New Capillary Gas Chromatographic Columns for the Analysis of Dioxins, Furans, and PCBs

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Abstract

The analyses of Dioxins, Furans, and PCBs are generally performed using at least 2 different methods, and if data for the co-planar PCBs is required a third method is often utilized. This can mean that for 1 sample it may be necessary to perform a dual-column ECD method for the non-coplanar PCBs, high resolution mass spec analysis for the dioxins and furans, and either a mass spec or another ECD analysis for the co-planar PCBs. Additionally common methodologies for these analyses can result in 1-hour long chromatographic separations, and different sample preparation procedures may also be required.

This investigation describes the preliminary data in the attempt to consolidate all of these analyses plus the toxaphene and PAH analyses into a single high resolution GC/MS separation.

Experimental

GC/MS

All separations using Agilent 6890 GC coupled to a Micromass Ultima HRMS @10,000RP; **Injection port:** 280°C; **Carrier gas:** He or H_2

Columns

20M: 0.10mm ID, 0.10µm Rtx®-5MS (Restek Corp.); **Column head pressure:** 100psi; **Oven program:** 100°C (hold 1 min.) to 200°C @ 100°C/min. to 235°C @ 13°C/min. to 300°C @ 27°C/min. (hold 4 min.); **Injection volume:** 0.2µL.

40M: 0.18mm ID, 0.18 µm Rtx®-5MS (Restek Corp.); **Column head pressure:** 61psi.; **Oven program:** 100°C (hold 0.62 min.) to 200°C @ 64.5°C/min. to 235°C @ 4.8°C/min. (hold 6.2 min.) to 300°C @ 9.7°C/min (hold 5.6 min); **Injection volume:** 1.0µL.

Extract Preparation

Extracts are prepared similar to the US EPA Method 8290, but the extracts are further cleaned using carbon SPE. This method allows for the collection of two sample extract fractions: one containing the non-coplanar PCBs, and the other containing the coplanar PCBs, dioxins, furans, and PAHs.

Separation Requirements

Dioxins and Furans

Chromatographic resolution and analysis times are dependant on column dimensions (length, i.d., phase thickness). The table below summarizes a number of column options for the analysis of dioxins/furans. The conventional 60M 5% diphenyl column is assigned a relative analysis time of 1. Experimentally it has been determined that 175,000 plates are required to obtain the necessary separation of 2,3,7,8-TCDD from its nearest neighbors (1,2,3,7/1,2,3,8-TCDD unresolved pair eluting before, and 1,2,3,9-TCDD eluting after). This criterion can be easily met on both the 40M, and the 60M columns, however, the analysis can be completed in nearly ½ of the time on the 40M column. The 20M column is also capable of meeting these requirements in about ¼ of the time, however, there is little room for trimming the column when the column performance begins to deteriorate with use. For the dioxin and furan analysis, therefore, a 40M column was selected for this work.

PCBs

In order to minimize the number of ions that must be simultaneously monitored, it is desirable to elute the bulk of the PCB compounds prior to the elution of the dioxin and furan compounds. This can be accomplished by injecting the non-coplanar PCB fraction into a 20M column that is parallel to the 40M column used for the separation of the dioxin/furan fraction.

Column Configuration

Columns are installed in parallel into an MS ion source, with PCB fraction being injected onto the 20M column, and the dioxin/furan fraction being injected onto the 40M column. Resulting analysis time is less than a single fraction on the conventional 60M column.

Analysis

Sample chromatograms are shown for the separation of several PCBs and dioxins by chlorination level. PCB data for the analysis of two reference materials (sediment and biota) are summarized in the tables below. This method was also evaluated for three different extracts, soil, biota, and air versus the conventional separation on the 60M column. This data appears as a comparison of the "fast" method to the "conventional" method in the table.

Analysis of PCB Congener Reference Sediment EC-3

PCB Congener	Expected Value ng/g	N	Average Value
18	9.0 +/- 4.7	8	9.2
28	18.6 +/- 8.6	8	14.7
52	35.6 +/- 12.9	8	28.9
105	13.1 +/- 4.3	8	18.9
118	28.5 +/- 5.4	8	28.6
138	25.2 +/- 6.3	8	26.0
153	24.2 +/- 4.1	8	22.6
170	8.9 +/- 1.3	8	9.6
180	15.4 +/- 6.6	8	13.7

Extract	Compound	Conventional GC/HRMS (60M)	Fast GC/HRMS (40M)
Soil	2,3,7,8-T_4CDD	2.2 ppt	2.3 ppt
Fish	2,3,7,8-T_4CDD	14 ppt	13 ppt
Air	1,2,3,7,8-P_5CDD	0.093 pg/M^3	0.093 pg/M^3

Summary

This presentation describes the initial attempt at method consolidation and throughput increase from a parallel-dual-column separation using GC-HRMS for the analysis of PCBs, Dioxins, Furans, and PAHs. The authors are continuing to refine this method, but initial results are very promising. This method should allow for the combining of several different analytical methods to a single instrument, whit a total analysis time of less than 30 minutes.

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✔ **Karen McPherson,** Ministry of the Environment—Ontatio, Canada

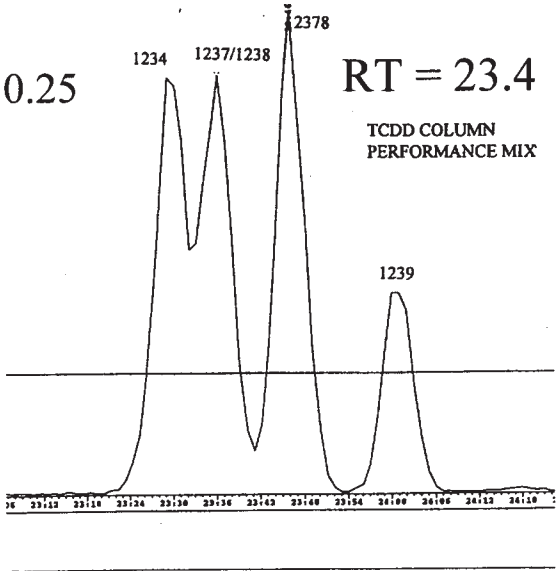
PCB Congener Analysis of NRC CARP-1 Reference Fish

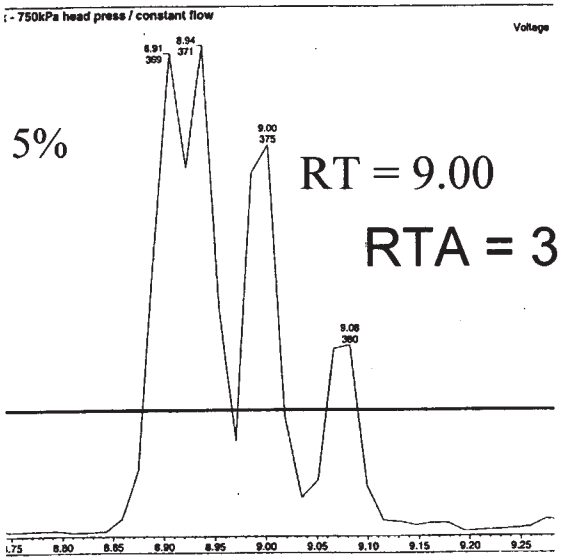
PCB CONGENER	CERTIFIED VALUE (ng/g)	N	AVERAGE
52	124 ± 32	3	141
101	124 ± 37	3	131
105	54 ± 24	3	51
118	132 ± 60	3	126
138	102 ± 23	3	102
153	83 ± 39	3	96
170	22 ± 8	3	22
180	46 ± 14	3	48
187	36 ± 16	3	39

Column Comparison: Dioxin

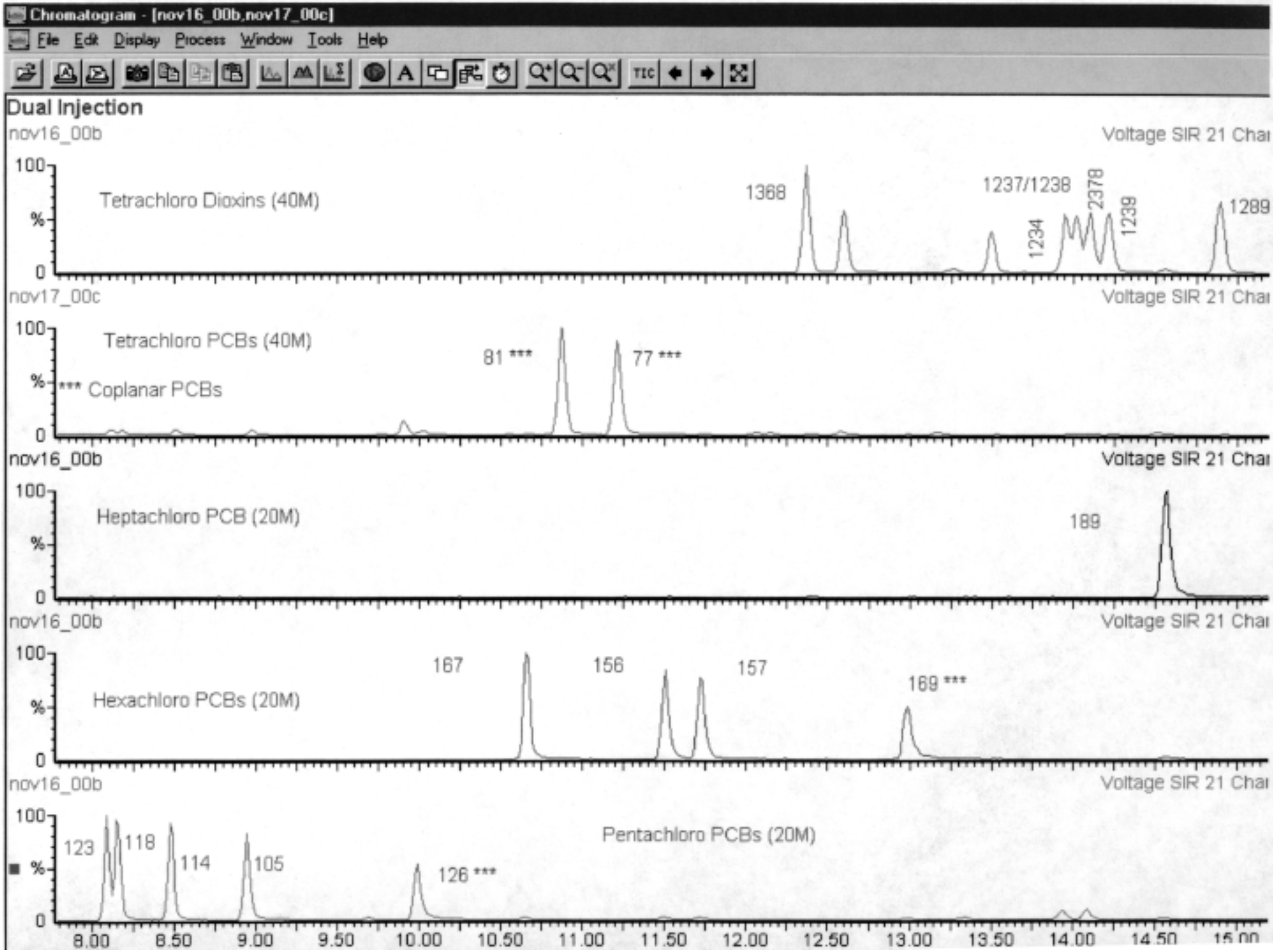
Column Length (m)	20	60	40
i.d. (mm)	0.1	0.25	0.18
Film Thickness (μm)	0.1	0.25	0.18
Theoretical Plates/m	8,600	3,300	5,300
Total Plates	172,000	198,000	212,000
Effective Plates (TCDD)	176,000	230,000	285,000
Relative Efficiency	0.93	1	1.03
Relative Anal. Time	0.33	1	0.55

60m - 0.25, 0.25
5% phenyl





20m - 0.1, 0.1 5%
phenyl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