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Journal of Chromatography B, 813 (2004) 269–285
JOURNAL OF CHROMATOGRAPHY B
www.elsevier.com/locate/chromb

Evaluation of four capillary columns for the analysis of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers in human serum for epidemiologic studies

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Received 25 June 2004; accepted 24 September 2004

Abstract

The separation of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ether (PBDE) congeners was evaluated on four capillary columns: 60 m × 0.25 mm i.d., 0.25 μm film thickness RTX-5MS and DB-XLB capillary columns, and 60 m × 0.18 mm i.d., 0.25 μm film thickness DB-XLB and DB-5MS capillary columns. Based on performance, capacity, and cost, the RTX-5MS (60 m × 0.25 mm i.d., 0.25 μm thickness) and the DB-XLB (60 m × 0.25 mm i.d., 0.25 μm film thickness) were selected for the analysis of human serum extracts by using gas chromatography/electron-capture detection. In contrast to previous studies, the oven temperature program affords the separation of congeners that are not separated by using other combinations of capillary columns, most notably PBDE-47 and PCB 180. In addition, the method enables determination of OCPs, PCBs, and PBDEs prevalent in a single extract of serum, which can lead to considerable time savings in the analysis of large number of samples collected for epidemiologic studies.

Keywords: Polychlorinated biphenyls (PCBs); Organochlorine pesticides; Polybrominated diphenyl ethers (PBDEs); Persistent organic pollutants (POPs); Capillary column; GC-ECD

1. Introduction

Epidemiologic studies that explore relationships between levels of halogenated persistent organic pollutants (POPs) in human serum and health outcomes (e.g., neurobehavioral deficits, effects on immune or reproductive systems) are critical to improve an understanding of health effects of POPs, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs). The POPs typically reported in human serum are PCBs with Ballschmiter nos. 28, 49, 52, 56, 66, 70, 74, 99, 101, 105, 110, 118, 137, 138, 146, 153, 156, 157, 170, 177, 180, 183, 187, 189, 190, 194, 199, and 203 and 4,4′-DDT, 4,4′-DDD, 4,4′-DDE, 2,4′-DDT, 2,4′-DDD, 2,4′-DDE, dieldrin, α- and β-BHC, hexachlorobenzene, heptachlor, heptachlor epoxide, oxychlordane, and *trans*-nonachlor [1–8], and PBDEs with nos. 47, 99, and 153 [9–12]. The chemical names of the PCB and PBDE congeners are listed in Table 1. The PCB congeners are numbered according to Ballschmiter except nos. 107, 108, 109, 199, 200, and 201, which are derived according to Guitart. The numbers for congeners 107, 108, 109, 199, 200, and 201 differ from the numbers assigned by Ballschmiter and Zell as 108, 109, 107, 201, 199, and 200, respectively. The Guitart numbers are typically used for congeners 107, 108, 109, 199, 200, and 201 [19].

In human serum, these chemicals exist at trace levels (from pg/g to ng/g lipid, or from pg/mL to ng/mL serum) in the presence of other chemicals that are present at much higher concentrations. Measurement of complex mixtures of OCPs,

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doi:10.1016/j.jchromb.2004.09.051

Table 1
Polychlorinated biphenyl and polybrominated diphenyl ether congeners typically reported in human serum extracts

No.	Congener
Polychlorinated biphenyls (PCBs)	
28	2,4,4′-Trichlorinated biphenyl
49	2,2′,4,5′-Tetrachlorinted biphenyl
52	2,2′,5,5′-Tetrachlorinated biphenyl
56	2,3,3′,4′-Tetrachlorobiphenyl
70	2,3′,4′,5-Tetrachlorbiphenyl
74	2,4,4′,6-Tetrachlorobihenyl
99	2,2′,4,4′,5-Pentachlorobiphenyl
101	2,2′,4,5,5′-Pentachlorobiphenyl
105	2,3,3′,4,4′-Pentachlorobiphenyl
110	2,3,3′,4′,6-Pentachlorobiphenyl
118	2,3′,4,4′,5-Pentachlorobiphenyl
137	2,2′,3,4,4′,5-Hexachlorobiphenyl
138	2,2′,3,4,4′,5′-Hexanchlorobiphenyl
146	2,2′,3,4′,5′-Hexachlorobiphenyl
153	2,2′,4,4′,5,5′-Hexachlorobiphenyl
156	2,3,3′,4,4′,5-Hexachlorobiphenyl
157	2,3,3′,4,4′,5′-Hexachlorobiphenyl
170	2,2′,3,3′,4,4′,5-Heptachlorobiphenyl
177	2,2′,3,3′,4′,6-Heptachlorobiphenyl
180	2,2′,3,4,4′,5,5′-Heptachlrobiphenyl
183	2,2′,3,4,4′,5′,6-Heptachlorobiphenyl
187	2,2′,3,4′,5,5′,6-Heptachlorobiphenyl
189	2,3,3′,4,4′,5,5′-Heptachlorobiphenyl
190	2,3,3′,4,4′,5,6-Heptachlorobiphenyl
194	2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl
199	2,2′,3,3′,4,5,5′,6-Octachlorobiphenyl
203	2,2′,3,4,4′,5,6,6′-Octachlorobiphenyl
209	2,2′,3,3′,4,4′,5,5′,6,6′-Decachlorobiphenyl
Polybrominated diphenyl ethers (PBDEs)	
47	2,2′,4,4-Tetrabrominated diphenyl ether
99	2,2′,4,4′,5-Pentabrominated diphenyl ether
153	2,2′,4,4′,5,5′-Hexbrominated diphenyl ether
209	2,2′,3,3′,4,4′,5,5′,6,6′-Decabrominated diphenyl ether

PCBs, and PBDEs, thus requires that the compounds be isolated from the bulk material, and enriched and concentrated prior to detection by using high-resolution gas chromatography (HRGC) along with mass spectrometry (MS) or electron-capture detection (ECD).

HRGC/MS is often the method of choice due to selectivity and sensitivity afforded by mass spectrometric detection. HRGC/ECD is also employed due to the low cost and ease of operation and the greater sensitivity of ECD compared to electron-ionization or electron-capture negative ionization mass spectrometry (ECNI). The major disadvantage of using HRGC/ECD is that co-eluting halogenated compounds cannot be differentiated from each other. No HRGC column exists that can separate all 209 PCB congeners, and PBDEs can co-elute with PCBs when using 30 m capillary columns with 5% diphenyl/95% dimethyl polysiloxane liquid stationary phases (e.g., DB-5, CP-Sil 8 CB, and RTX-5). Specifically, PBDE 47 was reported to co-elute with PCB 180 [13–15]. This co-elution problem was addressed by either altering the oven temperature program to increase the resolution or using MS to confirm the identity of the compounds [14,15]. Co-elution problems can also be addressed by employing two analytical columns with different liquid stationary phases [16–22], or by using column chromatography to isolate the OCPs and PCBs.

Dual chromatography relies on differences in the elution order of the PCBs and OCPs between the capillary columns. In previous work, we used a 60 m RTX-5MS (5% diphenyl/95% dimethyl polysiloxane) capillary column along with a 60 m RTX-1701 (4% cyanopropylphenyl/86% dimethyl polysiloxane) capillary column to identify and quantify PCBs and OCPs in human serum [23,24]. (These columns are equivalent to the DB-5 and DB-1701 capillary columns.) OCPs and PCBs can also be separated into two fractions by using column chromatography [4,25]. The separation of OCPs and PCBs is not perfect, however, and OCPs can be present in the extract that primarily contains the PCBs, or a specific compound may exist in both fractions. In addition, this approach necessitates analysis of at least two extracts, which is more time-consuming than if the analysis could be performed in a single fraction.

Two capillary columns worthy of further evaluation for separation of OCPs and PCBs are a 60 m DB-XLB column, a column with a stationary liquid phase equivalent in polarity to a 12% (phenylmethyl)-polysiloxane in concert with a 60 m 5% diphenyl/95% dimethyl polysiloxane (RTX-5MS or DB-5MS) capillary column [19,26]. In previous work, this combination was only evaluated for the analysis of PCB congeners. (The reader is referred to Cochran and Frame [19] for an extensive review of dual column chromatography of PCBs.) The higher temperature limit of the DB-XLB capillary column compared to the DB-17 column is advantageous for the analysis of higher molecular weight PBDEs that elute at later times than OCPs and PCBs [19,27–29].

Herein, separation of OCPs, PCBs, and PBDEs typically reported in human serum was evaluated on two DB-XLB capillary columns (60 m × 0.25 mm i.d., 0.25 μm film thickness; 60 m × 0.18 mm i.d., 0.18 μm film thickness) in concert with a RTX-5MS and a DB-5MS column. Based on this information, a method was developed that utilizes a long-temperature program and 60 m capillary columns. The method substantially reduces the time required to analyze these compounds in human serum.

2. Experimental

2.1. Solvents and standards

Florisil (60–100 mesh), sodium sulfate (10–60 mesh) and glacial acetic acid (99.7%) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Solvents employed were nanograde isooctane (Mallinckrodt, Paris, KY, USA), trace environmental analysis grade hexane (99.9%), methanol (99.9%), and dichloromethane (99.9%), and pesticide residue grade acetone (99.9%) and toluene (99.9%) (Burdick & Jackson, Muskegon, MI, USA). The nine PCB congener mixtures (10 μg/mL in isooctane; referred to as "Frame mixes"), neat individual PCB congeners, and neat pesticides were obtained from AccuStandard Inc. (New Haven, CT, USA). The PBDEs, 2,2′,4,4′-tetrabromodiphenyl ether (PBDE-47), 2,2′,4,4′, 5-pentabromodiphenyl ether (PBDE-99), and 2,2′4,4′5,5′-hexabromodiphenyl ether (PBDE-153) were purchased as 50 μg/mL solutions (>99% purity) in nonane from Cambridge Isotope Laboratories Inc. (Andover, MA, USA). A mixture of chlorinated pesticide standards was purchased from Chem Service Inc. (West Chester, PA, USA). Standard reference material 1589a (PCBs, Pesticides, and Dioxins/Furans in Human Serum) was purchased from the National Institute of Standards and Testing (Gaithersburg, MD, USA).

2.2. Serum samples

Serum samples were collected from distinct populations of women in the course of conducting three epidemiologic studies. Serum was obtained from women residing in the San Francisco Bay Area in the early 1960s and the late 1990s, and from women residing in Chiapas, Mexico in 1988. Serum samples from women in the 1960s were collected as part of the Child Health and Development Study (CHDS), a prospective cohort study that enrolled about 20,500 pregnant women attending prenatal clinics at Kaiser Foundation Health Plan Medical. This population was described by James et al., 2002 [23]. Between 1997 and 1999, serum was collected from a group of 50 Laotian immigrant women to conduct a study on reproductive effects [30] and the analysis of PBDE-47 in these populations was previously reported [31]. In addition, serum was collected in 1998 from women residing in Chiapas, Mexico, where DDT was used for malaria control [32].

2.3. Preparation of serum extracts

All glassware was washed, rinsed three times with a sequence of deionized water, acetone, toluene, and hexane. All glassware, except volumetric glassware was baked in a muffle furnace (Lindberg/Blue M model BF51828C, Asheville, NC, USA) at 575 °C for 3 h. Florisil was also baked in the muffle furnace then deactivated by adding 0.5 mL water to 100 g of florisil. The chromatography column for cleanup was assembled by addition of 1 g sodium sulfate, 11.5 g deactivated florisil, and 1 g sodium sulfate to an 11 mm diameter glass column.

After thawing, 1 mL of serum was transferred to a 15 mL test tube and enriched with 25 μL of surrogate solution (∼30 pg/μL PCBs 14, 65, 166, and ∼150 pg/μL tetrachloro-*m*-xylene (TCMX) in methanol), vortexed for 30 s and equilibrated for 1 h at room temperature. Samples were then denatured with 1 mL glacial acetic acid. Three milliliters of 10% dichloromethane in hexane (v/v) were added to the sample, vortexed for 1 min, and centrifuged for 1 min. The top organic layer was transferred into a second test tube. This procedure was repeated three more times, the four extracts were combined into one test tube, and the extract was concentrated to approximately 500 μL under a gentle stream of nitrogen. The extract was then added to a glass column filled with 11 g of florisil, which was conditioned with 60 mL hexane. The analytes were eluted with 60 mL hexane, and then 60 mL of dichloromethane/hexane (1:1, v/v). The eluates were combined and evaporated to approximately 2 mL using a rotary evaporator. The extract was transferred to a 15 mL conical bottom centrifuge tube. Three milliliters of isooctane were added to the sample and the sample was concentrated to ∼75 μL under nitrogen and enriched with 25 μL of internal standard solution (∼60 pg/μL PCBs 30, 204, 209 and pentachloronitrobenzene (PCNB) in isooctane). Validation of the method was accomplished by analysis of serum enriched with OCPs, PCBs, and PBDEs. The recovery of these compounds in the matrix spikes ranged from 70 to 120%.

2.4. Instrumentation

HRGC analyzes were performed using a Hewlett-Packard 6890 series gas chromatograph (Agilent Technologies, Palo Alto, CA, USA). The GC was equipped with two split–splitless injectors and two electron-capture detectors (ECD). Ultra high purity helium (99.999%) was used as the carrier gas with ultra high purity (99.999%) nitrogen as the make-up gas. Four different HRGC capillary columns were evaluated: An RTX-5MS (60 m × 0.25 mm i.d., 0.25 μm film thickness) from Restek Corporation (Bellefonte, PA, USA), a DB-XLB (60 m × 0.25 mm i.d., 0.25 μm film thickness), and two custom columns consisting of a DB-5MS (60 m × 0.18 mm i.d., 0.18 μm thickness) and a DB-XLB (60 m × 0.18 mm i.d., 0.18 μm film thickness) from Agilent Technologies (Palo Alto, CA, USA).

Two microliters of extract were injected onto the GC in the splitless mode with an injector temperature of 280 °C and a purge time of 1.6 min. The detector temperature was 310 °C, and the nitrogen makeup flow was 50 mL/min. Two different temperature programs were employed for GC separation of the analytes. For the two 0.25 mm i.d. columns, the initial temperature of the GC oven was 130 °C. This temperature was held for 1 min and then the temperature was increased at 1 °C/min to 261 °C, and then at a rate of 3 °C/min to 300 °C, where the temperature was held for 5 min. For the two 0.18 mm i.d. columns, the temperature was held at 130 °C for 1 min, increased at a rate of 1 °C/min to 261 °C and then further increased at a rate of 3 °C/min to 315 °C. The temperature was held at 315 °C for 10 min. The flow-rate for the 0.25 mm i.d. columns was 1.4 mL/min, and 1.2 mL/min for the 0.18 mm i.d. columns. The oven temperature program was slightly modified for the analysis of the serum extracts to optimize the analysis of the OCPs typically reported in human serum. The initial temperature of the oven was 100 °C. This temperature was held at 1.6 min and increased to 135 °C at a rate of 15 °C/min, increased to 261 °C at a rate of 1 °C/min, increased to 295 °C and a rate of 3 °C, and finally increased to 300 °C at a rate of 1 °C/min. The oven temperature was

Table 2
Retention time (RT) and relative retention time (RRT) of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers on 0.18 and 0.25 mm i.d. DB-XLB columns

0.18 mm i.d. Column				0.25 mm i.d. Column			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 1	29.369	0.5575	0.2062	PCB 1	27.797	0.5489	0.1980
PCB 2	36.280	0.6887	0.2548	PCB 2	34.524	0.6818	0.2460
PCB 3	37.606	0.7139	0.2641	PCB 3	35.816	0.7073	0.2552
PCB 4	39.381	0.7476	0.2765	PCB 4	37.546	0.7414	0.2675
PCB 10	39.442	0.7494	0.2770	PCB 10	37.656	0.7440	0.2684
TCMX[a]	41.133	0.7906	0.2886	TCMX[a]	38.932	0.7696	0.2774
PCB 9	44.685	0.8483	0.3138	PCB 9	42.760	0.8444	0.3047
PCB 7	44.848	0.8521	0.3150	PCB 7	42.956	0.8487	0.3062
PCB 6	46.302	0.8789	0.3251	PCB 6	44.349	0.8758	0.3160
PCB 5	47.426	0.9011	0.3331	PCB 5	45.483	0.8986	0.3242
PCB 8	47.965	0.9105	0.3368	PCB 8	45.983	0.9080	0.3276
α-BHC	48.758	0.9240	0.3424	α-BHC	46.583	0.9213	0.3320
HCB[b]	49.890	0.9447	0.3504	HCB[b]	47.689	0.9427	0.3398
PCB 19	50.457	0.9578	0.3543	PCB 19	48.434	0.9564	0.3451
PCB 14	51.104	0.9694	0.3586	PCB 14	49.035	0.9687	0.3495
PCB 30	52.724	1.0000	0.3703	PCB 30	50.615	1.0000	0.3608
γ- BHC	55.012	1.0425	0.3863	γ- BHC	52.767	1.0436	0.3761
PCB 11	55.180	1.0431	0.3876	PCB 11	52.878	1.0448	0.3768
PCB 18	55.053	1.0451	0.3866	PCB 18	52.980	1.0462	0.3775
PCNB[c]	55.554	1.0507	0.3898	PCNB[c]	53.335	1.0527	0.3798
PCB 17	55.555	1.0556	0.3902	PCB 17	53.494	1.0569	0.3813
PCB 12	56.086	1.0624	0.3936	PCB 12	53.870	1.0643	0.3840
PCB 13	56.830	1.0781	0.3988	PCB 13	54.683	1.0802	0.3897
PCB 27	56.819	1.0782	0.3990	PCB 27	54.695	1.0802	0.3898
PCB 24	57.292	1.0886	0.4024	PCB 24	55.200	1.0906	0.3934
PCB 16	58.314	1.1070	0.4095	PCB 16	56.195	1.1097	0.4004
PCB 15	58.724	1.1144	0.4124	PCB 15	56.579	1.1175	0.4032
PCB 32	58.972	1.1205	0.4142	PCB 32	56.865	1.1235	0.4053
PCB 54	60.567	1.1490	0.4250	PCB 54	58.355	1.1528	0.4159
PCB 34	60.698	1.1519	0.4262	PCB 34	58.542	1.1562	0.4172
PCB 23	61.092	1.1582	0.4294	PCB 23	58.838	1.1632	0.4194
PCB 29	61.712	1.1711	0.4333	PCB 29	59.539	1.1759	0.4243
β-BHC	62.213	1.1790	0.4369	β-BHC	59.959	1.1858	0.4273
PCB 26	63.188	1.2006	0.4438	PCB 26	61.048	1.2061	0.4351
PCB 50	63.489	1.2002	0.4459	PCB 50	61.122	1.2077	0.4355
PCB 25	63.739	1.2100	0.4476	PCB 25	61.585	1.2161	0.4388
PCB 31	65.266	1.2401	0.4584	PCB 31	63.100	1.2466	0.4497
PCB 53	65.437	1.2413	0.4592	PCB 53	63.199	1.2485	0.4504
PCB 28	65.773	1.2486	0.4619	PCB 28	63.602	1.2560	0.4532
Heptachlor	66.002	1.2508	0.4635	Heptachlor	63.665	1.2591	0.4537
PCB 21	66.249	1.2524	0.4653	PCB 21	63.864	1.2619	0.4551
PCB 33	66.252	1.2550	0.4650	PCB 33	63.940	1.2633	0.4558
PCB 20	66.277	1.2577	0.4654	PCB 20	64.051	1.2650	0.4565
δ-BHC	66.347	1.2574	0.4659	δ-BHC	64.045	1.2666	0.4565
PCB 51	66.553	1.2625	0.4670	PCB 51	64.304	1.2703	0.4583
PCB 45	67.872	1.2896	0.4767	PCB 45	65.653	1.2971	0.4679
PCB 22	68.299	1.2965	0.4796	PCB 22	66.094	1.3052	0.4709
PCB 46	68.979	1.3106	0.4845	PCB 46	66.747	1.3187	0.4757
PCB 73	69.934	1.3266	0.4908	PCB 73	67.673	1.3369	0.4823
PCB 36	70.416	1.3356	0.4946	PCB 36	68.159	1.3469	0.4858
PCB 69	70.532	1.3385	0.4953	PCB 69	68.276	1.3485	0.4866
PCB 43	70.867	1.3388	0.4978	PCB 43	68.430	1.3522	0.4877
PCB 52	71.066	1.3490	0.4990	PCB 52	68.861	1.3598	0.4906
PCB 48	71.539	1.3593	0.5025	PCB 48	69.300	1.3691	0.4939
Aldrin	71.685	1.3585	0.5034	Aldrin	69.292	1.3704	0.4938
PCB 49	71.990	1.3637	0.5053	PCB 49	69.643	1.3759	0.4964
PCB 104	72.619	1.3756	0.5097	PCB 104	70.248	1.3879	0.5007
PCB 39	72.602	1.3764	0.5103	PCB 39	70.270	1.3892	0.5009
PCB 47	72.676	1.3792	0.5103	PCB 47	70.394	1.3903	0.5017
PCB 65	72.876	1.3777	0.5119	PCB 65	70.457	1.3922	0.5020

Table 2 (*Continued*)

0.18 mm i.d. Column				0.25 mm i.d. Column			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 62	72.895	1.3820	0.5124	PCB 62	70.544	1.3946	0.5028
PCB 38	73.057	1.3811	0.5131	PCB 38	70.644	1.3959	0.5034
PCB 75	73.021	1.3852	0.5124	PCB 75	70.729	1.3972	0.5041
Dathal	73.723	1.3948	0.5174	Dathal	71.361	1.4108	0.5085
PCB 44	74.437	1.4130	0.5227	PCB 44	72.189	1.4255	0.5143
PCB 59	75.176	1.4240	0.5276	PCB 59	72.794	1.4382	0.5189
PCB 42	75.252	1.4280	0.5284	PCB 42	72.940	1.4406	0.5198
PCB 35	75.801	1.4379	0.5319	PCB 35	73.482	1.4516	0.5237
PCB 71	76.122	1.4450	0.5345	PCB 71	73.861	1.4586	0.5262
PCB 41	76.415	1.4519	0.5367	PCB 41	74.114	1.4642	0.5282
PCB 96	76.858	1.4577	0.5398	PCB 96	74.509	1.4724	0.5310
PCB 72	77.499	1.4699	0.5443	PCB 72	75.194	1.4860	0.5359
PCB 64	77.718	1.4722	0.5455	PCB 64	75.316	1.4880	0.5369
PCB 40	77.916	1.4786	0.5471	PCB 40	75.565	1.4924	0.5386
PCB 37	77.915	1.4804	0.5473	PCB 37	75.616	1.4939	0.5389
PCB 103	78.072	1.4834	0.5484	PCB 103	75.784	1.4972	0.5401
PCB 68	78.289	1.4842	0.5503	DCBP	75.957	1.5004	0.5410
DCBP	78.235	1.4856	0.5493	PCB 68	75.924	1.5010	0.5412
PCB 100	79.397	1.5062	0.5572	PCB 100	77.059	1.5223	0.5492
PCB 57	79.743	1.5075	0.5601	PCB 57	77.311	1.5276	0.5509
PCB 94	79.727	1.5115	0.5604	PCB 94	77.332	1.5288	0.5512
Oxychlordane	80.430	1.5459	0.5643	Oxychlordane	77.834	1.5386	0.5546
PCB 67	80.493	1.5280	0.5652	PCB 67	78.216	1.5445	0.5573
Heptachlor epoxide	80.701	1.5294	0.5667	PCB 58	78.211	1.5455	0.5574
PCB 58	80.682	1.5242	0.5668	Heptachlor epoxide	78.269	1.5480	0.5578
PCB 102	81.159	1.5343	0.5700	PCB 102	78.706	1.5551	0.5608
PCB 61	81.402	1.5388	0.5717	PCB 61	78.939	1.5598	0.5625
PCB 98	81.702	1.5496	0.5739	PCB 98	79.335	1.5678	0.5654
PCB 93	81.974	1.5556	0.5756	PCB 93	79.596	1.5720	0.5673
PCB 63	82.056	1.5543	0.5759	PCB 76	79.585	1.5727	0.5672
PCB 76	82.075	1.5505	0.5766	PCB 63	79.635	1.5733	0.5676
PCB 95	82.488	1.5673	0.5794	PCB 95	80.145	1.5834	0.5712
PCB 88	82.592	1.5658	0.5805	PCB 88	80.172	1.5850	0.5715
PCB 74	82.760	1.5710	0.5811	PCB 74	80.463	1.5889	0.5733
PCB 70	83.269	1.5821	0.5849	PCB 70	80.931	1.5989	0.5768
PCB 121	83.286	1.5790	0.5854	PCB 121	80.903	1.5994	0.5767
PCB 91	83.929	1.5898	0.5890	PCB 91	81.482	1.6098	0.5808
PCB 66	83.969	1.5940	0.5896	PCB 66	81.663	1.6126	0.5818
PCB 155	84.153	1.5954	0.5915	PCB 155	81.744	1.6161	0.5827
PCB 55	85.207	1.6097	0.5986	PCB 55	82.700	1.6342	0.5894
PCB 80	85.285	1.6169	0.5995	PCB 80	82.894	1.6388	0.5909
2,4-DDE	85.662	1.6220	0.6016	2,4-DDE	83.192	1.6446	0.5928
PCB 92	86.213	1.6360	0.6054	PCB 92	83.829	1.6557	0.5975
PCB 84	86.218	1.6382	0.6056	PCB 84	83.825	1.6561	0.5974
PCB 89	86.275	1.6364	0.6060	PCB 89	83.856	1.6571	0.5976
PCB 56	86.344	1.6391	0.6063	PCB 56	84.005	1.6589	0.5985
trans-Chlordane	87.203	1.6498	0.6120	*trans*-Chlordane	84.692	1.6743	0.6035
PCB 90	87.299	1.6561	0.6126	PCB 60	84.879	1.6769	0.6049
PCB 60	87.272	1.6582	0.6130	PCB 90	84.908	1.6773	0.6051
PCB 101	87.337	1.6574	0.6133	PCB 101	84.942	1.6776	0.6054
PCB 113	87.740	1.6587	0.6163	PCB 113	85.273	1.6849	0.6076
cis-Chlordane	87.855	1.6650	0.6166	*cis*-Chlordane	85.371	1.6877	0.6083
Endosulfan I	87.855	1.6650	0.6170	Endosulfan I	85.369	1.6884	0.6084
PCB 99	88.254	1.6753	0.6197	PCB 99	85.920	1.6967	0.6122
PCB 150	88.355	1.6751	0.6210	PCB 150	85.907	1.6984	0.6123
trans-Nonachlor	89.219	1.6894	0.6266	*trans*-Nonachlor	86.696	1.7138	0.6178
PCB 152	89.237	1.6925	0.6268	PCB 152	86.794	1.7152	0.6186
PCB 119	89.645	1.7012	0.6295	PCB 119	87.224	1.7227	0.6216
PCB 83	89.640	1.7032	0.6296	PCB 83	87.235	1.7235	0.6217
PCB 112	90.017	1.7006	0.6323	PCB 112	87.492	1.7289	0.6236
PCB 86	90.184	1.7049	0.6334	PCB 86	87.684	1.7325	0.6248
PCB 125	90.148	1.7091	0.6336	PCB 125	87.699	1.7338	0.6251
PCB 108	90.429	1.7084	0.6352	PCB 108	87.904	1.7371	0.6265

Table 2 (*Continued*)

0.18 mm i.d. Column				0.25 mm i.d. Column			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 145	90.552	1.7118	0.6360	PCB 145	88.037	1.7395	0.6273
PCB 97	90.684	1.7178	0.6365	PCB 97	88.192	1.7424	0.6286
PCB 79	90.874	1.7236	0.6383	PCB 79	88.452	1.7480	0.6304
PCB 116	91.601	1.7366	0.6439	PCB 116	89.114	1.7618	0.6352
PCB 148	91.804	1.7405	0.6453	PCB 148	89.353	1.7665	0.6369
PCB 78	92.087	1.7466	0.6468	PCB 78	89.646	1.7716	0.6389
PCB 87	92.273	1.7516	0.6479	PCB 87	89.888	1.7750	0.6404
PCB 136	92.577	1.7568	0.6501	PCB 136	90.095	1.7794	0.6421
PCB 117	92.776	1.7600	0.6511	Dieldrin	90.244	1.7848	0.6432
Dieldrin	92.781	1.7583	0.6515	PCB 117	90.320	1.7842	0.6437
4,4′-DDE	92.890	1.7604	0.6523	4,4′-DDE	90.466	1.7892	0.6448
PCB 115	92.936	1.7658	0.6528	PCB 115	90.496	1.7879	0.6450
PCB 85	93.196	1.7653	0.6541	PCB 85	90.676	1.7915	0.6463
PCB 154	93.282	1.7696	0.6546	PCB 111	90.718	1.7935	0.6466
PCB 111	93.158	1.7661	0.6548	PCB 154	90.838	1.7945	0.6474
PCB 110	94.083	1.7860	0.6606	PCB 110	91.686	1.8105	0.6532
PCB 120	94.357	1.7826	0.6628	PCB 120	91.833	1.8147	0.6545
PCB 81	94.452	1.7917	0.6628	2,4-DDD	91.879	1.8163	0.6547
2,4-DDD	94.406	1.7876	0.6630	PCB 81	91.993	1.8173	0.6556
PCB 82	95.672	1.8161	0.6718	PCB 82	93.238	1.8412	0.6643
PCB 151	95.744	1.8169	0.6723	PCB 151	93.257	1.8419	0.6646
PCB 135	96.094	1.8258	0.6750	PCB 135	93.628	1.8498	0.6673
PCB 77	96.491	1.8278	0.6772	PCB 77	93.953	1.8562	0.6697
Endrin	96.604	1.8308	0.6784	Endrin	94.035	1.8598	0.6702
PCB 144	96.665	1.8344	0.6788	PCB 144	94.164	1.8598	0.6711
PCB 147	97.345	1.8479	0.6835	PCB 147	94.918	1.8744	0.6763
PCB 149	97.536	1.8532	0.6851	PCB 149	95.055	1.8780	0.6775
PCB 139	98.103	1.8546	0.6890	PCB 139	95.574	1.8884	0.6810
PCB 143	98.096	1.8597	0.6895	PCB 143	95.576	1.8895	0.6813
PCB 124	98.304	1.8648	0.6899	PCB 124	95.816	1.8928	0.6829
PCB 140	98.472	1.8669	0.6922	PCB 140	95.961	1.8971	0.6840
PCB 107	98.884	1.8755	0.6945	PCB 107	96.394	1.9049	0.6870
PCB 123	99.180	1.8787	0.6961	PCB 123	96.622	1.9090	0.6887
PCB 109	99.181	1.8845	0.6966	PCB 109	96.693	1.9103	0.6891
PCB 106	99.431	1.8859	0.6984	PCB 106	96.929	1.9155	0.6908
Ethion	99.606	1.8844	0.6991	PCB 134	97.030	1.9164	0.6915
PCB 134	99.579	1.8897	0.6992	Ethion	97.103	1.9197	0.6919
2,4-DDT	99.735	1.8885	0.7004	2,4-DDT	97.153	1.9206	0.6923
PCB 142	99.934	1.8946	0.7024	PCB 142	97.382	1.9252	0.6941
PCB 188	99.934	1.8946	0.7024	PCB 188	97.382	1.9252	0.6941
PCB 118	100.193	1.9013	0.7035	PCB 118	97.668	1.9290	0.6961
PCB 131	100.264	1.9050	0.7042	PCB 131	97.735	1.9309	0.6966
PCB 133	100.619	1.9021	0.7067	PCB 133	98.104	1.9384	0.6990
cis-Nonachlor	100.962	1.9101	0.7086	*cis*-Nonachlor	98.358	1.9445	0.7009
PCB 122	101.340	1.9224	0.7112	PCB 122	98.808	1.9519	0.7042
PCB 184	101.329	1.9219	0.7117	PCB 184	98.813	1.9527	0.7042
PCB 165	101.578	1.9269	0.7128	PCB 165	99.064	1.9570	0.7060
PCB 146	101.799	1.9324	0.7148	PCB 114	99.304	1.9619	0.7078
PCB 114	101.899	1.9302	0.7152	PCB 146	99.359	1.9621	0.7079
PCB 161	102.338	1.9346	0.7188	PCB 161	99.810	1.9721	0.7112
Endosulfan II	102.378	1.9402	0.7189	4,4′-DDD	99.789	1.9736	0.7112
4,4′-DDD	102.618	1.9447	0.7206	Endosulfan II	100.110	1.9799	0.7135
PCB 132	102.886	1.9549	0.7227	PCB 132	100.330	1.9822	0.7151
PCB 153	103.036	1.9559	0.7235	PCB 168	100.420	1.9853	0.7158
PCB 168	102.937	1.9515	0.7235	PCB 153	100.581	1.9862	0.7166
PCB 179	104.135	1.9768	0.7312	PCB 179	101.629	2.0069	0.7241
Endrin Aldehyde	104.549	1.9813	0.7342	Endrin Aldehyde	101.937	2.0160	0.7265
PCB 105	104.784	1.9885	0.7358	PCB 105	102.182	2.0181	0.7283
PCB 141	105.006	1.9951	0.7375	PCB 141	102.459	2.0242	0.7302
PCB 176	105.491	1.9982	0.7404	PCB 176	102.845	2.0319	0.7331
PCB 137	106.140	2.0105	0.7449	PCB 137	103.510	2.0450	0.7378
PCB 127	106.278	2.0091	0.7465	PCB 186	103.685	2.0489	0.7390
PCB 186	106.336	2.0089	0.7470	PCB 127	103.735	2.0497	0.7392

Table 2 (*Continued*)

0.18 mm i.d. Column				0.25 mm i.d. Column			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 130	106.898	2.0278	0.7502	PCB 130	104.307	2.0605	0.7434
PCB 164	107.174	2.0363	0.7528	PCB 164	104.593	2.0664	0.7454
PCB 138	107.932	2.0489	0.7579	PCB 138	105.402	2.0814	0.7510
4,4′-DDT	107.973	2.0462	0.7582	4,4′-DDT	105.395	2.0844	0.7512
PCB 163	108.246	2.0534	0.7596	PCB 160	105.561	2.0869	0.7524
PCB 160	108.141	2.0502	0.7601	PCB 163	105.638	2.0868	0.7529
PCB 129	108.433	2.0540	0.7610	PCB 129	105.760	2.0895	0.7539
PCB 178	108.477	2.0611	0.7619	PCB 178	105.890	2.0920	0.7547
PCB 158	108.770	2.0641	0.7638	PCB 158	106.135	2.0962	0.7564
PCB 175	109.568	2.0785	0.7689	PCB 175	106.945	2.1127	0.7622
PCB 182	109.557	2.0779	0.7695	PCB 182	106.975	2.1140	0.7624
Endosulfan sulfate	110.026	2.0851	0.7726	Endosulfan sulfate	107.370	2.1235	0.7652
PCB 187	110.037	2.0888	0.7727	PCB 187	107.495	2.1227	0.7659
PCB 166	110.930	2.1040	0.7792	PCB 166	108.321	2.1406	0.7720
PCB 183	111.051	2.1100	0.7800	PCB 183	108.428	2.1422	0.7728
PCB 126	111.979	2.1169	0.7865	PCB 126	109.381	2.1613	0.7794
PCB 159	112.360	2.1227	0.7893	PCB 159	109.715	2.1681	0.7820
PCB 128	112.927	2.1430	0.7930	PCB 128	110.210	2.1767	0.7855
PCB 185	113.116	2.1427	0.7939	PCB 185	110.390	2.1810	0.7869
PCB 162	113.172	2.1456	0.7955	PCB 162	110.586	2.1863	0.7883
PCB 174	113.786	2.1600	0.7990	PCB 174	111.179	2.1955	0.7921
PCB 167	114.471	2.1683	0.8034	PCB 167	111.752	2.2079	0.7966
PCB 181	114.646	2.1673	0.8052	PCB 181	112.010	2.2132	0.7981
PCB 202	114.914	2.1799	0.8064	PCB 202	112.188	2.2162	0.7995
PCB 177	115.525	2.1930	0.8112	PCB 177	112.887	2.2292	0.8043
PCB 201	116.366	2.2075	0.8166	PCB 171	113.598	2.2443	0.8096
PCB 171	116.306	2.2098	0.8169	PCB 201	113.611	2.2443	0.8097
PCB 204	116.371	2.2072	0.8174	PCB 204	113.720	2.2473	0.8105
PCB 173	116.791	2.2170	0.8201	PCB 173	114.121	2.2536	0.8131
Methoxychlor	117.543	2.2276	0.8254	Methoxychlor	114.895	2.2723	0.8189
PCB 197	117.718	2.2367	0.8268	PCB 197	114.997	2.2719	0.8196
PCB 156	118.409	2.2429	0.8310	PCB 156	115.612	2.2841	0.8241
PCB 172	118.666	2.2547	0.8335	PCB 172	115.956	2.2909	0.8264
PCB 157	119.060	2.2594	0.8360	PCB 157	116.279	2.2966	0.8287
PCB 192	119.221	2.2523	0.8375	PCB 192	116.515	2.3024	0.8304
PCB 180	120.013	2.2782	0.8427	PCB 180	117.334	2.3170	0.8360
PCB 193	120.328	2.2863	0.8452	PCB 193	117.592	2.3232	0.8381
PCB 200	120.520	2.2863	0.8458	PCB 200	117.674	2.3246	0.8386
PCB 191	121.227	2.3005	0.8512	PCB 191	118.431	2.3391	0.8441
PBDE 47	121.717	2.3022	0.8539	PBDE 47	118.709	2.3467	0.8459
Mirex	124.693	2.3591	0.8751	Mirex	121.672	2.4054	0.8670
PCB 170	124.937	2.3738	0.8775	PCB 170	122.121	2.4127	0.8704
PCB 198	125.117	2.3637	0.8789	PCB 198	122.346	2.4177	0.8720
PCB 199	125.464	2.3817	0.8810	PCB 199	122.688	2.4227	0.8741
PCB 190	125.840	2.3880	0.8836	PCB 190	122.962	2.4285	0.8764
PCB 169	126.442	2.3903	0.8881	PCB 169	123.714	2.4445	0.8815
PCB 196	126.557	2.4046	0.8889	PCB 196	123.731	2.4445	0.8818
PCB 203	126.782	2.4067	0.8903	PCB 203	123.984	2.4483	0.8834
PCB 208	130.520	2.4768	0.9165	PCB 208	127.573	2.5196	0.9092
PCB 189	131.855	2.4976	0.9254	PCB 189	128.792	2.5445	0.9180
PCB 207	132.036	2.5056	0.9271	PCB 207	129.065	2.5491	0.9198
PCB 195	132.095	2.5075	0.9276	PCB 195	129.196	2.5513	0.9205
PCB 194	135.750	2.5769	0.9532	PCB 194	133.182	2.6300	0.9489
PCB 205	136.672	2.5968	0.9600	PCB 205	134.186	2.6511	0.9564
PBDE 99	139.703	2.6423	0.9801	PBDE 99	137.270	2.7136	0.9782
PCB 206	139.759	2.6530	0.9814	PCB 206	137.548	2.7162	0.9800
PCB 209	142.411	2.7034	1.0000	PCB 209	140.354	2.7716	1.0000
PBDE 153	149.786	2.8330	1.0509	PBDE 153	148.460	2.9348	1.0579

Experimental conditions: for the 0.18 mm i.d. column, the initial temperature of the oven was 130 °C. This temperature was held for 1 min and then increased at a rate of 1 °C/min. to 261 °C. The temperature was then increased at a rate of 3 °C/min to 315 °C and held at this temperature for 10 min. For the 0.25 mm i.d. column, the initial temperature of the oven was 130 °C. The temperature was increased at a rate of 1 °C/min to 261 °C, and then increased at a rate of 3 °C/min to 300 °C. The temperature was held at 300 °C for 5 min.

[a] Tetrachlorometaxylene.

[b] Hexachlorobenzene.

[c] Pentachloronitrobenzene.

Table 3
Retention time (RT) and relative retention time (RRT) of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers on 60 m × 0.18 mm i.d. and 0.25 mm i.d. 5% diphenyl/95% dimethyl polysiloxane columns

0.18 mm i.d. column (DB-5MS)				0.25 mm i.d. column (RTX-5MS)			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 1	25.375	0.5560	0.1880	PCB 1	23.715	0.5436	0.1787
PCB 2	30.833	0.6756	0.2285	PCB 2	28.696	0.6578	0.2162
PCB 3	31.503	0.6902	0.2335	PCB 3	29.259	0.6707	0.2205
TCMX	34.213	0.7433	0.2529	TCMX	32.379	0.7427	0.2438
PCB 4	34.273	0.7509	0.2540	PCB 4	32.453	0.7440	0.2445
PCB 10	34.328	0.7513	0.2543	PCB 10	32.476	0.7440	0.2446
PCB 7	38.530	0.8433	0.2854	PCB 9	36.294	0.8320	0.2735
PCB 9	38.556	0.8448	0.2857	PCB 7	36.347	0.8327	0.2738
PCB 6	40.160	0.8799	0.2976	PCB 6	38.019	0.8716	0.2865
α-BHC	40.911	0.8914	0.3028	α-BHC	38.953	0.8926	0.2934
HCB[a]	41.338	0.8981	0.3056	PCB 8	38.962	0.8932	0.2936
PCB 5	41.152	0.9007	0.3049	PCB 5	39.114	0.8961	0.2946
PCB 8	41.273	0.9043	0.3059	HCB	39.965	0.9167	0.3009
PCB 14	43.849	0.9572	0.3246	PCB 14	41.207	0.9444	0.3102
PCB 19	44.221	0.9689	0.3277	PCB 19	42.265	0.9689	0.3185
β-BHC	45.173	0.9842	0.3344	PCB 30	43.622	1.0000	0.3287
PCNB	45.456	0.9898	0.3363	β-BHC	43.638	1.0000	0.3287
PCB 30	45.856	1.0000	0.3391	γ-BHC	44.408	1.0176	0.3345
γ-BHC	46.454	1.0121	0.3438	PCB 11	44.472	1.0193	0.3351
PCB 11	47.244	1.0326	0.3502	PCNB	45.16	1.0368	0.3401
PCB 12	47.969	1.0495	0.3553	PCB 12	45.367	1.0406	0.3417
PCB 13	48.409	1.0567	0.3583	PCB 13	45.504	1.0429	0.3426
PCB 18	48.307	1.0584	0.3580	PCB 18	46.071	1.0561	0.3471
PCB 17	48.637	1.0645	0.3603	PCB 17	46.416	1.0634	0.3496
PCB 15	49.347	1.0792	0.3652	PCB 15	46.38	1.0635	0.3494
PCB 27	49.995	1.0934	0.3700	PCB 24	47.867	1.0966	0.3605
PCB 24	49.984	1.0940	0.3703	PCB 27	47.84	1.0970	0.3604
δ-BHC	51.557	1.1233	0.3816	δ-BHC	48.682	1.1156	0.3667
PCB 16	51.302	1.1241	0.3802	PCB 16	49.246	1.1289	0.3711
PCB 32	51.645	1.1304	0.3826	PCB 32	49.322	1.1299	0.3715
PCB 34	53.205	1.1636	0.3938	PCB 34	50.835	1.1656	0.3829
PCB 23	53.414	1.1648	0.3950	PCB 23	50.901	1.1680	0.3834
PCB 54	53.789	1.1742	0.3982	PCB 29	51.496	1.1808	0.3879
PCB 29	53.877	1.1783	0.3988	PCB 54	51.572	1.1820	0.3883
PCB 26	55.162	1.2073	0.4086	PCB 26	52.456	1.2017	0.3951
PCB 25	55.306	1.2118	0.4098	PCB 25	52.809	1.2106	0.3979
PCB 50	55.927	1.2224	0.4145	PCB 50	53.757	1.2321	0.4051
PCB 31	56.699	1.2410	0.4200	PCB 31	53.868	1.2341	0.4057
PCB 28	56.674	1.2418	0.4200	PCB 28	54.014	1.2382	0.4070
PCB 21	57.758	1.2624	0.4281	PCB 21	55.497	1.2719	0.4182
PCB 20	58.120	1.2710	0.4302	PCB 33	55.655	1.2766	0.4192
PCB 33	58.108	1.2713	0.4304	PCB 20	55.71	1.2774	0.4197
PCB 53	58.168	1.2697	0.4306	PCB 53	55.894	1.2811	0.4208
Heptachlor	58.851	1.2822	0.4356	Heptachlor	56.213	1.2882	0.4235
PCB 51	59.049	1.2890	0.4371	PCB 51	56.704	1.2996	0.4269
PCB 22	59.435	1.3023	0.4404	PCB 22	56.982	1.3063	0.4293
PCB 45	60.068	1.3147	0.4450	PCB 45	57.889	1.3262	0.4360
PCB 36	61.122	1.3301	0.4531	PCB 36	57.979	1.3290	0.4368
PCB 46	61.387	1.3436	0.4548	PCB 46	59.271	1.3579	0.4464
PCB 69	61.972	1.3553	0.4587	PCB 39	59.458	1.3643	0.4478
PCB 73	62.320	1.3604	0.4613	PCB 69	59.706	1.3691	0.4498
PCB 39	62.619	1.3656	0.4630	PCB 52	60.128	1.3784	0.4531
PCB 52	62.827	1.3766	0.4656	PCB 73	60.217	1.3801	0.4534
PCB 43	62.888	1.3742	0.4665	PCB 43	60.683	1.3911	0.4574
PCB 49	63.478	1.3888	0.4702	PCB 49	60.844	1.3957	0.4583
PCB 38	63.618	1.3905	0.4716	PCB 38	61.068	1.3996	0.4602
PCB 48	63.720	1.3946	0.4720	PCB 47	61.308	1.4058	0.4618
PCB 47	63.877	1.3970	0.4728	PCB 75	61.412	1.4075	0.4624
PCB 75	63.928	1.3955	0.4732	PCB 48	61.505	1.4090	0.4632
PCB 65	63.958	1.3979	0.4741	PCB 65	61.898	1.4186	0.4664

Table 3 (*Continued*)

0.18 mm i.d. column (DB-5MS)				0.25 mm i.d. column (RTX-5MS)			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 62	64.350	1.4033	0.4758	Aldrin	62.012	1.4211	0.4671
Aldrin	64.972	1.4156	0.4809	PCB 62	62.07	1.4243	0.4675
PCB 104	65.065	1.4236	0.4820	PCB 104	62.81	1.4408	0.4731
PCB 35	65.832	1.4370	0.4873	PCB 35	62.926	1.4422	0.4738
PCB 44	66.062	1.4475	0.4896	PCB 44	63.662	1.4594	0.4797
Dathal	66.217	1.4447	0.4907	PCB 59	64.018	1.4685	0.4822
PCB 59	66.362	1.4519	0.4916	PCB 37	64.211	1.4710	0.4836
PCB 42	66.588	1.4562	0.4928	PCB 42	64.234	1.4729	0.4839
PCB 37	67.098	1.4686	0.4971	DCBP	64.364	1.4797	0.4851
PCB 71	67.815	1.4859	0.5025	PCB 72	65.197	1.4945	0.4912
PCB 41	67.991	1.4881	0.5037	Dathal	65.173	1.4948	0.4907
DCBP	68.058	1.4907	0.5040	PCB 71	65.579	1.5033	0.4941
PCB 64	68.300	1.4943	0.5059	PCB 41	65.779	1.5070	0.4954
PCB 72	68.295	1.4862	0.5062	PCB 64	65.786	1.5090	0.4956
PCB 68	68.811	1.5006	0.5088	PCB 68	65.994	1.5143	0.4971
PCB 96	69.013	1.5018	0.5116	PCB 96	66.531	1.5251	0.5013
PCB 40	69.371	1.5171	0.5134	PCB 40	67.17	1.5402	0.5060
PCB 103	69.579	1.5229	0.5154	PCB 103	67.292	1.5416	0.5068
PCB 57	70.114	1.5325	0.5197	PCB 57	67.48	1.5466	0.5085
PCB 100	70.672	1.5427	0.5231	PCB 100	68.255	1.5644	0.5139
PCB 67	70.852	1.5524	0.5250	PCB 67	68.221	1.5639	0.5140
PCB 58	71.266	1.5572	0.5286	PCB 58	68.824	1.5777	0.5187
PCB 94	71.921	1.5684	0.5318	Oxychlordane	69.226	1.5879	0.5212
PCB 63	71.877	1.5726	0.5324	PCB 63	69.196	1.5872	0.5212
Oxychlordane	72.172	1.5679	0.5335	Heptachlor epoxide	69.273	1.5874	0.5218
Heptachlor epoxide	72.078	1.5704	0.5335	PCB 94	69.623	1.5976	0.5244
PCB 61	72.095	1.5758	0.5344	PCB 74	69.847	1.6012	0.5263
PCB 74	72.571	1.5901	0.5378	PCB 61	69.877	1.6015	0.5266
PCB 102	73.077	1.5972	0.5417	PCB 70	70.603	1.6175	0.5318
PCB 76	73.062	1.5965	0.5420	PCB 98	70.76	1.6220	0.5331
PCB 93	73.240	1.6017	0.5421	PCB 76	70.745	1.6218	0.5332
PCB 98	73.140	1.5917	0.5421	PCB 102	70.902	1.6250	0.5343
PCB 70	73.467	1.6080	0.5442	PCB 80	71.035	1.6300	0.5350
PCB 95	73.699	1.6131	0.5460	PCB 93	71.145	1.6314	0.5359
PCB 66	73.752	1.6160	0.5465	PCB 66	71.13	1.6306	0.5359
PCB 121	74.113	1.6162	0.5480	PCB 95	71.338	1.6343	0.5373
PCB 80	74.113	1.6162	0.5480	PCB 121	71.726	1.6458	0.5402
PCB 88	74.376	1.6219	0.5500	PCB 88	71.726	1.6458	0.5402
PCB 91	74.794	1.6364	0.5541	PCB 91	72.38	1.6603	0.5452
PCB 55	75.130	1.6416	0.5573	PCB 55	72.63	1.6650	0.5474
PCB 155	76.228	1.6623	0.5636	*trans*-Chlordane	73.391	1.6833	0.5526
trans-Chlordane	76.298	1.6647	0.5654	PCB 155	73.633	1.6896	0.5546
PCB 56	76.456	1.6752	0.5666	PCB 56	74.026	1.6970	0.5578
PCB 60	76.619	1.6770	0.5676	PCB 60	74.114	1.6979	0.5582
PCB 92	77.047	1.6850	0.5702	PCB 92	74.409	1.7062	0.5605
PCB 84	77.192	1.6895	0.5718	2,4-DDE	74.852	1.7169	0.5635
2,4-DDE	77.525	1.6842	0.5730	PCB 84	74.957	1.7172	0.5645
PCB 90	77.840	1.6992	0.5762	PCB 89	75.299	1.7261	0.5673
PCB 89	77.759	1.6922	0.5764	PCB 101	75.384	1.7286	0.5679
PCB 101	78.101	1.7080	0.5780	Endosulfan I	75.407	1.7280	0.5680
PCB 113	78.227	1.7098	0.5798	PCB 90	75.462	1.7296	0.5681
Endosulfan I	78.447	1.7092	0.5806	PCB 113	75.956	1.7408	0.5724
cis-Chlordane	78.576	1.7144	0.5822	*cis*-Chlordane	76.093	1.7453	0.5730
PCB 99	78.754	1.7255	0.5836	PCB 99	76.242	1.7478	0.5745
trans-Nonachlor	79.262	1.7220	0.5859	PCB 79	76.445	1.7523	0.5760
PCB 79	79.554	1.7312	0.5897	*trans*-Nonachlor	76.885	1.7635	0.5788
PCB 119	79.741	1.7439	0.5902	PCB 119	77.361	1.7739	0.5828
PCB 150	79.989	1.7444	0.5915	PCB 150	77.406	1.7762	0.5830
PCB 112	79.920	1.7463	0.5928	PCB 112	77.697	1.7811	0.5856
PCB 83	80.384	1.7594	0.5955	PCB 108	78.103	1.7904	0.5887
PCB 108	80.311	1.7549	0.5957	PCB 83	78.193	1.7914	0.5889
PCB 152	80.959	1.7618	0.6001	PCB 78	78.162	1.7917	0.5889

Table 3 (*Continued*)

0.18 mm i.d. column (DB-5MS)				0.25 mm i.d. column (RTX-5MS)			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 78	81.129	1.7655	0.6014	PCB 152	78.678	1.8035	0.5928
PCB 97	81.391	1.7808	0.6029	PCB 97	79.049	1.8133	0.5955
PCB 86	81.348	1.7780	0.6030	PCB 86	79.177	1.8147	0.5966
PCB 125	81.807	1.7840	0.6049	PCB 125	79.477	1.8237	0.5986
PCB 111	82.013	1.7885	0.6064	PCB 117	79.826	1.8296	0.6010
PCB 117	82.080	1.7917	0.6076	PCB 81	79.826	1.8296	0.6010
PCB 145	82.088	1.7942	0.6085	PCB 111	79.806	1.8313	0.6011
PCB 115	82.344	1.8023	0.6100	PCB 116	79.806	1.8313	0.6011
PCB 87	82.519	1.8080	0.6115	PCB 145	79.807	1.8291	0.6014
PCB 116	82.730	1.8041	0.6117	PCB 87	79.945	1.8327	0.6024
PCB 81	82.705	1.8054	0.6122	Dieldrin	79.985	1.8329	0.6025
PCB 148	82.933	1.8086	0.6132	PCB 115	80.058	1.8341	0.6030
PCB 85	83.101	1.8182	0.6156	PCB 148	80.551	1.8483	0.6067
Dieldrin	83.305	1.8150	0.6166	4,4′-DDE	80.565	1.8462	0.6069
4,4′-DDE	83.419	1.8175	0.6174	PCB 85	80.657	1.8501	0.6076
PCB 136	83.541	1.8270	0.6183	PCB 120	80.672	1.8493	0.6081
PCB 120	83.467	1.8238	0.6192	PCB 136	81.101	1.8596	0.6109
PCB 110	84.053	1.8417	0.6229	PCB 77	81.601	1.8718	0.6147
PCB 154	84.204	1.8381	0.6233	PCB 110	81.663	1.8721	0.6153
2,4-DDD	84.474	1.8352	0.6244	2,4-DDD	81.902	1.8786	0.6166
PCB 77	84.497	1.8487	0.6259	PCB 154	81.931	1.8778	0.6168
PCB 82	85.771	1.8793	0.6356	PCB 82	83.54	1.9151	0.6295
PCB 151	86.143	1.8839	0.6376	Endrin	83.65	1.9169	0.6301
Endrin	86.808	1.8914	0.6425	PCB 151	83.813	1.9218	0.6314
PCB 135	86.771	1.8992	0.6428	PCB 135	84.594	1.9380	0.6371
PCB 144	86.991	1.9024	0.6438	PCB 144	84.623	1.9404	0.6375
PCB 147	87.351	1.9139	0.6473	PCB 124	84.86	1.9449	0.6389
PCB 124	87.696	1.9143	0.6492	PCB 147	85.167	1.9524	0.6417
PCB 107	87.962	1.9142	0.6520	PCB 107	85.322	1.9558	0.6429
PCB 109	88.080	1.9278	0.6525	PCB 109	85.417	1.9569	0.6433
PCB 139	88.148	1.9266	0.6534	Endosulfan II	85.46	1.9584	0.6438
PCB 149	88.204	1.9305	0.6534	PCB 123	85.773	1.9675	0.6461
PCB 123	88.288	1.9317	0.6540	PCB 139	85.82	1.9669	0.6467
PCB 140	88.990	1.9406	0.6580	PCB 149	85.934	1.9687	0.6472
PCB 106	88.803	1.9325	0.6582	PCB 106	86.149	1.9748	0.6491
Endosulfan II	88.945	1.9379	0.6583	PCB 118	86.197	1.9765	0.6493
PCB 118	88.984	1.9460	0.6586	PCB 140	86.388	1.9823	0.6507
PCB 143	89.793	1.9582	0.6640	PCB 143	87.421	2.0060	0.6584
PCB 134	89.759	1.9630	0.6643	PCB 134	87.634	2.0094	0.6601
cis-Nonachlor	89.877	1.9609	0.6660	4,4′-DDD	87.836	2.0128	0.6617
PCB 131	90.506	1.9809	0.6705	*cis*-Nonachlor	87.876	2.0155	0.6617
PCB 114	90.573	1.9816	0.6709	PCB 122	88.018	2.0173	0.6627
PCB 142	90.753	1.9791	0.6711	PCB 114	88.041	2.0195	0.6632
PCB 133	90.554	1.9792	0.6712	PCB 133	88.071	2.0185	0.6637
4,4′-DDD	90.832	1.9790	0.6723	2,4-DDT	88.161	2.0207	0.6642
PCB 122	90.893	1.9841	0.6728	PCB 131	88.383	2.0248	0.6657
PCB 165	91.005	1.9865	0.6737	PCB 142	88.423	2.0290	0.6660
2,4-DDT	91.147	1.9802	0.6737	PCB 165	88.861	2.0366	0.6690
PCB 188	91.306	1.9911	0.6751	PCB 188	88.91	2.0402	0.6697
Endrin Aldehyde	91.623	1.9963	0.6782	Endrin Aldehyde	88.902	2.0373	0.6697
PCB 161	91.552	2.0010	0.6786	Ethion	89.184	2.0455	0.6715
Ethion	91.615	1.9988	0.6789	PCB 146	89.13	2.0432	0.6716
PCB 146	91.676	2.0087	0.6794	PCB 161	89.368	2.0482	0.6734
PCB 184	92.495	2.0129	0.6856	PCB 184	90.041	2.0640	0.6784
PCB 153	92.816	2.0337	0.6878	PCB 153	90.143	2.0665	0.6792
PCB 168	93.054	2.0293	0.6881	PCB 132	90.543	2.0743	0.6819
PCB 132	92.882	2.0329	0.6881	PCB 168	90.595	2.0788	0.6824
PCB 105	93.218	2.0386	0.6899	PCB 105	90.696	2.0797	0.6832
PCB 127	93.716	2.0483	0.6947	PCB 127	90.736	2.0796	0.6838
PCB 179	94.746	2.0759	0.7021	PCB 141	92.341	2.1155	0.6955
PCB 141	94.948	2.0781	0.7034	PCB 179	92.491	2.1203	0.6969
Endosulfan sulfate	95.871	2.0888	0.7096	Endosulfan sulfate	93.005	2.1313	0.7006

Table 3 (*Continued*)

0.18 mm i.d. column (DB-5MS)				0.25 mm i.d. column (RTX-5MS)			
Compound	RT (min)	RRT to PCB 30	RRT to PCB 209	Compound	RT (min)	RRT to PCB 30	RRT to PCB 209
PCB 137	95.839	2.0969	0.7100	PCB 137	93.451	2.1436	0.7040
PCB 176	96.122	2.1030	0.7120	PCB 176	93.741	2.1503	0.7061
PCB 130	96.314	2.1024	0.7130	PCB 130	94.018	2.1548	0.7078
PCB 163	97.059	2.1187	0.7185	4,4′-DDT	94.189	2.1584	0.7095
PCB 164	97.010	2.1233	0.7186	PCB 164	94.768	2.1711	0.7138
PCB 160	97.450	2.1251	0.7206	PCB 163	94.857	2.1741	0.7142
PCB 138	97.312	2.1322	0.7211	PCB 138	94.829	2.1739	0.7145
4,4′-DDT	97.475	2.1238	0.7215	PCB 160	95.014	2.1802	0.7156
PCB 158	97.537	2.1331	0.7219	PCB 158	95.232	2.1837	0.7174
PCB 186	97.441	2.1292	0.7228	PCB 186	95.182	2.1820	0.7174
PCB 129	98.393	2.1527	0.7289	PCB 129	96.157	2.2057	0.7243
PCB 178	98.456	2.1549	0.7294	PCB 126	96.272	2.2065	0.7255
PCB 126	99.096	2.1659	0.7345	PCB 178	96.362	2.2076	0.7258
PCB 175	99.442	2.1707	0.7361	PCB 166	97.181	2.2276	0.7322
PCB 166	99.455	2.1643	0.7372	PCB 175	97.335	2.2309	0.7328
PCB 187	99.954	2.1901	0.7407	PCB 182	97.72	2.2400	0.7363
PCB 182	100.056	2.1774	0.7417	PCB 187	97.727	2.2403	0.7364
PCB 159	100.472	2.1954	0.7453	PCB 159	97.754	2.2409	0.7368
PCB 183	100.907	2.2086	0.7475	PCB 183	98.625	2.2595	0.7428
PCB 162	101.796	2.2199	0.7527	PCB 162	98.748	2.2659	0.7438
PCB 128	101.756	2.2253	0.7531	PCB 128	99.428	2.2799	0.7490
PCB 167	102.514	2.2429	0.7594	PCB 167	99.713	2.2873	0.7511
PCB 185	102.736	2.2478	0.7610	PCB 185	100.325	2.3013	0.7557
PCB 174	103.948	2.2776	0.7703	PCB 174	101.646	2.3302	0.7659
PCB 181	104.036	2.2739	0.7711	PCB 181	101.804	2.3332	0.7672
PCB 177	104.748	2.2951	0.7762	PCB 177	102.544	2.3507	0.7726
PCB 202	105.253	2.2975	0.7791	PCB 202	103.224	2.3658	0.7771
PCB 171	105.602	2.3113	0.7823	PCB 171	103.347	2.3676	0.7784
PCB 156	106.161	2.3227	0.7864	PCB 156	103.503	2.3742	0.7797
PCB 173	106.358	2.3304	0.7882	PCB 173	104.219	2.3891	0.7853
PCB 201	106.684	2.3288	0.7897	PCB 157	104.461	2.3953	0.7869
PCB 157	106.944	2.3388	0.7915	PCB 201	104.563	2.3965	0.7872
PCB 204	107.113	2.3310	0.7940	Methoxychlor	104.723	2.3998	0.7889
PCB 192	107.549	2.3500	0.7978	PCB 204	104.717	2.4004	0.7890
PCB 172	107.858	2.3607	0.7990	PCB 172	105.382	2.4142	0.7937
Methoxychlor	108.003	2.3532	0.7994	PCB 192	105.34	2.4148	0.7940
PCB 197	108.061	2.3651	0.8005	PCB 197	105.74	2.4225	0.7964
PCB 180	109.032	2.3890	0.8080	PCB 180	106.393	2.4390	0.8016
PCB 193	109.103	2.3879	0.8082	PBDE 47	106.727	2.4480	0.8035
PCB 191	109.800	2.4013	0.8127	PCB 193	106.898	2.4490	0.8051
PBDE 47	110.171	2.3989	0.8150	PCB 191	107.524	2.4655	0.8100
PCB 200	110.723	2.4170	0.8196	PCB 200	108.404	2.4846	0.8161
PCB 169	112.648	2.4621	0.8350	Mirex	109.581	2.5133	0.8251
PCB 190	113.718	2.4869	0.8417	PCB 169	109.807	2.5167	0.8275
PCB 170	113.651	2.4875	0.8419	PCB 170	111.315	2.5502	0.8384
Mirex	114.466	2.4974	0.8482	PCB 190	111.41	2.5546	0.8392
PCB 198	114.345	2.4985	0.8482	PCB 198	112.143	2.5708	0.8453
PCB 199	114.982	2.5193	0.8521	PCB 199	112.729	2.5842	0.8494
PCB 203	115.945	2.5404	0.8592	PCB 203	113.554	2.6031	0.8556
PCB 196	116.011	2.5391	0.8594	PCB 196	113.73	2.6055	0.8566
PCB 189	118.882	2.6010	0.8806	PCB 189	116.086	2.6628	0.8745
PCB 208	120.614	2.6378	0.8927	PCB 208	118.268	2.7119	0.8909
PCB 195	120.747	2.6456	0.8948	PCB 195	118.469	2.7158	0.8926
PCB 207	122.087	2.6700	0.9036	PCB 207	119.597	2.7424	0.9009
PCB 194	124.524	2.7284	0.9228	PCB 194	121.87	2.7938	0.9183
PCB 205	125.107	2.7382	0.9268	PCB 205	122.775	2.8127	0.9247
PBDE 99	129.565	2.8212	0.9584	PBDE 99	125.749	2.8843	0.9467
PCB 206	130.308	2.8551	0.9656	PCB 206	127.897	2.9319	0.9637
PCB 209	134.944	2.9567	1.0000	PCB 209	132.718	3.0425	1.0000
PBDE 153	143.362	3.1217	1.0605	PBDE 153	140.793	3.2294	1.0600

Experimental conditions: the initial temperature of the GC oven was held 130 °C for 1 min. The temperature was increased at a rate of 1 °C/min to 261 °C, then at a rate 3 °C/min to 300 °C. The temperature was maintained at 300 °C for 5 min.

[a] Hexachlorobenzene.

held at 300 °C for 10 min. The initial oven temperature was lowered from 130 to 100 °C to provide separation of dieldrin and 4, 4′-DDE, and the rate at which the oven temperature was increased was altered to decrease the time of analysis and increase the number of samples that could be analyzed in a week. A rate of 15 °C/min was used in the portion of the program where analytes of interest were not emerging. The rate was then decreased to 1 °C/min during the period in which analytes were eluting to minimize any co-elution problems.

2.5. Determination of retention and relative retention times

The retention times for all 209 PCBs were determined using the nine Frame mixes and individual PCB standards. The retention times for the PBDEs, OCPs, and surrogates were determined by the analysis of individual standard solutions and a mixture of OCPs. Finally, a complete mix containing all compounds was analyzed to further evaluate co-elution problems. This process was repeated for each of the four columns.

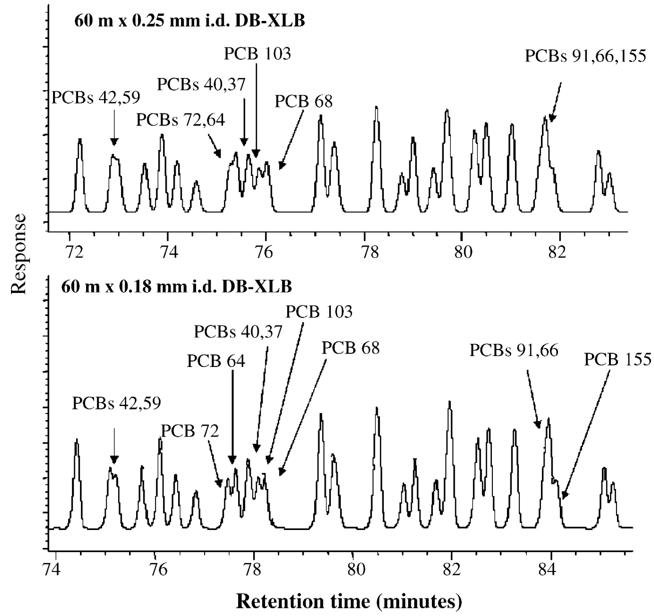

Fig. 1. Comparison of separation of select PCBs in a standard solution (100 pg/mL) on a 0.25 mm and a 0.18 mm i.d. 60 m DB-XLB capillary columns.

3. Results and discussion

3.1. Retention time and order of OCPs, PCBs, and PBDEs on 0.18 mm i.d. and 0.25 mm i.d. DB-XLB columns, and 0.18 mm i.d. DB5-MS and 0.25 mm i.d. RTX-5MS columns

In Table 2, the retention time and relative retention time to PCBs 209 and 30 are presented on 0.18 mm i.d. and 0.25 mm i.d. DB-XLB columns. In Table 3, the retention time and relative retention time to PCBs 209 and 30 are presented for a 0.18 mm i.d. DB-5MS and a 0.25 mm i.d. RTX-5MS column.

The average peak width at half height for PCBs 30 and 209 was calculated. Compounds having retention time differences greater than 1.5 times the average peak width were considered resolved. This resolution was adequate for quantifying analytes that do not have significantly different concentrations, and do not exhibit baseline resolution. For the four columns evaluated, this corresponded to a RRT of the analyte to PCB 209 of 0.0012, 0.0014, 0.0013, and 0.0016 for the 0.18 mm i.d. DB-XLB, 0.25 mm i.d. DB-XLB, 0.18 mm i.d. DB-5MS, and 0.25 mm i.d. RTX-5MS columns, respectively. In the analysis of the serum extracts, identification of the analytes was based on the RRT of the analyte to PCB 30 for compounds that eluted prior to PCB 56. The RRT of the PCBs that eluted later was calculated relative to PCB 209.

3.2. Comparison of separation by using 0.25 mm i.d. and 0.18 mm i.d. DB-XLB capillary columns.

Reducing the i.d. of the capillary column should improve the separation by affecting the mass transfer term (*C*) in the van Deemter equation, resulting in an improvement in column efficiency due to lowering the height of the theoretical plates and increasing the number of the theoretical plates. For example, a 0.18 mm i.d. capillary column will have 1.4 times more theoretical plates (6600 plates per meter) than a 0.25 mm i.d. column (4750 plates per meter), and result in 1.2× resolution compared to the 0.25 mm i.d. column. However, the use of a narrower i.d. column can also require more time for the analytes to elute from the column. The extent of improvement is a balance between the increase in column efficiency by reducing the i.d. diameter of the column, and band-broadening that result from an analyte spending more time on the capillary column.

As demonstrated in Fig. 1, for certain compounds the resolution was improved by using a 0.18 mm i.d. column. A slight improvement was observed between PCBs 91 and 66 and 155. The difference in the relative retention time between PCBs 66 and 155 was improved from 0.0019 on the 0.25 mm i.d. column to 0.0025 on the 0.18 mm i.d. column. In contrast, little improvement was observed between other compounds, such as PCBs 40 and 37. Overall, however, the changes were not sufficient to report the congeners as separate compounds.

3.3. Comparison of separation by using a 0.18 mm i.d. DB-5MS and 0.25 mm i.d. RTX-5MS capillary columns

The 5% phenyl/95% methylpolysiloxane liquid stationary phase is reportedly the same phase used on the DB-5MS and RTX-5MS capillary columns. We thus, expected that any differences in the retention time of the analytes observed between a 0.18 mm i.d. DB-5MS and 0.25 mm i.d. RTX-5MS would be due to the difference in the i.d.

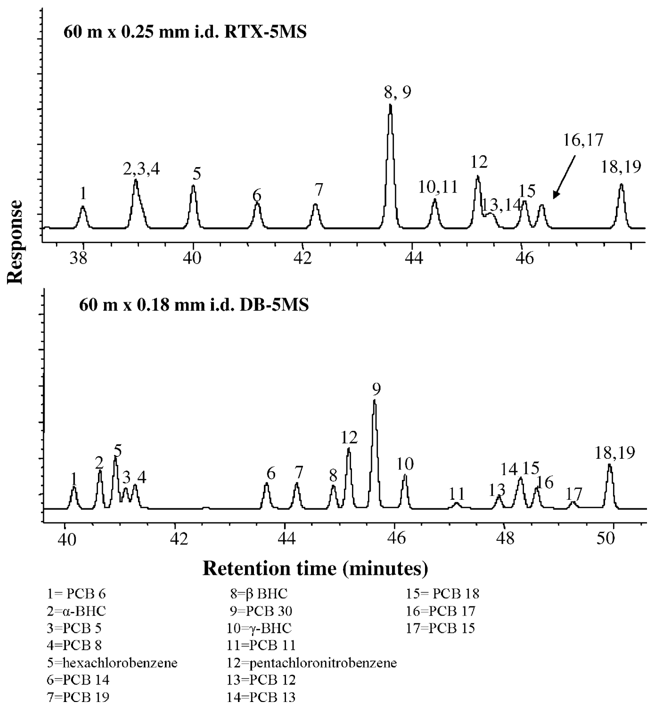

Fig. 2. Comparison of separation of select OCPs and PCBs in a standard solution (100 pg/mL) on a 60 m × 0.25 mm RTX-5MS and 60 m × 0.18 mm i.d. DB-5MS capillary columns. (The dimensions and liquid phase of the capillary columns are identical. The only difference between the columns were that two different companies manufactured them.)

of the columns. Surprisingly, the retention order for specific compounds was different. For example, as presented in Fig. 2 (top), the retention order for the first five compounds on the 0.25 mm i.d. RTX-5MS column is PCB 6, α-BHC, PCBs 5 and 8, and hexachlorobenzene. On the 0.18 mm i.d. DB-5MS column (Fig. 2, bottom), hexachlorobenzene elutes after α-BHC and prior to PCB 5. Another example concerns the elution order of PCB 19, β-BHC, PCB 30, γ-BHC, and PCB 11 and pentachloronitrobenzene. In this case, pentachloronitrobenzene elutes after β-BHC and before PCB 30 on the 0.18 mm i.d. DB-5MS column, whereas pentachloronitrobenzene elutes after β-BHC on the 0.25 mm i.d. RTX-5MS column (Fig. 2). These observations indicate differences between the liquid stationary phases produced by the two manufacturers. This result is significant because analysts often assume that the retention order is the same on capillary columns produced by different manufacturers.

Since some variability likely exists between the liquid stationary phases, it is difficult to state whether the improved separation among α-BHC, PCBs 5 and 8, and between β-BHC and PCB 30, and between PCBs 15 and 17 on the 0.18 mm i.d. column is due to the reduced i.d. of the column. The results do suggest, however, that overall; the 0.18 mm i.d. DB-5MS capillary column improves separation of the PCBs and OCPs.

3.4. The complementary nature of using a 0.25 mm i.d. 12% (phenylmethyl)-polysiloxane (e.g., DB-XLB) and 0.25 mm i.d. 5% phenyl/95% dimethyl (polysiloxane) (e.g., RTX-5MS) capillary columns to analyze POPs in human serum extracts

Although the 0.18 mm i.d. DB-XLB capillary column exhibited better separation for certain PCB congeners compared to the 0.25 mm i.d. DB-XLB capillary column, we chose to employ the 0.25 mm i.d. DB-XLB because it has a greater capacity than the 0.18 mm i.d. column (50 ng on the 0.18 mm i.d. column versus 75 ng on the 0.25 mm i.d. column), it cost less than the 0.18 mm i.d. column, and at the time that this work was underway the 0.18 mm i.d. column was manufactured by special request. The 0.18 mm i.d. DB-XLB column is now commercially available, but is about US$ 150 more expensive than the 0.25 mm i.d. capillary column.

To determine the complementary nature of the 0.25 mm i.d. DB-XLB and 0.25 mm i.d. RTX-5MS columns, the data were further evaluated to determine which compounds co-elute on each capillary column. In Table 4, a summary of the OCPs that co-elute in the analysis of these compounds in human serum extracts is presented. OCPs and PCBs that can potentially interfere in the analysis of these compounds on the 0.25 mm i.d. DB-XLB and the 0.25 mm i.d. RTX-5MS capillary columns are listed in the second and third columns, respectively. The column that we recommend to employ for quantification of the analytes is presented in the fourth column. The compounds in bold are compounds which have been previously reported in human serum, and thus are of primary concern. Of the 52 compounds listed there are only nine compounds which are typically reported in human serum for which the presence of co-eluting compounds may be a problem. However, for all these compounds, the co-elution problem is evident on only one of the columns, enabling accurate quantification by using the data obtained from the other column. According to the scheme presented, accurate quantification can be obtained by analyzing certain compounds using data obtained from the analysis of serum extracts on the 60 m × 0.25 mm i.d. RTX-5MS column, and analyzing other compounds by using data from the 60 m × 0.25 mm i.d. DB-XLB column. One must recognize, however, the potential for the other co-eluting compounds to be present. For these compounds, the absence of a co-eluting interferent is inferred if the concentration determined for the compound is the same within a reasonable error (e.g., 20% relative difference).

3.5. Analysis of OCPs, PCBs, and BDEs in human serum extracts

While the analysis conducted above provides the basis for choosing which column to use to quantify the compounds, the analyst must evaluate the chromatograms for the presence or absence of interferences, and to verify the choice of column to employ for quantification of the analytes. In the analysis of 500 serum extracts by using 0.25 mm i.d. DB-XLB and

Table 4
Summary of potential co-eluting compounds that interfere with measurement of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers on 60 m × 0.25 mm i.d. DB-XLB and RTX-5MS columns[a]

Analyte	Compounds that co-elute on DB-XLB	Compounds that co-elute on RTX-5MS	Suggested column for quantification[b]
PCB 14			Either
PCB 28	**Heptachlor**		RTX-5MS
PCB 30		**β-BHC**	DB-XLB
PCB 49		PCB 43	DB-XLB
PCB 52		PCB 73	DB-XLB
PCB 56	PCB 92, PCB 84, PCB 89	PCB 60	
PCB 65	PCB 39, PCB 47, PCB 62	PCB 62, Aldrin	
PCB 66	PCB 91, PCB 155	PCB 80, PCB 93, PCB 95	
PCB 70	PCB 121	PCB 98, PCB 76	
PCB 74		PCB 61	DB-XLB
PCB 99	PCB 150		RTX-5MS
PCB 101	PCB 60, PCB 90	PCB 89, PCB 90, Endosulfan I	
PCB 105		PCB 132, PCB 168, PCB 127	DB-XLB
PCB 110		PCB 77	DB-XLB
PCB 118	PCB 131	PCB 106	
PCB 137	PCB 186		RTX-5MS
PCB 138	**4,4′-DDT**, PCB 160	PCB 163, PCB 164, PCB 160	RTX-5MS
PCB 146	PCB 114	Ethion	
PCB 153	PCB 168	PCB 184	
PCB 156			Either
PCB 157		PCB 201	DB-XLB
PCB 166	**PCB 183**	PCB 175	RTX-5MS
PCB 170		**PCB 190**	DB-XLB
PCB 177			Either
PCB 180			Either
PCB 183	**PCB 166**	PCB 162	RTX-5MS
PCB 187	Endosulfan sulfate	PCB 182, PCB 159	
PCB 189			Either
PCB 190		**PCB 170**	DB-XLB
PCB 194			Either
PCB 199			Either
PCB 203		PCB 196	DB-XLB
PCB 204	PCB 171, PCB 201	Methoxychlor	
PCB 209			Either
2,4′-DDT	PCB 106, PCB 134, Ethion	PCB 114, PCB 133	
2,4′-DDD	PCB 120, PCB 81	PCB 154	
2,4′-DDE		PCB 84	
4,4′-DDT	PCB 138, PCB 160		RTX-5MS
4,4′-DDD	PCB 161	PCB 122, *cis*-Nonachlor	
4,4′-DDE	PCB 115, PCB 117, PCB 85	PCB 148, PCB 85, PCB 120	
α-BHC		PCB 5, PCB 8	DB-XLB
β-BHC		**PCB 30**	DB-XLB
Heptachlor	PCB 28, PCB 21		RTX-5MS
Heptachlor epoxide	PCB 67, PCB 58	Oxychlordane, PCB 63	
Hexachlorobenzene			Either
trans-Nonachlor	PCB 152		RTX-5MS
Tetrachloro-*m*-xylene			Either
Pentachloronitrobenzene			Either
PBDE 47			Either
PBDE 99			Either
PBDE 153			Either

[a] Compounds in bold have been reported in human serum, and thus are of major concern.
[b] In cases where potential interferences are not typically reported in human serum, the responses should be equivalent on both columns in the absence of interferences.

RTX-5MS columns, quantification of most analytes could be accomplished by using data from either column. However, certain cases arose in which quantification was accomplished using the response from either the DB-XLB or RTX-5MS capillary columns. The choice of which column to use was determined by comparing the response of the analyte on the DB-XLB and RTX-5MS columns and by examining the chromatograms. We assume that in the absence of a co-eluting interferent on either column, that the difference in the response on both columns will be less than 20%. Conversely, we assume the presence of a co-eluting interferent if the response differs by greater than 20%. In such cases, the lowest concentration was reported.

In the following section, two cases are presented that serve to exemplify the decision-making process in determining which data to employ for quantification of the POPs.

3.5.1. Case 1: quantification of PCBs 153 and 180 accomplished by using either column

Overall, the analysis of over 500 human serum extracts for PCBs 153 and 180 resulted in good agreement between the concentrations calculated by using data from the DB-XLB versus the RTX-5MS. As an example we present a plot of the response of PCB 153 on the DB-XLB versus RTX-5MS column in Fig. 3. This result indicates that PCBs 168 and 184, which can co-elute with PCB 153 are not present in the human serum extracts.

In certain cases, however, the concentrations of PCBs 153 and 180 calculated using data from each column were different. In one case, the presence of an interferent with PCB 153 was obvious by the presence of a shoulder on the peak. The concentration for PCB 153 calculated using the response on the DB-XLB column was 0.78 ng/mL and the concentration calculated using the response on the RTX-5MS column that incorporated the shoulder was 0.83 ng/mL. If the shoulder was removed, the concentration was reduced to 0.53 ng/mL. This corresponds to a 32% relative difference, and thus the concentrations are different, if the criterion that the concentrations be equivalent within a 20% relative difference is employed. In the second case, the presence of a co-eluting interferent was indicated by a larger response for PCB 180 on the DB-XLB column compared to the RTX-5MS column. This difference was sufficient to cause a 96% relative difference between the concentrations calculated using data from each column. We calculated a concentration of 11.62 ng/mL by using the response on the DB-XLB column, and 0.43 ng/mL by using the response on the RTX-5MS column. In this case, we chose to report the lower concentration, recognizing, however, that an interferent may be present on either column.

3.5.2. Case 2: quantification of PCB 99 and trans-nonachlor on the RTX-5MS column

In contrast to PCBs 153 and 180, relative differences of >20% between the concentration obtained by using data from the DB-XLB and RTX-5MS columns were observed for PCB 99 and *trans*-nonachlor (Fig. 4). For example, the concentration reported using the data on the DB-XLB column was lower (0.44 ng/mL) than by using the data from the RTX-5MS

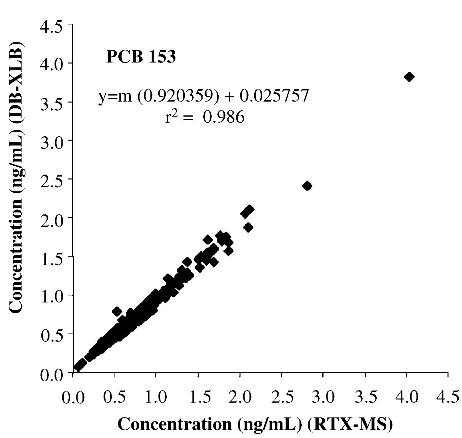

Fig. 3. Concentration of PCB 153 obtained from the analysis of 500 serum extracts ($N = 500$) on a 0.25 mm DB-XLB column vs. the concentration of PCB 153 obtained from the analysis of 500 serum extracts ($N = 500$) on a 0.25 mm RTX-5MS column. (Since higher values may be due to co-elution of PCPs and PCBs, in cases where the concentration yielded on one column was higher than the other, the lower value was reported as the concentration in the serum extract.)

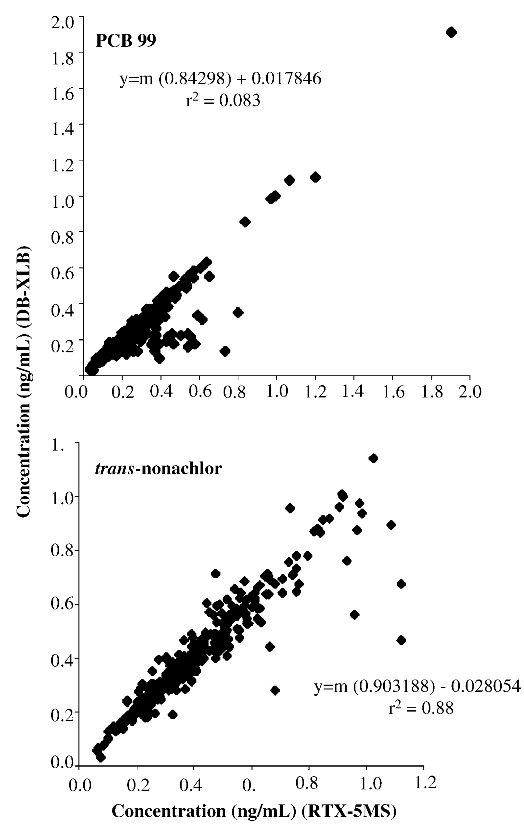

Fig. 4. Concentration of PCB 99 and *trans*-nonachlor obtained from the analysis of 500 serum extracts ($N = 500$) on a 0.25 mm DB-XLB column vs. the concentration of PCB 99 and *trans*-nonachlor obtained from the analysis of 500 serum extracts ($N = 500$) on a RTX-5MS column.

column (0.67 ng/mL). In this case, about a 30% relative difference was observed between the values, and the lower value was reported.

4. Summary

Herein, new information is provided on the retention time of a mixture of persistent organic pollutants prevalent in human serum, including 14 OCPs, 27 PCBs, and 3 PBDE congeners, on an RTX-5MS (60 m × 0.25 mm i.d., 0.25 μm film thickness), a DB-XLB (60 m × 0.25 mm i.d., 0.25 μm film thickness), a DB-XLB (60 m × 0.18 mm i.d., 0.18 μm film thickness), and a DB-5MS (60 m × 0.18 mm i.d., 0.18 μm film thickness) capillary columns. Although, the stationary liquid phase on the RTX-5MS and DB-5MS are supposedly the same (5% diphenyl/95% dimethyl polysiloxane), differences were observed in the retention order, which indicate differences between the phases. Two 60 m × 0.25 mm i.d., 0.25 μm film thickness columns (RTX-5MS and DB-XLB) were employed to measure 14 OCPs, 27 PCBs, and 3 PBDEs in 500 human serum extracts collected from diverse populations of women at different periods reflecting different use patterns and concentrations of OCPs, PCBs, and PBDEs. For example, the concentrations of PCB 153, DDT, DDE, and PBDE 47 ranged from 7 to 410 ng/g lipid, from 60 to 23,200 ng/g lipid, from 110 to 42,000 ng/g lipid and from <10 to 510 ng/g lipid, respectively. The method was, thus validated over a wide range of OCPs, PCBs, and PBDEs. Typically, the concentrations reported using data from each column were similar (<20% relative difference). Cases did arise, however, in which the concentrations were not the same. In these cases, the lower concentration was reported.

Three major advantages of the method developed herein are that: (1) PCB and PBDE congeners critical to assess risk can be resolved, (2) OCPs, PCBs, and PBDEs which are typically reported in human serum can be analyzed in one extract, and (3) our method affords separation of OCPs, PCBs, and PBDEs that is not provided by methods used by other investigators. Silica and florisil columns are commonly used to fractionate OCPs, PCBs, and PBDEs [15,33–35]. In spite of time consuming and laborious procedures used to isolate OCPs and PCBs, and the use of a 60 m DB-17 capillary column and a 25 mm Sil-8 capillary column in series with an HT-5 capillary column, difficulties arose quantifying PCBs 41, 56/60, 70, 92/84, and 196/203 [18,36]. In contrast, PCBs 41, 56, 70, 92/84, and 196/203 can be quantified by using our method. Our method also affords separation of PCBs 28, 52, 101, 118, 138, 153, and 180, seven PCB congeners, used as indicators of PCBs for regulatory purposes and risk assessment [33–35], and separation of PBDE 47 and PCB 180 was attained in contrast to methods reported by others [13–15]. The seven PCB congeners can be resolved by using other methods, but the approaches used are more time-consuming and laborious. For example, Bucholski et al., employed fractionation followed by dual column chromatography [35] and Galceran et al., [33] and Hajslová et al., [34] achieved separation by analyzing the extracts on four to six separate capillary columns.

Fractionation of OCPs, PCBs, and PBDEs typically yields three extracts. Complete separation of these classes of molecules is difficult to achieve, however, leading to compound overlap among the extracts. Compound overlap is not a problem using our method because the OCPs, PCBs, and PBDEs are present in one extract. Regarding the time to analyze three versus one extract, we estimate that it would take 40 h to analyze a batch of 10 samples compared to 30 h to analyze the same batch using our method. This estimate is based on the assumption that OCPs are analyzed using a single column and an analytical time of 1 h; PCBs are analyzed by using dual chromatography and an analytical time of 2 h, and that PBDEs can be analyzed using a single column with an analytical time of about 1 h. The HRGC/ECD analysis of the 500 human extracts conducted in this study would, thus take 833 days using other methods compared to 625 days using our method, resulting in a time savings of 208 days (about 7 weeks). The time savings is actually likely to be greater because differences in time to isolate the analytes or to analyze the chromatograms is not considered. The only potential disadvantage of our method is band-broadening of the higher molecular weight PBDEs due to their long retention times.

Acknowledgements

This study was partially supported by the National Institute of Environmental Health Sciences (R29 ES09042 and RO1 ES08324).

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