Using Classifications and Mass Spectral Filtering to Process GCxGC-TOFMS Data for Polychlorinated Biphenyls

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Key Words: GCxGC-TOFMS, Classifications, Scripts, PCB's

1. Introduction

A relatively new way to solve separation problems for complex environmental samples is to use comprehensive two-dimensional GC (GCxGC). GCxGC increases peak capacity by applying two independent separations to a sample in one analysis. Typically, GCxGC involves a serial column configuration (employing orthogonal phases) separated by a thermal modulator.

Due to modulation, most GCxGC peaks are on the order of 50 to 250 ms wide, requiring a fast detector. When MS is used, only Time-of-Flight (TOF) has the necessary acquisition rates (hundreds of spectra/second). The ability of the thermal modulator to create narrow peaks (thereby increasing their height) prior to their detection also affords the ability to increase TOFMS sensitivity.

GCxGC-TOFMS offers the possibility of handling complex samples, but the data generated is itself complex. This makes data processing routines very important if the full potential of GCxGC-TOFMS is to be realized. One of the ways that data can be processed is by taking advantage of the structure of GCxGC chromatograms; certain compounds elute in certain areas of the contour plot under the right conditions, and can be grouped. Another way is to employ mass spectral filtering, which can be done in conjunction with grouping, or geographical classification of compounds.[1,2] In this work, Classifications and Scripts (mass spectral filtering) software was employed to process polychlorinated biphenyls (PCBs) data generated using GCxGC-TOFMS. Although not illustrated here, mass spectral filtering can also be used to selectively view certain compounds, or groups of compounds, in a contour plot.

2. Experimental Conditions

Samples

PCB standard solutions and dilutions of Aroclors were obtained from AccuStandard.

Instrument Conditions

Pegasus 4D GCxGC-TOFMS

GCxGC Column:

Integral column from Restek Corporation, 50 m x 0.18 mm x0.18 µm; Rtx-1 x 10 m x 0.10 mm x 0.10 µm Rtx-PCB (installed so that 4 m of the Rtx-PCB resided in a secondary oven past a modulator)

Primary Oven:

70°C (1 min), 50°/min to 120°, 8°/min to 340° (0.5 min)

Secondary Oven:

20°C positive offset from the primary oven

Modulation:

Quad-jet, dual-stage

Modulation Period:

2 seconds

Carrier Gas:

Helium at 1.5 mL/min constant flow

TOFMS Conditions

Ionization:	EI at 70 eV
Source Temp:	225°C
Stored Mass Range:	120 to 520u
Acquisition Rate:	100 spectra/second

Instrument Control and Data Processing

The autosampler, the GC, the thermal modulator, and the TOFMS were all fully controlled through LECO ChromaTOF® software. In addition, all data processing (including Automated Peak Find, Spectral Deconvolution, GCxGC Slice Combine, Classifications, and Scripts) was also accomplished with ChromaTOF.

3. Results and Discussion

Figure 1 shows a contour plot for a mix of PCBs with Classifications of the various chlorination levels shown as ovals. Inevitably, there will be chromatographic overlap of PCB congeners for the various chlorination levels and a Peak Table generated from the Classifications scheme will reflect that by showing individual PCBs belonging to several chlorination classes when obviously they should only belong to one (Figure 2). In addition, compounds that were located by an automatic peak find routine and fall into the geographic space for the PCB classes will also be noted in the Peak Table, even though they may not be PCBs.

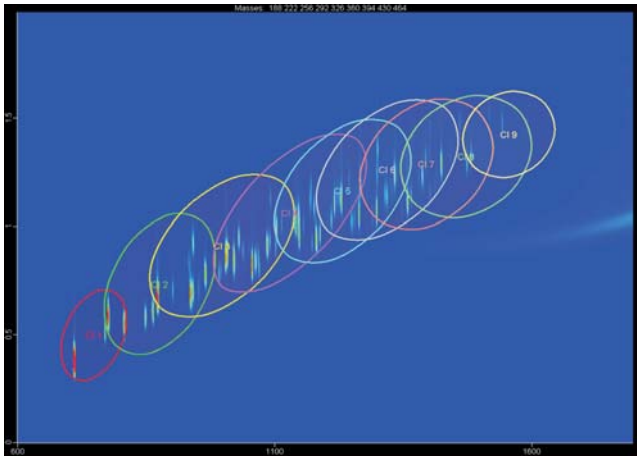

Figure 1. Contour plot of PCBs with Classifications (ovals) for the various chlorination levels. Note the chromatographic overlap for different PCB homolog groups.

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Peak Table (1)

Peak #	R.T. (s)	Name	Classifications	UniqueMass	Area	S/N
140	1224 , 0.880	Cyclotetrasiloxane, (iodomethyl)heptamethyl-	Cl 5	267	24815	459.11
141	1226 , 1.130	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 4; Cl 5; Cl 6	360	44818	2408.2
142	1228 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	4149.6	83.792
143	1230 , 1.130	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 4; Cl 5; Cl 6	326	257010	9344.0
144	1230 , 1.320	1,1'-Biphenyl, 2,3',5,5'-tetrachloro-	Cl 4; Cl 5; Cl 6	292	7404.8	339.94
146	1232 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	1428.0	88.742
147	1234 , 0.880	Cyclotetrasiloxane, octamethyl-	Cl 5	267	52120	500.03
148	1236 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	4416.7	96.520
149	1242 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	4376.4	91.570
150	1244 , 1.220	1,1'-Biphenyl, 2,2',3,5,6-Pentachloro-	Cl 4; Cl 5; Cl 6	254	20593	867.20
152	1250 , 1.020	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 5; Cl 6	290	68986	2207.8
153	1252 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	7676.7	98.641
154	1254 , 1.030	1,1'-Biphenyl, 2,2',3,3',4,5-hexachloro-	Cl 5; Cl 6	360	23512	1173.1
155	1256 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	3301.4	102.53
156	1256 , 1.040	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 5; Cl 6	360	10958	674.05
157	1256 , 1.120	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 4; Cl 5; Cl 6	326	7075.2	256.26
158	1260 , 1.170	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 4; Cl 5; Cl 6	326	14988	342.38
159	1262 , 0.920	Cyclohexasiloxane, dodecamethyl-	Cl 5	341	3216.6	100.06
160	1264 , 1.060	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 5; Cl 6	360	188146	9514.1
161	1266 , 0.920	1,3,5,7,9-Pentaethyl-1,9-dibutoxypentasiloxane	Cl 5	341	1824.0	105.01
162	1266 , 1.200	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 4; Cl 5; Cl 6; Cl 7	326	169076	6626.6
163	1278 , 1.150	1,1'-Biphenyl, 2,2',3,3',4,5-hexachloro-	Cl 5; Cl 6; Cl 7	360	7519.5	284.26
164	1282 , 1.260	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 5; Cl 6; Cl 7	326	7330.9	151.46
165	1284 , 1.170	1,1'-Biphenyl, 2,2',3,3',4,5-hexachloro-	Cl 5; Cl 6; Cl 7	360	1989.7	79.550
166	1290 , 1.040	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 5; Cl 6	290	19069	911.64
167	1292 , 0.950	Cyclohexasiloxane, dodecamethyl-	Cl 6	327	1295.8	50.205
168	1298 , 1.070	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 5; Cl 6; Cl 7	360	189808	10610
169	1298 , 1.250	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 5; Cl 6; Cl 7	325	30085	657.96
170	1300 , 1.360	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 5; Cl 6; Cl 7	324	45494	1976.5
171	1304 , 1.010	9,12,15-Octadecatrienoic acid, 2,3-bis[(trimethyl	Cl 5; Cl 6	149	2656.9	72.125
172	1314 , 1.150	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 5; Cl 6; Cl 7	360	35609	2074.7
173	1318 , 1.140	1,1'-Biphenyl, 2,2',3,4,5,6,6'-Heptachloro-	Cl 5; Cl 6; Cl 7	396	67661	2778.4
174	1322 , 1.190	1,1'-Biphenyl, 2,2',4,4',5,6-Hexachloro-	Cl 5; Cl 6; Cl 7	290	4081.4	257.21
175	1326 , 1.170	1,1'-Biphenyl, 2,2',3,4,5,6,6'-Heptachloro-	Cl 5; Cl 6; Cl 7	396	14877	482.07
176	1326 , 1.210	1,1'-Biphenyl, 2,2',3,4,5,6'-Hexachloro-	Cl 5; Cl 6; Cl 7	290	9601.4	266.23
177	1332 , 1.250	1,1'-Biphenyl, 2,2',4,4',5,6-Hexachloro-	Cl 5; Cl 6; Cl 7	360	167136	5382.9
178	1338 , 1.250	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 5; Cl 6; Cl 7	360	18667	805.73
179	1344 , 1.250	1,1'-Biphenyl, 2,2',3,3',4,5-hexachloro-	Cl 5; Cl 6; Cl 7	290	6007.1	277.36
180	1348 , 1.080	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 6; Cl 7	324	17878	689.43
181	1352 , 1.390	[1,1'-Biphenyl]-4-ol, acetate	Cl 5; Cl 6; Cl 7	170	758.52	54.730
182	1354 , 1.110	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 6; Cl 7	394	2582.9	146.90
183	1354 , 1.390	Unknown 8	Cl 5; Cl 6; Cl 7	170	877.55	55.579
184	1356 , 1.390	4-Benzylpyridazine	Cl 5; Cl 6; Cl 7	170	845.37	54.306

Figure 2. Peak Table with Classifications (PCB chlorination level) based on geographic location of compounds alone. Note the assignment to more than one class for some PCBs and the labeling of compounds other than PCBs in the classes.

Peak Table (1)

Peak #	R.T. (s)	Name	Classifications	UniqueMass	Area	S/N
133	1210 , 1.030	1,1'-Biphenyl, 2,2',3,5,6-Pentachloro-	Cl 5	326	56197	2208.7
135	1216 , 1.110	1,1'-Biphenyl, 2,2',3,5,6-Pentachloro-	Cl 5	254	91817	3731.4
137	1220 , 1.130	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 5	326	6617.0	278.32
139	1222 , 1.140	1,1'-Biphenyl, 2,2',3,5,6-Pentachloro-	Cl 5	326	27655	1283.4
141	1226 , 1.130	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 6	360	44818	2408.2
143	1230 , 1.130	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 5	326	257010	9344.0
144	1230 , 1.320	1,1'-Biphenyl, 2,3',5,5'-tetrachloro-	Cl 4	292	7404.8	339.94
150	1244 , 1.220	1,1'-Biphenyl, 2,2',3,5,6-Pentachloro-	Cl 5	254	20593	867.20
152	1250 , 1.020	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 6	290	68986	2207.8
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165	1284 , 1.170	1,1'-Biphenyl, 2,2',3,3',4,5-hexachloro-	Cl 6	360	1989.7	79.550
166	1290 , 1.040	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 6	290	19069	911.64
168	1298 , 1.070	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 6	360	189808	10610
169	1298 , 1.250	1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	Cl 6	325	30085	657.96
170	1300 , 1.360	1,1'-Biphenyl, 2,3,3',4,6-Pentachloro-	Cl 5	324	45494	1976.5
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181	1354 , 1.110	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	394	2582.9	146.90
185	1358 , 1.110	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	394	127730	6452.0
186	1364 , 1.140	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	324	39858	1682.7
187	1366 , 1.440	1,1'-Biphenyl, 2,2',3,3',4,5-hexachloro-	Cl 6	360	17823	548.89
188	1372 , 1.300	1,1'-Biphenyl, 2,3,3',4,5,6-hexachloro-	Cl 6	360	4063.9	247.13
190	1380 , 1.230	1,1'-Biphenyl, 2,2',3,4,5,6,6'-Heptachloro-	Cl 7	394	12349	636.40
191	1386 , 1.240	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	396	80408	2477.7
194	1394 , 1.310	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	324	34847	1515.7
196	1400 , 1.330	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	324	12106	547.83
198	1400 , 1.450	1,1'-Biphenyl, 2,2',3,3',6,6'-hexachloro-	Cl 6	360	13204	551.54
203	1406 , 1.480	1,1'-Biphenyl, 2,2',3,3',4,4',5-hexachloro-	Cl 6	360	2348.0	126.75
207	1414 , 1.260	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	324	8256.6	240.77
213	1424 , 1.290	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	324	146574	6450.4
215	1428 , 1.280	1,1'-Biphenyl, 2,3,3',4,5,5',6-heptachloro-	Cl 7	396	6346.6	373.88
238	1460 , 1.460	1,1'-Biphenyl, 2,2',3,4,4',5,6'-Heptachloro-	Cl 7	394	31706	884.06
242	1464 , 1.480	1,1'-Biphenyl, 2,2',3,4,5,6,6'-Heptachloro-	Cl 7	394	10188	467.22

Figure 3. Peak Table showing Classifications for PCBs generated from GCxGC elution area and mass spectral filters (Scripts). All PCBs were properly assigned to class.

If a Script, or mass spectral filter, is employed to work in conjunction with the geographic location of a compound in the GCxGC data (contour plot), then the Classification of a PCB can be specific. An example of a ChromaTOF Script (uses Microsoft Visual Basic Scripting Edition) for tetrachlorobiphenyl is shown below. Rank(1) defines the base peak of the mass spectrum, and Abundance() is the intensity of the m/z ion in the spectrum based on a normalization of the base peak to 999. Essentially what the Script says is that the base peak must be 292 (a molecular ion of tetrachlorobiphenyl) or 222 (from the loss of Cl2) and that the abundance (in the deconvoluted mass spectrum) of 292 and 222 must be greater than 500. Similar Scripts were written for other homolog groups of the PCBs. A Peak Table using PCB elution area and Scripts together resulted in no overlap of the Classifications (Figure 3). Scripts can include arithmetic, comparison, and logical operators, and/or conditional statements (e.g. If…Then…Else) and/or loops.

```
FUNCTION Cl4PCBs()
 Cl4PCBs = (Rank(1) = 292 OR Rank(1) = 220) AND
Abundance(292)>500 AND Abundance(220)>500
END FUNCTION
```

4. Conclusions

Classifications and Scripting (mass spectral filters) are powerful mechanisms for processing GCxGC-TOFMS data.

5. References

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