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Short communication

Enhanced comprehensive two-dimensional gas chromatographic resolution of polychlorinated biphenyls on a non-polar polysiloxane and an ionic liquid column series☆

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ABSTRACT

A total of 196 out of 209 polychlorobiphenyl (PCB) congeners were resolved using GC × GC–TOFMS with a non-polar/ionic liquid column series consisting of poly(50%-*n*-octyl-50%-methyl)siloxane and (1,12-di(tripropylphosphonium)dodecane bis(trifluoromethansulfonyl)amide) in the first and second dimension, respectively. It has been found that 13 PCB congeners overlap in five doublets (CB12 + CB13, CB62 + CB75, CB70 + CB76, CB97 + CB125 and CB153 + CB168) and one triplet (CB90 + CB101 + CB113). All toxic, "dioxin like" congeners were separated with no interferences from any PCB congener. The 109 PCBs present in Aroclor 1242 and the 82 PCBs present in Aroclor 1260 were resolved GC × GC–TOFMS analysis on this column set.

1. Introduction

The separation of the 209 polychlorinated biphenyls (PCBs) remains a significant challenge in capillary column gas chromatography (HRGC) and complete separation has not been reported so far.

PCBs in samples analyzed for environmental and regulatory purposes usually consist of complex mixtures of up to ∼150 of the 209 possible different chlorine-substituted biphenyl congeners, derived from technical formulations [1–3]. Additional congeners may be encountered in samples where processes such as photolytic, microbial, thermal or chemical dechlorination, or metabolism in higher animals have acted upon the initial distribution found in the technical mixtures [1]. Many research applications, particularly those investigating the alteration processes listed above, require comprehensive, quantitative, congener-specific (CQCS) analyses [1]. No single column can separate all 209 congeners, or even all those typically encountered in applications requiring CQCS methods. Four columns were particularly effective for one-dimensional CQCS analyses [1–3]:

(i) poly(dimethylsiloxy-1,4-bis((dimethylsiloxy)phenylen)siloxane) (DB-XLB),
(ii) phenyl polycarborane-siloxane (HT-8),
(iii) poly-(50%-*n*-octyl-50%-methyl)siloxane (SPB-Octyl), and
(iv) a non-specified polysiloxane polymer (Rtx-PCB) [4].

The following conclusion on PCB congener separation may be deduced for the first three columns [1]:

- 104 singlets, 33 doublets, 4 triplets, 3 tetraplets and 1 pentaplet on the SPB-Octyl column,
- 128 singlets, 24 doublets and 11 triplets on the DB-XLB column, and
- 100 singlets, 23 doublets, 15 triplets, 3 tetraplets and 1 hexaplet on the HT-8 column.

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From the retention data published by Fix and Libardoni [5] on Rtx-PCB column it may be concluded that 35 of PCB peak pairs were separated with resolution factor $Rs < 0.7$ and 14 peak pairs were fully overlapped ($Rs = 0.00$). Moreover the toxic CB 77 fully overlaps with CB 149.

In comprehensive two-dimensional gas chromatographic (GC × GC) separations of the 209 PCBs, combinations of HT-8, DB-XLB and Rtx-PCB columns "selective for co-planar PCB congeners" used in the first dimension with polar columns in the second dimension represent the most effective column series [6–8]. Focant et al. separated 188 of the 209 PCB congeners by GC × GC–TOFMS with the 50 m HT-8/2.5 m BPX-50 (50% phenyl)-polysilphenylene-siloxane column series. Four PCB congeners were resolved by mass spectral deconvolution leading to a total of 192 congeners resolved in 146 min [6]. Harju et al. resolved 194 of the 209 PCBs in 240 min by GC × GC-μECD on a 60 m DB-XLB/2.25 m BPX-70 (70% cyanopropylphenyl polysiloxane) column series [7]. Osemwiege and Sovocool described the separation of 196 PCBs by GC × GC–TOFMS using a 40 m Rtx-PCB/1 m DB-17 column series [8].

The SPB-Octyl column has yet not been used for comprehensive two-dimensional separations of PCBs in spite of the fact that all toxic "dioxin like PCBs" except CB 156 and CB 157 were successfully separated on this column [9].

The aim of this study was to enhance the separation of the 209 PCBs by GC × GC–TOFMS on the "traditional column combination" in which the ^{1}D column is non-polar and the ^{2}D column polar. The polarity of SPB-Octyl approaches that of squalane, and is substantially lower than that of the widely used polydimethylsiloxane column [10]. The low polarity of SPB-Octyl therefore offers more non-polar interactions with the PCBs than any of the other columns used so far for separation of PCBs. The application of a SPB-Octyl column in the first dimension separates PCBs according to their boiling points. We have recently demonstrated that the ionic liquid (1,12-di(tripropylphosphonium)dodecane bis(trifluoromethansulfonyl)amide) – SLB-IL59) used in the ^{2}D dimension exhibits unique selectivity for PCBs that are not separated on polydimethylsiloxane column used in ^{1}D first dimension. [11].

The present study evaluates the capability of a GC × GC–TOFMS system to enhance the separation of the 209 PCB congeners using a SPB-Octyl/ionic liquid SLB-IL59 column series.

2. Experimental

2.1. PCB standards

The nine PCB standard solutions of all 209 PCBs labeled as C-CS-01 to C-CS-09 contain mixtures of 12–39 PCB congeners at a concentration of 10 μg/mL in isooctane (AccuStandard Inc., New Haven, CT, USA) [12]. Aliquots of the nine multi-congener solutions (C-CS-01 to 09) were mixed to produce a solution containing all 209 congeners at 1 μg/mL. Aroclors 1242 and 1260 were purchased from Supelco (Bellefonte, PA, USA). Individual PCBs congeners were labeled using the IUPAC numbering. All standard solutions and Aroclor formulations were separated by GC × GC–TOFMS on a SPB-Octyl/SLB-IL59 column series. Considering both experimental as well as published retention data on a SPB-Octyl column by Frame [1] and in US EPA Method 1668B [9], as well as measured and tabulated mass spectra, all peaks and peak clusters on the two-dimensional retention planes were unambiguously identified.

2.2. GC × GC–TOFMS separations

A LECO Pegasus 4D (LECO Corporation, St. Joseph, MI, USA) consisting of an Agilent 7890 gas chromatograph and automatic liquid sampler HP 7683 (Agilent, Palo Alto, CA, USA) equipped with a split/splitless injector, dual-stage thermal modulator and secondary oven connected to a Time-of-Flight Mass Spectrometer, was used.1 μL of sample containing all 209 PCBs in a concentration 1 μg/mL of isooctane was injected splitless at 300 °C with 1 min purge off. Stored mass range of m/z 29–520 with an acquisition rate of 50 spectra/s was used. Helium was the carrier gas at 1 mL/min flow (99.999%, Linde AG, Wiesbaden, Germany). The primary oven was programmed from 80 °C (2 min) to 250 °C (30 min) at 3 °C/min. The temperature offset between secondary and primary oven was 5 °C. Other experimental parameters were: modulation frequency 5 s, temperature offset of modulation 50 °C, temperature of transfer line 280 °C, temperature of ion source 250 °C and electron ionization energy 70 eV. Data analysis was performed using the LECO ChromaTOF software for automated peak find and spectral deconvolution. The signal-to-noise ratio for the peak find processing was set to 50. Peak identification was performed with NIST mass spectral library search using a required minimum similarity of 700 out of 1000.

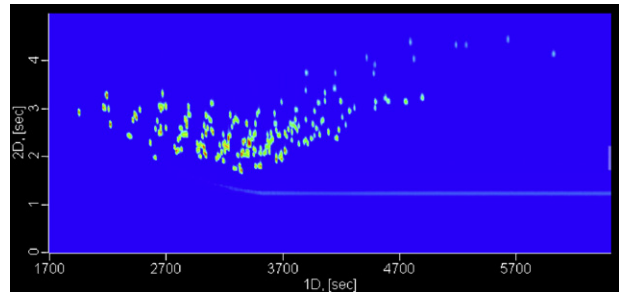

Fig. 1. Contour plot obtained by GC × GC–TOFMS analysis of all 209 PCB congeners on a SPB-Octyl/SLB-IL59 column series.

2.3. Column series

A SPB-Octyl (30 m × 250 μm I.D. coated with 0.25 μm film thickness of poly(50%-n-octyl-50%-methyl)siloxane) column was used in the ^{1}D dimension. An ionic liquid SLB-IL59 column of 1.8 m × 100 μm I.D. coated with 0.24 μm film thickness of (1,12-di(tripropylphosphonium)dodecane bis(trifluoromethansulfonyl)amide) column was used in the ^{2}D dimension. Both columns were donated by Supelco (Bellefonte, PA, USA).

3. Results and discussion

Fig. 1 shows the contour plot obtained for the GC × GC–TOFMS separation of the 209 PCBs on the SPB-Octyl/SLB-IL59 column series. Retention times in the primary and secondary dimensions were recorded for each of the 209 PCB congeners and are listed in Table 1. The retention times in the ^{1}D dimension were used to predict critical pairs of congeners that may be difficult to separate. Table 1 shows 70 PCB congeners that had the primary retention time within one modulation period on the SPB-Octyl column (22 doublets, 6 triplets and 2 tetraplets). All the other PCB congeners differ on this column with at least one modulation period (5 s) of each other. Differences in retention times and the mean peak widths at the base ($w_{b,1D} = 0.12$ min) were used to calculate resolution factors of all neighboring peaks separated by the first dimension. Neighboring peaks differing with at least one modulation period with resolution factor $Rs_{,1D} \geq 0.6$ ($Rs_{,1D} = \Delta t_{R,1D}/w_{b,1D}$) were considered as resolved in the ^{1}D dimension. PCB congeners overlapping on the ^{1}D column were resolved by ChromaTOF software with automated peak find and mass spectral deconvolution

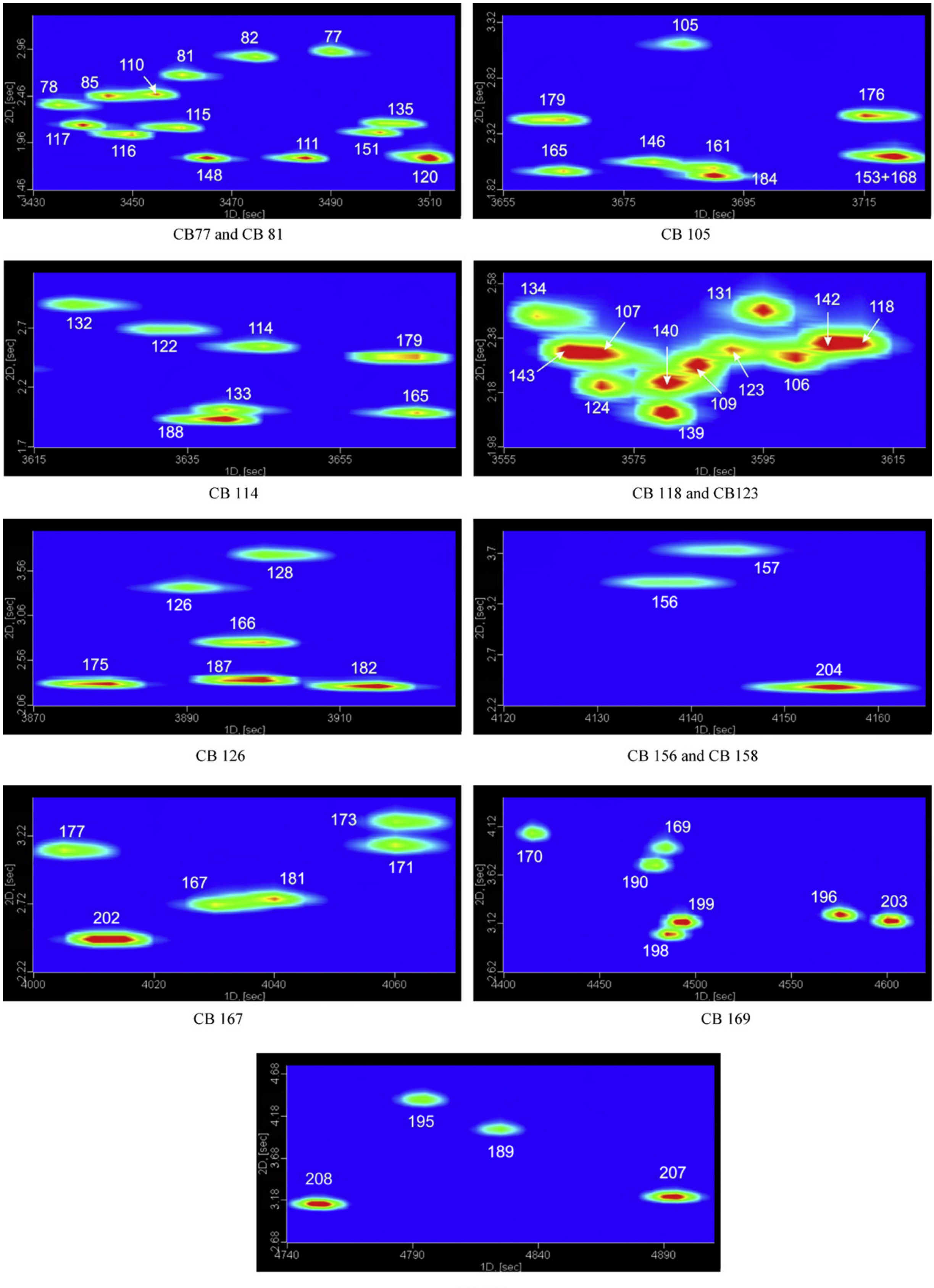

Fig. 2. Contour plots by GC × GC–TOFMS for the toxic "dioxin like" PCBs.

Table 1
Elution order of PCB congeners on SPB-Octyl/SLB-IL59 column series, 5 °C offset.

IUPAC No	Cl position	$^{1}t_R$, s	$^{2}t_R$, s	IUPAC No	Cl position	$^{1}t_R$, s	$^{2}t_R$, s
1	2	1960	2.92	79	3,3',4,5'	3405	2,28
2	3	2170	3.02	97	2,2',3',4,5	3405	2,32
3	4	2190	3.28	125	2',3,4,5,6'	3405	2,32
4	2,2'	2215	3.00	86	2,2',3,4,5	3410	2,30
10	2,6	2230	2.68	87	2,2',3,4,5'	3410	2,50
9	2,5	2385	2.44	78	3,3',4,5	3435	2,36
7	2,4	2395	2.44	117	2,3,4',5,6	3440	2.16
6	2,3'	2415	2.76	85	2,2',3,4,4'	3445	2.46
5	2,3	2440	2.88	116	2,3,4,5,6	3450	2.04
8	2,4'	2450	2.82	110	2,3,3',4',6	3455	2.48
19	2,2',6	2475	2.98	115	2,3,4,4',6	3460	2.12
14	3,5	2570	2.28	81	3,4,4',5	3460	2.68
30	2,4,6	2605	1.98	148	2,2',3,4',5,6'	3465	1.80
18	2,2',5	2610	2.58	82	2,2',3,3',4	3475	2.88
11	3,3'	2630	2.74	111	2,3,3',5,5'	3485	1.80
17	2,2',4	2635	2.50	77	3,3',4,4'	3490	2.94
27	2,3',6	2650	2.62	151	2,2',3,5,5',6	3500	2.10
12	3,4	2650	2.98	135	2,2',3,3',5,6'	3505	2.16
13	3,4'	2650	2.98	154	2,2',4,4',5,6'	3510	1.78
24	2,3,6	2660	2.50	120	2,3',4,5,5'	3510	1.84
16	2,2',3	2670	3.02	144	2,2',3,4,5',6	3530	2.08
15	4,4'	2670	3.30	149	2,2',3,4',5',6	3545	2.20
54	2,2',6,6'	2695	3.04	147	2,2',3,4',5,6	3550	2.10
32	2,4',6	2700	2.60	134	2,2',3,3',5,6	3560	2.46
34	2',3,5	2780	2.20	143	2,2',3,4,5,6'	3565	2.34
23	2,3,5	2790	2.12	124	2',3,4,5,5'	3570	2.20
29	2,4,5	2810	2.12	107	2,3,3',4,5'	3570	2.34
26	2,3',5	2810	2.36	139	2,2',3,4,4',6	3580	2.10
25	2,3',4	2825	2.40	140	2,2',3,4,4',6'	3580	2.22
50	2,2',4,6	2830	2.14	109	2,3,3',4',5	3585	2.28
53	2,2',5,6'	2830	2.58	123	2',3,4,4',5	3590	2.34
31	2,4',5	2845	2.46	131	2,2',3,3',4,6	3595	2.48
28	2,4,4'	2860	2.46	106	2,3,3',4,5	3600	2.30
20	2,3,3'	2865	2.76	142	2,2',3,4,5,6	3605	2.36
45	2,2',3,6	2870	2.78	118	2,3',4,4',5	3610	2.36
51	2,2',4,6'	2875	2.46	132	2,2',3,3',4,6'	3620	2.90
21	2,3,4	2875	2.64	122	2',3,3',4,5	3630	2.68
33	2',3,4	2875	2.72	188	2,2',3,4',5,6,6'	3640	1.94
46	2,2',3,6'	2890	3.04	133	2,2',3,3',5,5'	3640	2.02
22	2,3,4'	2900	2.88	114	2,3,4,4',5	3645	2.54
52	2,2',5,5'	2970	2.28	165	2,3,3',5,5',6	3665	1.98
73	2,3',5',6	2975	2.14	179	2,2',3,3',5,6,6'	3665	2.46
43	2,2',3,5	2985	2.24	146	2,2',3,4',5,5'	3680	2.08
36	3,3',5	2990	2.16	105	2,3,3',4,4'	3685	3.12
69	2,3',4,6	2995	2.00	184	2,2',3,4,4',6,6'	3690	1.94

Table 1 (*Continued*)

49	2,2',4,5'	3000	2.26	161	2,3,3',4,5',6	3690	2.02
39	3,4',5	3010	2.42	176	2,2',3,3',4,6,6'	3715	2.48
48	2,2',4,5	3015	2.22	153	2,2',4,4',5,5'	3720	2.12
104	2,2',4,6,6'	3025	2.18	168	2,3',4,4',5',6	3720	2.12
64	2,3,5,6	3030	2.08	141	2,2',3,4,5,5'	3735	2.42
47	2,2',4,4'	3030	2.20	186	2,2',3,4,5,6,6'	3750	2.56
44	2,2',3,5'	3030	2.64	130	2,2',3,3',4,5'	3760	2.68
62	2,3,4,6	3045	2.06	127	3,3',4,5,5'	3770	2.34
75	2,4,4',6	3045	2.06	137	2,2',3,4,4',5	3775	2.52
38	3,4,5	3045	2.48	164	2,3,3',4',5',6	3785	2.66
59	2,3,3',6	3045	2.50	163	2,3,3',4',5,6	3805	2.62
96	2,2',3,6,6'	3050	2.86	138	2,2',3,4,4',5'	3805	2.76
42	2,2',3,4'	3060	2.60	129	2,2',3,3',4,5	3810	2.98
35	3,3',4	3075	2.78	160	2,3,3',4,5,6	3820	2.54
71	2,3',4',6	3085	2.56	178	2,2',3,3',5,5',6	3830	2.26
41	2,2',3,4	3085	2.74	158	2,3,3',4,4',6	3830	2.64
40	2,2',3,3'	3090	3.10	175	2,2',3,3',4,5',6	3880	2.30
64	2,3,4',6	3100	2.50	126	3,3',4,4',5	3890	3.38
37	3,4,4'	3100	3.10	187	2,2',3,4',5,5',6	3900	2.34
72	2,3',5,5'	3140	1.96	186	2,3,4,4',5,6	3900	2.76
103	2,2',4,5',6	3150	1.98	128	2,2',3,3',4,4'	3900	3.74
68	2,3',4,5'	3155	2.04	182	2,2',3,4,4',5,6'	3915	2.28
94	2,2',3,5,6'	3165	2.24	183	2,2',3,4,4',5',6	3945	2.38
57	2,3,3',5	3180	2.08	185	2,2',3,4,5,5',6	3960	2.68
95	2,2',3,5',6	3190	2.46	159	2,3,3',4,5,5'	3965	2.44
58	2,3,3',5'	3195	2.26	174	2,2',3,3',4,5,6'	3970	2.94
100	2,2',4,4',6	3200	1.92	162	2,3,3',4',5,5'	3990	2.58
67	2,3',4,5	3205	2.12	177	2,2',3,3',4',5,6	4005	3.12
93	2,2',3,5,6	3205	2.28	202	2,2',3,3',5,5',6,6'	4010	2.46
102	2,2',4,5,6'	3210	2.22	167	2,3',4,4',5,5'	4030	2.72
98	2,2',3',4,6	3215	2.22	181	2,2',3,4,4',5,6	4040	2.76
63	2,3,4',5	3220	2.20	171	2,2',3,3',4,4',6	4060	3.16
61	2,3,4,5	3235	2.18	173	2,2',3,3',4,5,6	4060	3.32
88	2,2',3,4,6	3235	2.24	201	2,2',3,3',4,5',6,6'	4090	2.52
74	2,4,4',5	3240	2.24	156	2,3,3',4,4',5	4135	3.42
76	2',3,4,5	3240	2.36	157	2,3,3',4,4',5'	4145	3.74
70	2,3',4',5	3240	2.40	204	2,2',3,4,4',5,6,6'	4155	2.38
91	2,2',3,4',6	3240	2.40	197	2,2',3,3',4,4',6,6'	4175	2.56
66	2,3',4,4'	3255	2.44	200	2,2',3,3',4,5,6,6'	4195	3.14
84	2,2',3,3',6	3255	2.86	172	2,2',3,3',4,5,5'	4205	2.82
55	2,3,3',4	3265	2.62	192	2,3,3',4,5,5',6	4235	2.66
89	2,2',3,4,6'	3280	2.72	193	2,3,3',4',5,5',6	4265	2.94
121	2,3',4,5',6	3290	1.76	180	2,2',3,4,4',5,5'	4270	2.94
56	2,3,3',4'	3295	2.78	191	2,3,3',4,4',5',6	4310	3.00
60	2,3,4,4'	3305	2.74	170	2,2',3,3',4,4',5	4415	4.06

Table 1 (*Continued*)

92	2,2',3,5,5'	3315	2.04	190	2,3,3',4,4',5,6	4480	3.72
80	3,3',5,5'	3320	1.80	198	2,2',3,3',4,5,5',6	4485	3.02
155	2,2',4,4',6,6'	3335	1.70	169	3,3',4,4',5,5'	4485	3.90
113	2,3,3',5',6	3345	2.06	199	2,2',3,3',4,5,5',6'	4495	3.14
101	2,2',4,5,5'	3345	2.06	196	2,2',3,3',4,4',5',6	4575	3.22
90	2,2',3,4',5	3345	2.06	203	2,2',3,4,4',5,5',6	4600	3.15
152	2,2',3,5,6,6'	3350	2.30	208	2,2',3,3',4,5,5',6,6'	4755	3.14
150	2,2',3,4',6,6'	3355	2.10	195	2,2',3,3',4,4',5,6	4795	4.38
99	2,2',4,4',5	3375	2.04	189	2,3,3',4,4',5,5'	4825	4.02
83	2,2',3,3',5	3375	2.32	207	2,2',3,3',4,4',5,6,6'	4895	3.22
136	2,2',3,3',6,6'	3380	2.68	194	2,2',3,3',4,4',5,5'	5175	4.32
112	2,3,3',5,6	3385	2.10	205	2,3,3',4,4',5,5',6	5265	4.32
145	2,2',3,4,6,6'	3395	2.24	206	2,2',3,3',4,4',5,5',6	5625	4.44
119	2,3',4,4',6	3405	2.04	209	2,2',3,3',4,4',5,5',6,6'	6010	4.14
108	2,3,3',4,6	3405	2.10				

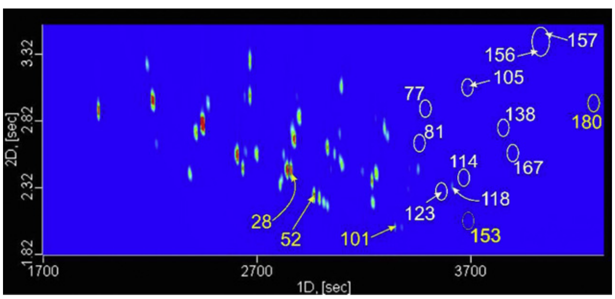

Fig. 3. Contour plot of the GC × GC–TOFMS analysis of PCBs present in Aroclor 1242.

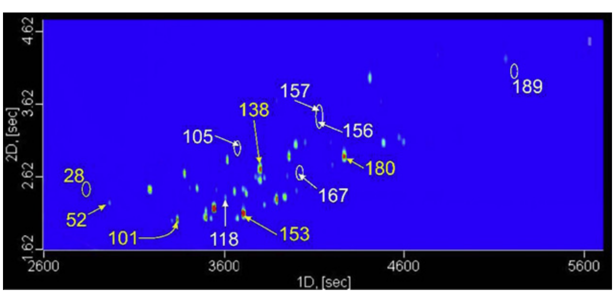

Fig. 4. Contour plot of the GC × GC–TOFMS analysis of PCBs present in Aroclor 1260.

if the resolution factor $Rs_{,2D} \geq 0.4$ (for $\Delta t_{R,2D} \geq 0.08$ s and the mean peak width at the base on ^{2}D column $w_{b,2D} = 0.2$ s). Table 1 indicates that 196 of the PCB congeners are resolved by GC × GC using a combination of chromatographic separation and mass spectral deconvolution.

Thirteen congeners overlap in five doublets (CB12 + CB13, CB62 + CB75, CB70 + CB76, CB97 + CB125 and CB153 + CB168) and one triplet (CB90 + CB101 + CB113). Fig. 2 shows the separation of all toxic "dioxin like" congeners (CB77, CB81, CB105, CB114, CB118, CB123, CB126, CB156, CB157, CB167, CB169 and CB189) with no interferences from any other PCB congener. From seven regulations relevant PCBs (CB28, CB52, CB101, CB118, CB138, CB153 and CB180) five are separated under these conditions. Two congeners CB101 and CB153 overlap on this column series with CB90 + CB-113 and CB-168 congeners, respectively. These interferences, however, are irrelevant in *real world* samples since congeners PCB-90, PCB-113 and PCB-168 are not present in any Aroclor formulations [2]. Figs. 3 and 4 show ^{2}D contour plots of the GC × GC–TOFMS separation of PCBs present in the Aroclor 1242 and Aroclor 1260 technical formulations. All PCB congeners in Aroclor 1242, except of CB12 + CB13 (109 PCBS) and in Aroclor 1260 (82 PCBs) were separated on this column set. Positions of toxic and relevant congeners on the ^{2}D retention plane are labeled in both Figs. 3 and 4.

4. Conclusion

The separation of 209 individual PCB congeners using GC × GC–TOFMS on a SPB-Octyl/SLB-IL59 column series has been studied. 203 peaks were detected on the ^{2}D retention plane. One hundred and ninety-six of the PCBs were resolved by separation and/or mass spectral deconvolution using the ChromaTOF software. All PCBs present in Aroclor 1242 and Aroclor 1260 formulations were resolved.

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