Analysis of Polychlorinated Biphenyl (PCB) Congeners Using an Application-Specific Capillary GC Column with TOFMS

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Abstract

"Weathering" of Aroclor mixes that have been in the environment for more than 30 years and changes in Aroclor patterns in tissue samples, due to bioaccumulation have made identification and quantification of Aroclor mixes difficult. Consequently, many laboratories are analyzing long lists of PCB congeners, using the data to determine specific congener patterns, and compiling congener results to obtain an accurate total PCB concentration. Identification and quantification of PCB congeners is chromatographically challenging because there are 209 possible combinations in which chlorine atoms can be added to the biphenyl structure, ranging from addition of single chlorine (monochlorobiphenyls) to addition at every available carbon atom (decachlorobiphenyl). In 1996, George Frame published work he performed in order to determine which PCB congeners are present in Aroclor mixes. Using this work as a guide, the list of 209 possible PCB congeners can be reduced to a target list of 158 congeners. Several congeners not found in Aroclors but found in animal tissues, such as PCB#169, have been added. The list encompasses the seven European indicator compounds and the 12 most toxic congeners listed by the World Health Organization (WHO) list.

Introduction

There are many different lists of PCB Congeners that laboratories use in their analytical methods. These lists of reported PCB congeners are determined by different organizations that include: country's health organizations (International), state agencies (domestic), the World Heath Organization (WHO), NOAA, and PCB congeners that are most prevalent in tissue and serum samples (CDC list), to name a few.

Following are examples of PCB congener lists:

- 7 Indicator Congeners (European):
  - 28,52,101,118,138,153,180
  - Indicate presence/absence of PCB's
- 12 Most Toxic Congeners (WHO):
  - 77,81,126,169
  - 105, 114, 118, 123, 156, 157, 167, 189
- 18 NOAA Status & Trend Congeners
  - 8, 18, 28, 52, 44, 66, 101, 118, 153, 105, 138, 187, 128, 180, 170, 195, 206, and 209
- 36 CDC PCB congener list (congeners found in biological samples)
  - 18, 28, 44, 49, 52, 66, 74, 87, 99, 101, 105, 110, 118, 128, 138, 146, 149, 151, 153, 156, 157, 167, 170, 172, 177, 178, 180, 183, 187, 189, 194, 195, 196, 199, 206, and 209
- 159 Congeners Quantified in Aroclor Mixes
  - Frame, et. al. (Fresenius J. Anal .Chem. 357, 714-22)
  - List includes coplanar congeners not found in the Aroclor mixes

There is the potential to analyze and report all 209 PCB congeners, however it is difficult to chromatographically resolve all the PCB congeners on one, or even two fused silica capillary columns. And secondly, there may not be good reason to put all the effort into resolving all 209 PCB congeners because they may not exist in the environment.

In 1996, George Frame et. al. published literature showing which PCB congeners are found in Aroclor mixes (>0.01%w/w). This information is very valuable because from the work it can be determined there are approximately 157 PCB congeners that would normally be found in the environment. Using this information and combining PCB congener lists from different agencies the 209 possible PCB congeners can be reduced to a target list of 159. PCB congeners not included on the target list are listed in Table 1.

PCB#	PCB#	PCB#	PCB#	PCB#	PCB#	PCB#	PCB#	PCB#	PCB#
14	50	68	79	106	113	140	152	162	184
30	58	69	80	107	116	143	155	165	186
36	61	72	98	108	120	145	159	168	188
38	62	73	100	111	121	148	160	181	192
39	65	78	104	112	127	150	161	182	204

Table 1 - PCB congeners not included in the target list

Experimentation

Following is an analysis showing the experimentation performed using the Rtx-PCB fused silica column. Utilizing this unique stationary phase it has been determined that many of the 159 PCB congeners can be resolved using one analytical GC/MS analysis. The analysis was performed using GC/MS because it offers the advantage to spectrally resolve coeluting congeners of different chlorination level. Secondly, GC/MS is common in most laboratories and the analysis can be performed using one column. The one disadvantage of the GC/MS is it is not as sensitive as an electron capture detector.

The column selected for this analysis is the Rtx-PCB column due to unique separations achieved versus other traditional columns. The Rtx-XLB column is the second column of choice for performing PCB congener analysis. Other columns historically used include the Rtx-1, Rtx-5 (most common), Rtx-CLPesticides, Rtx-CLPesticides2, Rtx-500 (carborane phase), Rtx-35, and Rtx-1701.

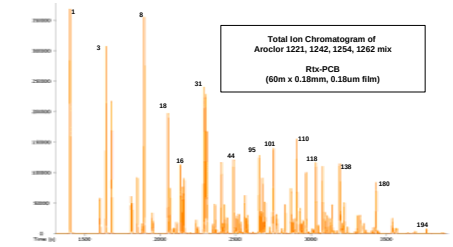
Following were the goals and conditions of the following analysis.

1. Determine retention times for all 209 PCBs on the Rtx-PCB capillary column
   - The 9 mixes referenced in George Frame's work were used to determine retention time of each PCB congener
   - Hexachlorobenzene was used as a reference marker for relative retention times
2. Analyze mix of Aroclors 1221:1242:1254:1262 at a 1:2:2:2 ratio
   - Show chromatogram with 158 congeners labeled
   - Show how compounds will be quantified for different congener subsets

Instrument Test Conditions

- **Gas Chromatography**
  - One microliter splitless injection, 60 sec splitless hold
  - Injection port temperature: 250°C
  - 60 m x 0.18 mm x 0.18 µm Rtx-PCB column
    - Constant flow helium, 1.5 mL/minute
    - 70°C (1 min), 50°/min to 120°, 3°/min to 360° (1 min)
- **Mass Spectrometry LECO Pegasus III**
  - Source temperature: 225°C
  - Electron ionization: 70 eV
  - Stored mass range: 120 to 520 u
  - Acquisition rate: 5 spectra/sec

Below is the total ion chromatogram of the Aroclor mix with major peaks identified.



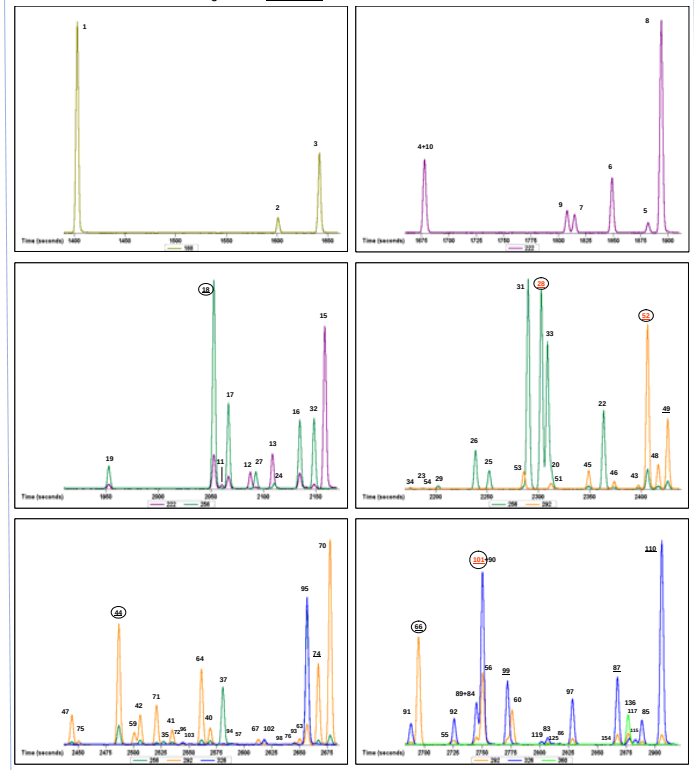
PCB Congener Identification

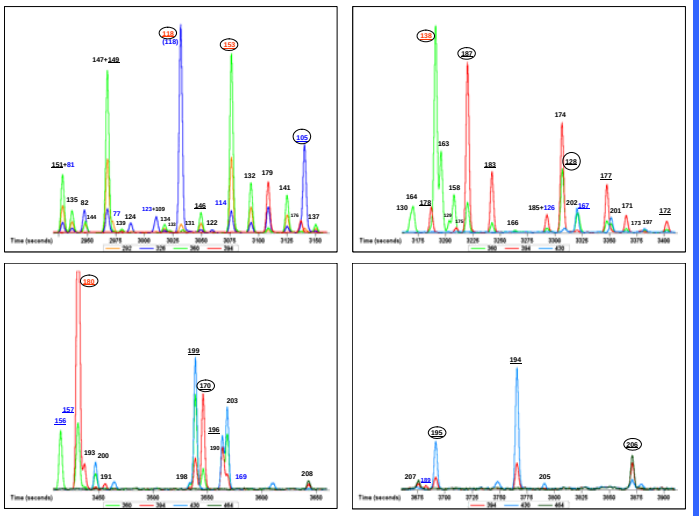
To determine the PCB congener elution in the Aroclor mix the extracted ion was used along with the determined retention times from the individual congener mixes. Following is the detailed work showing the elution of the PCB congeners in the Aroclor mix acquired above. The overlaid ion chromatograms are plotted to show windows of the Aroclor mix and extracted ions of the congeners that elute in the region. For this work the mass/charge ratios for the extracted ions shown are:

•Monochlorinated	m/z 188	•Hexachlorinated	m/z 360
•Dichlorinated	m/z 222	•Heptachlorinated	m/z 394
•Trichlorinated	m/z 256	•Octachlorinated	m/z 430
•Tetrachlorinated	m/z 292	•Nonachlorinated	m/z 464
•Pentachlorinated	m/z 326		

The extracted ion chromatograms are labeled to indicate which group the PCB congener belongs to. All congeners labeled are the congener target list determined from George Frame's research work. The following are the subgroups and how they are indicated on the extracted ion chromatograms:

- 7 European Indicator congeners => (red font)
- 12 Most Toxic Congeners => (blue font)
- 18 NOAA Status & Trends Congeners => circled
- 36 CDC PCB Congeners => underlined





Chromatographic Results

159 Congeners Found in Aroclor Mixes

- 139 PCB congeners can be identified and quantified
- 16 PCB congeners would be reported in 8 pairs due to coelution and being at the same chlorination level: 4+10, 33+20, 95+88, 89+84, 101+90, 147+149, 123+109, 130+164
- The following congeners can not be reported accurately because they coelute with a congener that is 2 chlorination levels above: 81, 77, 126, and 167

12 Most Toxic Congeners (WHO list)

- 5 congeners elute as single components: 169, 105, 118, 156 and 189
- 2 congeners can be spectrally resolved: 114 w/153, 157 w/180
- 1 congener coelutes with a congener of the same chlorination level and cannot be spectrally resolved: 123 w/109
- 4 congeners coelute with a congener 2 chlorination levels higher: 77 w/147+149, 81 w/151, 126 w/185, 167 w/202

7 European Indicator Congeners

- 5 congeners elute as single components: 28, 52, 118, 138, 153
- PCB 101 elutes with 56+90. PCB 90 has been accepted as a coelution with 101, and 56 is spectrally resolved
- PCB 180 coelutes with 157, which can be spectrally resolved

18 NOAA Status & Trends Congeners

- 16 congeners elute as single components: 8, 18, 28, 44, 49, 52, 66, 105, 118, 138, 153, 170, 180, 187, 195, 206 and 209
- 1 congener can be spectrally resolved: 128 w/174
- 1 congener coelutes with a congener of the same chlorination level and cannot be spectrally resolved: 101 w/90

36 CDC Congeners

- 29 congeners elute as single components: 18, 28, 44, 49, 52, 66, 74, 99, 105, 110, 118, 138, 146, 153, 156, 157, 170, 172, 177, 178, 180, 183, 187, 189, 194, 195, 199, 206 and 209
- 4 congeners can be spectrally resolved: 87 w/154, 128 w/174, 151 w/81, 196 w/190
- 3 congeners coelute with congeners of the same chlorination level and cannot be spectrally resolved: 101 w/90, 149 w/147
- 1 congener coelutes with a congener 2 chlorination levels higher resulting in an estimated value: 167 w/202

Conclusion

- The Rtx-PCB column is a good choice for quantification of the 148 PCB congeners
- The Rtx-PCB column does not separate all of the 12 most toxic PCB congeners (WHO list) adequately for the level of accuracy needed when reporting the coplanar congeners. Carbon cleanup which is used to separate the coplanar PCB congeners from the noncoplanar congeners will still be needed.
- The Rtx-PCB column can be used for quantification of the European Indicator PCB congeners with GC/MS
- The Rtx-PCB column can be used for quantification of the NOAA Status & Trends PCB congeners with the following limitations:
  - 101 combined with 90
- The Rtx-PCB column can be used for the CDC congener list with the following limitations:
  - 101 combined with 90
  - 149 combined with 147
  - 167 quantified as an estimated value due to coelution with 202

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