Dioxin '97, Indianapolis, Indiana, USA

A NEW LIQUID CRYSTAL POLYSILOXANE COLUMN FOR ISOMER-SPECIFIC SEPARATION OF 2,3,7,8-TCDD BY GC-MS

K. P. Naikwadi*
University College of Cape Breton
1250 Grand Lake Road, P.O. Box 5300,
Sydney, Nova Scotia, CANADA B1P 6L2

P. P. Wadgaonkar
J & K Environmental Ltd.
1240, Grand Lake Road, P.O Box 1042
Marconi Campus, Sydney,
Nova Scotia, CANADA B1P 6L2

ABSTRACT

Several new side chain liquid crystal polysiloxanes (SCLCP) were synthesized for their application as stationary phases in gas chromatography columns. The capillary columns developed using SCLCP stationary phases exhibited high thermal stability and efficiency. Also, they have shown unique selectivity for the separation of 2,3,7,8-TCDD from other tetra- isomers. Analysis of polychlorinated dibenzo-p-dioxins (PCDD) on SCLCP capillary column showed the separation of the most toxic isomers, in particular, 2,3,7,8-substituted isomers from the other isomers. The analysis of 2,3,7,8-TCDD and total PCDD in a single GC-MS run is a promising feature of the new SCLCP capillary columns.

INTRODUCTION

Low molecular mass liquid crystals (LMMLC) were used in capillary columns due to their extraordinary selectivity for the separation of structural and positional isomers. However, their drawbacks were high column bleed, poor column efficiency and non-reproducible retention times. To overcome these drawbacks, the LMMLC were blended with conventional polysiloxane stationary phases[1,2]. Attempts in this regard had limited success. So, there was a need to synthesize liquid crystals suitable for use in capillary columns and overcome the difficulties of lower column efficiency and stability encountered with the LMMLC. The logical step was to use liquid crystal polymers as stationary phases.

The SCLCP consists of two components, the pendent liquid crystalline moieties and the polymer main chain to which they are attached. A large number of LMMLC which proved to be good as stationary phases in packed column can be used in the preparation of SCLCP suitable as stationary phases for capillary columns. Thus, the combination of modified main chain and LMMLC allows a manifold variation to obtain a variety of SCLCP. So far, only substituted phenyl- and biphenyl-containing SCLCP were used as stationary phases. Their use as stationary phases for analysis of environmental samples has been reported[3,6].

Taking into account the correlation between the structure, liquid crystalline range and thermal stability, in the current investigation SCLCP were developed to overcome the difficulties encountered with LMMLC and previously reported SCLCP columns[3-6]. Initially, several new 2,6-disubstituted naphthylene containing liquid crystalline olefins were synthesized. Those olefins were then attached to polysiloxane backbone by hydrosilylation reaction. The resulting new SCLCP containing disubstituted naphthylene were used for the first time as stationary phases in capillary columns.

The analysis of environmental samples for PCDD requires rigorous methodology for positive identification and quantification. Environmental samples are difficult to analyze due to sample complexity and strong interferences from other chlorinated organic compounds. The current techniques for the analysis of 2,3,7,8-TCDD in environmental samples are time consuming and are not completely satisfactory. The liquid crystal column developed under current investigation shows the unique selectivity for the separation of 2,3,7,8-TCDD from other tetra- isomers.

EXPERIMENTAL METHODS

Several liquid crystalline olefins containing 2,6-disubstituted naphthylene moiety were synthesized and reacted with poly(methylhydrosiloxane) to obtain SCLCP. Then the SCLCP were used to make fused silica capillary columns. The columns were made using the static coating technique. In a typical procedure, a calculated amount of SCLCP was dissolved in dichloromethane. A pre-treated fused silica capillary tubing of desired length was then filled with the stationary phase solution. The filled tubing was sealed at one end and the solvent was removed by applying vacuum to the other end. The coated column was conditioned by heating from 40°C to 295 °C at 4°C/min, and was held at 295°C for 5 hours. The SCLCP used as stationary phase had a wide liquid crystalline range 140°C to 324°C. A SCLCP column, 30m x 0.25 mm, 0.125 μm film was used in the current studies. A mixture of PCDD/PCDF synthesised in our laboratory and individual standards of 2,3,7,8-substituted PCDD/PCDF isomers available from commercial sources were used to determine the selectivity of the newly developed 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. Hewlett Packard 5890 GC-MSD instrumentation was used to evaluate the performance of columns for PCDD separations.

RESULTS AND DISCUSSION

GC-MS in the electron impact selected ion monitoring (EISIM) mode is generally used for analysis of PCDD. The separation of TCDD from other interfering compounds can be achieved using HRGC-MS/EISIM or HRGC-HRMS or HRGC-MS/MS techniques. However these techniques are

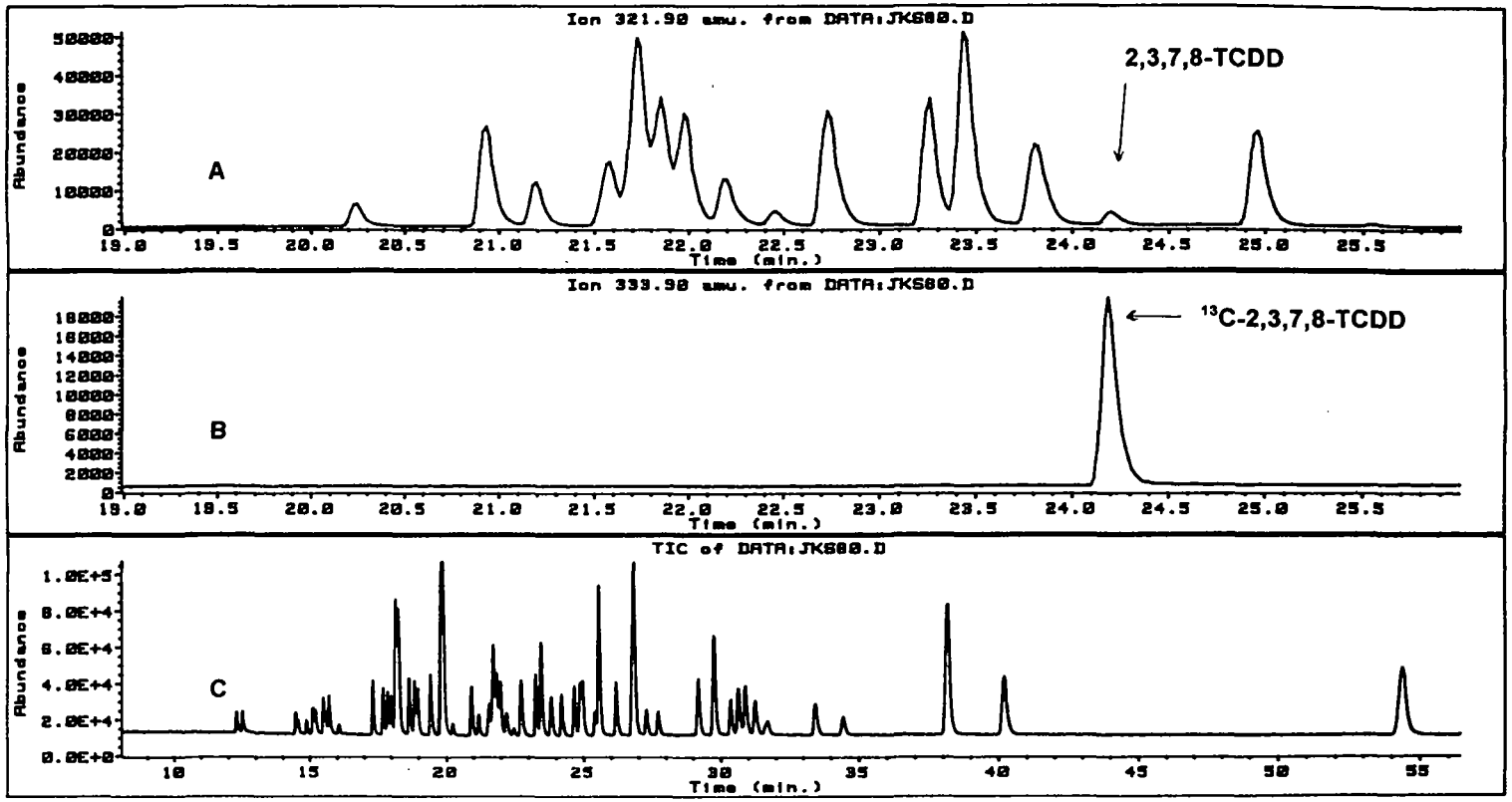

Figure 1.
Separation of 2,3,7,8-TCDD from other TCDD isomers, GC-MS/EISIM data, **A**: mass chromatogram of M+2 ion of T_4CDD (m/z=321.9) for a synthetic mixture of PCDDs, **B**: mass chromatogram of M+2 ion of ^{13}C-TCDD (m/z=333.9) for a spiked labelled standard. **C**: Total ion chromatogram of a synthetic mixture of PCDDs, two ions (M and M+2, or M+2 and M+4) for each mono to octa-CDD were monitored. Chromatographic conditions: Liquid Crystal Polysiloxane (LCP-1) column (30 m X 0.25 mm i.d., 0.125 μm film), initial oven temperature 100°C, programmed to 250°C at 10°C/minute, programmed to 285°C at 5°C/minute, final time 40 minutes.

not useful for the separation of 2,3,7,8-TCDD from other tetra isomers. 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 and dibenzofurans. The complete separation of 2,3,7,8-TCDD from all other tetra-CDD isomers using newly developed capillary column by GC-MS is shown in Figure 1: A. The separation and retention time of 2,3,7,8-TCDD was confirmed from the retention time of the spiked ^{13}C-TCDD, Figure 1, B. It can be seen from Figure 1: A and B that 2,3,7,8-TCDD is completely separated from all other tetra-CDD isomers. The selectivity of this new 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-TCDD is the most symmetrical and linear of all 22 TCDD isomers and hence retain longer. The separation achieved using the new column and GC-MS selected ion monitoring (SIM) technique for a synthetic mixture containing mono- to Octa-chlorodibebzop-dioxin isomers is shown in Figure 1, C. There are several advantages of the newly developed column for analysis of environmental samples. It can be used for the analysis of the total PCDD/PCDF in addition to 2,3,7,8-TCDD in all environmental samples. The separation of 2,3,7,8-TCDD from other tetra- isomers and analysis of all mono- to octa- chlorinated dibenzo-p-dioxins in a single run is a promising feature of this column. Separation and identification of 2,3,7,8-substituted all PCDD and PCDF isomers using new SCLCP column is presentely under investigation.

CONCLUSIONS

The new column developed in this study can be used for the analyses of total PCDD/PCDF in addition to 2,3,7,8 TCDD in complicated environmental samples, in a single run. The most toxic 2,3,7,8-TCDD is separated from remaining 21 tetra-CDD isomers.

ACKNOWLEDGEMENT

The authors express their thanks to the National Research Council and Enterprise Cape Breton Corporation for the financial support.

LITERATURE CITED

1) Laub, R.J.; Purnell J.H., *J. Am. Chem. Soc.* **1976**, 98, 30.
2) Kong, R.C.; Lee, M. L.; Tominaga, Y.; Pratap, R.; Iwao, M; Castle, R. N., *J. Chromatogr. Sci.* **1982**, 20, 502.
3) Patterson, D.G. Jr.; Reddy, V. V.; Barnhart, E.R.; Ashley, D.L.; Lapeza, C.R. Jr.; Alexander, L.R.; Gelbaum, L.T. *Chemosphere,* **1989**, 19, 233-240.
4) Swerev, M.; Ballschmiter, K. *J. High. Resolut. Chromatogr. Chromatogr. Commun.*, **1987**, 10, 544.
5) Albrecht, I.D.; Naikwadi K. P.; Karasek, F.W. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1991**, 14, 143-146.
6) Albrecht, I.D.; Naikwadi, K. P.; Karasek, F. W.; Hatano, H. *Anal. Sci.*, **1991**, 7, 215.