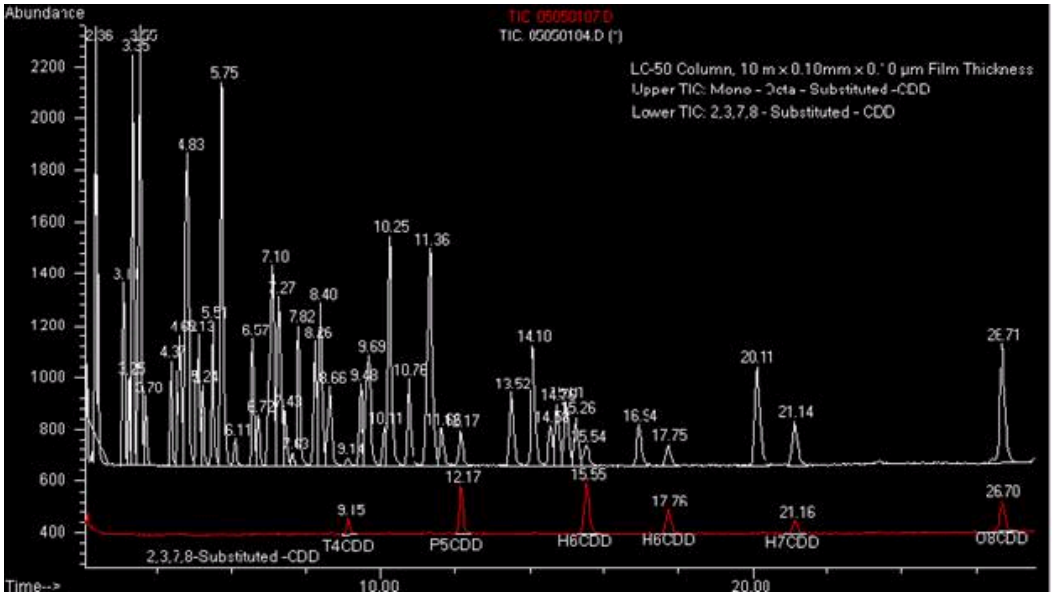

Figure 1: GC/MSD/EISIM TIC for mono-to octachlorodibenzo-p-dioxins. One ion (M+2 or M+4) for each mono- to octachlorodibenzo-p-dioxin congener was monitored. Chromatographic conditions: Oven Temperature 100^0C, programmed to 170^0C @ 40^0C/min-270^0C @ 3 ^{0}C/min, 10 minutes at 270^0C. Upper TIC for mono- to octa-CDD in a laboratory standard containing all possible dioxin isomers. Lower TIC is for 2,3,7,8-substituted CDD standard.