Quantification of Dioxin-Like Polychlorinated Biphenyls Using GCxGC-ECD with a Selective Column in the Second Dimension

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1. Introduction

Certain polychlorinated biphenyls (PCBs), those with no or only one ortho-chlorine substitution, exhibit dioxin-like toxicity due to their ability to take planar shapes in space. When determining PCBs in a variety of environmental samples, many analytical schemes focus on those congeners, and it is important that any quantitative values are free from bias. This is sometimes a challenge due to the fact that there are 209 possible PCB congeners, and also because dioxin-like PCBs are almost always at much lower concentrations in samples than other PCBs. For these reasons, the chromatographic separation of PCBs must be highly efficient.

Comprehensive two-dimensional GC (GCxGC) is one way to determine dioxin-like PCBs with a higher degree of selectivity. GCxGC increases peak capacity by applying two independent separations to a sample in one analysis with one detector. This application note will demonstrate the possibility of using GCxGC-ECD to quantify dioxin-like PCBs in environmental samples with an example of their quantification in an Aroclor 1254 dilution.

Standards

PCB standard mixes that included the dioxin-like PCBs shown in Table 1 and Aroclor 1254 were obtained from AccuStandard (New Haven, Connecticut, USA). An organochlorine pesticide standard mix was obtained from Restek Corporation (Bellefonte, Pennsylvania, USA).

2. Experimental Conditions

LECO GCxGC-ECD

Agilent 6890 GC-ECD equipped with a LECO Quad Jet—Dual-Stage Thermal Modulator

Column 1:
50 m x 0.18 mm x 0.18 µm Rtx-1 (Restek)

Column 2:
1.5 m x 0.18 mm x 0.10 µm Rtx-PCB (Restek)

Carrier:
Helium at 1.3 mL/minute, constant flow

Injection:
1 µL split at 250°C, split ratio 20:1

Oven 1 Program:
160°C (0.2 minute), 2°/minute to 280°C

Oven 2 Program:
20°C offset from oven 1

Modulation Time: 8 seconds

Detector:
ECD, 325°C, N_2 makeup gas at 148.7 mL/minute, 50 Hz

Table 1. World Health Organization non- and mono-ortho substituted polychlorinated biphenyls.

PCB #	Cl #	Cl Position
77	4	34-34
81	4	345-4
105	5	234-34
114	5	2345-4
118	5	245-34
123	5	345-24
126	5	345-34
156	6	2345-34
157	6	234-345
167	6	245-345
169	6	345-345
189	7	2345-345

3. Results and Discussion

The second dimension column chosen for this work is highly selective for those PCBs that can form planar configurations, which makes it an ideal column for use with GCxGC to determine the dioxin-like PCBs. Table 2 shows how the PCBs with fewer ortho-chlorines (which allows the planar shape to occur), generally elute later in the second dimension than those with more ortho-chlorines. It is important to note that even though the retention time differences shown in this table seem rather small, the distances are in most cases adequate for quantification due to the very narrow peaks produced using GCxGC (in this work they are approximately 200 ms at half-height). In addition, the first dimension separation afforded by the Rtx-1 cannot be ignored for reducing the potential for interferences while trying to determine dioxin-like PCBs.

Table 2. Second dimension retention times in seconds (RT 2) for dioxin-like PCBs (on top) compared to those with greater degrees of ortho-chlorine substitution (on bottom).

PCB #	Cl Position	RT 2
77	34-34	6.42
81	345-4	6.28
105	234-34	6.50
114	2345-4	6.28
118	245-34	5.94
123	345-24	6.04
126	345-34	6.78
156	2345-34	6.72
157	234-345	6.72
167	245-345	6.12
169	345-345	7.08
189	2345-345	6.92

PCB #	Cl Position	RT 2
49	24-25	5.06
52	25-25	5.00
87	234-25	5.82
95	236-25	5.80
99	245-24	5.56
101	245-25	5.50
110	236-34	5.90
132	234-236	6.14
138	234-245	6.18
149	236-245	6.12
153	245-245	5.88
180	2345-245	6.30

To test the accuracy of GCxGC-ECD, dioxin-like PCBs in an Aroclor 1254 dilution were quantified against GCxGC-ECD calibration curves prepared using hexachlorobenzene as an internal standard. The values produced were compared against those from a detailed study conducted by Frame et. al, where numerous GC column sets and mass spectrometry were used to define Aroclor PCB concentrations (Table 3). The numbers are in good agreement, except for PCB 77, where a large concentration of PCB 110, a pentachlorobiphenyl, may have thwarted the quantification effort for PCB 77. This is interesting from the standpoint that these congeners are resolved chromatographically in the second dimension using Rtx-PCB when they exist in approximately equal concentrations in a sample (Figure 1A). Figure 1B shows the same chromatographic area as Figure 1A, but for Aroclor 1254. PCB 110, which is at 325 pg/µL as calculated from Frame et. al, is the dominant PCB, and PCB 77 cannot be detected.

Table 3. Dioxin-like PCB concentrations in Aroclor 1254 (pg/µL) as calculated from the study of Frame et. al, and with GCxGC-ECD.

PCB #	Frame et. al	GCxGC-ECD
77	1.05	**
81	ND	ND
105	105	101
114	6.30	7.41
118	257	201
123	5.25	5.41
126	ND	ND
156	28.7	32.6
157	6.65	6.96
167	9.45	11.1
169	ND	ND
189	0.35	1.44

*ND = not detected. **possible coelution from PCB 110.*

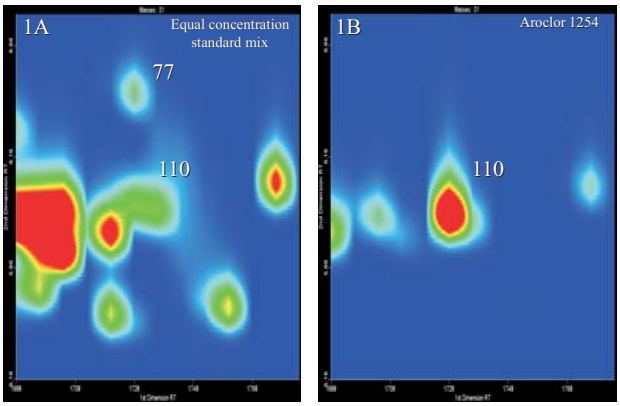

Figure 1. Contour plots of (1A) standard mix containing equal concentrations of PCBs 110 and the dioxin-like PCB 77 and (1B) Aroclor 1254. As calculated from the study of Frame et. al, PCB 110 is at 325 pg/µL in the Aroclor 1254 dilution, while PCB 77 only has a concentration of 1.05 pg/µL.

The selectivity of GCxGC-ECD for dioxin-like PCBs, even when they are in the presence of bulk PCBs in an Aroclor, has been adequately demonstrated by the data in Table 3, except for PCB 77. In this case, a better chromatographic separation may be necessary to determine this PCB in an unbiased fashion should PCB 110 be elevated in the same sample. To further demonstrate the selectivity of GCxGC-ECD for dioxin-like PCBs, the Aroclor 1254 dilution was made more complex by spiking it with an organochlorine pesticide (OCP) mix that contained aldrin, chlordanes, DDD, DDE, DDT, dieldrin, endosulfans, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, hexachlorocyclohexanes, and methoxychlor at 100 pg/µL for each pesticide. In environmental samples it is not unusual to find OCPs with PCBs, which complicates the determination of both species. Table 4 demonstrates that the OCPs did not

interfere with the determination of dioxin-like PCBs in an Aroclor mix, highlighting the selectivity of the GCxGC-ECD technique.

Table 4. Dioxin-like PCB concentrations in Aroclor 1254 (pg/µL) as calculated from the study of Frame et. al, and with GCxGC-ECD. The Aroclor was spiked with an OCP standard to make the determination more challenging and demonstrate the selectivity of GCxGC.

PCB #	Frame et. al	GCxGC-ECD
77	0.95	**
81	ND	ND
105	94.2	96.4
114	5.67	6.54
118	232	193
123	4.73	4.90
126	ND	ND
156	25.8	33.1
157	5.99	6.74
167	8.51	10.5
169	ND	ND
189	0.32	0.85

ND = not detected. **possible coelution from PCB 110.

4. Conclusions

GCxGC-ECD with a selective column in the second dimension offers a way to substantially improve separations for the important group of dioxin-like PCBs, even in the presence of PCBs that are normally at higher concentrations in environmental samples. Due to the increase in peak capacity afforded with GCxGC, organochlorine pesticides did not interfere with dioxin-like PCB determinations either.

5. Reference

G.M. Frame, J.W. Cochran and S.S. Bowadt, Complete PCB Congener Distributions for
17 Aroclor Mixtures Determined by 3 HRGC Systems Optimized for Comprehensive, Quantitative, Congener-Specific Analysis, *J. High Resol. Chromatogr.*, 19 (1996) 657-668.

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