THE APPLICATION OF SIDE CHAIN LIQUID CRYSTAL POLYSILOXANES AS STATIONARY PHASES IN HRGC SEPARATIONS OF PCDD AND PCDF

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ABSTRACT

Two different side chain liquid crystal polysiloxanes were examined as stationary phases for the isomer specific analysis of 2,3,7,8-substituted PCDD/F. The selectivities amongst the two phases were different. With one phase 2,3,7,8-T4CDD eluted last in its congener group, while with the other it eluted second to last. In general the 2,3,7,8-T4CDD/F were retained longer than most of the other T4CDD/F isomers.

INTRODUCTION

Liquid crystals have been used extensively as stationary phases in gas chromatography for the separation of various isomeric organic compounds [1-3]. The separations of close-boiling compounds are provided on the basis of their molecular geometry, where characteristics such as rigidity, planarity and length-to-breadth (L/B) ratios are related to analyte retention [1,3,4] such that planar and elongated solutes are retained longer than bulky or flexible isomeric counterparts. Side chain liquid crystal polysiloxanes have provided a means of overcoming the difficulties encountered with low molecular weight phases. Due to their polymeric nature these substances have much higher thermal stabilities thereby significantly reducing the problem of column bleed. Furthermore, their ability for thin film formation has led to acceptable efficiencies. Recently capillary columns coated with a smectic biphenyl carboxylate ester polysiloxane stationary phase, developed by Lee and co-workers [5,6], became commercially available. This phase has given promising results for the separations of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) [7-9], however difficulties regarding reproducibility have been encountered [9]. A nematic phase developed earlier by Laub and his co-workers [10, 11] has been used in the gas chromatography of various polycyclic aromatic compounds. We have synthesized several liquid crystalline polysiloxane phases in our laboratory. Preliminary results for the separations of PCDD/F on two of these phases will be presented.

EXPERIMENTAL

Fractional dissolution of the prepolymer (Polymethylhydrosiloxane, purchased from Fluka, DP = 35) was carried out according to the method described by Apfel et. al. [10]. The polyhydrosilylation reaction was carried out as described by Lee et. al. [12] using PVMS solution purchased from Petrarch as the catalyst.

The GC-MS system used was a Hewlett Packard 5890/5970 MSD with cool on-column injection and ion source temperature of 200°C.

Two portions of fused silica capillary tubing (25m x 0.32 mm i.d.) were coated with the liquid crystalline phases using the static method (Column 1: Phase 1, D_f=0.16μm ; Column 2: Phase 2, D_f=0.20μm). The columns were conditioned by heating from 40°C to 250°C (column 1) or 260°C (column 2) at 2°C/min. The temperature programming used for the analyses are indicated on the illustrated chromatograms.

Standard solutions containing 2,3,7,8-substituted PCDD/F isomers were purchased from CIL Inc., and a reference standard containing all PCDD/F isomers was synthesized in our laboratory.

RESULTS AND DISCUSSION

Two characteristic ions for each congener group of tetra- to octa- chlorinated dibenzo-p-dioxins and dibenzofurans were monitored using GC-MS in selected ion monitoring mode. Figures 1(a) and 2(a) illustrate the TIC tracings obtained for the mixture of PCDD/F, containing all isomers in each congener group, using columns 1 and 2 respectively. The liquid crystal polysiloxane phases show good thermal stability since no column bleed is apparent in these chromatograms. The operating temperatures were kept well below that of the clearing temperatures of the phases, by at least 10 °C, in order to preserve column performances.

The mass fragmentograms corresponding to the tetrachlorinated dibenzo-p-dioxins (T4CDDs) and the tetrachlorinated dibenzofurans (T4CDFs) of the lab standard and the individual 2,3,7,8-T4CDD/F isomers are also shown in figures 1 and 2. The ions monitored to obtain these traces were 321.9 amu for T4CDD and 305.9 amu for T4CDF.

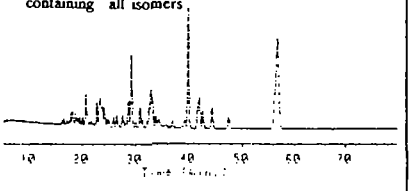
Chlorine substitution on all lateral positions provides the most elongated structures possible for PCDD and therefore according to the correlation of L/B and retention times reported in the literature, 2,3,7,8-T4CDD is expected to be retained longest in its congener group. In figure 1(b) this predicted behaviour is shown to be true, however column 2 shows a different selectivity as is seen in figure 2(b), for which there is another isomer which elutes after 2,3,7,8-T4CDD. The separations of the T4CDFs are illustrated in Figures 1(c) and 2(c). In neither case does the 2,3,7,8-T4CDF elute last. The difference between the dioxins and furans, with respect to the retentions of 2,3,7,8-substituted isomers,

Figure 1 GC-MS of PCDD/F solution: Column 1

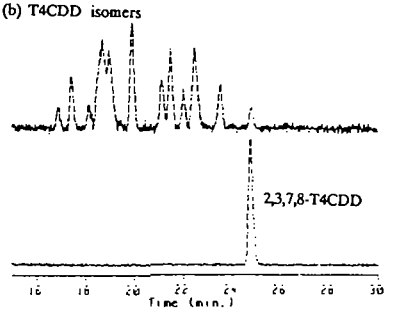
Temperature Programming:

Initial : 120 °C (1 min)
Ramp 1 : 5 °C/min
Final 1 : 210 °C
Ramp 2 : 2 °C/min
Final 2 : 250 °C (41 min)

(a) TIC of PCDD/F solution containing all isomers



(b) T4CDD isomers



(c) T4CDF isomers

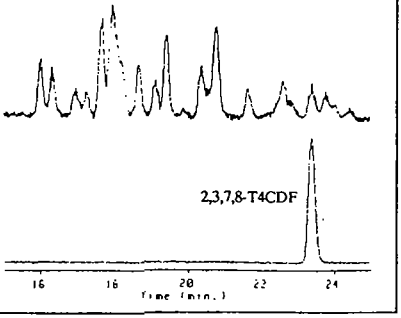
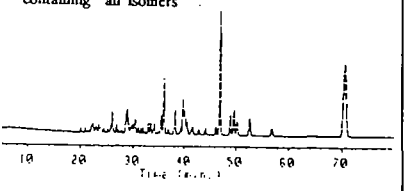


Figure 2 GC-MS of PCDD/F solution: Column 2

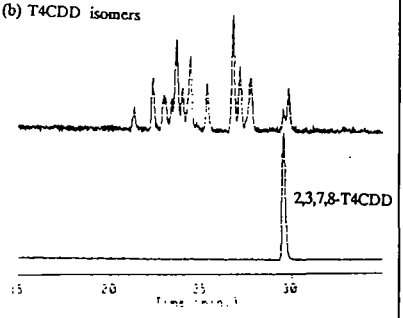
Temperature Programming:

Initial : 120 °C (1 min)
Ramp 1 : 5 °C/min
Final 1 : 210 °C
Ramp 2 : 2 °C/min
Final 2 : 260 °C (36 min)

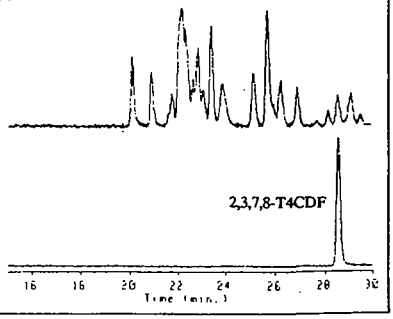
(a) TIC of PCDD/F solution containing all isomers



(b) T4CDD isomers



(c) T4CDF isomers



is not unexpected since their geometries are also different. The differences between the two columns in their overall selectivities is under investigation. Further work is being pursued to confirm the non-existence of coeluting isomers with the 2,3,7,8-T4CDD/F, and to observe the selectivities of these phases for the higher chlorinated congeners.

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