Liquid Crystal Capillary Column as a Tool for Identifying or Eliminating Interferences in the GC-MS Determination of PCDD and PCDF

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Abstract

The shape selective characteristics of a newly developed liquid crystal polysiloxane stationary phase were explored to provide a means of simplifying the identification and determination of PCDD/F in certain sample extracts. The results obtained with a liquid crystal capillary column were compared against those obtained with a DB-5 column, and indicate that this technique may in some cases provide a viable alternative to other more cumbersome clean up procedures.

Introduction

Liquid crystal stationary phases offer a shape selective parameter in chromatographic separations. Isomeric compounds have been observed to elute in an order that approximately follows their increasing length-to-breadth ratios (L/B)[1-3] which has served as the basis for exploring the potential use of these types of stationary phases for the isomer specific analysis of PCDD and PCDF[4-7]. The development of a homopolymeric liquid crystal stationary phase geared for the separations of all 2,3,7,8-substituted PCDD/F isomers is currently being pursued in our laboratories. However, another important property of liquid crystal stationary phases is that the degree of rigidity and planarity of solutes also determine their retention times[1], which may provide a simple means to separate PCDD/F from other interfering classes of compounds with molecular structures possessing less rigidity and planarity.

In this work the shape selectivity of a newly developed liquid crystal stationary phase is illustrated by showing the relative retentions of an Aroclor mixture with respect to the PCDD/F retention windows on the liquid crystal capillary column compared to a DB-5 column. Furthermore, the application of this phase for the analysis of ^{13}C labelled PCDD/F in sample extracts from experiments investigating *deNovo* synthesis of PCDD/F is demonstrated and compared to the performance of the DB-5 column.

Experimental

A new side chain liquid crystal polysiloxane was synthesized according to a method outlined previously[7], but with a slight variation in the terminal group, which gave rise to a product having a mesophase range of 77-281°C. Fused silica tubing (0.25 mm i.d.) was purchased from Polymicro Technologies, from which a length of 20m was coated with the liquid crystal product using the static coating technique to give a film thickness of 0.2μm. The 30m x 0.32 mm i.d., D_f = 0.25μm DB-5 column was purchased from J&W Scientific.

The GC-MS system was a HP 5890/5970 MSD with an ion source temperature of 200°C. The MS operating mode was electron impact selected ion monitoring (EISIM), and a minimum of 2 characteristic ions were monitored for each PCDD/F congener group containing 4 to 8 chlorines. The carrier gas was helium, and column head pressures were 7psi (liquid crystal column) or 9psi (DB-5 column). Cool on-column injection was used. Temperature programs are specified in the figures.

A mixture of a variety of AROCLOR from our laboratory stock was prepared to give a solution containing mono to nona chlorinated biphenyls. A reference standard containing all 210 isomers of PCDD/F was prepared in our laboratories[8].

A mixture of annealed fly ash containing 1%KCl, 1%$CuCl_2$ and 1% Charcoal was prepared and reacted at 300°C under an air stream of 45 mL/min according to the methods outlined by Steiglitz et.al[9], with the exception that ^{13}C-labelled charcoal was employed instead of unlabelled charcoal. The products were extracted with 250 mL toluene and concentrated to volumes of approximately 100μL.

Results and Discussion

Figure 1 offers an example of how the liquid crystal column may be used to remove or minimize interferences from the target analyte retention windows. The presence of PCB results in interference in the M+2 and M+4 ion of PCDD, owing to the M-HCl fragment of PCB containing two more Cl and the M ion of PCB containing one more Cl, respectively. These interferences may prevent unambiguous confirmation of PCDD by preventing the accurate verification of isotopic abundances. Clearly the lack of rigidity of the PCB, compared to PCDD, is reflected by their earlier relative elution on the liquid crystal column. This results in minimal interference, occurring only in the T4CDD window, and well in advance of the elution of 2,3,7,8-T4CDD, whose determination has historically been complicated by the presence of PCB.

Our initial experiments involving the *deNovo* sythesis of labelled PCDD/F were frustrated by the presence of unidentified interferences which coeluted with lower chlorinated PCDD/F on a DB-5 column. The extracts were also chromatographed on our liquid crystal column in hopes that this would provide an alternative to further clean up procedures. Figure 2 illustrates the comparison of mass chromatograms obtained for T4CDF. Clearly the compactness of the retention window of the DB-5 column makes positive identification difficult. Some peaks, such as 'X' which passed both the t_R and the isotopic abundance criteria on the DB-5 column, were found on the liquid

crystal column not to be representative of T4CDF. Complete results of the determinations for both extracts on both columns are given in Table 1. Lower results were obtained from the liquid crystal column for T4CDD/F through H6CDD/F, which indicates that several interfering compounds eluted within their retention windows on the DB-5 column. However, the results for the higher chlorinated species where interferences were few, were comparable on both columns. These preliminary results suggest that, depending upon the molecular structures of the interferences, liquid crystal capillary columns in GC may be used as an alternative to other more labour intensive clean-up procedures.

References

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Figure 1 *TIC tracings of PCDD/F standard (top) and AROCLOR mixture (bottom) using DB-5 (left, temp. prog: 110°C, 1min, 15°C/min, 230°C, 3°C/min, 300°C, 10 min) and LIQUID CRYSTAL (right, temp. prog: 180°C, 5min, 2°C/min, 275°C, 7.5 min)*

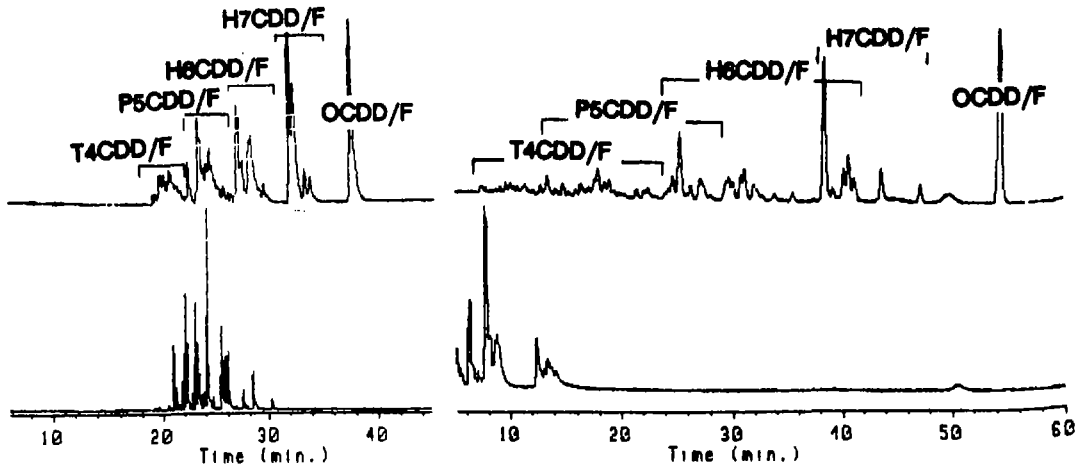

Figure 2 *Comparison of ion chromatograms obtained for standard (top) and a sample extract (ion = 315.9 amu (middle) and ion = 317.9 amu (bottom)) for the analysis of Labelled T4CDF using DB-5 (left) and LIQUID CRYSTAL (right). Peaks marked with dots were rejected. Peak 'X' is discussed in text. Temperature programs are given in Figure 1.*

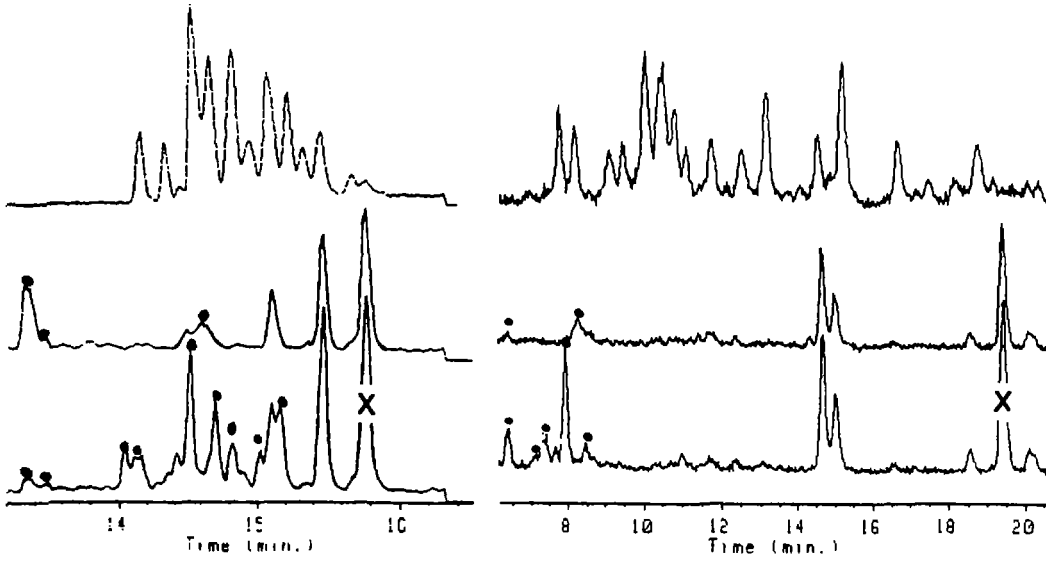

Table 1: *Comparison of results obtained for determination of ^{13}C-Labelled PCDD and PCDF in sample extracts #1 and #2 (ng/g flyash mixture) using DB-5 and LIQUID CRYSTAL columns*

	EXTRACT #1		EXTRACT #2	
CONGENER GROUP	DB-5	LIQUID CRYSTAL	DB-5	LIQUID CRYSTAL
T4CDF	20	6.4	31.5	16.2
T4CDD	nc	nd	nc	nd
P5CDF	80	52	147	98
P5CDD	nc	nd	nc	nd
H6CDF	133	108	260	195
H6CDD	22	10	28	20
H7CDF	170	171	312	318
H7CDD	55	67	84	76
OCDF	227	272	387	427
OCDD	96	120	133	146