Organohalogen Compounds, Volume 60, Pages 41-44 (2003)

THE DETERMINATION OF LIQUID CHROMATOGRAPHIC ELUTION PATTERNS IN THE SEPARATION OF PCB ISOMERS PRIOR TO ANALYSIS

C. Sueper[1], E. Kehoe[1], B. Gaylord[1], J. Palausky[2], D. Friedrich[1], S. Hannan[1]

[1]Pace Analytical Services, Inc., 1700 Elm St., Minneapolis, MN 55414
[2]Terrachem, Inc., 8600 Shawnee Mission Pkwy, Suite 305, Shawnee Mission, KS 66202

Introduction

The interest in polychlorinated biphenyl (PCB) congeners has shown a steady increase in recent years. Since Aroclor marketing was halted in the United States in 1977[1], the Aroclors have been affected by "weathering" due to photolysis and biodegradation. Due to the effects of weathering, the PCB isomer patterns seen in the original Aroclor mixtures are becoming more difficult to identify and may produce false negative results when using conventional gas chromatography methodology for identification. This has led to techniques used to identify individual congeners, thus providing both a fingerprint of the PCB isomers and a reliable value for the total PCB concentration remaining in the sample.

As part of the fingerprinting process, it may be useful to target only selected PCB isomers. Although current methodology does allow individual identification of a large number of isomers, many are not completely resolved by the typical suite of columns (SPB-Octyl, DB-5MS, DB-1, etc.). Therefore, information related to the elution sequence of selected isomers during the analyte enrichment procedure could potentially be used to provide further separation of specific isomers and eliminate the need for multi-column analyses when only selected PCB isomers are targeted. The use of liquid chromatography to increase the options for improving the separation of selected PCB isomers was the goal of this experiment.

Materials and Methods

The elution patterns were tested using the full suite of native isomers available from AccuStandard, New Haven, CT, USA (M-1668A-0.01X-SET). The combined 209 isomer stock solution (Method 1668A[2], Section 7.8.2.2) was prepared and an aliquot was added to each sample tested. Initially, a 1 mL aliquot of hexane was spiked with an aliquot of the combined 209 isomer stock solution and processed through an automated Power Prep™ clean-up system (Fluid Management Systems, Waltham, MA, USA). The Power Prep™ system was set up to utilize the multi-layer silica and alumina columns available from FMS. The tests were performed both with and without the use of FMS carbon columns in order to determine the elution scheme of selected isomers. All solvents were Optima grade purchased from Fisher Scientific.

In order to determine which isomers eluted throughout the elution of each particular column, spiked samples were loaded onto the Power Prep™ system and the PCBs were eluted. First, 90 mL of hexane was used to elute the PCBs through the silica column onto the alumina column with the hexane eluent from the alumina column directed to a waste container. The alumina column

was then eluted sequentially to a carbon column with 60 mL of 2% (v/v) methylene chloride/hexane (2%DCM) and 120 mL of 50% (v/v) methylene chloride/hexane (50%DCM). Fractions of 2%DCM and 50%DCM were collected in 30 mL volumes. The carbon column was then eluted with 16 mL of 50% (v/v) ethyl acetate/toluene (50%EtTol) followed by 10 mL of hexane as a line and valve rinse, both in the forward direction. Fractions of 50%EtTol were collected in 4 mL volumes.

After separation, each fraction was spiked with the Method 1668A labeled toxics/LOC/window defining standard spiking solution and the labeled clean-up standard spiking solution (Method 1668A, sections 7.12 and 7.13). By adding the native analytes before separation and the labeled standards after completion, the levels of native analytes in each fraction can be accurately quantified and not be affected by the elution of the related labeled standards. Each fraction was then concentrated, spiked with the labeled injection internal standard spiking solution (Method 1668A, Section 7.14) and analyzed using a Micromass Autospec Ultima high resolution mass spectrometer. The mass spectrometer was operated in the electron impact/selected ion recording mode and utilized a 30 meter Supelco SPB-Octyl capillary column fitted into an Agilent 6890 gas chromatograph.

Results and Discussion

Table 1 presents elution information for all 209 congeners based on the elution scheme discussed above. The table is organized by solvent system and then by PCB IUPAC number. It should be noted that the majority of congeners were recovered in more than one elution solvent system. The table, however, only lists the solvent system where the majority (>50% of total) of the congener was found. It was observed that several congeners were recovered in roughly equal amounts in the 2 % and 50 % methylene chloride/hexane fractions. These congeners are listed under the combined solvent systems of 2 % and 50 % DCM. These results suggest that further separation of these isomers may be obtained with modifications to the alumina column elution scheme. Additionally, octa- through deca-substituted congeners generally had lower recoveries in the 2% fractions. Further tests without the use of a carbon column yielded significantly improved recoveries for these analytes. This suggests that these isomers are retained by the carbon column when this elution scheme is utilized.

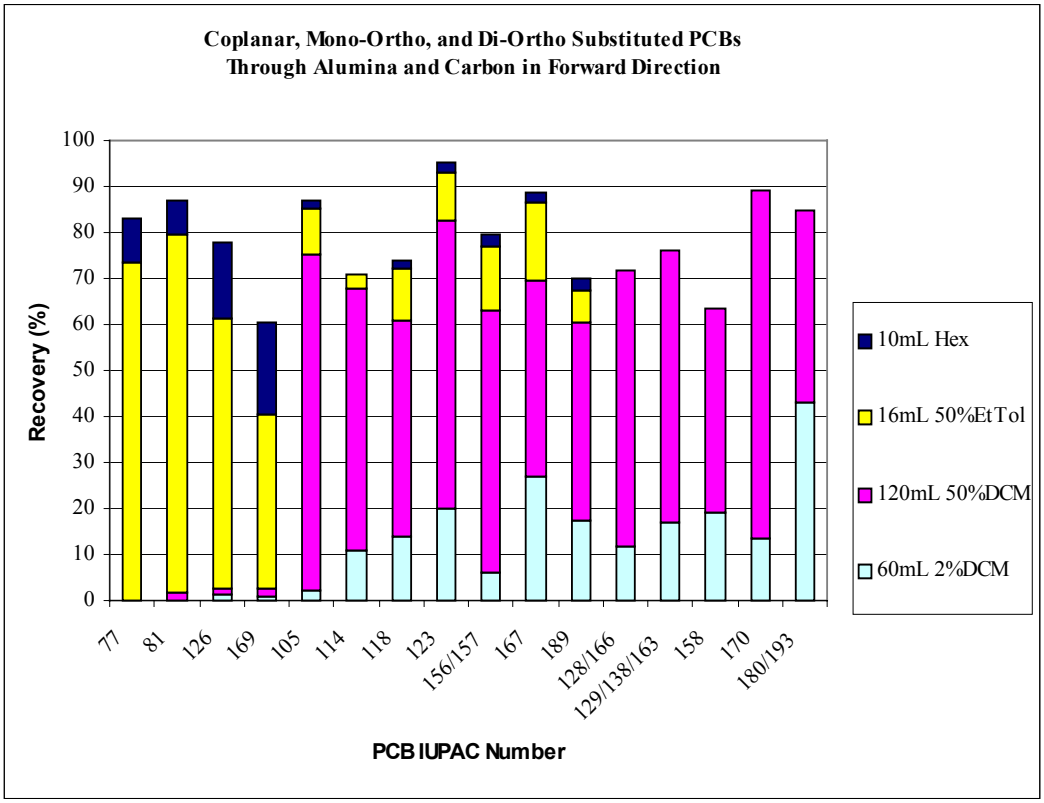
Figure 1 summarizes the recoveries for the coplanar, mono-ortho, and di-ortho substituted congeners by elution solvent. This information can be used to direct fraction collection for the isolation of specific congeners with the ultimate goal of reducing background in analysis. For example, coplanar PCBs (i.e, 81, 77, 126, and 169) are typically found in lower concentrations than the majority of PCBs. The presence of non-coplanar PCBs can cause elevation of noise measurements in HRMS which will in turn cause elevation in detection limits. Utilizing the information shown in Table 1 and Figure 1, however, the majority of non-coplanar PCB interferences can easily be removed providing a cleaner extract for analysis.

Table 1. PCB Congener Recovery by Elution Solvent

IUPAC #	Total Recovery*	IUPAC #	Total Recovery*	IUPAC #	Total Recovery*	IUPAC #	Total Recovery*
2% DCM		72	68.9	45/51	94.6	132	69.6
92	82.2	73	93.4	46	96.0	134/143	67.0
103	72.9	90/101/113	85.9	48	96.5	136	86.0
104	78.8	94	153	50/53	92.0	137	81.5
111	83.6	120	87.7	52	95.2	139/140	72.5
121	61.6	135/151	85.4	54	82.4	152	85.7
133	58.5	141	50.3	55	75.8	156/157	79.4
144	77.2	145	84.0	56	76.1	158	63.5
146	76.8	147/149	64.7	57	73.0	160	66.8
148	54.2	159	67.4	58	73.2	167	88.8
150	72.1	162	59.4	59/62/75	97.7	170	89.3
153/168	66.9	164	55.5	60	74.2	171/173	79.3
154	55.2	180/193	84.9	61/70/74/76	74.6	174	67.1
155	32.7	186	84.5	63	75.1	177	71.3
161	44.2	**50% DCM**		64	101	181	106
165	65.7	1	106	66	75.5	189	70.0
172	79.3	4	83.9	67	71.8	190	88.8
175	65.7	5	77.0	82	89.5	194	74.6
176	82.7	6	72.9	83	114	195	76.0
178	73.7	7	74.1	84	90.7	205	76.6
179	84.1	8	75.6	85/116/117	98.4	**50% EtTol+Hex**	
182	54.8	9	70.1	86/87/97/108/119/125	86.8	2	119
183/185	80.8	10	85.4	88/91	88.3	3	125
184	31.2	16	83.4	89	89.0	11	88.6
187	81.1	17	81.2	93/98/100/102	85.8	12/13	84.3
188	33.9	18/30	79.4	95	88.8	14	85.9
191	83.0	19	79.4	96	132	15	93.5
192	73.9	20/28	77.4	99	104	35	85.7
196	87.3	21/33	79.1	105	87.2	36	85.2
197/200	48.8	22	82.3	106	51.4	37	98.1
198/199	77.1	23	77.1	107/124	75.3	38	83.6
201	47.6	24	81.0	109	81.3	39	83.6
202	44.7	25	76.0	110/115	83.1	77	82.9
203	63.6	26/29	76.9	112	60.9	78	82.4
204	26.9	27	78.9	114	70.7	79	82.5
206	62.6	31	75.9	118	74.1	80	81.7
207	29.9	32	79.1	122	92.1	81	86.8
208	35.3	34	76.7	123	95.2	126	77.8
209	23.5	40/41/71	103	128/166	71.8	127	81.9
2% and 50% DCM		42	103	129/138/163	76.1	169	60.6
49/69	94.5	43	93.4	130	78.5		
68	69.7	44/47/65	96.9	131	75.0		

* Total recovery values represent the analyte recovery in the fraction indicated.

Figure 1. Elution of Toxic PCBs Using FMS Power Prep™



Using this information, the fraction collection can be modified to include all isomers in a single extract, remove unwanted isomers from the sample extract or to provide multiple fractions from a single extract. It is common in the industry to separate the coplanar and mono-ortho isomers listed in the World Health Organization (WHO) toxic isomer list from the remaining isomers prior to analysis. This experiment demonstrates that isomers that potentially co-elute with the WHO toxic isomers when alternate gas chromatographic columns or conditions are used can be separated from the more toxic isomers during enrichment procedures. This could be used in a similar manner to eliminate unwanted isomers when certain analyte sub-lists are requested. These separations have also been utilized on "typical" environmental matrices to demonstrate the reproducibility of the elution scheme.

Acknowledgements and References

1. Erickson, Mitchell D. (1992), Analytical Chemistry of PCBs, Lewis Publishers, Inc., ISBN 0-87371-702-3
2. USEPA Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS.