Analyses of Polychlorinated Biphenyl (PCB) Mixtures and Individual Congeners by GC

Widespread use of PCBs has made them an environmental problem. Consequently, the US Environmental Protection Agency has issued guidelines for monitoring PCBs in various matrices. Described here are gas chromatographic columns and conditions for monitoring PCBs in simple or difficult samples. A 2-meter glass column packed with 1.5% SP-2250/ 1.95% SP-2401 or 3% SP-2100 on 100/120 SUPELCOPORT support is suitable for identifying Aroclor PCB mixtures in most samples. Degraded or highly complex mixtures can be separated on SPB-Octyl, SPB-608, or SPB-5 capillary columns. Studies of individual congeners are best conducted on SPB-Octyl columns.

Key Words:
- polychlorinated biphenyls ● PCBs ● Aroclor
- environmental analyses

Polychlorinated biphenyls (PCBs) formerly were widely used as dielectric and heat-transferring fluids, as fluids in hydraulic and vacuum systems, as plasticizers, and as flame retardants. Their widespread use and stable molecular structures, and the high toxicity of a few of these molecules, have made PCBs a persistent environmental problem. PCBs have been found in water, soil, and other environmental matrices, and in foods. Concern over their pervasiveness in the environment prompted the US Environmental Protection Agency (US EPA) to issue guidelines limiting PCB levels in various matrices (1), and to promote methods for PCBs analysis (2-5). A typical EPA method includes sample work-up, clean-up procedures to minimize interference, and analysis by gas chromatography using an electron capture detector (ECD).

Because PCBs often were used in complex mixtures, their identification and quantification can be difficult. In the United States, the most commonly used PCB mixtures were marketed under the trade name Aroclor.® Aroclor PCB mixtures were manufactured by simply chlorinating biphenyl to specific weight percentages of chlorine.* Consequently, each Aroclor PCB mixture is a complex mixture of biphenyl molecules incorporating 1 to 10 chlorine atoms, with positional isomers at each level. (In total, there are 209 PCB congeners.) Furthermore, minor variations in manufacturing conditions caused batch-to-batch differences in the exact proportions of each congener in a mix. Taken in total, however, the multiple components of each Aroclor PCB mixture produce a characteristic chromatographic pattern. By comparing the pattern for an unknown PCB mixture with patterns for standard Aroclor PCB mixtures, the unknown often can be identified.

The extraction technique to use in a PCB analysis depends on the sample matrix. Transformer oil or waste oil samples typically have been diluted with solvent (2). PCBs in wastewater, sedimentary, or biological samples have been extracted with a solvent, then concentrated (3,4). Modern extraction methods include solid phase extraction (request Application Note 67) and solid phase microextraction (described in this bulletin). Samples prepared by any of these approaches can be analyzed on the same GC column.

For many PCB-containing samples, analysis by packed column GC is sufficient. Two packings produced by Supelco meet all requirements of US EPA Method 608 (5) for monitoring organochlorine pesticides and PCBs in wastewater: 1.5% SP™-2250/1.95% SP-2401 on 100/120 SUPELCOPORT™ support and 3% SP-2100 on 100/120 SUPELCOPORT. These packings also can be used to analyze PCBs in transformer oil or waste oil (2).

An undegraded, relatively pure Aroclor mixture easily can be identified and quantified by using a 2m x 4mm ID glass column filled with 1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT or a 2m x 2mm ID glass column filled with 3% SP-2100 on 100/120 SUPELCOPORT. Figures A and B show the unique PCB patterns of prevalent Aroclor mixtures. Most notable in these patterns is the increasing proportion of later-eluting peaks that accompanies the increase in percent chlorine. Aroclor 1254, containing 54% chlorine by weight, but with an elution pattern showing many early-eluting peaks, is the exception to this trend. Because the chlorine content of Aroclor mixtures 1232, 1242, and 1016 is similar, the peak patterns also are similar. Fortunately, the proportions of the common peaks differ, and each mixture produces a recognizable pattern.

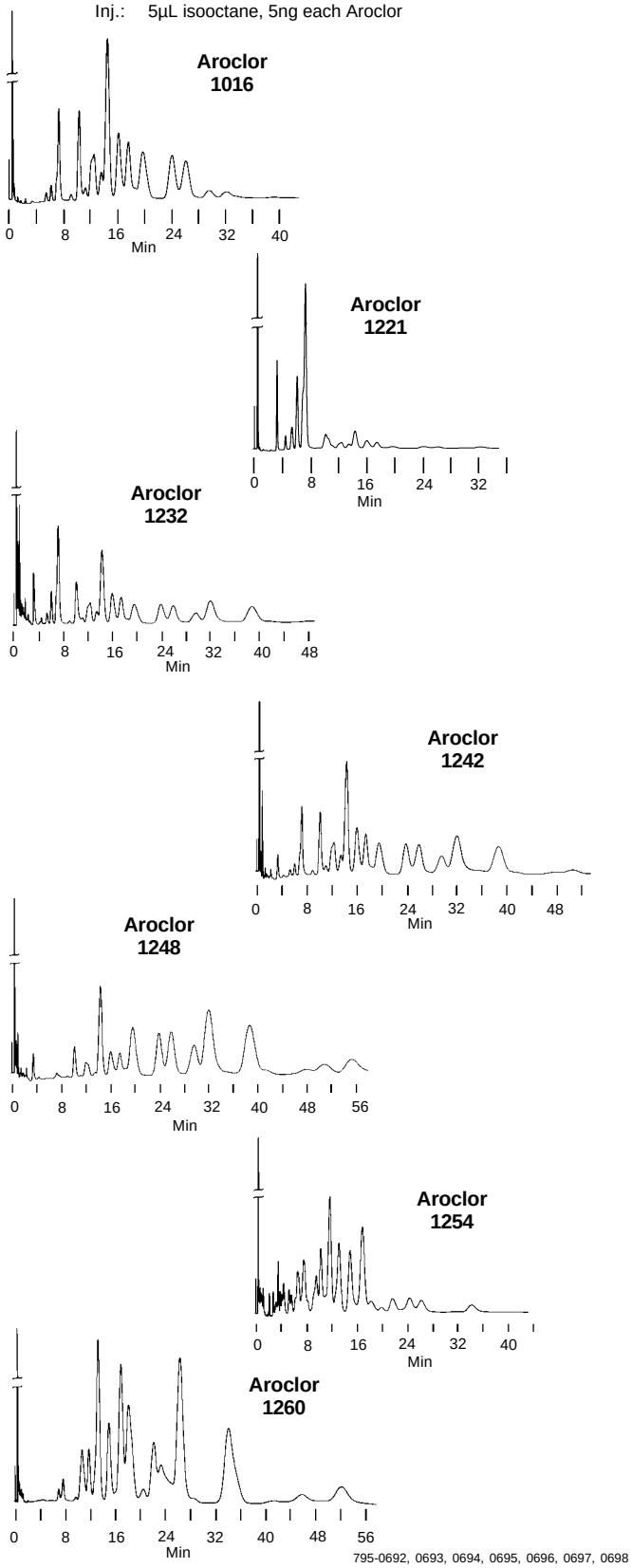
Often, an analysis method will dictate the column to use. For example, US EPA Method 608 lists the SP-2250/SP-2401 packing as the primary packing and an SP-2100-type packing for confirmation; SW-846 methods are based solely on capillary columns. If the choice is open, however, there are advantages and disadvantages to using either packing. The SP-2250/ SP-2401 packing spreads the peaks, aiding in pattern recognition and peak measurement but requiring longer run times. If you are unfamiliar with PCB analysis, you may find the more open patterns easier to identify. The SP-2100 packing offers faster analyses, but the peaks are more difficult to measure and there is slight loss of detail. You might prefer this packing if you are familiar with identifying PCB mixtures or have many samples to analyze. When a PCB pattern is unclear, you can use both packings and compare the results.

An Aroclor PCB mixture can be quantified when the pattern of the

*Aroclor mixtures are characterized by a four-digit number (e.g., Aroclor 1242). The last two digits represent the weight percent of chlorine in the mixture (e.g., Aroclor 1242 is 42% chlorine by weight). Aroclor 1016, the exception to this nomenclature, contains 41% chlorine.

Figure A. Aroclor PCB Mixtures on 1.5% SP-2250/1.95% SP-2401

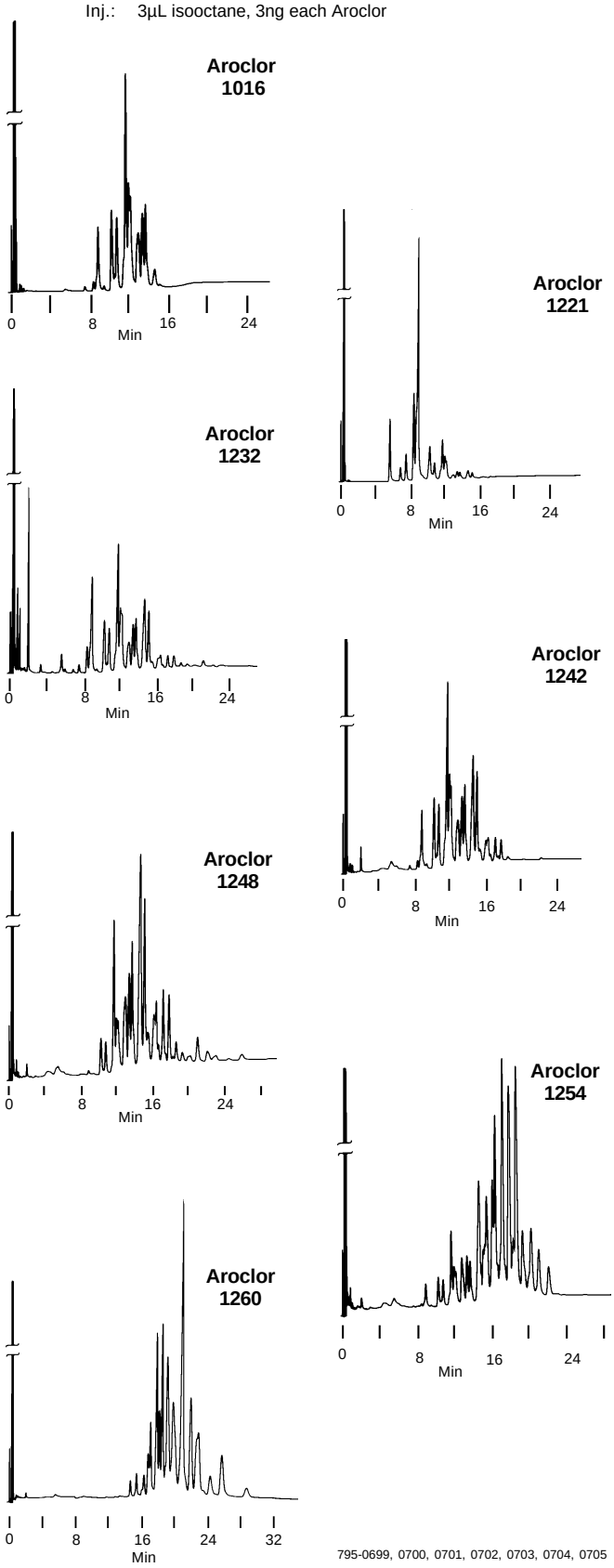
Packing: **1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT**
Cat. No.: **11947** (20g/bottle)
Column: 2m x 4mm ID TightSpec™ glass
Oven: 160°C or 200°C (Aroclor 1254 & 1260)
Carrier: nitrogen, 60mL/min
Det.: ECD
Inj.: 5µL isooctane, 5ng each Aroclor



795-0692, 0693, 0694, 0695, 0696, 0697, 0698

Figure B. Aroclor PCB Mixtures on 3% SP-2100

Packing: **3% SP-2100 on 100/120 SUPELCOPORT**
Cat. No.: **11738** (20g/bottle)
Column: 2m x 2mm ID TightSpec glass
Oven: 140°C (Aroclor 1221 & 1232) or 170°C
Carrier: nitrogen, 40mL/min
Det.: ECD
Inj.: 3µL isooctane, 3ng each Aroclor



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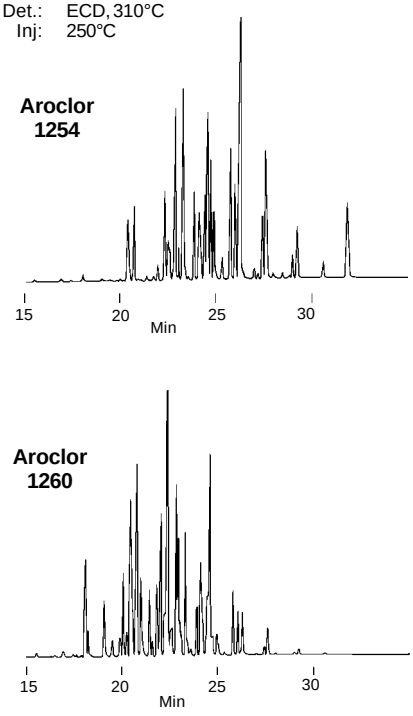
sample closely resembles that of a standard. Quantification requires area summation of all components, and comparison to the summed area from the corresponding Aroclor standard. Alternatively, you can measure selected peaks (height or area) and compare them to corresponding peaks from Aroclor standards. Sometimes, however, a complex mixture of PCBs is difficult to identify and quantify. The peak pattern for a chemically or biologically degraded Aroclor mixture can differ significantly from that of the manufactured form. Problems also arise when a sample contains two or more Aroclor mixtures, or a non-Aroclor mixture of PCBs (e.g., Kaneclor, Clophen, or Phenoclor). Similarly, extraneous peaks from non-PCB sample components can obscure PCB patterns. Samples should be prepared carefully, to reduce the potential for interference.

If you are unable to identify a pattern by using a packed column, you can resolve individual PCB congeners on a high resolution capillary column, such as an SPB™-608 column (Figure C), an SPB-5 column (Figure D), or a PTE-5 column. The congeners then can be compared to PCB standards (Figure E), making quantification as well as identification often possible. If your instrument is not equipped for capillary chromatography, a wide bore (0.53mm ID or 0.75mm ID) capillary column offers sample resolution similar to that from a 0.25mm or 0.32mmm column, in equipment designed for packed column use. (compare Figure F to Figures C and D). Even when used in a packed column instrument, a wide bore capillary column can provide the resolution needed to identify combinations of Aroclors (Figure G).

Figure C. Aroclor PCB Mixtures on an SPB-608 Capillary Column (by US EPA Method 608)

Column: **SPB-608, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24103**
Oven: 150°C (4 min) to 290°C at 6°C/min, hold 13 min
Carrier: helium, 25cm/sec
Det.: ECD, 310°C
Inj: 250°C



92-0030
92-0031

Figure D. Aroclor PCB Mixtures on an SPB-5 Capillary Column

Column: **SPB-5, 30m x 0.32mm ID, 0.25µm film**
Cat. No.: **24048**
Oven: 30°C (4 min) to 300°C at 10°C/min, hold 10 min
Carrier: helium, 25cm/sec (set at 150°C)
Det.: ECD
Inj.: 1µL isooctane, 1ng each Aroclor, splitless

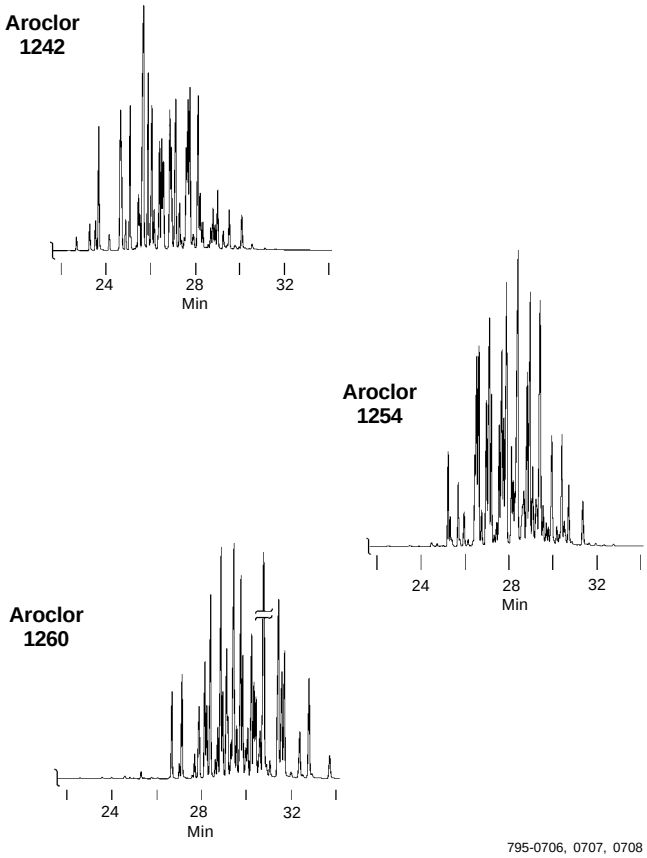


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Figure E. Monochloro - Decachloro PCB Congeners on a Capillary Column

Column: **SPB-5, 30m x 0.32mm ID, 0.25µm film**
Cat. No.: **24048**
Oven: 30°C (4 min) to 300°C at 10°C/min, hold 10 min
Carrier: helium, 25cm/sec (set at 150°C)
Det.: ECD
Inj.: 1µL Cat. No. 4-8738 (analyte quantities listed on figure), splitless

1. 2-Chlorobiphenyl (100ng)
2. 3,3'-Dichlorobiphenyl (100ng)
3. 2,4,5-Trichlorobiphenyl (10ng)
4. 2,2',4,4'-Tetrachlorobiphenyl (10ng)
5. 2,3',4,5',6-Pentachlorobiphenyl (10ng)
6. 2,2',3,3',6,6'-Hexachlorobiphenyl (10ng)
7. 2,2',3,4,5,5',6-Heptachlorobiphenyl (5ng)
8. 2,2',3,3',4,4',5,5'-Octachlorobiphenyl (5ng)
9. 2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl (5ng)
10. 2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl (5ng)

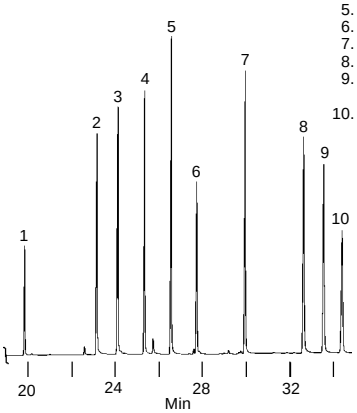

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Figure F. Aroclor PCB Mixtures on a 0.75mm ID Capillary Column

Column: **SPB-5, 60m x 0.75mm ID (glass), 1.0µm film**
Cat. No.: **23721**
Oven: 180°C (2 min) to 300°C at 8°C/min, hold 10 min
Carrier: helium, 20cm/sec (set at 180°C) (5cc/min flow, flow controlled)
Det.: ECD
Inj.: 0.1µL isooctane, 0.1ng Aroclor 1242 or 0.5µL isooctane, 0.5ng Aroclor 1254 or 1260 on-column injection

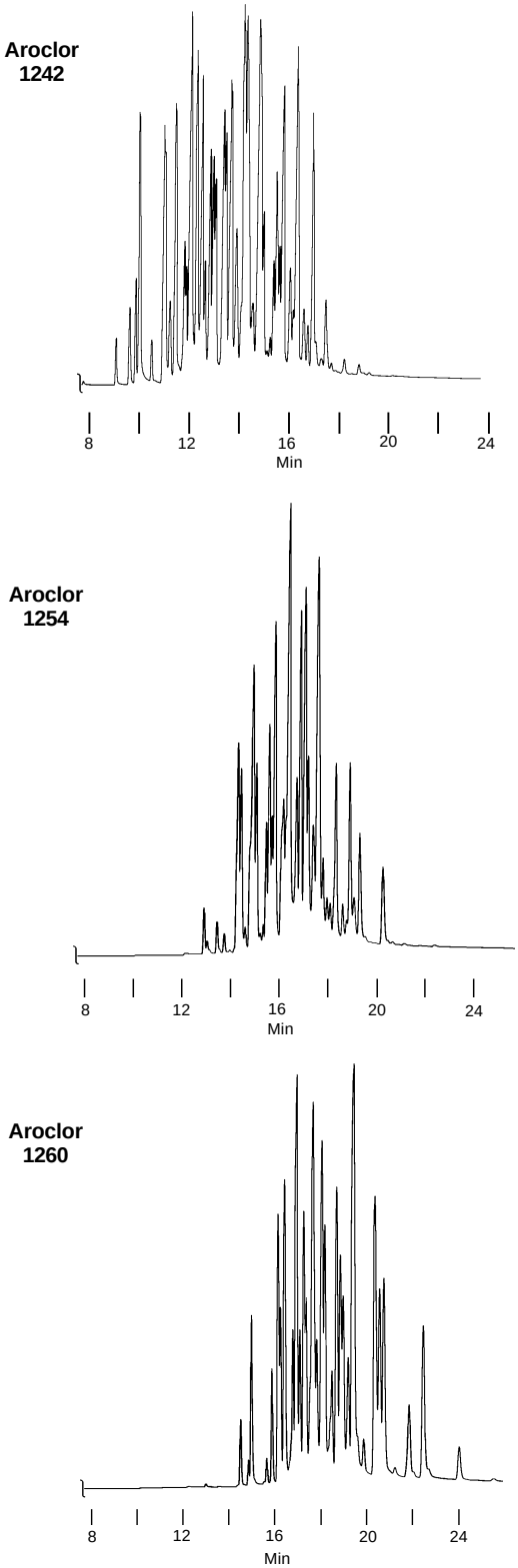

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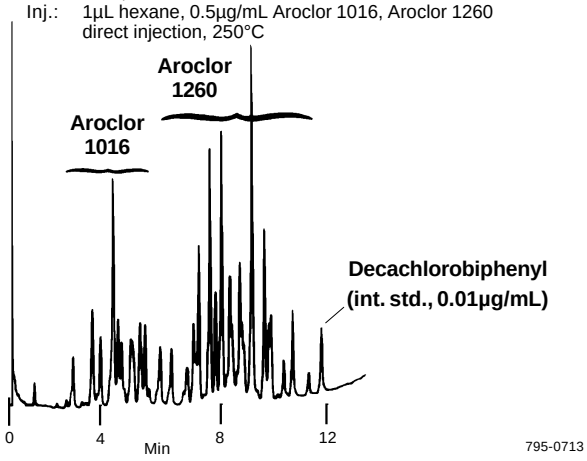
Figure G Mixed Aroclors Resolved and Identified, Using a 0.53mm ID Capillary Column in a Packed Column Chromatograph

Column: **PTE-5 QTM, 15m x 0.53mm ID, 0.5µm film**
Cat. No.: **25355**
Oven: 150°C (2 min) to 275°C at 10°C/min
Carrier: helium, 6.8mL/min (30mL/min nitrogen make-up gas)
Det.: ECD, 350°C
Inj.: 1µL hexane, 0.5µg/mL Aroclor 1016, Aroclor 1260 direct injection, 250°C



795-0713

Detailed Analyses of Polychlorinated Biphenyl Congeners, Using a Bonded Octyl Methyl Polysiloxane Stationary Phase

Individual members (cogeners) of the 209-member PCB family (Table 1) usually must be isolated by capillary GC. Congener-specific GC separations of PCBs have received considerable attention (6-14) because the high toxicities of a dozen of these congeners are similar to the toxicities of several dioxins. The analysis of individual PCB congeners is challenging in several respects. Synthetic PCB mixtures are commonly retained in soil, sludge, clay and airborne particles, but are quite insoluble in water. On the other hand, PCBs bioaccumulate in food chains, and can be traced from soil and air to plant life, from plants to herbivores, and from herbivores to various levels of carnivores. Both aquatic and terrestrial animals accumulate PCBs, mainly in fat tissue and vital organs. The most toxic PCB congeners are in low abundance in synthetic PCB mixtures, but exist in higher concentrations in incinerator fly-ash. Escalating the challenge is the large number of possible PCB congeners, 209, with as many as 10-15 congeners eluting per minute from a GC column. The sheer complexity has resulted in quantitation often being reported for two coeluting congeners.

The key to the toxicity of certain PCB and dioxin congeners to mammals is found in their chemical structures. On the right in Figure H are two of the 209 possible PCB congeners, chosen because they commonly coelute on SPB-5 columns. PCB 77 is highly toxic and is found in low abundance in synthetic PCB mixtures, while PCB 110 is quite abundant but is relatively non-toxic. In PCB 77 there is unrestricted rotation of the bond that links the phenyl groups. Therefore, the phenyl rings can achieve geometries that are essentially coplanar. The most toxic dioxins contain the common 2,3,7,8-tetrachloro- substitution with aromatic rings that also are rigid and coplanar (Table 2). On the other hand, the phenyl rings of PCB 110 are restricted to noncoplanar conformations, due to the chloro- substitution in the two ortho positions. An interesting note is that the aromatic rings of the most toxic chloro- substituted aromatics (dibenzodioxins, dibenzofurans and naphthalenes) are rigid and planar, whereas the most toxic PCB congeners are flexible and coplanar.

The effect of chloro-substitution in the ortho positions can be

Table 1. PCB Congeners

No.	Structure	No.	Structure	No.	Structure	No.	Structure	No.	Structure
MonochloroBiph		*TetrachloroBiph*		*PentachloroBiph*		*HexachloroBiph*		*HeptachloroBiph*	
1	2	**40**	2,2',3,3'	**82**	2,2',3,3',4	**128**	2,2',3,3',4,4'	**170**	2,2',3,3',4,4',5
2	3	**41**	2,2',3,4	**83**	2,2',3,3',5	**129**	2,2',3,3',4,5	**171**	2,2',3,3',4,4',6
3	4	**42**	2,2',3,4'	**84**	2,2',3,3',6	**130**	2,2',3,3',4,5'	**172**	2,2',3,3',4,5,5'
		43	2,2',3,5	**85**	2,2',3,4,4'	**131**	2,2',3,3',4,6	**173**	2,2',3,3',4,5,6
DichloroBiph		**44**	2,2',3,5'	**86**	2,2',3,4,5	**132**	2,2',3,3',4,6'	**174**	2,2',3,3',4,5,6'
4	2,2'	**45**	2,2',3,6	**87**	2,2',3,4,5'	**133**	2,2',3,3',5,5'	**175**	2,2',3,3',4,5',6
5	2,3	**46**	2,2',3,6'	**88**	2,2',3,4,6	**134**	2,2',3,3',5,6'	**176**	2,2',3,3',4,6,6'
6	2,3'	**47**	2,2',4,4'	**89**	2,2',3,4,6'	**135**	2,2',3,3',6,6'	**177**	2,2',3,3',4',5,6
7	2,4	**48**	2,2',4,5	**90**	2,2',3,4',5	**136**	2,2',3,4,4',5	**178**	2,2',3,3',5,5',6
8	2,4'	**49**	2,2',4,5'	**91**	2,2',3,4',6	**137**	2,2',3,4,4',5'	**179**	2,2',3,3',5,6,6'
9	2,5	**50**	2,2',4,6	**92**	2,2',3,5,5'	**138**	2,2',3,4,4',5'	**180**	2,2',3,4,4',5,5'
10	2,6	**51**	2,2',4,6'	**93**	2,2',3,5,6	**139**	2,2',3,4,4',6	**181**	2,2',3,4,4',5,6
11	3,3'	**52**	2,2',5,5'	**94**	2,2',3,5,6'	**140**	2,2',3,4,4',6'	**182**	2,2',3,4,4',5,6'
12	3,4	**53**	2,2',5,6'	**95**	2,2',3,5',6	**141**	2,2',3,4,5,5'	**183**	2,2',3,4,4',5',6
13	3,4'	**54**	2,2',6,6'	**96**	2,2',3,6,6'	**142**	2,2',3,4,5,6	**184**	2,2',3,4,4',6,6'
14	3,5	**55**	2,3,3',4	**97**	2,2',3',4,5	**143**	2,2',3,4,5,6'	**185**	2,2',3,4,5,5',6
15	4,4'	**56**	2,3,3',4'	**98**	2,2',3',4,6	**144**	2,2',3,4,5',6	**186**	2,2',3,4,5,6,6'
		57	2,3,3',5	**99**	2,2',4,4',5	**145**	2,2',3,4,6,6'	**187**	2,2',3,4',5,5',6
TrichloroBiph		**58**	2,3,3',5'	**100**	2,2',4,4',6	**146**	2,2',3,4',5,5'	**188**	2,2',3,4',5,6,6'
16	2,2',3	**59**	2,3,3',6	**101**	2,2',4,5,5'	**147**	2,2',3,4',5,6	**189**	2,3,3',4,4',5,5'
17	2,2',4	**60**	2,3,4,4'	**102**	2,2',4,5,6'	**148**	2,2',3,4',5,6'	**190**	2,3,3',4,4',5,6
18	2,2',5	**61**	2,3,4,5	**103**	2,2',4,5',6	**149**	2,2',3,4',5',6	**191**	2,3,3',4,4',5',6
19	2,2',6	**62**	2,3,4,6	**104**	2,2',4,6,6'	**150**	2,2',3,4',6,6'	**192**	2,3,3',4,5,5',6
20	2,3,3'	**63**	2,3,4',5	**105**	2,3,3',4,4'	**151**	2,2',3,5,5',6	**193**	2,3,3',4',5,5',6
21	2,3,4	**64**	2,3,4',6	**106**	2,3,3',4,5	**152**	2,2',3,5,6,6'		
22	2,3,4'	**65**	2,3,5,6	**107**	2,3,3',4',5 (IUPAC 109)	**153**	2,2',4,4'5,5'	*OctachloroBiph*	
23	2,3,5	**66**	2,3',4,4'	**108**	2,3,3',4,5' (IUPAC 107)	**154**	2,2',4,4',5,6'	**194**	2,2',3,3',4,4',5,5'
24	2,3,6	**67**	2,3',4,5	**109**	2,3,3',4,6 (IUPAC 108)	**155**	2,2',4,4',6,6'	**195**	2,2',3,3',4,4',5,6
25	2,3',4	**68**	2,3',4,5'	**110**	2,3,3',4',6	**156**	2,3,3',4,4',5	**196**	2,2',3,3',4,4',5,6'
26	2,3',5	**69**	2,3',4,6	**111**	2,3,3',5,5'	**157**	2,3,3',4,4',5'	**197**	2,2',3,3',4,4',6,6'
27	2,3',6	**70**	2,3',4',5	**112**	2,3,3',5,6	**158**	2,3,3',4,4',6	**198**	2,2',3,3',4,5,5',6
28	2,4,4'	**71**	2,3',4',6	**113**	2,3,3',5',6	**159**	2,3,3',4,5,5'	**199**	2,2',3,3',4,5,5',6' (IUPAC 200)
29	2,4,5	**72**	2,3',5,5'	**114**	2,3,4,4',5	**160**	2,3,3',4,5,6	**200**	2,2',3,3',4,5,6,6' (IUPAC 201)
30	2,4,6	**73**	2,3',5',6	**115**	2,3,4,4',6	**161**	2,3,3',4,5',6	**201**	2,2',3,3',4,5',6,6' (IUPAC 199)
31	2,4',5	**74**	2,4,4',5	**116**	2,3,4,5,6	**162**	2,3,3',4',5,5'	**202**	2,2',3,3',5,5',6,6'
32	2,4',6	**75**	2,4,4',6	**117**	2,3,4',5,6	**163**	2,3,3',4',5,6	**203**	2,2',3,4,4',5,5',6
33	2',3,4	**76**	2',3,4,5	**118**	2,3',4,4',5	**164**	2,3,3',4',5',6	**204**	2,2',3,4,4',5,6,6'
34	2',3,5	**77**	3,3',4,4'	**119**	2,3',4,4',6	**165**	2,3,3',5,5',6	**205**	2,3,3',4,4',5,5',6
35	3,3',4	**78**	3,3',4,5	**120**	2,3',4,5,5'	**166**	2,3,4,4',5,6		
36	3,3',5	**79**	3,3',4,5'	**121**	2,3',4,5',6	**167**	2,3',4,4',5,5'	*NonachloroBiph*	
37	3,4,4'	**80**	3,3',5,5'	**122**	2',3,3',4,5	**168**	2,3',4,4',5',6	**206**	2,2',3,3',4,4',5,5',6
38	3,4,5	**81**	3,4,4',5	**123**	2',3,4,4',5	**169**	3,3',4,4',5,5'	**207**	2,2',3,3',4,4',5,6,6'
39	3,4',5			**124**	2',3,4,5,5'			**208**	2,2',3,3',4,5,5',6,6'
				125	2',3,4,5,6'				
				126	3,3',4,4',5			*DecachloroBiph*	
				127	3,3',4,5,5'			**209**	2,2',3,3',4,4',5,5',6,6'

From Ballschmiter and Zell, *Fresenius' Z. Anal. Chem.,* **302:** 20-31 (1980).

Table 2. Toxic, Dioxin-Like PCBs: Toxic Equivalency Factors (TEF)

IUPAC No.	Structure	TEF*
Non-*ortho*		
77	3,3',4,4'-TCB	0.0005
126	3,3',4,4',5-PeCB	0.1
169	3,3',4,4',5,5'-HxCB	0.01
Mono-*ortho*		
105	2,3,3',4,4'-PeCB	0.0001
114	2,3,4,4',5-PeCB	0.0005
118	2,3',4,4',5-PeCB	0.0001
123	2',3,4,4',5-PeCB	0.0001
156	2,3,3',4,4',5-HxCB	0.0005
157	2,3,3',4,4',5'-HxCB	0.0005
167	2,3',4,4',5,5'-HxCB	0.00001
189	2,3,3',4,4',5,5'-HpCB	0.0001
Di-*ortho*		
170	2,2',3,3',4,4',5-HpCB	0.0001
180	2,2',3,4,4',5,5'-HpCB	0.00001

*2,3,7,8-tetrachlorodibenzo-p-dioxin = 1.0; PCB 126 has 1/10 toxicity of 2,3,7,8-TCDD, etc.

Data from Ahlborg, *et al.* (8).

classified into six categories (Figure I). Non-ortho and mono-ortho- substituted PCB congeners can achieve coplanar conformations, since the phenyl groups are free to rotate. Rotation about the common bond of di-ortho-substituted PCB congeners diminishes, due to steric hindrance. Achieving coplanarity is impossible, even at normal body temperature, since two chloro groups or a chloro and a hydro group repulse each other as the phenyl groups approach coplanarity. The number of conformations is limited further by tri-ortho- and tetra-ortho- substitution. The phenyl groups of tetra-ortho-substituted PCBs can rotate less than 90° in either direction.

On the left in Figure H is the chemical structure of the SPB-Octyl stationary phase. The polarity of this phase is dominated by the

Note:

The toxic PCB congeners all contain chloro-substitutions in the 3,3',4,4' or 3,4,4' or 3',4,4' positions and either 0, 1, or 2 chloro groups in the *ortho* positions.

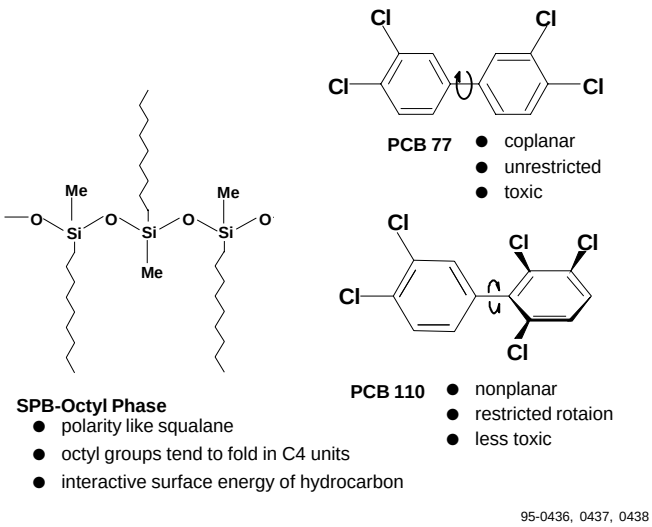
The 3 non-*ortho* congeners are rarely reported in environmental samples but are the most toxic group. Of the mono-*ortho* and di-*ortho* chloro-substituted congeners, 118, 105, 156, 170, and 180 make up about 20% of the total PCBs reported in animal tissue. Congeners 114, 123, 157, 167, and 189 have rarely been reported in animal tissue but have moderately high toxicity.

hydrocarbon character of the octyl groups. The octyl groups do not line up as depicted here, but tend to bend back upon themselves between the fourth and fifth carbons. Using SPB-Octyl columns, we have observed examples of shape selectivity that may be excellent examples of true boiling point separations. First reported for separating PCB congeners by Ballschmiter, *et al.* (6), the SPB-Octyl phase has unique selectivity for coplanar PCBs. Investigators in private industry, government agencies, and universities now are pioneering the use of SPB-Octyl columns for PCB, dioxin, and chloronaphthalene investigations.

We investigated the potential for separating all 209 PCB congeners, using ECD and MSD detection with splitless injections. The limits of detection were approximately 0.5ppb/congener by ECD and 10ppb/congener for MSD. The last congener, PCB 209, always eluted before 280°C during temperature programming.

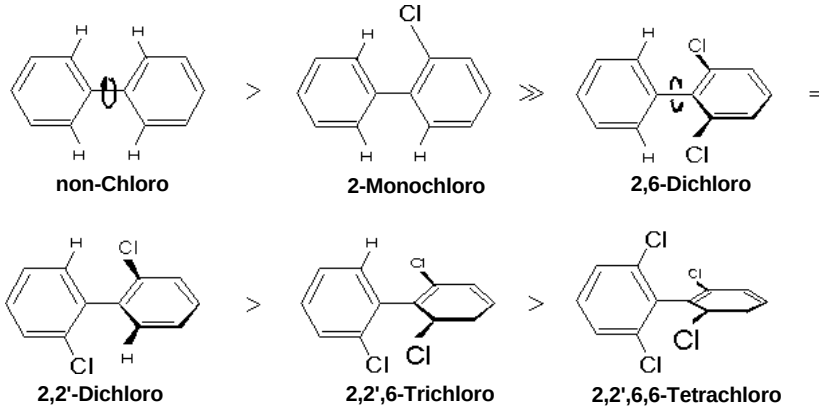
The ECD chromatogram in Figure J illustrates the complexity of PCB congener separations, with nearly 100 congeners eluting within an eight-minute span. The brackets below the chromatogram mark the elution ranges of PCB homologs: trichloro-,

Figure H. Chemical Structures: SPB-Octyl Phase, PCB Congeners



95-0436, 0437, 0438

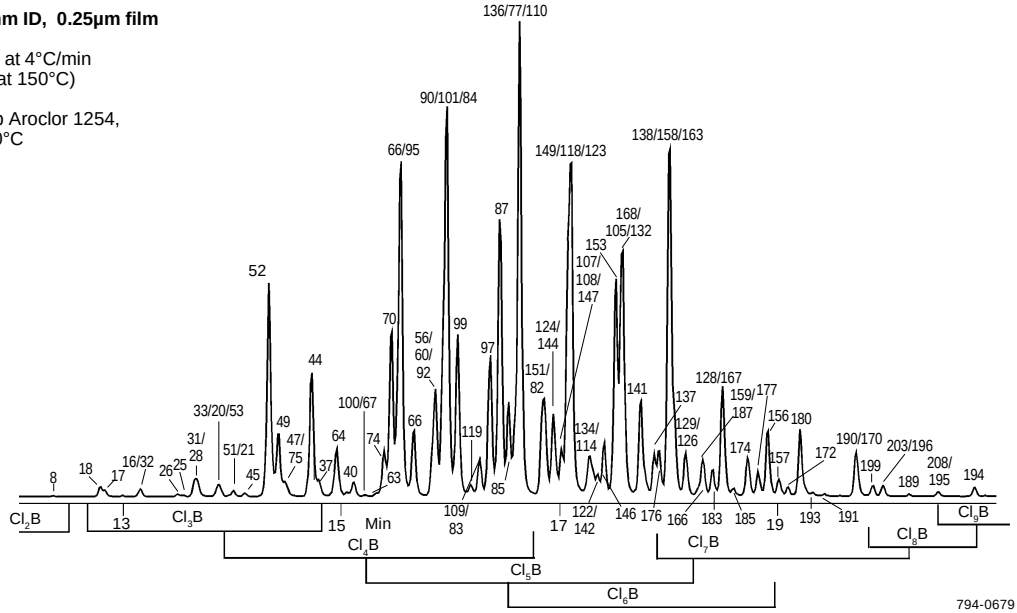
Figure I. Order of Decreasing Rotational Freedom of PCB Congeners (substitution in *ortho* positions)



95-0071

Figure J. Complexity of PCB Congener-Specific Separations

Column: **PTE™-5, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24135**
Oven: 150°C (1 min) to 280°C at 4°C/min
Carrier: helium, 40cm/sec (set at 150°C)
Det.: ECD
Inj.: 1µL isooctane, 400ppb Aroclor 1254, splitless (0.5 min), 280°C



794-0679

tetrachloro-, pentachloro-, hexachloro-, heptachloro- and octachloro- biphenyls. There are 30 possible tetrachloro-, 46 pentachloro-, and 42 hexachloro- biphenyl congeners. This complexity leads to coelution of PCB homologs and overlapping of elution ranges for PCBs of different homologs (e.g., pentachloro- and hexachloro- biphenyls).

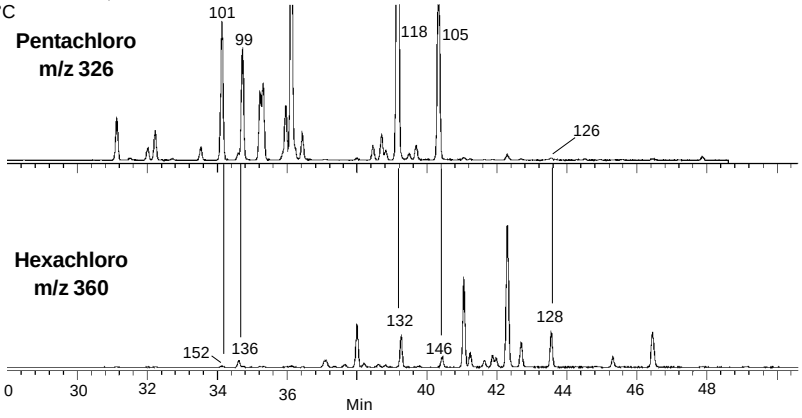
With a mass-selective detector (MS, MSD, or ion trap), the congeners of each chloro-homolog can be extracted from the total ion chromatogram. In Figure K, pentachlorobiphenyls (m/z 326) and hexachlorobiphenyls (m/z 360) are stacked separately, thereby overcoming the overlapping of elution ranges. For instance, partially coeluting PCB 118 and PCB 132 can be correctly identified by retention time or retention index and accurately quantified by using extracted ion plots. ECD is more sensitive to PCB congeners, but mass spectrometric detection is more selective and enhances the chromatographic separation.

The overlap between ortho-substitution classes of PCBs increases with increasing phenyl-substitution in the stationary phase in a column. With an SPB-5 column (5% phenyl) there is some overlap of the di-ortho- (2,6 and 2,2') with the tri-ortho- (2,2',6) substituted pentachlorobiphenyls. With an SPB-20 column (20% phenyl) the overlap increases, because the greater phenyl content widens the elution range of the ortho-substitution classes. With an SPB-50 column (50% phenyl) the elution zones are approximately twice as wide as for an SPB-5 column. The basis of the widening of the elution zones is the increased average dipole-induced dipole interactions between the polarizable phenyl-containing phases and the moderately polar PCB congeners.

With an SPB-Octyl column, in contrast, the elution zones for ortho-substitution classes are narrow and well separated (Figure L). The chemical icons on the figure help to show that, for each group of chloro-homologs, the noncoplanar congeners (e.g., tetra-ortho) elute first and the flexible coplanar congeners (e.g., non-ortho) elute last. One of the most toxic PCB congeners, non-ortho-substituted, coplanar PCB 126, elutes last and well separated in the

Figure K. PCB Congeners: MS Extracted Ions

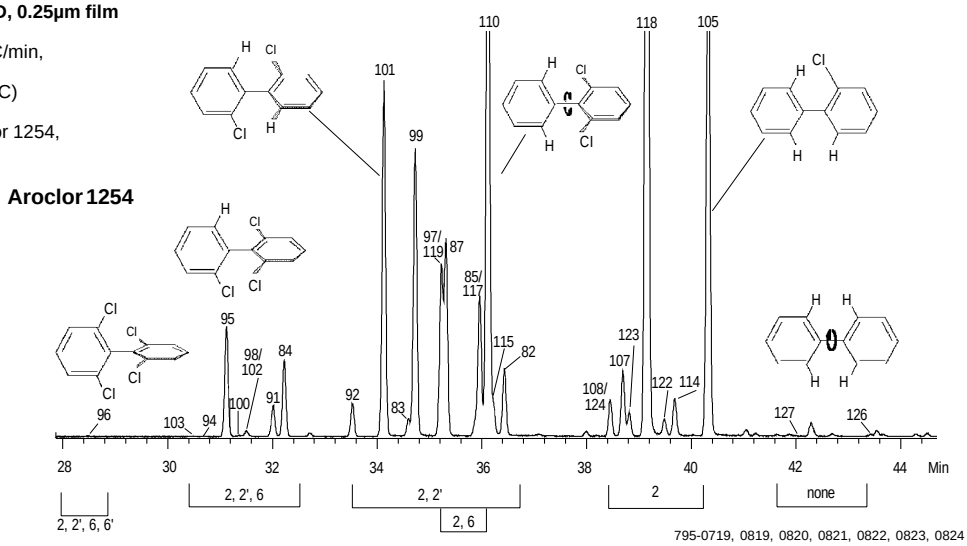
Column: **SPB-Octyl, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24218**
Oven: 75°C (2 min) to 150°C at 15°C/min, then to 290°C at 2.5°C/min
Carrier: helium, 40cm/sec (set at 40°C)
Det.: MS
Inj.: 1µL isooctane, 40ppm Aroclor 1254, splitless (0.5 min), 280°C



795-0718

Figure L. Effect of ortho-Substitution: SPB-Octyl Phase, Pentachlorobiphenyls

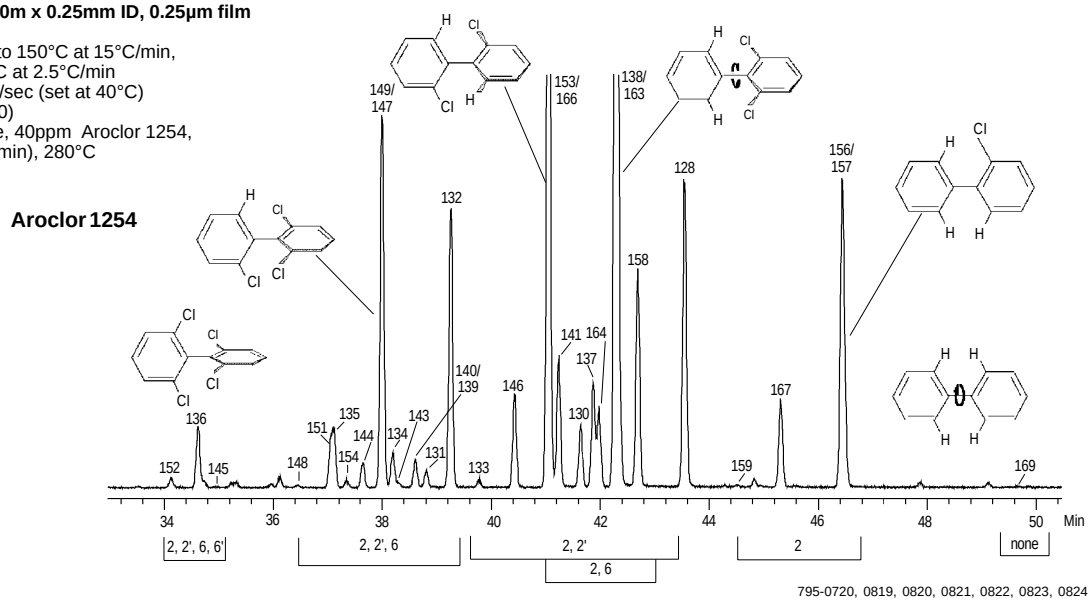
Column: **SPB-Octyl, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24218**
Oven: 75°C (2 min) to 150°C at 15°C/min, then to 290°C at 2.5°C/min
Carrier: helium, 40cm/sec (set at 40°C)
Det.: MS (m/z = 326)
Inj.: 1µL isooctane, 40ppm Aroclor 1254, splitless (0.5 min), 280°C



795-0719, 0819, 0820, 0821, 0822, 0823, 0824

Figure M. Effect of ortho-Substitution: SPB-Octyl Phase, Hexachlorobiphenyls

Column: **SPB-Octyl, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24218**
Oven: 75°C (2 min) to 150°C at 15°C/min, then to 290°C at 2.5°C/min
Carrier: helium, 40cm/sec (set at 40°C)
Det.: MS (m/z = 360)
Inj.: 1µL isooctane, 40ppm Aroclor 1254, splitless (0.5 min), 280°C



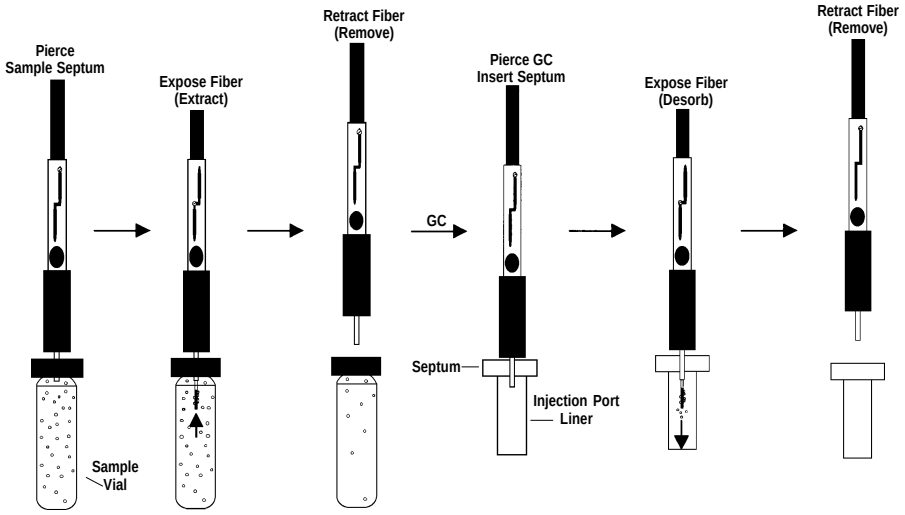
795-0720, 0819, 0820, 0821, 0822, 0823, 0824

group of pentachlorobiphenyls. The same pattern is evident for the hexachlorobiphenyls (Figure M). Another of the most toxic PCB congeners, PCB 169, also a non-ortho- substituted, coplanar congener, elutes last among the hexachloro- homologs. The elution of PCB congeners on an SPB-Octyl column best correlates with increasing boiling point (vapor pressure). The accentuated resolution attained by using an SPB-Octyl column indicates a unique selectivity of this column for PCB congeners.

Solid Phase Microextraction of PCBs

Solid phase microextraction (SPME), is a highly effective sample preparation technique for rapidly extracting PCB congeners from soil, for separation by capillary GC. Figure N shows the process of microextracting and concentrating organic compounds from a water, soil, or sludge sample. By immersing into the sample the 1cm, polysiloxane-coated fiber at the tip of the SPME device, or exposing it to the headspace above the sample, an analyst can extract and concentrate PCB congeners without using solvents, usually in 15-30 minutes. The extracted PCBs are desorbed in the injection port, where they are transferred to the column. Figure O shows the SPME-extracted organics from a stream sediment, collected downstream from a site where transformer oils accidentally leaked into the stream more than 10 years ago. Except for the increased abundance of several dichloro- and trichloro- biphenyls, the extracted PCB profile is nearly identical to that of Aroclor 1242. To indicate the sensitivity of the extraction, PCB 44/65 was present at 700 parts per trillion and PCB 105 was present at 50 parts per trillion. With SPME, a minimum extraction limit of less than 5 parts per trillion is attainable, in an extraction time of only 60 minutes.

Figure N. Solid Phase Microextraction

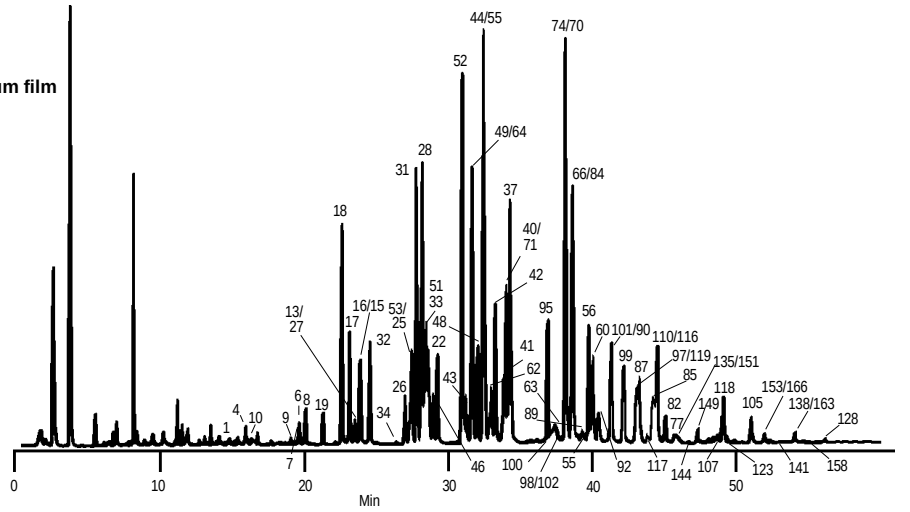


795-1345

Figure O. PCB Congeners in Stream Sediment, Using Solid Phase Microextraction/Capillary GC

SPME Fiber: **100µm polydimethylsiloxane**
Cat. No.: **57300**
Sampling: headspace (20 min)
10 sec desorption (splitless mode)

Column: **SPB-Octyl, 30m x 0.25mm ID, 0.25µm film**
Cat. No.: **24218**
Oven: 50°C (1min) to 150°C at 15°C/min, then to 280°C at 1.5°C/min
Carrier: helium, 40cm/sec (set at 150°C)
Det.: ECD
Inj.: headspace SPME sample from 3g stream sediment, splitless (0.5 min), 280°C



795-0716

Ordering Information:

Description	Cat. No.
1.5% SP-2250/1.95% SP-2401 on 100/120 SUPELCOPORT	
20g bottle	**11947**
3% SP-2100 on 100/120 SUPELCOPORT	
20g bottle	**11738**

For columns packed for your instrument, please call our Ordering Department.

Capillary Columns

SPB-608, 30m x 0.25mm ID, 0.25µm film	**24103-U**
SPB-5, 30m x 0.32mm ID, 0.25µm film	**24048**
SPB-5, 60m x 0.75mm ID glass, 1.0µm film	**23721**
PTE-5, 30m x 0.25mm ID, 0.25µm film	**24135-U**
PTE-5 QTM, 15m x 0.53mm ID, 0.5µm film	**25355**
SPB-Octyl, 30m x 0.25mm ID, 0.25µm film	**24218-U**

DCMA PCB Mixture

Use this qualitative mix of isomers for identifying PCBs in pigments and other materials. Prepared according to Dry Colors Manufacturers' Association specifications.

In hexane.

2-Chlorobiphenyl, 100µg/mL
3,3'-Dichlorobiphenyl, 100µg/mL
2,4,5-Trichlorobiphenyl, 10µg/mL
2,2',4,4'-Tetrachlorobiphenyl, 10µg/mL
2,3',4,5',6-Pentachlorobiphenyl, 10µg/mL
2,2',3,3',6,6'-Hexachlorobiphenyl, 10µg/mL
2,2',3,4',5,5',6-Heptachlorobiphenyl, 5µg/mL
2,2',3,3',4,4',5,5'-Octachlorobiphenyl, 5µg/mL
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl, 5µg/mL
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl, 5µg/mL

Description	Cat. No.
10mL	**48738**

PCB Congener Mix 1

10µg/mL each component in isooctane.

2,6-Dichlorobiphenyl
2,4,4´-Trichlorobiphenyl
2,2´,5,5´-Tetrachlorobiphenyl
2,2´,3,4,4´5,5´-Heptachlorobiphenyl
2,2´4,4´5,5´-Hexachlorobiphenyl
2,2´3,4,4´,5´-Hexachlorobiphenyl

Description	Cat. No.
10mL	**47330-U**

CEN PCB Congener Mix-1

10µg/mL in heptane.

2,2´,5-Trichlorobiphenyl
2,4´,5-Trichlorobiphenyl
2,4,4´-Trichlorobiphenyl
2,2´,5,5´-Tetrachlorobiphenyl
2,2´,3,5´-Tetrachlorobiphenyl
2,2´,4,5,5´-Pentachlorobiphenyl
2,3´,4,4´,5-Pentachlorobiphenyl
2,2´,3,4´,5´,6-Hexachlorobiphenyl
2,2´,4,4´,5,5´-Hexachlorobiphenyl
2,2´,3,4,4´,5´-Hexachlorobiphenyl
2,2´,3,4,4´,5,5´-Heptachlorobiphenyl
2,2´,3,3´,4,4´,5,5´-Octachlorobiphenyl

Description	Cat. No.
1mL	**47927**

PCB Locator Mix

Use this qualitative mix for identifying PCBs in transformer and waste oils. Prepared according to US EPA specifications. Quality monitored by GC (ECD or Hall® detector), but also suitable for HPLC or TLC analyses.

At concentrations indicated in isooctane.

2-Chlorobiphenyl, 0.1µg/mL
3-Chlorobiphenyl, 0.1µg/mL
Aroclor 1242, 0.5µg/mL
Aroclor 1260, 0.5µg/mL
Decachlorobiphenyl, 0.1µg/mL

Description	Cat. No.
1mL	**48730-U**

Aroclor PCB Mixtures

Neat		in Solvent		in Diala AX Oil Solution (5mL)	
Qty.	Cat. No.	Concentration	Cat. No.	Concentration	Cat. No.
Aroclor 1016					
50mg	**48591**	1000µg/mL in isooctane	**48097**	50mg/kg	**47925**
		200µg/mL in methanol	**48701**	500mg/kg	**47962**
		1000µg/mL in methanol	**48050-U**		
Aroclor 1221					
50mg	**48587**	1000µg/mL in methanol	**48051**	50mg/kg	**47963**
		1000µg/mL in isooctane	**48098**	500mg/kg	**47964**
		200µg/mL in methanol	**48705**		
Aroclor 1232					
10mg	**48588**	1000µg/mL in isooctane	**44805**	50mg/kg	**47967-U**
		1µg/mL in isooctane	**44811**	500mg/kg	**47968**
		200µg/mL in methanol	**48702**		
		1000µg/mL in methanol	**48052**		
Aroclor 1242					
50mg	**48585**	1000µg/mL in isooctane	**44806**	50mg/kg	**48732**
		1µg/mL in isooctane	**44812**	500mg/kg	**48731**
		200µg/mL in methanol	**48706**		
		1000µg/mL in methanol	**48053-U**		
Aroclor 1248					
50mg	**48589**	1000µg/mL in isooctane	**44807**	50mg/kg	**47965-U**
		1µg/mL in isooctane	**44813**	500mg/kg	**47966**
		200µg/mL in methanol	**48703**		
		1000µg/mL in methanol	**48054**		
Aroclor 1254					
50mg	**48586**	1000µg/mL in isooctane	**44808**	50mg/kg	**48734**
		1µg/mL in isooctane	**44814**	500mg/kg	**48733**
		200µg/mL in methanol	**48707**		
		1000µg/mL in methanol	**48055-U**		
Aroclor 1260					
50mg	**48590**	1000µg/mL in isooctane	**44809**	50mg/kg	**48736**
		1µg/mL in isooctane	**44815**	500mg/kg	**48735**
		200µg/mL in methanol	**48704**		
		1000µg/mL in methanol	**48056**		
Aroclor 1262					
—	—	1000µg/mL in isooctane	**44810**	50mg/kg	**47482**
		1µg/mL in isooctane	**44816**	500mg/kg	**47483**

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EMSL, Cincinnati = Environmental Monitoring and Support Laboratory, Office of Research and Development, US Environmental Protection Agency, Cincinnati, Ohio 45268

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SP, SPB, Supelco,
SUPELCOPORT, PTE , TightSpec – Supelco, Inc.

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