IMPROVED PCB CONGENERS SPECIFIC ANALYSIS BY HRGC-HRMS

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Abstract
A study was proposed to simultaneously monitor all 209 PCB congeners in various matrices. A state of the art DFS HRGC-HRMS coupled with a newly developed SGE column were employed in achieving lower detection limits and better chromatographic separation. The results indicated detection limits for tissue samples were 1~10 ng/kg (ppt), 10 pg/L for water samples. A total of one hundred & eighty nine peaks were resolved, consisting of 172 individual congeners and 17 coelutions.

Introduction
Environmental samples, especially tissue, do not give results that resemble Aroclors, therefore they are difficult to quantify based on traditional methods[1]. Hence, congener speciation has to be achieved to fulfill various analysis requests. The study was carried out using U.S. EPA Method 1668B[2] as our reference.

Materials and Methods
HRGC-HRMS congener specific method uses 27 internal standards ($^{13}C_{12}$-labelled congeners) which are: all twelve dioxin-like PCBs (dlPCBs), first and last elute congener in each level of chlorination (LOC); three $^{13}C_{12}$-labelled clean-up standards and five $^{13}C_{12}$-labelled recovery standards. A six point (0.2~2000 ng/mL) calibration was created for the quantification of dlPCBs and LOC PCBs. A single point calibration was used for all remaining PCB congeners.

A newly developed SGE GC column was adopted for better congener chromatographic separation in our study.
SGE HT8 PCB, 8% phenyl (equiv.) polycarborane-siloxane, 60m , 0.25mm i.d., 0.15um film thickness.
A Thermo DFS HRMS with dual Thermo Trace GCs with split/splitless injection was used with the following conditions: Initial temp 90 ^{o}C for 1 min, ramp 20 ^{o}C/min to 190 ^{o}C, then ramp 1.5 ^{o}C/min to 250 ^{o}C and ramp 4.0 ^{o}C/min to 300 ^{o}C for 4.2 mins.

Results and Discussion
Fig. 1 demonstrates from mono- to deca-CBs, 189 out of 209 PCB congeners or congener pairs were resolved. Table 1 lists the retention time of the congener peaks in this study. All dioxin-like PCBs were resolved from other congeners in the given level of chlorination. PCB105 has shoulder separation from PCB127, however the latter is a rarely occurring congener. PCB110 gives a fragment ion (M-Cl) that resolves from PCB081, however high concentrations of PCB110 in environmental samples may mask the low concentrations usually found for PCB081.

Fig.2 shows excellent sensitivity of 0.2 pg/µL PCB Std solution on DFS HRMS. Fig.3 (a)(b)(c) indicates better chromatographic resolution with SGE HT8 PCB column. The combination of the SGE column resolution and DFS HRMS sensitivity allows for a more dilute (200 µL) final sample volume. This leads to less environmental matrix effects, thus increasing the system stability and ultimately sample throughput. Fig.4 (a)(b) demonstrates the results from a fish tissue sample. During the course of six weeks, and over 250 injections of fish extracts, the column maintained its chromatographic resolution. Fig.5 (a)(b)(c) shows the results from serum samples.

Acknowledgements
Pacific Rim Laboratories would like to thank Wellington Laboratories with gratitude for their long-term support. And in appreciation of SGE in collaboration of column performance testing and study.

References
1. Bernhard T., Petron S., *PCB Congeners in Ecological Risk Assessment*, 2001
2. U.S. EPA, *Method 1668B* 2008.

Table 1 The retention time of the congeners peaks in this study

Congener Number	9 Pt Std	CS209
PCB-001	10.38	10.29
PCB-002	13.02	12.94
PCB-003	13.30	13.23
PCB-010	14.18	14.04
PCB-004	14.29	14.22
PCB-009	16.35	16.31
PCB-007	16.60	16.49
PCB-006	17.78	17.76
PCB-008	18.31	18.30
PCB-005	18.39	
PCB-014	19.95	19.88
PCB-011	22.45	22.47
PCB-013	23.17	23.16
PCB-012	23.19	
PCB-015	24.02	23.96
PCB-019	19.56	19.50
PCB-030	20.41	20.38
PCB-018	22.27	22.25
PCB-017	22.67	22.61
PCB-024	23.24	23.21
PCB-027	23.75	23.73
PCB-032	24.66	24.62
PCB-016	24.90	24.88
PCB-023	25.95	25.95
PCB-034	26.41	26.39
PCB-029	26.61	26.59
PCB-026	27.56	27.54
PCB-025	27.99	27.98
PCB-031	28.50	28.49
PCB-028	29.03	29.03
PCB-021	29.98	29.99
PCB-020	30.55	30.56
PCB-033	30.59	
PCB-022	31.49	31.51
PCB-036	32.70	32.73
PCB-039	33.78	33.85
PCB-038	35.41	35.43
PCB-035	37.36	37.43
PCB-037	38.64	38.72

Congener Number	9 Pt Std	CS209
PCB-054	25.37	25.37
PCB-050	27.37	27.35
PCB-053	28.95	28.98
PCB-051	29.71	29.73
PCB-045	30.56	30.56
PCB-046	32.09	32.09
PCB-069	32.90	33.01
PCB-052	33.01	
PCB-073	33.27	33.31
PCB-043	33.45	33.68
PCB-049	33.68	
PCB-065	33.95	33.94
PCB-075	34.23	
PCB-062	34.39	34.27
PCB-048	34.35	34.38
PCB-047	34.40	
PCB-044	36.33	36.35
PCB-059	36.56	36.59
PCB-042	36.98	36.99
PCB-064	37.85	37.86
PCB-072	38.27	
PCB-071	38.28	38.18
PCB-041	38.37	38.33
PCB-068	39.08	39.11
PCB-040	39.81	39.83
PCB-057	40.37	40.40
PCB-067	41.32	41.35
PCB-063	41.69	41.73
PCB-058	41.92	41.93
PCB-061	42.18	42.20
PCB-074	42.73	42.78
PCB-070	43.54	43.59
PCB-055	43.78	43.78
PCB-066	44.36	44.39
PCB-080	44.37	44.49
PCB-076	45.58	45.61
PCB-060	46.94	47.00
PCB-056	47.22	47.26
PCB-079	49.75	49.84
PCB-078	51.27	51.36
PCB-081	52.51	52.59
PCB-077	54.16	54.20

Congener Number	9 Pt Std	CS209
PCB-104	33.92	33.90
PCB-096	37.12	37.15
PCB-103	38.48	38.50
PCB-100	39.55	39.55
PCB-094	40.55	40.59
PCB-093	41.75	41.81
PCB-102	41.89	
PCB-098	41.96	
PCB-095	42.11	
PCB-088	42.55	42.59
PCB-091	43.15	43.15
PCB-121	43.69	43.73
PCB-084	45.76	45.80
PCB-092	45.98	45.99
PCB-089	46.18	46.22
PCB-090	46.84	46.88
PCB-101	47.17	47.19
PCB-113	47.65	47.68
PCB-099	48.10	48.12
PCB-112	49.10	49.12
PCB-119	49.34	
PCB-083	49.59	49.72
PCB-109	49.73	49.72
PCB-086	50.31	50.48
PCB-125	50.43	
PCB-117	50.48	
PCB-097	50.63	50.91
PCB-116	50.87	
PCB-115	51.11	51.16
PCB-087	51.19	
PCB-111	51.78	51.89
PCB-085	51.91	51.99
PCB-110	52.60	52.65
PCB-120	52.68	52.73
PCB-082	54.02	54.05
PCB-124	55.49	55.51
PCB-108	55.81	55.86
PCB-107	55.84	
PCB-123	56.14	56.15
PCB-106	56.28	56.30
PCB-118	56.59	56.61
PCB-114	57.27	57.29
PCB-122	57.87	57.91
PCB-105	59.08	59.09
PCB-127	59.26	59.28
PCB-126	61.33	61.36

Congener Number	9 Pt Std	CS209
PCB-155	43.35	43.37
PCB-150	46.70	46.70
PCB-152	47.77	47.77
PCB-145	50.01	48.99
PCB-136	50.05	50.06
PCB-148	50.58	50.58
PCB-154	51.88	51.89
PCB-151	52.99	52.99
PCB-135	53.51	53.52
PCB-144	53.73	53.87
PCB-147	53.80	53.81
PCB-149	54.56	54.59
PCB-139	54.59	
PCB-140	55.08	55.10
PCB-143	55.41	55.43
PCB-134	55.61	55.63
PCB-142	56.03	56.02
PCB-131	56.25	56.27
PCB-133	56.70	56.70
PCB-165	57.25	57.25
PCB-132	57.45	57.50
PCB-146	57.50	57.50
PCB-161	57.78	57.78
PCB-153	58.29	58.32
PCB-168	58.39	58.39
PCB-141	59.06	59.08
PCB-137	59.51	59.52
PCB-130	59.70	59.70
PCB-163	60.06	60.08
PCB-164	60.07	
PCB-138	60.19	60.21
PCB-160	60.21	60.31
PCB-158	60.37	60.39
PCB-129	60.53	60.53
PCB-166	60.79	60.79
PCB-159	61.47	61.49
PCB-128	61.59	61.61
PCB-162	61.74	61.76
PCB-167	62.09	62.09
PCB-156	62.98	62.97
PCB-157	63.17	63.17
PCB-169	64.43	64.46

Congener Number	9 Pt Std	CS209
PCB-188	55.30	55.31
PCB-184	56.25	56.27
PCB-179	57.48	57.50
PCB-176	58.31	58.31
PCB-186	58.91	58.93
PCB-178	59.98	60.00
PCB-175	60.39	60.41
PCB-182	60.54	60.56
PCB-187	60.56	
PCB-183	60.94	60.95
PCB-185	61.38	61.38
PCB-174	61.66	61.66
PCB-181	61.74	61.74
PCB-177	61.90	61.89
PCB-171	62.19	62.20
PCB-173	62.40	62.40
PCB-172	62.99	62.99
PCB-192	63.13	63.14
PCB-180	63.32	63.35
PCB-193	63.35	63.45
PCB-191	63.55	63.57
PCB-170	64.24	64.24
PCB-190	64.35	64.38
PCB-189	65.67	65.68
PCB-202	61.42	61.45
PCB-200	61.85	61.87
PCB-204	61.97	61.97
PCB-197	62.26	62.27
PCB-201	62.79	62.81
PCB-198	64.05	64.08
PCB-199	64.10	64.13
PCB-196	64.37	64.39
PCB-203	64.41	64.43
PCB-195	65.37	65.36
PCB-194	66.60	66.60
PCB-205	66.96	66.95
PCB-208	64.69	64.72
PCB-207	65.04	65.05
PCB-206	67.59	67.59
PCB-209	68.05	68.05

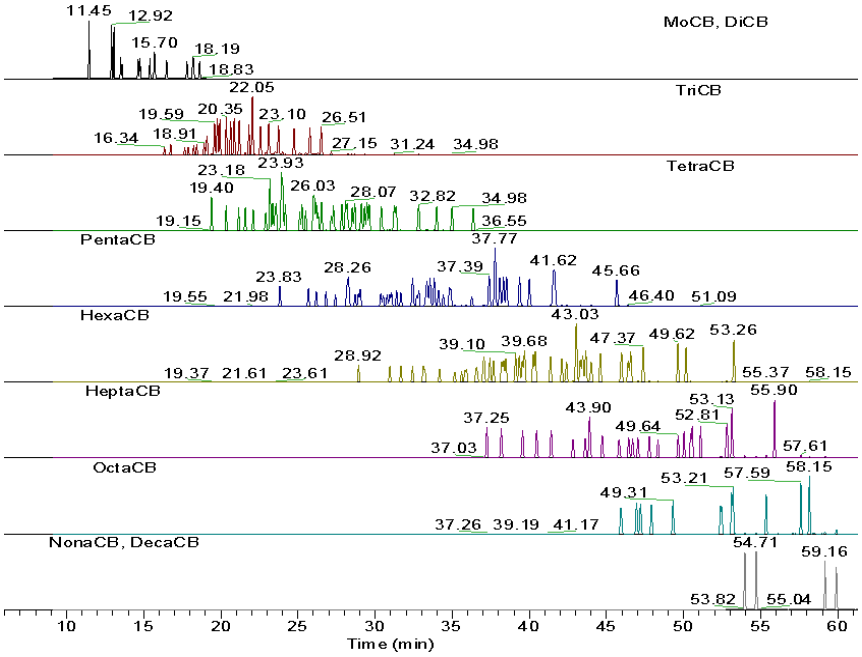

Fig. 1 Mono- to deca-CBs

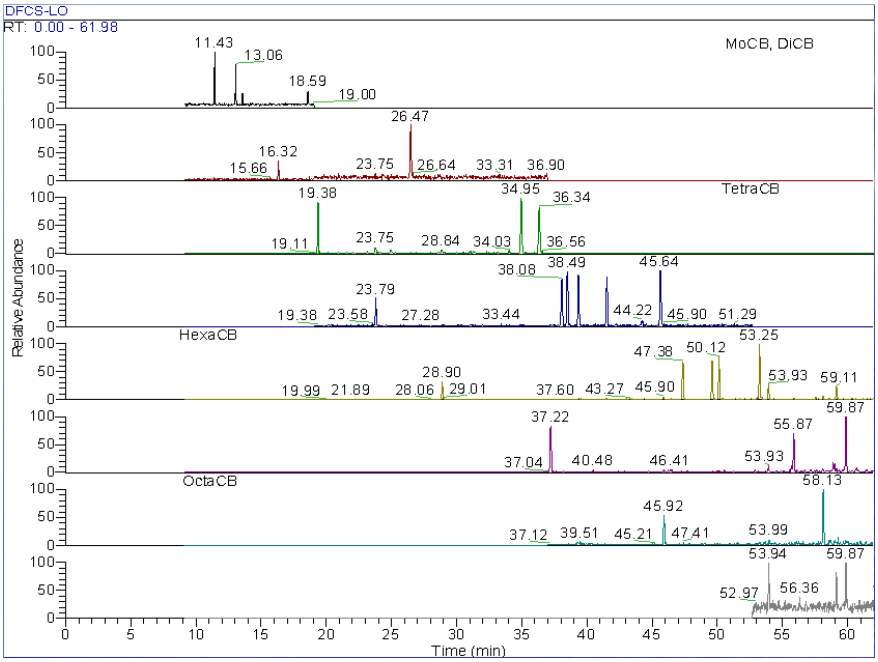

Fig. 2(a) PCB CS-Lo Std at 0.2 pg/uL

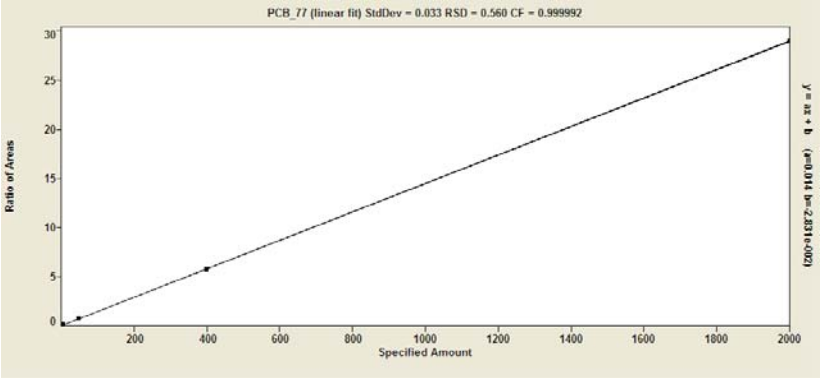

Fig. 2(b) 6 point calibration results at 0.2 ~2000 ng/mL

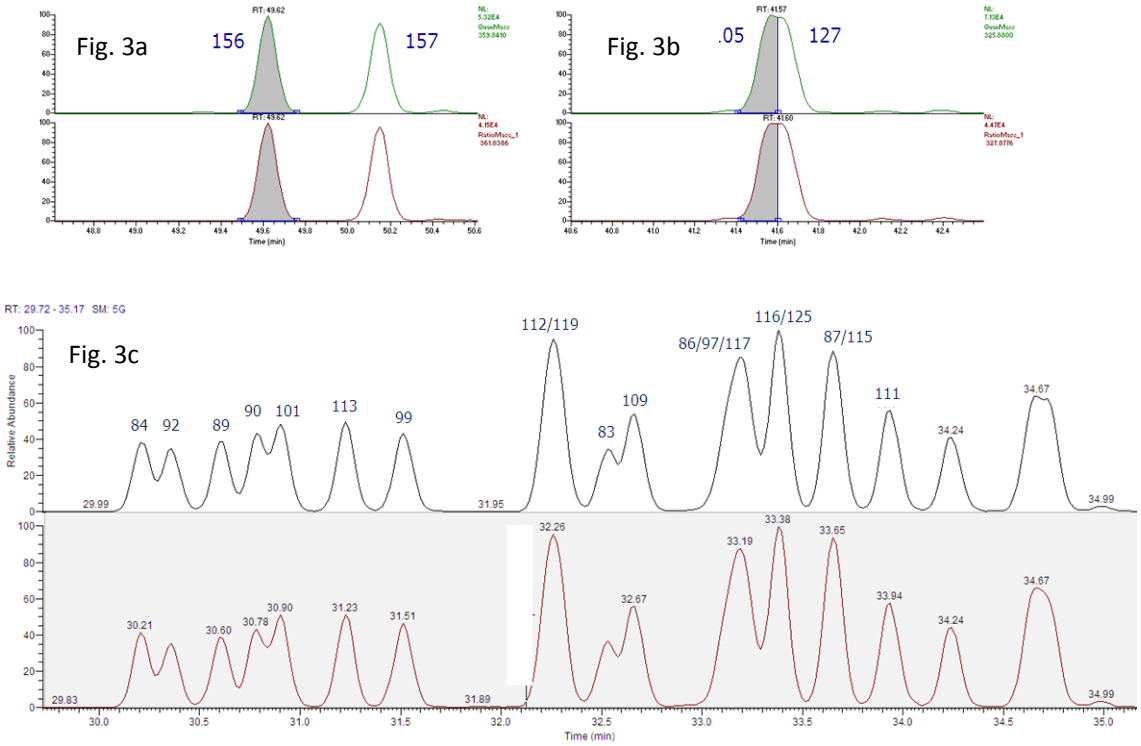

Fig.3 (a)(b)(c) Chromatographic resolution with SGE HT8 PCB column

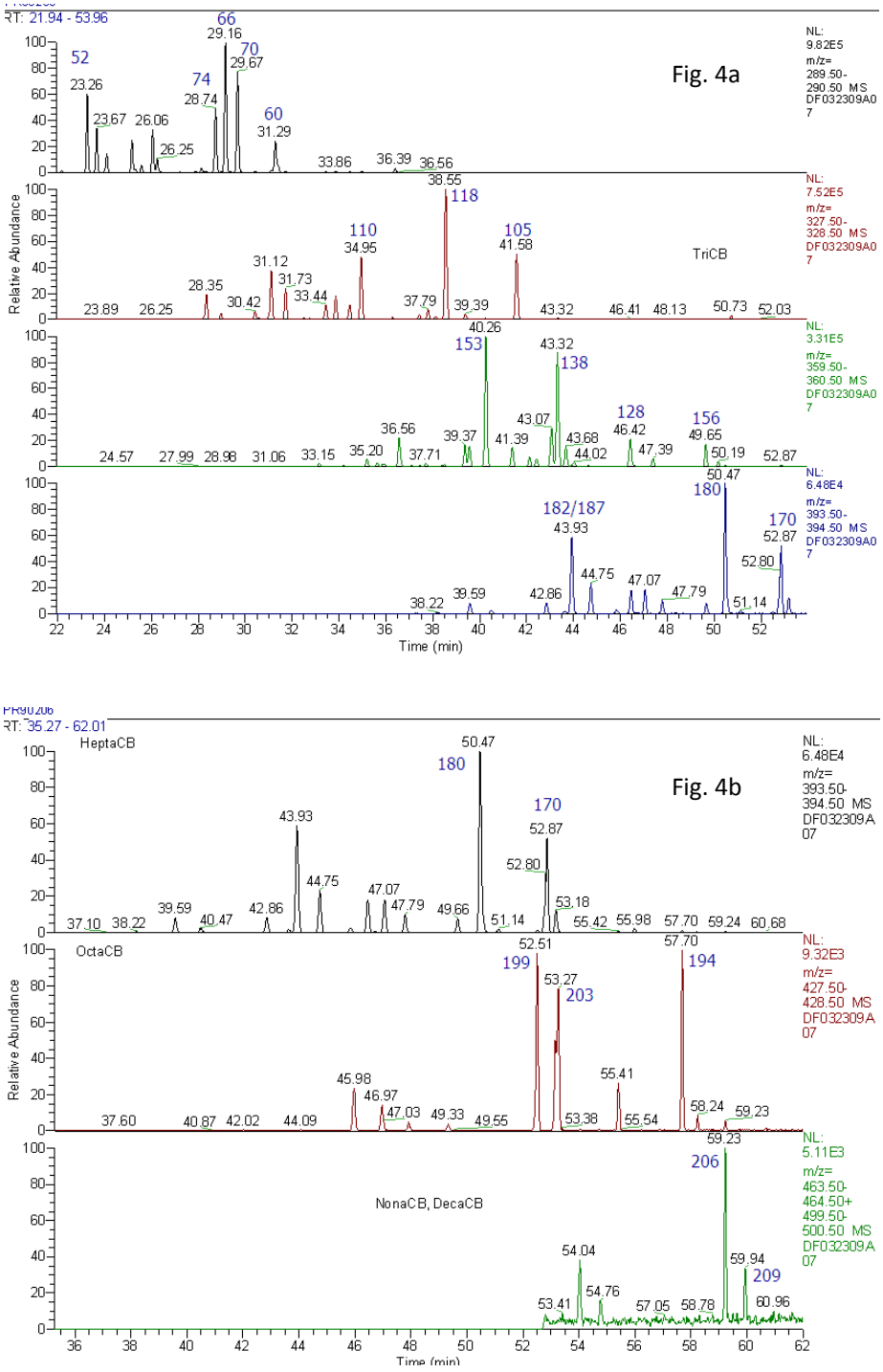

Fig.4 (a)(b) The results from fish tissue sample

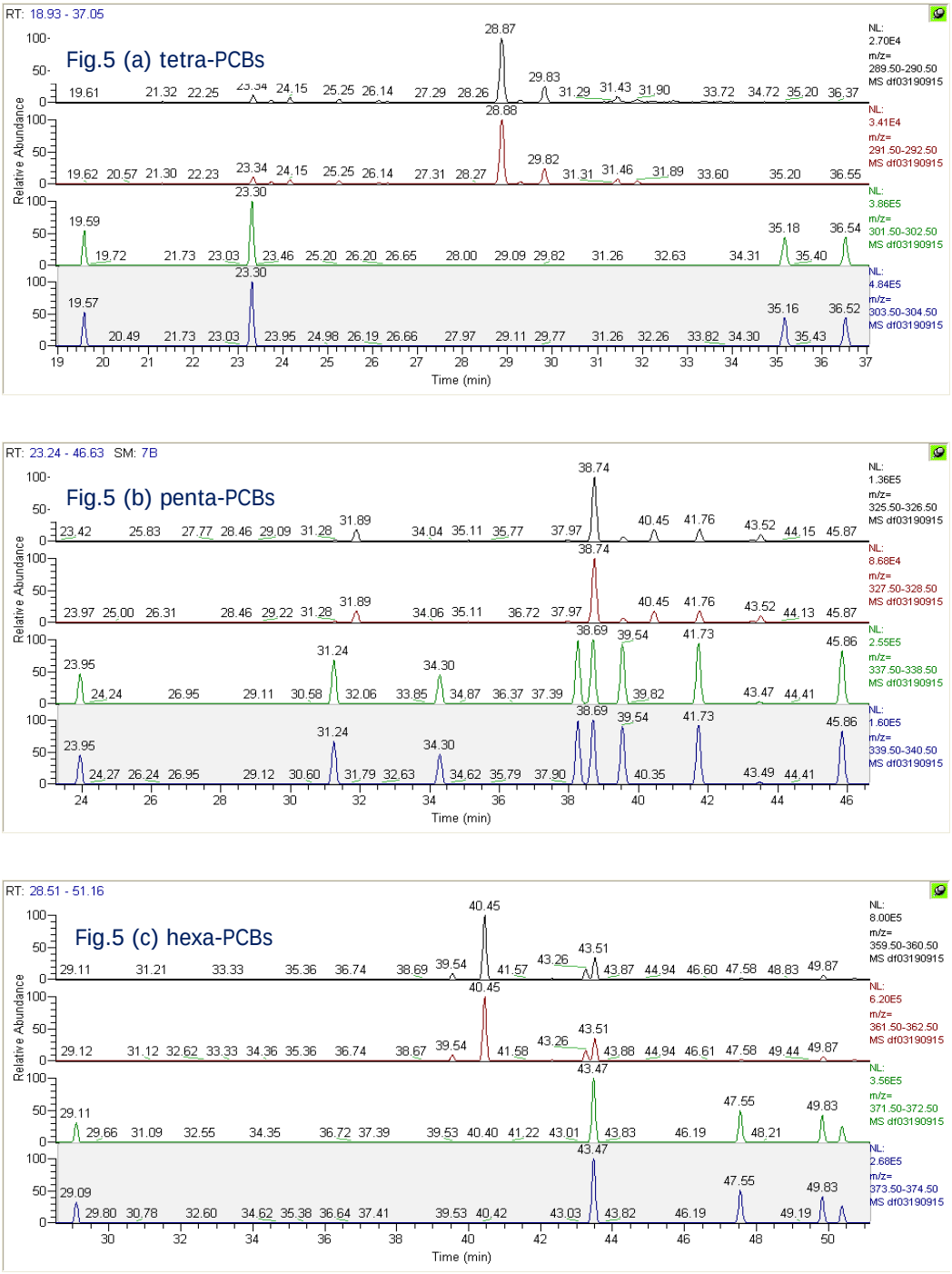

Fig.5 (a)(b)(c) The results from a serum sample