Fast Gas Chromatography–Time-of-Flight Mass Spectrometry of Polychlorinated Biphenyls and Other Environmental Contaminants

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Abstract

Practical applications of fast gas chromatography (GC) with time-of-flight mass spectrometry (TOFMS) are presented. A narrow-bore column (0.10-mm i.d.) is used to analyze over 100 specific polychlorinated biphenyl congeners in an Aroclor mix and a sediment sample in 10.5 min. Sample preparation is minimized for the sediment to more closely match the speed advantage gained by using fast GC–TOFMS. The possibility of using a 0.53-mm-i.d. column operated under vacuum-outlet conditions for fast GC–TOFMS is established for Aroclors and a suite of environmental contaminants. Fast acquisition rates and automated peak-find and spectral deconvolution capabilities are demonstrated for TOFMS.

Introduction

The current interest in fast gas chromatography (GC) is motivated by the promise the technique has offered since it was first explored in the 1950s and 1960s (1–6), which is increasing the speed of analysis and improving signal-to-noise with narrower peaks. A wealth of papers on the theory of fast GC is available in the literature (7–11), including a recent review by Cramers and Leclercq (12) that defines limits and offers guidelines for optimization of the technique.

In order to take full advantage of the benefits of fast GC with narrow-bore columns, careful attention to injector and detector parameters is necessary. Any extra-column contribution to band-broadening defeats the efficiency proffered by these columns (13,14). In particular, inlet-liner inside diameter, split ratio, and splitless injection volume are critical. Van Ysacker et al. (15) explored nonsplitting injections in detail, including on-column injection. Another recent publication used "large volume" (1–3 µL) on-column injection for a 0.10-mm column (16). Some injections rely on more specialized techniques to produce narrow input bands, such as cryofocusing and thermal desorption (17–21). Standard GC detectors must have small volumes or use high dilution gas flow rates (13).

Up until now in this introduction, the definition of fast (or high-speed) GC has been carefully avoided. Bertsch even noted in a 1997 editorial (22) that terms such as fast, very fast, and ultra-fast chromatography were introduced at a scientific meeting. They have since shown up in at least one publication (23). The recent definitions put forth by Hinshaw on the four levels of capillary GC (including those that are fast) are based on the relative speed of analysis, column dimensions, and the type of GC equipment necessary: conventional or specialized (24). The philosophical question though is that if a GC analysis is reduced from 75 to 15 min (no matter the method in which it is achieved) is that fast GC. The answer is probably yes, until that same analysis is reduced to 75 s. Generally though, fast GC is characterized by narrow-bore columns (0.10 mm or less), fast temperature programming, and high carrier gas velocities.

Column choice in fast GC depends on the application. If a method that takes 30 min on a 0.25-mm column is already optimized for the necessary resolution, then miniaturization may be the only choice (e.g., going to a 0.10-mm column) in order to increase speed (25). If resolution is at a premium, then shortening the column, increasing the carrier flow rate, or both are options for increasing the analysis speed. In addition to approaches that use narrow-bore columns (20,25,26), other options for fast GC include the use of packed capillaries (14,27), multicapillaries (11,27,28), very fast column temperature programming through resistive heating (20,29–32), and vacuum-outlet GC (33,34). More specialized methods are pressure-tunable column ensembles (35–37), supersonic molecular beams (38,39), and comprehensive two-dimensional GC (40–45). Comprehensive two-dimensional GC is not always fast in the first dimension, in which separations are on the order of minutes, but second-dimension chromatograms are performed in seconds.

A recent development in vacuum-outlet GC concerns the use of a capillary restrictor in front of a short 0.53-mm column that terminates in the source of a mass spectrometer (MS) (46,47). The restrictor allows for the proper operation of a normal GC inlet while low-pressure conditions favoring fast GC are maintained in the 0.53-mm column by the vacuum of the MS. Mastovska et al. (48) used this setup to great practical advantage for the analysis of pesticides in carrots, noting a three-fold increase in the speed of separation, better sensitivity, and increased sample capacity. Another benefit was an improved analysis of thermally labile pesticides.

The utility of fast GC is greatly enhanced when it is combined with an MS. Unfortunately, most scanning MSs such as quadrupole filters, ion traps, and magnetic sectors do not have the necessary spectral acquisition speed to adequately define the narrow peaks generated by fast GC, especially if they are operated across a wide *m/z* range (35,36). Only one to a few spectra per second are typically acquired with these systems (49), although van Ysacker et al. (50) reported 10-spectra/s rates for a small, fast magnet operated from 50 to 500 u. One way to get around the acquisition speed limitation is to use selected ion recording (SIR), in which only a few *m/z* channels are monitored during a GC run. The quantitative value of SIR though is severely limited.

The introduction of time-of-flight MS (TOFMS) with time array detection offers an elegant solution to recording mass spectra at a speed compatible with fast GC (51,52). This method allows for the potential collection of hundreds of spectra per second with high efficiency. TOFMS also has the unique capability to produce nonskewed mass spectra, unlike slow scanning MSs in which the sample concentration changes that occur in the source during the elution of a chromatographic peak cause distortion of the mass spectrum (52). TOFMS is a "snapshot" technique in which ion packets are extracted and the mass is analyzed almost simultaneously (53). Nonskewed spectra are what make peak-find and spectral deconvolution algorithms possible for overlapping chromatographic peaks. In essence, TOFMS adds another separation dimension to fast GC, which makes a loss of chromatographic resolution for the sake of speed more forgiving. Because of these characteristics, TOFMS has been evaluated as a detector for fast GC (23,35,36,54,55) and comprehensive two-dimensional GC (45,56).

This study demonstrates practical applications of fast GC coupled with TOFMS using instrumentation that is already available commercially. A standard injector operated in splitless mode is used to introduce samples to either a 0.53-mm column operated in vacuum-outlet mode or a 0.1-mm column. For the 0.10-mm column, emphasis is placed on achieving quantitative values for as many specific polychlorinated biphenyl (PCB) congeners as is practical in an Aroclor mix and a Great Lakes sediment extract, keeping the analysis time fast. A simple extraction and cleanup method is proposed for the sediment, which is very short compared with more conventional methods.

The possibilities of using vacuum-outlet GC for speed combined with TOFMS as another separation dimension are explored for PCBs and a standard containing a suite of environmentally significant compounds. The impact of acquisition speed on producing deconvoluted mass spectra from coeluting compounds is discussed.

Experimental

Standards and samples

All solvents were GC[2] grade and obtained from Burdick and Jackson (Muskegon, MI). PCB stock standards were obtained from AccuStandard (New Haven, CT) as congener mixes 1–5, representing the congeners contained in Aroclors 1242, 1254, and 1260. Dilutions of these mixes for calibration standards were prepared in isooctane. Aroclor standards in isooctane (35 µg/mL) were also purchased from AccuStandard. A test sample of Aroclors 1221, 1242, 1254, and 1262 was prepared by mixing together 20, 40, 40, and 40 µL, respectively, of the Aroclor standards. The PCB-contaminated reference sediment (EC-1) was purchased from Wellington Laboratories (Guelph, ON, Canada). The sediment was a freeze-dried, ground composite from various locations in the Great Lakes basin that had certified concentration values for select PCB congeners.

In order to test the vacuum-outlet GC–TOFMS system, a complex standard of organophosphorus and organochlorine pesticides, nitroaromatics, phenols, and base–neutral priority pollutants (including polynuclear aromatic hydrocarbons) was prepared in hexane from stocks obtained from Restek Corporation (Bellefonte, PA). Concentrations ranged from 0.5 to 2.5 ng/µL.

Extraction of sediment

A Bransonic 2510 ultrasonic bath (Branson, Danbury, CT) was used for extracting PCBs from sediment samples. Approximately 5 g of freeze-dried sediment was placed into a 15-mL glass vial. Ten milliliters of hexane was added, a polytetrafluoroethylene-lined cap was placed on the vial, and the vial contents were shaken vigorously to wet the sediment thoroughly with the hexane. The vial was placed into the ultrasonic bath at 55°C and sonicated for 10 min. The vial was then removed from the bath, allowed to set for 20 min, and the clear extract was pipetted off the top of the sediment into a clean glass bottle. Two additional extractions were performed under the same conditions, but only 5 mL of hexane was used for each of these extractions. The extracts were combined and filtered through approximately 7.5-g copper sticks (LECO Corporation, St. Joseph, MI) atop a small amount of anhydrous sodium sulfate (J.T. Baker, Phillipsburg, NJ). Whatman (Maidstone, U.K.) 125-mm Dia 40 filter papers were used to contain the copper and sodium sulfate.

Extracts were concentrated to approximately 0.5 mL with a gentle stream of dry nitrogen while in a heating block at 45°C. Additional hexane was used to rinse the concentration vial and bring the final volume of the extracts to 1.0 mL.

Cleanup of sediment extract

Supelclean LC-Si SPE tubes 6 mL in volume and containing 1 g of silica were obtained from Supelco (Bellefonte, PA). A

Table I. RRTs for PCBs on a 40-m × 0.10-mm × 0.10-µm DB-XLB

IUPAC no.*	Cl no.	Cl position	RT (s)	RRT†
1	1	2	226.4	0.748
2	1	3	253.6	0.838
3	1	4	258.5	0.854
4‡	2	2-2	265.1	0.876
10‡	2	26	265.5	0.877
9	2	25	283.9	0.938
7	2	24	284.7	0.941
6	2	2-3	289.7	0.957
5	2	23	293.9	0.971
8	2	2-4	295.5	0.976
HCBz	6		302.7	1.000
19	3	26-2	304.3	1.005
14	2	35	305.7	1.011
18	3	25-2	319.5	1.055
17	3	24-2	321.3	1.062
12	2	34	322.8	1.066
27‡	3	26-3	325.1	1.075
13‡	2	3-4	325.2	1.075
24	3	236	327.3	1.081
16	3	23-2	330.7	1.092
15	2	4-4	331.6	1.096
32	3	26-4	332.7	1.099
34‡	3	35-2	337.7	1.116
54‡	4	26-26	337.8	1.117
29	3	245	341.3	1.128
26	3	25-3	346.2	1.144
25	3	24-3	348.0	1.150
31‡	3	25-4	353.1	1.167
53‡	4	25-26	353.2	1.168
28	3	24-4	354.7	1.172
33‡	3	34-2	356.1	1.177
20‡	3	23-3	356.3	1.178
51	4	24-26	357.0	1.180
45	4	236-2	361.9	1.196
22	3	23-4	363.2	1.200
46	4	23-26	365.5	1.208
73	4	26-35	367.5	1.215
69	4	246-3	369.5	1.221
52	4	25-25	371.3	1.227
48	4	245-2	373.4	1.234
49	4	24-25	374.1	1.236
104‡	5	246-26	376.6	1.244
47‡	4	24-24	376.5	1.244
75	4	246-4	377.5	1.248
44	4	23-25	382.6	1.264
59	4	236-3	384.6	1.271
42	4	23-24	385.0	1.273
35	3	34-3	386.7	1.279
71	4	26-34	388.0	1.282
41	4	234-2	389.3	1.286
64	4	236-4	392.8	1.298
103‡	5	246-25	393.7	1.301
37‡	3	34-4	393.9	1.301
40‡	4	23-23	393.8	1.302
100	5	246-24	397.6	1.315
67	4	245-3	401.6	1.327
63‡	4	235-4	406.3	1.342
93‡	5	2356-2	406.4	1.343
95	5	236-25	408.1	1.348
74	4	245-4	408.9	1.351
70	4	25-34	410.4	1.356
91‡	5	236-24	412.4	1.362
66‡	4	24-34	412.7	1.363
92	5	235-25	418.9	1.385
84‡	5	236-23	420.2	1.388
56‡	4	23-34	420.6	1.389
101‡	5	245-25	422.5	1.397
90‡	5	235-24	422.5	1.397
60	4	234-4	423.6	1.399
99	5	245-24	425.8	1.407
119‡	5	246-34	430.0	1.421
83‡	5	235-23	430.6	1.423
97	5	245-23	433.6	1.433
87	5	234-25	438.8	1.450
136‡	6	236-236	439.8	1.454
117‡	5	2356-4	440.0	1.455
115‡	5	2346-4	441.0	1.457
154‡	6	245-246	441.0	1.458
85‡	5	234-24	441.6	1.459
110	5	236-34	444.4	1.468
81	4	345-4	445.5	1.473
151	6	2356-25	448.9	1.484
82	5	234-23	449.9	1.486
135	6	235-236	450.5	1.488
77‡	4	34-34	452.0	1.493
144‡	6	2346-25	452.0	1.494
147	6	2356-24	454.5	1.501
149	6	236-245	454.9	1.503
124	5	345-25	456.8	1.510
123‡	5	345-24	459.9	1.519
109‡	5	235-34	460.0	1.520
134	6	2356-23	461.4	1.525
118	5	245-34	462.9	1.530
131	6	2346-23	464.0	1.533
165‡	6	2356-35	466.7	1.543
122‡	5	345-23	466.8	1.543
146	6	235-245	467.7	1.545
114	5	2345-4	468.8	1.549
153‡	6	245-245	471.7	1.558
132‡	6	234-236	472.0	1.560
179	7	2356-236	475.8	1.572
105‡	5	234-34	477.7	1.579
141‡	6	2345-25	478.1	1.580
176	7	2346-236	479.9	1.585
137	6	2345-24	481.6	1.591
130	6	234-235	483.8	1.600
164	6	236-345	485.0	1.602
138	6	234-245	487.4	1.610
163	6	2365-34	487.8	1.613

Continued on next page

* IUPAC number explanation shown in PCB nomenclature subsection.
† RRT = RT of PCB / RT of HCBz.
‡ Coeluting congeners.

Table I. RRTs for PCBs on a 40-m × 0.10-mm × 0.10-µm DB-XLB *(continued)*

IUPAC no.*	Cl no.	Cl position	RT (s)	RRT†	IUPAC no.*	Cl no.	Cl position	RT (s)	RRT†
178‡	7	2356-235	488.7	1.615	157	6	234-345	521.5	1.724
129‡	6	2345-23	489.1	1.616	180	7	2345-245	524.2	1.732
158	6	2346-34	489.6	1.618	193	7	2356-345	525.3	1.735
175	7	2346-235	491.7	1.626	200	8	23456-236	526.1	1.739
187	7	2356-245	493.5	1.630	191	7	2346-345	527.7	1.744
183	7	2346-245	496.7	1.641	170	7	2345-234	540.1	1.784
185‡	7	23456-25	503.3	1.663	199	8	2345-2356	541.2	1.788
128‡	6	234-234	503.1	1.663	190	7	23456-34	542.5	1.793
174	7	2345-236	505.5	1.670	196	8	2345-2346	544.6	1.799
167	6	245-345	506.9	1.675	203	8	23456-245	545.3	1.801
202	8	2356-2356	508.4	1.681	208	9	23456-2356	556.8	1.840
177	7	2356-234	511.1	1.688	189	7	2345-345	560.3	1.851
201‡	8	2346-2356	512.8	1.695	*207*‡	9	23456-2346	561.5	1.856
171‡	7	2346-234	513.4	1.696	195‡	8	23456-234	562.0	1.857
173	7	23456-23	515.4	1.703	194	8	2345-2345	574.1	1.897
197	8	2346-2346	517.5	1.710	205	8	23456-345	577.9	1.909
156	6	2345-34	519.5	1.716	206	9	23456-2345	590.6	1.951
172	7	2345-235	520.0	1.718	*209*	10	23456-23456	603.3	1.994

* IUPAC number explanation shown in PCB nomenclature subsection.
† RRT = RT of PCB / RT of HCBz.
‡ Coeluting congeners.

Table II. Quantitation Masses for PCBs

Cl no.	No. of PCBs	Masses
1	2	188+190
2	10	222+224
3	18	256+258+260
4	24	290+292+294
5	22	324+326+328
6	23	358+360+362
7	18	394+396+398
8	10	428+430+432
9	2	462+464+466

cartridge was placed into a Visiprep solid-phase extraction manifold (Supelco) and vacuum-eluted with 5 mL hexane (discard). A 0.5-mL sediment extract was placed on top of the cartridge via a syringe. The cartridge was eluted with 6 mL hexane to collect the PCBs. The PCB fraction was concentrated to just under 0.5 mL, as described previously, after the addition of 0.5 mL isooctane. A small amount of isooctane was used to rinse the concentration vial and bring the final volume to 0.5 mL.

GC–TOFMS (narrow bore)

Samples were analyzed using a LECO Pegasus III GC–TOFMS in electron ionization (EI) mode. Simply described, ion packets formed by EI were (*a*) pulsed at 5 kHz into a field-free drift tube at the same energy, in which they were (*b*) separated in time according to the different velocities of different *m/z* ions with (*c*) subsequent detection as a transient representing a complete mass spectrum. Transients were summed according to the necessary spectra collection rate, with 500 spectra/s being the maximum (10 summed transients), before being written to a file.

The TOFMS source temperature was set at 220°C. The detector was operated at 1850 V. The stored mass range was 120 to 520 u collected at 20 spectra/s. The transfer line temperature was constant at 260°C.

Mass spectral data were processed using automated peak-find and deconvolution software that was part of the Pegasus platform. Entering chromatographic peak widths and minimum desired signal-to-noise were the only requirements.

Fast splitless injections of 0.25 µL were made with an Agilent (Wilmington, DE) 7683 injector into a 2-mm Siltek open liner (Restek) that was set at 260°C. The split valve was opened after 60 s. Hydrogen at a constant flow of 0.7 mL/min was used for the carrier gas. The linear velocity at a GC oven temperature of 225°C was approximately 40 cm/s. A 40-m × 0.10-mm × 0.10-µm DB-XLB column from J&W Scientific (Folsom, CA) in an Agilent 6890 GC was programmed as follows: 75°C for 0.5 min, 50°C/min to 125°C, and then 20°C/min to 305°C. The run time was 10.5 min. An oven insert ("pillow") from Agilent was used to reduce the GC oven volume by approximately 50% for more accurate heating and faster cooling.

GC–TOFMS (vacuum-outlet)

For the vacuum-outlet PCB work, the TOFMS instrumentation and conditions were the same as described previously, except that the transfer line was operated at 240°C and spectra were collected 15 times per second. A 3-m × 0.18-mm piece of uncoated, deactivated fused silica was connected to a 5-m × 0.53-mm × 0.5-µm CP-Sil 8 CB column (Varian Chrompack International B.V., Middleburg, The Netherlands) via a press-fit. A similar, prebuilt configuration commercially available from Varian Chrompack is the Rapid-MS column. The GC oven program for PCBs was 60°C for 0.25 min, 120°C/min to 120°C, and then 40°C/min to 260°C. The run time was 4.25 min. Fast splitless injections of 1 µL were

Table III. Congener-Specific PCB Quantitation for an Aroclor Mix

IUPAC no.*	Cl position	Actual† (pg/µL)	Measured‡ (pg/µL)	Coelution
1	2	1840	1610	
3	4	1040	820	
4	2-2	634	627	10
5	23	50.0	61.9	
6	2-3	338	300	
7	24	111	126	
8	2-4	1340	1100	
9	25	150	128	
10	26	60.0	440	4
12	34	35.5	50.7	
13	3-4	76.0	88.8	
15	4-4	518	338	
16	23-2	335	300	
17	24-2	346	431	
18	25-2	936	768	
19	26-2	85.0	87.8	
20	23-3	71.5	587	33
22	23-4	294	247	
24	236	14.0	19.7	
25	24-3	61.5	70.9	
26	25-3	134	182	
27	26-3	42.5	57.6	
28	24-4	733	592	
29	245	8.5	24.0	
31	25-4	792	939	
32	26-4	204	251	
33	34-2	538	765	20
34	35-2	2.0	15.1	
35	34-3	7.0	17.3	
37	34-4	207	211	
40	23-23	91.0	120	
41	234-2	71.5	126	
42	23-24	136	154	
44	23-25	612	516	
45	236-2	100	154	
46	23-26	38.0	57.0	
47	24-24	115	113	
48	245-2	134	178	
49	24-25	384	495	
51	24-26	56.0	36.2	
52	25-25	913	774	
53	25-26	89.0	91.8	
56	23-34	245	242	
59	236-3	39.5	42.4	
60	234-4	141	244	
63	235-4	15.0	29.6	
64	236-4	244	281	
66	24-34	458	357	
67	245-3	15.0	31.8	
70	25-34	749	993	
71	26-34	124	116	
74	245-4	279	269	
75	246-4	5.0	21.8	
77	34-34	30.5	88.4	144
82	234-23	140	154	
83	235-23	60.0	93.0	119
84	236-23	284	438	
85	234-24	169	238	115
87	234-25	464	376	
91	236-24	118	157	
92	235-25	143	146	
95	236-25	783	1090	
97	245-23	313	346	
99	245-24	363	288	
101	245-25	987	942	
105	234-34	369	349	
109	235-34	45.0	73.3	123
110	236-34	1060	833	
114	2345-4	23.0	31.6	
115	2346-4	24.0	221	85
117	2356-4	26.0	74.4	
118	245-34	830	667	
119	246-34	8.0	57.0	83
122	345-23	11.0	35.1	
123	345-24	18.0	70.0	109
124	345-25	32.0	76.4	
128	234-234	163	195	
129	2345-23	41.0	264	158
130	234-235	63.0	55.5	
131	2346-23	19.0	35.5	
132	234-236	341	1640	153
134	2356-23	48.0	69.0	
135	235-236	128	296	
136	236-236	172	201	
137	2345-24	43.0	49.2	
138	234-245	829	670	
141	2345-25	262	442	
144	2346-25	65.0	95.9	
146	235-245	124	128	
147	2356-24	10.0	1060	149
149	236-245	1010	1280	
151	2356-25	383	429	
153	245-245	1060	1240	132
156	2345-34	98.0	136	
157	234-345	19.0	28.8	
158	2346-34	101	149	129
163	2356-34	253	275	

Continued on next page

* IUPAC no. explanation shown in PCB nomenclature subsection.
† The calculated concentration of congeners from reference 58.
‡ The measured value from a GC–TOFMS analysis of the Aroclor mix.

Table III. Congener-Specific PCB Quantitation for an Aroclor Mix *(continued)*

IUPAC no.*	Cl position	Actual† (pg/µL)	Measured‡ (pg/µL)	Coelution	IUPAC no.*	Cl position	Actual† (pg/µL)	Measured‡ (pg/µL)	Coelution
164	236-345	63.0	108		**189**	2345-345	4.0	5.1	
167	245-345	29.0	47.6		**190**	23456-34	81.0	101	
170	2345-234	357	619		**191**	2346-345	13.0	21.4	
171	2346-234	99.0	189		**193**	2356-345	70.0	134	
172	2345-235	70.0	144		**194**	2345-2345	380	363	
173	23456-23	3.0	135	**171**	**195**	23456-234	139	173	
174	2345-236	690	583		**196**	2345-2346	241	279	
175	2346-235	19.0	25.1		**197**	2346-2346	14.0	26.9	
176	2346-236	77.0	112		**199**	2345-2356	492	554	
177	2356-234	302	287		**200**	23456-236	69.0	78.7	
178	2356-235	134	234		**201**	2346-2356	66.0	81.9	
179	2356-236	374	353		**202**	2356-2356	120	127	
180	2345-245	1440	1180		**203**	23456-245	413	346	
183	2346-245	307	554		**205**	23456-345	16.0	51.0	
185	23456-25	93.0	133		**206**	23456-2345	122	153	
187	2356-245	980	873		**208**	23456-2356	30.0	28.7	

* IUPAC no. explanation shown in PCB nomenclature subsection.
† The calculated concentration of congeners from reference 58.
‡ The measured value from a GC–TOFMS analysis of the Aroclor mix.

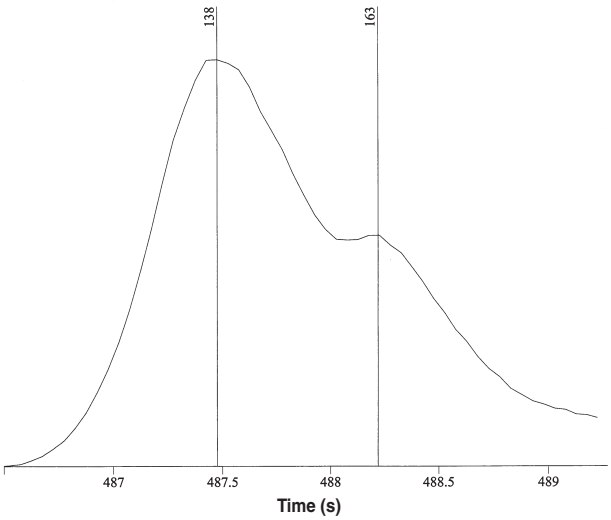

Figure 1. Separation of hexachlorobiphenyls 138 and 163 in an Aroclor mix on a 40-m × 0.10-mm × 0.10-µm DB-XLB column.

made into a 4-mm CarboFrit-packed gooseneck liner (Restek) that was set at 260°C. The split valve was opened after 15 s. Helium carrier gas was set to be constant at 5 mL/min, although vacuum readings from the MS indicated that this flow was probably inaccurate for the hybrid column system. The linear velocity was estimated at 175 cm/s at a GC oven temperature of 200°C.

For the semivolatiles work using the complex standard described previously, mass spectra were acquired at 5, 10, 20, and 40 spectra/s in the range of 45 to 520 u. The transfer line was at 270°C. The GC oven was programmed from 40°C (0.25 min) to 295°C at 60°C/min for a total run time of 4.5 min. Splitless injection conditions were as described for the PCB vacuum-outlet GC work.

Results and Discussion

Use of hydrogen for narrow-bore column analyses

Although safety concerns tend to lead analysts in the United States to use helium as a carrier gas, hydrogen is a better choice for speed and efficiency (12,57). In fact, its use is almost mandated for 0.10-mm (or less) columns because of the high head pressures necessary to produce an optimum velocity for helium. For this work, which employed a 40-m × 0.10-mm column, the range of head pressure necessary to keep the hydrogen flow constant at 0.7 mL/min across the GC oven temperature range of 75°C to 305°C was 86 to 139 psi. If helium had been used, a head pressure greater than 200 psi would have been needed in the upper temperature range of the GC oven program. This pressure is not possible with most GC systems.

PCB nomenclature

PCBs are listed by their IUPAC number in the tables of this study. A simple convention for the single-ring chlorine substitution pattern is used to denote structure (e.g., 234–245 is 2,2',3,4,4',5'-hexachlorobiphenyl). Congeners are classified according to their significance in Aroclors 1242, 1254, or 1260 (58) as (*a*) boldfaced for a congener between 0.05% and 1.0% (w/w), (*b*) boldfaced and underlined for a congener greater than 1.0% (w/w), and (*c*) italicized for a trace or undetected congener.

Table IV. Certified PCB Values and Fast GC–TOFMS Measured Values for a Great Lakes Basin Sediment Extract

IUPAC no.*	Cl position	Certified† (ng/g)	Certified‡ (pg/µL)	Ext. #1§ (pg/µL)	Ext. #2§ (pg/µL)	Total (pg/µL)	Ext. #1§ %recovery	Total (ng/g)	High limit** (ng/g)
18	25-2	47.4	253	337	70.9	408	83	76.5	63.5
28	24-4	48.7	260	278	67.0	345	81	64.6	65.7
44	23-25	64.7	345	548	125	674	81	126.2	96.1
52	25-25	99.4	530	689	154	842	82	157.8	142.6
87	234-25	44.9	240	359	94.8	454	79	85.0	59.4
101	245-25	109.4	584	927	214	1141	81	213.9	183.8
105	234-34	34.2	183	292	82.4	374	78	70.1	47.7
110	236-34	120.1	641	751	195	946	79	177.2	187.4
118	245-34	79.8	426	602	171	773	78	144.9	116.9
128	234-234	14.5	77.4	138	57.9	196	71	36.8	20.9
137	2345-24	3.8	20.3	39.2	n.d.††	39.2	100	7.3	4.8
138	234-245	72.0	384	568	141	709	80	132.9	98.3
141	2345-25	19.4	104	211	37.1	248	85	46.5	23.4
151	2356-25	16.6	88.6	192	54.5	246	78	46.1	21.5
153	245-245	68.2	364	745	206	951	78	178.2	90.3
170	2345-234	16.8	89.7	177	48.0	225	79	42.2	24.4
180	2345-245	44.9	240	299	80.1	379	79	71.0	68.1
183	2346-245	15.2	81.1	149	21.0	170	88	31.9	22.8
194	2345-2345	13.1	69.9	97.0	30.5	127	76	23.9	18.7
201	2346-2356	7.3	39.0	18.2	n.d.	18.2	100	3.4	12.3
206	23456-2345	7.0	37.4	43.2	12.4	55.6	78	10.4	10.0
209	23456-23456	1.4	7.5	n.d.	n.d.	n.d.	n.d.	n.d.	2.2

* IUPAC no. explanation shown in PCB nomenclature subsection.
† Certified reference value of sediment.
‡ Certified reference value of sediment based on extracted sample size.
§ Sequential extractions labeled as Ext. #1 and Ext. #2.
** The high range of certified values.
†† n.d., not detected.

Table V. EDLs for Key PCBs*

IUPAC no.	Cl no.	Masses	EDL (pg/µL)	EDL† (pg)
4	2	222+224	1.1	0.28
8	2	222+224	1.0	0.24
18	3	256+258+260	2.4	0.60
28	3	256+258+260	2.2	0.56
44	4	290+292+294	3.1	0.76
52	4	290+292+294	2.5	0.61
101	5	324+326+328	3.9	0.96
118	5	324+326+328	5.2	1.3
138	6	358+360+362	8.7	2.2
153	6	358+360+362	5.7	1.4
174	7	394+396+398	8.8	2.2
180	7	394+396+398	8.4	2.1
194	8	428+430+432	12	2.9
199	8	428+430+432	9.1	2.3
206	9	462+464+466	16	4.0
209	10	496+498+500	16	3.9

* IUPAC no. explanation shown in PCB nomenclature subsection.
† Based on a 0.25-µL injection.

PCBs on a narrow-bore column

Prior to the analysis of PCBs on the narrow-bore column, three parameters were defined: optimal injection volume, sample capacity, and TOFMS acquisition rate. Splitless injections of 1 µL resulted in severely broadened or split peaks, and 0.25-µL injections resulted in narrow peaks with widths at a half height of approximately 0.7 s. Injection of a standard that contained 10 ng/µL of several PCBs resulted in fronting peaks (although the width at half-height remained at 0.7 s), which was an indication of an overload of the 0.10-mm × 0.10-µm DB-XLB column. With an injection volume of 0.25 µL, this corresponded with 2.5 ng of each PCB on-column. A 2.5-ng/µL standard (625 pg injected) showed good peak shapes and was used as the sample capacity limit for the narrow-bore XLB, although in reality the capacity of the column is somewhere between 625 and 2500 pg. For chromatographic peaks that were approximately 1.5-s wide at their base, an acquisition rate of 20 spectra/s was chosen to adequately define the peak, especially for quantitative purposes.

Relative retention times (RRTs) for the 144 PCBs in mixes 1–5 are shown in Table I for the narrow-bore XLB column. There were 17 coelutions involving 34 PCBs, which can be considered significant on the basis of congener concentration in Aroclors (or environmental samples in which substantial

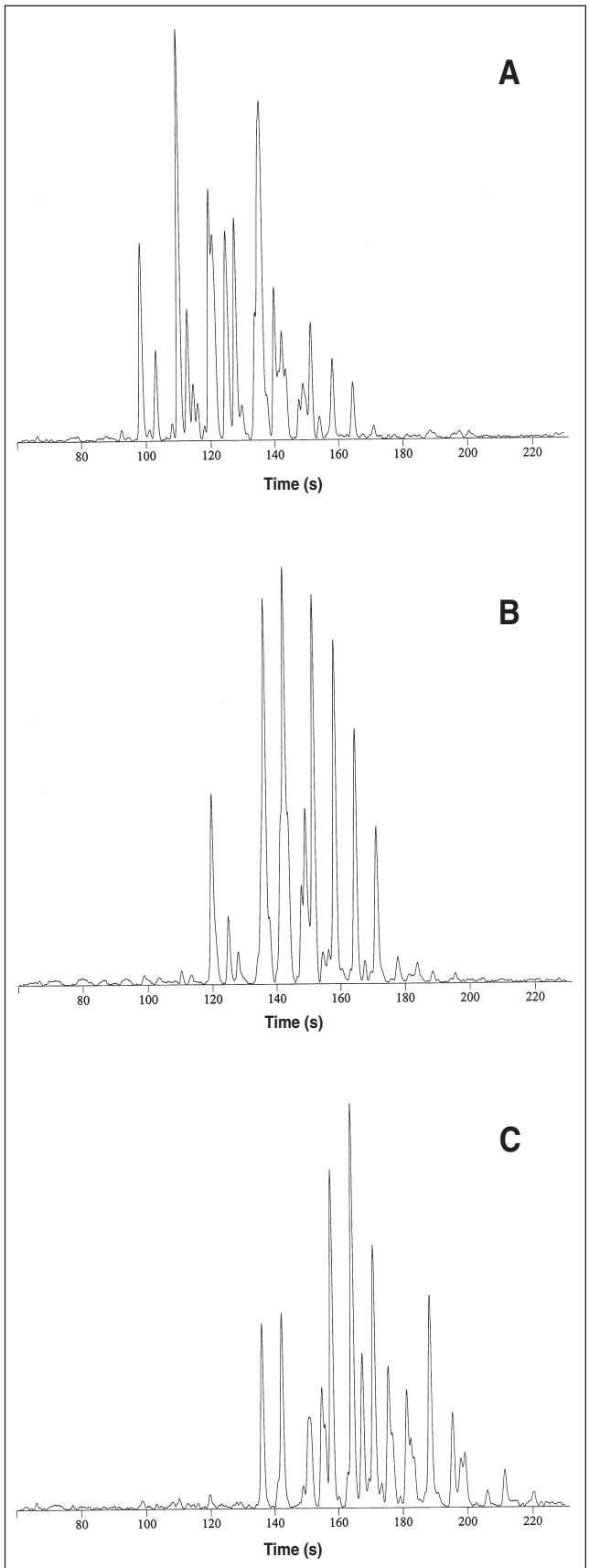

Figure 2. Reconstructed ion chromatograms of Aroclors analyzed using vacuum-outlet GC–TOFMS: (A) Aroclor 1248, (B) Aroclor 1254, and (C) Aroclor 1260.

degradation or transformation has not occurred). Of the 34 PCBs involved in the coelutions, 21 could be measured separately by MS because they are in a different homologue group than their coeluter. A special case was the 77–144 pair, in which PCB 144 can be identified or quantitated by its 358–360–362–364 molecular ion group, but its fragmentation loss of Cl2 produces a 288–290–292–294 cluster that interferes with the molecular ion group from PCB 77 (a tetrachlorobiphenyl). PCB 77 (34–34) is significant not only because of its concentration in Aroclors, but also because it is one of the coplanar PCBs, which are believed to be more toxic than those PCBs that cannot assume a planar configuration.

Of the remaining coelutions, probably the most important was the 153–132 pair. Both congeners exist in substantial quantities in Aroclors, and PCB 153 is on many "short lists" for monitoring purposes (59). The XLB achieves one resolution, which is tough to do on any phase (that of the 138–163 pair). PCB 138 is a congener on short lists, and 163 is significant in Aroclors and has toxic potential (60). When combined with TOFMS, the highly efficient XLB column used in this work should be capable of measuring up to 116 of the 129 primary congeners that compose Aroclors 1242, 1254, and 1260 in 10.5 min. This is likely the fastest congener-specific PCB work ever reported for that many congeners, rivaled only by the reports of Larsen (60,61), and adds to the reputation of DB-XLB being a superior phase for PCB analysis when combined with MS (58,62–65).

Aroclor mix quantitation for PCBs

Calibration curves were generated from PCB standard concentrations of 25, 50, 100, 250, 500, 1000, and 2500 pg/µL using hexachlorobenzene (HCBz) as an internal standard. The quantitation masses are shown in Table II. For HCBz, the sum of three ions was used (282+284+286). All calculations were based on peak area. Upon inspection, some of the curves were not linear through the 2500-pg/µL point, thus it was eliminated. This did not affect most of the results, because they fell within the 25- to 1000-pg/µL range. For those few Aroclor mix PCBs that were above 1000 pg/µL, a two-point curve of 1000 to 2500 pg/µL was employed for quantitation. Table III summarizes the results of the quantitative analysis of the Aroclor mix by fast GC–TOFMS with the narrow-bore XLB column. Generally speaking, the measured values were close to the calculated values (generated from reference 58) and demonstrated the validity of the fast congener-specific analysis. As might be expected for an analysis in which concentration ranges vary by an order of magnitude or more, a few additional coelutions were noted. Specifically, it appears that the values for PCBs 129, 147, and 173 were biased high because of coelutions with congeners 158, 149, and 171, respectively. The separation of PCB 138 and 163 was good enough for the quantitative estimates of each congener (Figure 1).

Sediment quantitation for PCBs

In order to fully utilize the value of a fast GC method, the sample preparation step should also be reasonably fast and allow for easy multiple processing of samples. Most Soxhlet extraction methods for solids run between 18 and 24 h, and

Table VI. RTs of Semivolatile Compounds for a Low-Pressure GC–TOFMS System

No.	Compound	RT (s)	No.	Compound	RT (s)
1	Benzaldehyde	37.60	53	2-Methyl-4,6-dinitrophenol	119.88
2	Phenol	40.95	54	Propachlor	120.23
3*	2-Chlorophenol	41.11	55	Dichloroprop methyl ester	120.83
4	Bis(2-chloroethyl)ether	41.18	56*	*N*-Nitrosodiphenylamine	120.83
5	Bis(2-chloroisopropyl)ether	49.98	57*	Demoton O	120.97
6	2-Methylphenol	50.25	58	2,4-D-Methyl ester	123.23
7	Acetophenone	51.08	59	Ethoprop	123.38
8	Hexachloroethane	51.48	60	Naled	125.05
9	*N*-Nitrosodi-*n*-propylamine	52.53	61	4-Bromophenyl phenyl ether	128.05
10	1,2-Dibromo-3-chloropropane	52.78	62	α-BHC	128.40
11	4-Methylphenol	53.08	63	Phorate	129.00
12	Nitrobenzene	53.50	64*	*trans*-Diallate	129.25
13	Isophorone	58.28	65*	Sulfotepp	129.41
14	2-Nitrophenol	59.60	66	Hexachlorobenzene	129.60
15	2,4-Dimethylphenol	62.80	67	Trifluralin	129.70
16	2-Nitrotoluene	63.75	68*	1,3,5-Trinitrobenzene	130.18
17	Bis(2-chloroethoxy)methane	64.23	69	2,4,6-Trinitrotoluene	130.88
18	2,4-Dichlorophenol	64.55	70	Monocrotophos	131.28
19	Naphthalene	66.15	71	Dimethoate	132.85
20	3-Nitrotoluene	68.60	72	Demoton S	133.18
21	4-Chloroaniline	69.38	73*	β-BHC	134.31
22	4-Nitrotoluene	70.83	74*	Simazine	134.70
23	Hexachlorobutadiene	71.25	75	Pentachlorophenol	134.70
24*	Caprolactam	77.88	76	γ-BHC	135.03
25	Dichlorvos	77.88	77	Atrazine	135.78
26	2-Methylnaphthalene	80.93	78	2,4,5-TP methyl ester	136.05
27	4-Chloro-3-methylphenol	81.95	79	Phenanthrene	136.35
28	Hexachlorocyclopentadiene	86.53	80	Anthracene	137.33
29	2,4,6-Trichlorophenol	88.93	81	2,4,5-T methyl ester	139.00
30	2,4,5-Trichlorophenol	89.68	82	δ-BHC	140.18
31	2-Chloronaphthalene	91.05	83	Disulfoton	140.95
32	Biphenyl	92.03	84	Diazinon	141.76
33	2-Nitroaniline	95.80	85	Chlorothalonil	141.90
34*	Mevinphos	95.80	86	Carbazole	142.85
35	Acenaphthylene	99.90	87	2,4-DB methyl ester	145.65
36	1,3-Dinitrobenzene	101.30	88	Dinoseb methyl ester	145.88
37	Etridazole	101.83	89	Metribuzin	147.98
38	Dimethyl phthalate	102.20	90	Heptachlor	148.80
39	2,6-Dinitrotoluene	102.63	91	Methyl parathion	148.98
40	Acenaphthene	104.20	92	Alachlor	150.88
41	3-Nitroaniline	105.35	93	Ronnel	151.65
42	2,4-Dinitrophenol	107.65	94	4-Amino-2,6-dinitrotoluene	153.50
43	Dibenzofuran	108.13	95*	3,5-Dinitroaniline	154.81
44	Chloroneb	109.03	96	Aldrin	155.08
45	Dicamba methyl ester	109.48	97	Di-*n*-butyl phthalate	156.40
46	2,4-Dinitrotoluene	111.18	98	Metolachlor	157.50
47	4-Nitrophenol	112.48	99	Malathion	157.68
48	Fluorene	115.60	100*	2-Amino-4,6-dinitrotoluene	158.16
49	4-Chlorophenyl phenyl ether	117.65	101	Fenthion	158.25
50	Diethyl phthalate	118.70	102	Chlorpyrifos	158.63
51*	TEPP	118.84	103	Parathion	158.80
52	4-Nitroaniline	119.15			

Continued on next page

* Not located automatically by peak-find software.

Table VI. RTs of Semivolatile Compounds for a Low-Pressure GC–TOFMS System *(continued)*

No.	Compound	RT (s)	No.	Compound	RT (s)
104	DCPA	159.35	125	Sulprofos	185.85
105	Cyanazine	159.70	126	Endosulfan sulfate	187.15
106	Isodrin	160.20	127	4,4'-DDT	188.80
107	Trichloronate	160.45	128	Butyl benzyl phthalate	189.45
108	Heptachlor epoxide	162.80	129	Endrin ketone	194.65
109	Fluoranthene	163.05	130*	Chrysene	195.35
110	γ-Chlordane	167.18	131	Benzo[*a*]anthracene	196.03
111	Pyrene	167.50	132	EPN	198.13
112*	Endosulfan I	169.19	133	Methoxychlor	199.73
113	α-Chlordane	169.98	134	Azinphos methyl	203.58
114	Stirofos	171.38	135	Bis(2-ethylhexyl)phthalate	205.60
115	Dieldrin	173.88	136	*cis*-Permethrin	215.90
116	Tokuthion	174.10	137	*trans*-Permethrin	217.15
117	4,4'-DDE	175.08	138	Coumaphos	217.15
118	Merphos	175.75	139	Benzo[*b*]fluoranthene	218.53
119	Endrin	177.42	140	Benzo[*k*]fluoranthene	218.53
120	Endosulfan II	179.41	141	Di-*n*-octyl phthalate	219.03
121	Chlorobenzilate	181.33	142	Benzo[*a*]pyrene	224.03
122	Fensulfothion	182.20	143	Indeno[123-*cd*]pyrene	244.08
123	4,4'-DDD	182.38	144	Dibenz[*ah*]anthracene	245.30
124	Endrin aldehyde	182.88	145	Benzo[*ghi*]perylene	248.08

* Not located automatically by peak-find software.

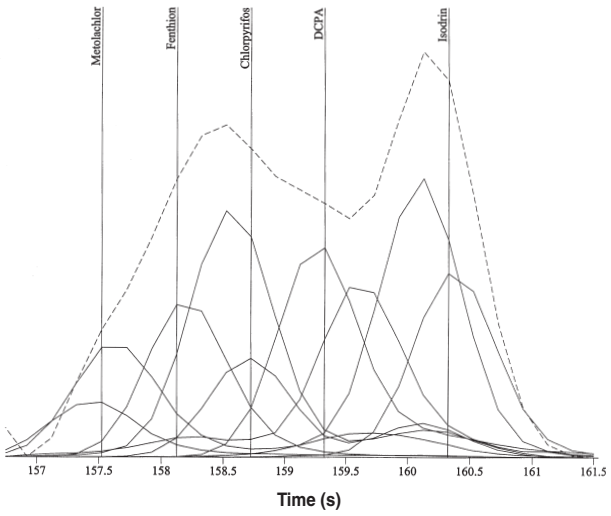

Figure 3. Chromatogram of pesticides using vacuum-outlet GC–TOFMS at 5 spectra/s. Unique ions and TIC (dashed line) are plotted. Only 5 of the 10 compounds were located automatically by TOFMS software.

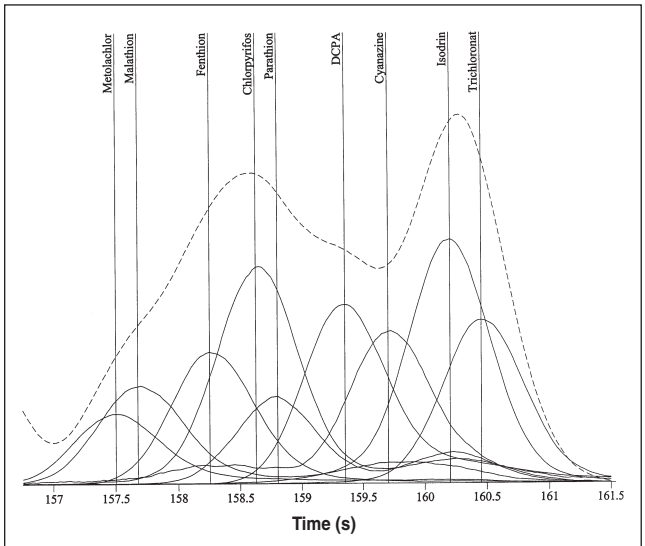

Figure 4. Chromatogram of pesticides using vacuum-outlet GC–TOFMS at 40 spectra/s. Unique ions and TIC (dashed line) are plotted. A faster acquisition rate allowed automatic peak location for 9 of the 10 compounds.

although several can be processed together, a shorter extraction is desirable. In order to demonstrate the possibility of increasing sample preparation speed, a sediment sample that has been certified for specific PCB congeners was extracted using the very simple method described in the Experimental section. Preliminary work used hexane–acetone (50:50) as the extraction solvent, but upon concentration the acetone was volatilized and polar coextractives precipitated out before a 1-mL final volume could be achieved. Additional groundwork with hexane extraction solvent indicated that sonication for 5 min in a bath at 50°C was insufficient to fully recover the PCBs (average recovery was 31%). Extending the time to 10 min and increasing the bath temperature to 55°C resulted in a better extraction. The results for two sequential extractions of the same sediment using the method in the Experimental section with fast GC–TOFMS

analysis are compared with certified values in Table IV.

The first extraction recovered most of the PCBs (if you consider the sum of extractions 1 and 2 to represent all of the PCBs that could be recovered from the sediment). The fast extraction/fast GC–TOFMS results were approximately twice the certified values for almost all of the PCBs, and most were outside the upper limit of the certified values. The reason for this is not understood and of course cannot be defined with only one extraction. One possibility is that it was a nonhomogeneous sample. Only 5 g of sediment was taken from a 30-g sample; perhaps a "hot spot" was sampled. Another possibility is that the extraction with hot solvent and ultrasound energy was more efficient. This is unlikely considering that the certified PCB values represent composites from an interlaboratory study in which a wide variety of extractions was used, including sonication. Still, the point of the extraction work was only to show that an abbreviated extraction/sample preparation process might be possible; defining an extraction that will produce certified values was outside the scope of this study. Additional fast extraction/fast analysis results will be presented in another communication.

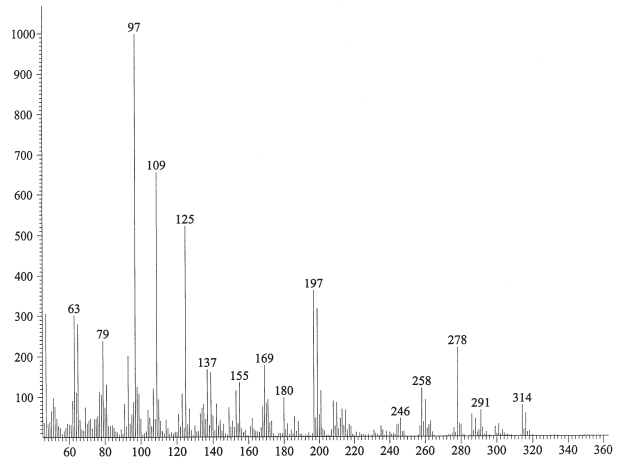

Figure 5. Mass spectrum taken at the peak apex of the TIC in which fenthion, chlorpyrifos, and parathion coeluted. All pesticides contributed ions to the mass spectrum.

Detection limits of key PCBs using fast GC–TOFMS on a narrow-bore column

Estimated detection limits (EDLs) (Table V) were calculated by determining the picograms-per-microliter amount of a PCB that would give a signal-to-noise ratio of 3. Signal-to-noise measurements from the summed quantitation masses as calculated by the Pegasus software were used to extrapolate these values from the 25-pg/µL standards. Also included in Table V are the picogram detection limits, which represent the on-column amount of each PCB based on the 0.25-µL injection volume. For full-mass range acquisition data, these are excellent detection limits.

PCBs using a vacuum-outlet GC system

Two benefits to using vacuum-outlet GC with a 0.53-mm column were anticipated: high speed of analysis and increased sample capacity. Separation power was expected to decrease, and plotting RRTs for PCBs in mixes 1–5 provided confirmation of this expectation. A large number of coelutions between congeners in the same homologue group eliminate vacuum-outlet GC (as operated in this study) from consideration for congener-specific PCB work. However, this setup may have some value for Aroclor determinations in capacitor fluids or Aroclor spills, in which congener-specific measurements are not necessary. Speed and sample capacity may be more important in these analyses. Three Aroclors analyzed in less than 4 min are shown in Figure 2.

A not altogether unexpected result of this work (but still impressive) was the very narrow peak widths (1.5 s at the base) obtained using the 0.53-mm column. As noted in other studies on vacuum-outlet GC (23), this is because of high diffusion coefficients.

Semivolatile compounds using a vacuum-outlet GC system

The reason vacuum-outlet GC fails for congener-specific PCB work is a lack of separation power that results in coelu-

Table VII. Peak-Find Results for Different Acquisition Rates of a TOFMS

No.	Compound	RT (s)	Difference* (s)	Acquisition rate (spectra/s) 5	10	20	40
98	Metolachlor	157.50		×†	×	×	×
99	Malathion	157.68	0.18			×	×
100	2-Amino-4,6-dinitrotoluene	158.16	0.48				
101	Fenthion	158.25	0.09	×	×		×
102	Chlorpyrifos	158.63	0.38	×	×	×	×
103	Parathion	158.80	0.17				×
104	DCPA	159.35	0.55	×	×	×	×
105	Cyanazine	159.70	0.35			×	×
106	Isodrin	160.20	0.50	×	×	×	×
107	Trichloronate	160.45	0.25		×	×	×

* The difference between the retention times of the peak and the previous peak.
† A peak that was automatically located by the software.

tions of isomers that cannot be differentiated on the basis of their mass spectra. For other environmental pollutants in which compounds have some differences in their mass spectra, TOFMS offers a powerful solution to the coelution problem and allows for a full use of the speed offered by vacuum-outlet GC. Peak-find and deconvolution algorithms built around the acquisition speed and spectral reproducibility of TOFMS offer another separation dimension and produce library-searchable mass spectra. For the 144 compounds shown in Table V analyzed in 4.5 min, almost all could be identified quantitatively based on deconvoluted mass spectra.

Acquisition speed of the MS is critical, not only to define the peak for quantitation (10–20 spectra), but also for the deconvolution process. For the vacuum-outlet GC work in this study, the peak widths were approximately 1.5 s at the base. If the only consideration was to define a chromatographic peak for quantitation purposes, acquisition rates of approximately 5–15 spectra/s would be adequate. However, as Table VI illustrates for a group of 10 compounds eluting in a 3-s window, 40 spectra/s was needed to automatically locate the most peaks and produce deconvoluted spectra. Only 2-amino-4,6-dinitrotoluene was not located at the 40-spectra/s rate. The chromatographic representation of the peak-find results is illustrated in Figures 3 and 4 for the 5- and 40-spectra/s acquisition rates.

When one considers that a 4-spectra difference in component peak elutions is sufficient for the deconvolution algo-

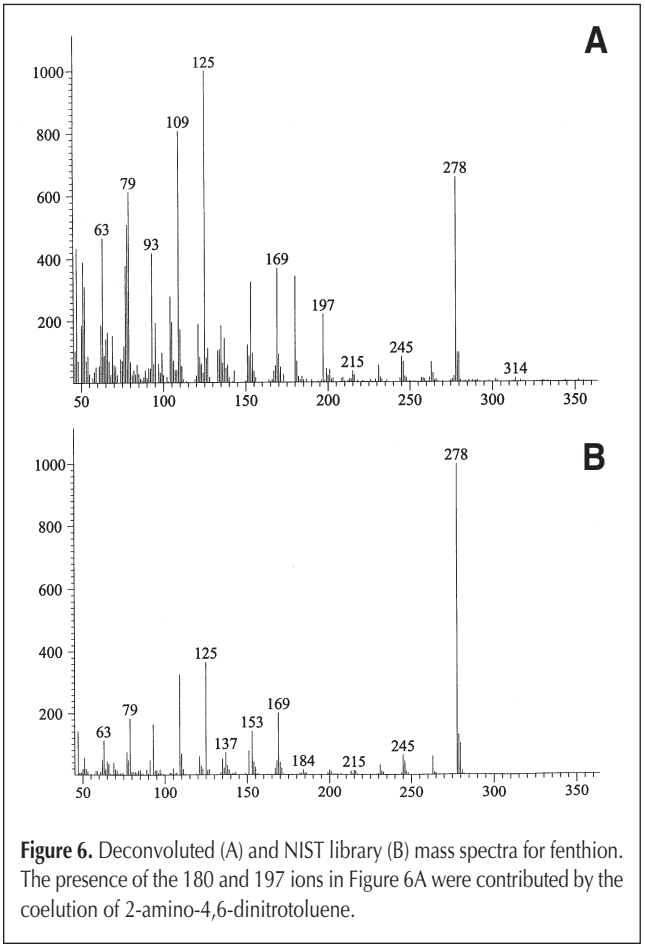

Figure 6. Deconvoluted (A) and NIST library (B) mass spectra for fenthion. The presence of the 180 and 197 ions in Figure 6A were contributed by the coelution of 2-amino-4,6-dinitrotoluene.

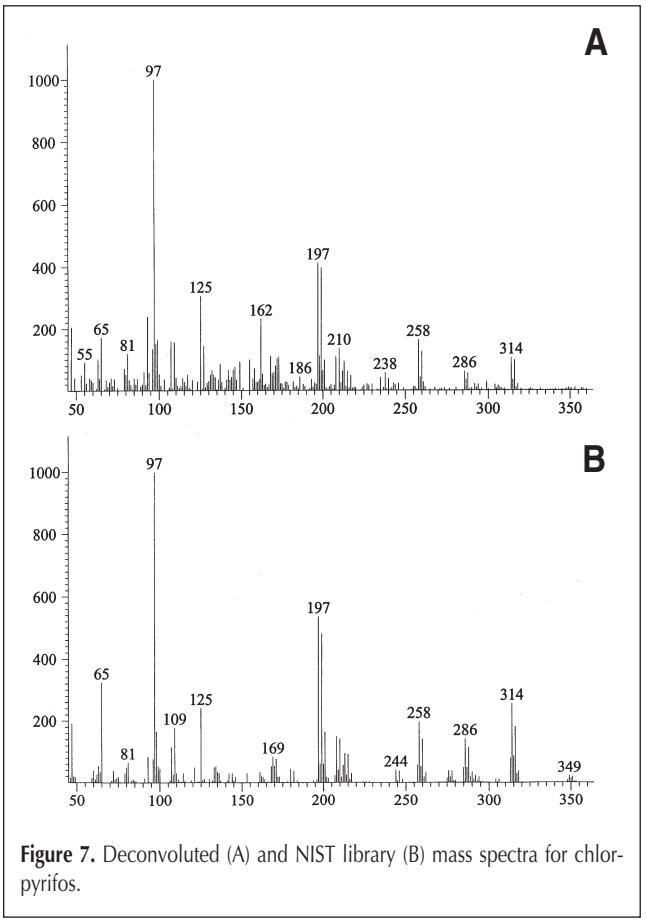

Figure 7. Deconvoluted (A) and NIST library (B) mass spectra for chlorpyrifos.

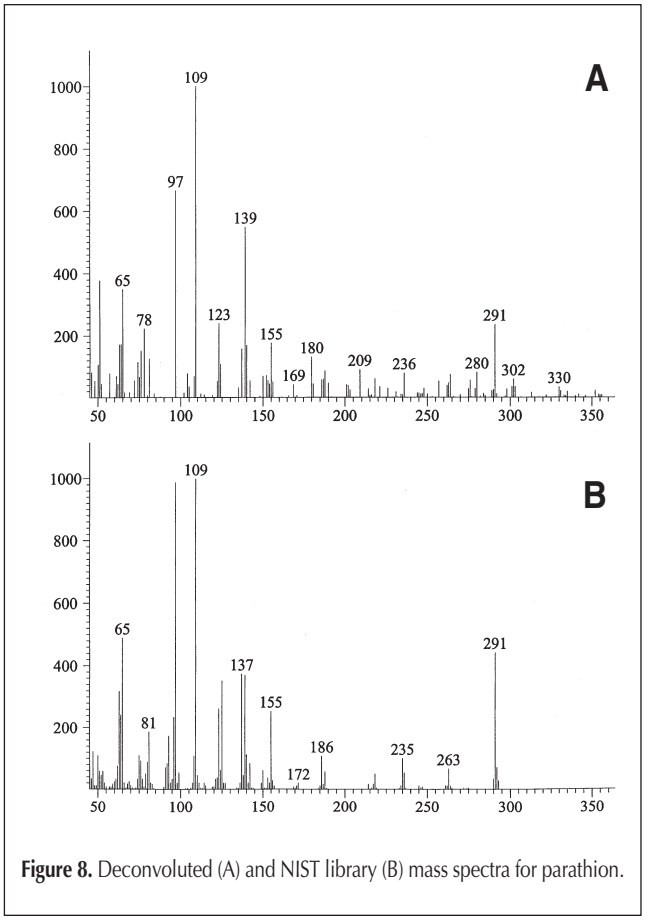

Figure 8. Deconvoluted (A) and NIST library (B) mass spectra for parathion.

rithm (53), the peak-find results in Table VII are more easily interpreted. The 40-spectra/s rate allows for the collection of 4 spectra between peaks that are only 0.10 s apart. This could explain why 2-amino-4,6-dinitrotoluene was not located (it elutes too close to fenthion). Theoretically, an 80-spectra/s acquisition rate should easily allow peak-find and deconvolution for all ten peaks in the example chromatogram, but 2-amino-4,6-dinitrotoluene was not located under 80-spectra/s TOFMS conditions, even though it appeared to have a unique ion at 180 *m/z*.

The peaks that eluted most closely together in Figure 4 were fenthion, chlorpyrifos, and parathion, spanning an RT range of barely 0.5 s. The mass spectrum taken at the peak apex of the total ion chromatogram (TIC) in this region is shown in Figure 5. As expected, it represents a combination of spectral characteristics from the coeluting compounds. Deconvoluted spectra (peak true) are shown in Figures 6, 7, and 8 versus NIST library spectra. The NIST spectra were obtained by searching the library against each compound's deconvoluted mass spectrum across the acquired range (45 to 520 u) while limiting the molecular weight possibilities from 180 to 400. Under these conditions, every first-hit library spectrum was correct.

Conclusion

Fast GC–TOFMS with instrumentation already available offers practical quantitative solutions to difficult application problems, such as the congener-specific analysis of PCBs. No complex injection systems are necessary to produce the narrow peaks required for the efficient operation of 0.10-mm columns. A 40-m × 0.10-mm column requires the use of hydrogen as a carrier gas, because of the prohibitively high head pressure required for helium. Hydrogen is more efficient anyway and should be used for fast GC whenever possible. The DB-XLB is an excellent phase for PCB analysis. Using this phase in a 40-m × 0.10-mm × 0.10-µm configuration in combination with TOFMS may offer the most efficient tool yet for trace-level, congener-specific PCB work.

Trace analysis is achievable with 0.10-mm columns (even with 0.25-µL injections) as evidenced by the excellent detection limits for select PCBs. One reason is that a narrower peak is a taller peak; proper operation of a narrow-bore column produces narrow peaks. The other reason is because of the sensitivity of TOFMS.

Sample capacity could be a concern for 0.10-mm × 0.10-µm columns and is estimated to be in the low-nanogram range for individual components that are compatible with the stationary phase. However, this should be no problem for those analysts that are doing trace-level work.

Vacuum-outlet GC (0.53 mm) offers high speed and high capacity. A loss of separation power is offset by the deconvolution capabilities of TOFMS for compounds that have at least some differences in their mass spectra. Automated peak-find accuracy has been shown to increase for close-eluting compounds when spectral acquisition speed is increased. The resulting deconvoluted mass spectra are NIST-library searchable.

TOFMS is uniquely positioned to be the detector of choice for fast GC because of its high-speed acquisition rates and nonskewed spectra that allow for powerful peak-find and deconvolution algorithms.

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