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Complete PCB Congener Distributions for 17 Aroclor Mixtures Determined by 3 HRGC Systems Optimized for Comprehensive, Quantitative, Congener-Specific Analysis

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Summary

Three HRGC systems (1: 30m DB-XLB capillary with MS-SIM detection; 2: 60m DB-XLB capillary with full-scan, ion-trap MS detection; and 3: Parallel dual-column DB-17 and series-coupled HP5/HT5 with ECD detection) were used to completely characterize multiple lots of 8 different-numbered Aroclor mixtures by quantitative calibration against 9 solutions containing primary standards of all 209 PCB congeners. Despite lower absolute sensitivity and more Aroclor congener coelutions than the dual-column ECD system, the MS systems enabled measurement of more congeners per Aroclor since their greater linear response range did not require dilution of samples and standards. Pairs of different lots of Aroclors 1248 and 1254 displayed markedly different proportions of congeners, and the 1254 pair displayed strong differences in the extent of *ortho*-chlorine substitution. The tables of congener weight percent distributions among Aroclors are more comprehensive and quantitatively precise than those of prior publications. However, the limitations of single-level calibration precluded measurement of all congeners to the $\pm 10\%$ accuracy desirable for establishing these Aroclors as secondary standards for comprehensive, quantitative congener-specific PCB analysis.

1 Introduction

Polychlorinated biphenyls (PCBs) are comprised of 209 distinct chlorine-substituted biphenyl structures (congeners). About 140 to 150 of these are observed in the commercial mixtures produced by catalytic chlorination of biphenyl (Trade Name Aroclor in USA, formerly manufactured by Monsanto, Corp., St. Louis, MO, USA). The dispersion of these PCB congeners by uncontrolled releases into the environment, their long-term stability, their lipophilicity resulting in biomagnification up food chains, and questions of possible toxicity, together cause concern for their effects on the environment and have engendered a vast body

of research over the past three decades. The measurement of the large number of PCB congeners in commercial or environmentally altered PCB mixtures requires the use of high resolution gas chromatography (HRGC) with sensitive, selective detection by electron capture detection (ECD) or selected-ion-monitoring mass spectrometry (MS-SIM). Current regulatory analytical methods in the USA and Europe simplify the analytical task by specifying quantitation either as a combination of one or more Aroclor congener distributions [1], or by specifying short lists of selected priority congeners for individual quantitation [2,3]. Analyses supporting some research applications, which must account for as many as possible of significant Aroclor congeners and sometimes additional congeners not originally in Aroclors, make even greater demands on HRGC systems. Examples include studies of Aroclors or PCBs in environmental samples which have undergone photolytic dechlorination [4], anaerobic microbial dechlorination [5], or aerobic microbial degradation [6]. The latter results in selective congener removal without production of new congeners. This most complete category of PCB analysis will be referred to herein as *comprehensive, quantitative, congener-specific* analysis (abbreviated CQCS). A CQCS PCB analysis is defined as one in which a substantial majority of congeners are resolved, all congeners at significant levels are correctly assigned to the HRGC peak in which they elute, and the PCB content of each resolved peak (including coeluting congeners of different chlorine number if separately quantified by MS) is accurately quantified against appropriate primary or secondary standards.

Hess *et al.* have recently provided a lengthy critical review of the analysis of non- and mono-*ortho*-chlorobiphenyls [7]. This covered all aspects of such analyses, with particularly useful and detailed discussions of the capabilities and problems of ECD,



MS-SIM, and full-scan ion-trap MS detection, as well as the shortcomings of single-point calibrations. Larsen [8] has recently provided in this journal a critical review of HRGC separations of PCB congeners. His laboratory has provided both an example of a dual-column HRGC-ECD system (parallel DB-17 and series-coupled Sil8/HT5) optimized for CQCS PCB analysis [9,10], as well as identifying a single column (HT8) particularly suited for CQCS and priority list congener PCB analysis when used with MS detection [11]. One of us (Frame) recently organized a worldwide consortium of laboratories to obtain complete retention and coelution data for all 209 PCB congeners on 27 HRGC systems encompassing 20 different stationary phase coatings [12]. Samples of Aroclors 1221, 1016, 1242, 1254, 1260, and 1262 were analyzed against the 209 individual congener standards on 18 of these systems, and the results were combined and averaged to produce comprehensive congener weight percent distributions for these 6 Aroclors [13]. Some of the most significant results from this pair of linked studies are the following:

1. The Aroclor distribution study enabled identification of all significant Aroclor congeners (about 140 of the 209), and when predicted coelutions of this subset were evaluated for all systems in the retention database, one newly developed stationary phase (DB-XLB, J&W Scientific, Folsom, CA, USA) displayed great promise, if used with MS-SIM detection, for enabling the CQCS measurements of an exceptional number of Aroclor congeners. The HT8 column (SGE Pty Ltd, Ringwood, Victoria, Australia) was likewise evaluated in the study, and Aroclor congener resolution information almost completely confirmed Larsen's evaluation of it [11,12]. While DB-XLB data predicted its ability to measure a slightly larger total of Aroclor congeners, it appeared unable to resolve extremely significant priority congeners 138 and 153 from 163 and 132, respectively, while HT8 isolated them from all significant Aroclor congeners. Both these phases have siloxane backbones modified by substitution of some oxygens with bulky organic groups to inhibit polymer thermal degradation leading to column bleed at high temperatures. This makes them especially suitable for CQCS PCB methods employing sensitive MS detection. The DB-XLB resolution predictions had not yet been confirmed by actual analysis of Aroclor mixtures.
2. Hewlett-Packard 5972 bench-top GC-MS-SIM systems operating with above-average new-model electron-multiplier tubes (either K&M or Galileo 5778 Channeltron) and similarly priced Varian Saturn Ion-Trap GC-MS systems operating in full-scan mode displayed exceptional ability to detect and quantify minor Aroclor components. Their *effective* sensitivity in this study was similar or slightly better than the inherently more sensitive ECD detectors because the MS detectors' wider linear response range did not require the dilution of samples and standards needed to include all Aroclor and internal standard peaks within the ECD linear range.
3. The retention database facilitated the distribution of almost all significant Aroclor congeners plus a few "non-Aroclor congeners" among only 5 calibration solutions totaling 144 congeners, while the remaining 65 "non-Aroclor conge-

ners" plus a few very minor Aroclor congeners could be distributed among an additional 4 solutions. Each solution's congener distribution was structured such that there would be a minimum of close elutions on 12 of the stationary phases deemed most useful for CQCS PCB analysis. Tables of elution order for the components of each solution on each of the 12 phases were produced, enabling peak assignments and primary PCB congener standard single-level calibration to be made on a particular analyst's system using one of these phases after only 5 injections for the Aroclor congeners and an additional 4 injections for all 209. A commercial US standards supplier (AccuStandard, New Haven, CT, USA) has formulated the 9 congener mixture solutions according to this scheme, and provides them with the elution order tables described above.

A comparison of the GC-ECD and GC-MS Aroclor congener quantitations in the collaborative study suggested that even after dilution of the samples and standards for GC-ECD analysis, the ECD detectors were measuring many peaks in a non-linear response range rendering the single point calibration inadequate for accurate quantitation. Statistics on quantitation averages indicated that the values should be considered only "semi-quantitative" (*i.e.* between 10% and 50% different from actual values depending on concentration). Congener distributions for Aroclors 1232 and 1248 were compiled from only one pair of systems. Comparison with published congener weight percent distributions for other Aroclor 1254 lots [14], led us to suspect that the Aroclor 1254 used in the collaborative study might have an abnormal distribution. This raises a broader question of the degree of similarity of such distributions among different lots of the same numbered Aroclors over the whole range of chlorine weight percentages (denoted by the last two digits of the Aroclor designation [except Aroclor 1016]). This is significant since many CQCS PCB analysis methods specify calibration against secondary standards of Aroclors [15-18]. This method of calibration has advantages of convenience, cost of standards, and, in some cases, similarity of the standard and sample congener distributions, but its accuracy ultimately depends both on how well the Aroclor standards' congener distributions have been determined and how closely the lot being used matches the one from which the congener weight percent distributions have been compiled.

The purposes of the work reported here are: to confirm the predictions [12] and optimize the performance of DB-XLB columns by CQCS PCB analysis of actual Aroclor distributions using both MS-SIM and full-scan, ion-trap MS detection; to analyze the same sample set using a version of the Larsen/Bøwadt dual column GC-ECD system [9,10] and compare the congener resolution and quantitation performance with the GC-MS systems; and to use all three systems to compile complete congener weight percent distributions of multiple lots of the complete range of Aroclors (except Aroclors 1268 and 1270) by calibration against the 9 new AccuStandard primary standard congener mixtures.

2 Experimental

2.1 Materials

Aroclor lots were obtained from 3 sources, designated by letter-number(#) combinations in **Tables 3 and 4**. 1000 µg/ml iso-octane solutions in ampoules from AccuStandard (New Haven, CT, USA) are designated A# and those from Supelco (Bellefonte, PA, USA) are designated S#. A1, A2, A3, A4, A5, and A6 are the same solutions profiled in the study of reference [13]. Neat Aroclors obtained from the manufacturer (Monsanto Corp., St. Louis, MO, USA) are the same lots used as secondary HRGC calibration standards by GE Corporate R&D [17] and are designated G#. The MS internal standard (IS), 2-fluorobiphenyl (2F-BP), was purchased from Aldrich Chemical Co. (Milwaukee, WI, USA), and the ECD IS, decachlorobiphenyl (PCB 209), from AccuStandard. The primary calibration standards (containing 10 ppm each of all 209 PCBs distributed among 9 different mixtures) were purchased from AccuStandard. Iso-octane was OmniSolve (E. Merck, New Jersey, USA) distilled GC-grade. The DB-17 (50% diphenyl dimethylpolysiloxane) and DB-XLB (proprietary polysiloxane) capillary GC columns were obtained from J&W Scientific. The HP5 (5% diphenyl dimethylpolysiloxane) column was obtained from Hewlett-Packard (Palo Alto, CA, USA) and the HT5 (1,10-dicarba-closo-dodecaborane dimethylpolysiloxane) column from SGE, and they were series-coupled in that order using a Restek Press-Tight fused-silica column connector.

2.2 Sample and Standards Preparation

1.00 ml of each of the 9 standard congener calibration mixtures was separately diluted together with appropriate volumes of the two IS stock solutions to 10.00 ml in volumetric flasks with iso-octane to produce solutions containing 1.00 µg/ml of each congener and 4.00 µg/ml of each IS. 1000 µg/ml stocks of Aroclors were similarly diluted with the 2 IS's and iso-octane in 25.00 ml volumetric flasks to produce solutions containing 40 µg/ml of Aroclor and 4.00 µg/ml of each IS. Because of the greater absolute sensitivity and non-linear response of ECD detectors to major Aroclor components and especially the high concentration of decachlorobiphenyl IS, samples and standards were diluted 16-fold with iso-octane prior to injection on the dual-column GC-ECD system.

2.3 Gas Chromatographic Analysis

Samples and standards were analyzed on the four systems summarized in **Table 1**. **Systems 1, 2, and 3** employed splitless injections of 1.0 µL, while that of **System 4** was a 1.0 µL on-column injection to a 0.53 mm i.d. × 2 m deactivated Hewlett-Packard capillary fused silica retention gap split to the series-coupled HP5/HT5 (**4A**) and DB-17 (**4B**) columns using a Restek Press-Tight fused-silica "T-piece". **System 1** employed MS-SIM detection at the most intense of either the M⁺, (M + 2)⁺, or (M + 4)⁺ masses, with acquisition at 5 scans per second. The exact masses and SIM acquisition groups were the same as in [12]. The electron multiplier was upgraded to the K&M model employed in an HP 5972 GC-MS, and peak areas were integrated with the HP ChemStation integrator after Gaussian-smoothing, which caused slight losses of peak resolution but greatly improved the quantitative peak area measurement of minor peaks by enabling more accurate and consistent automated placement of peak baselines. **System 2** employed the new HP-1801-GCD

GC-MS instrument. It was operated similarly to the HP 5971 of **System 1**, but its software limitations (maximum mass = 425 m/z) required acquisition of signals for 8, 9, and 10-chlorine-substituted biphenyl congeners at the (M - 2Cl)⁺ or (M - 4Cl)⁺ fragment masses (*i.e.* 359.8 or 395.8 m/z for 8 and 10, or 9 chlorobiphenyls respectively), and integration of unsmoothed peaks. Its new diffusion pump fluid permitted employment of hydrogen as carrier gas with a capillary GC column. **System 3** employed MS-Ion Trap detection which acquired full-scan spectra from 150 to 520 m/z at 1 scan/s. Peak areas were acquired by integration of peaks obtained by extraction of 2 or 3 of the major mass peaks of the M⁺ cluster.

Table 1. HRGC systems used for CQCS PCB analysis.

Investigator	Frame	Frame	Cochran	Bowadt	Bowadt
Parameter	System 1	System 2	System 3	System 4A	System 4B
Column	DB-XLB	DB-XLB	DB-XLB	HP5/HT5	DB-17
Length (m)	29.6	28	60	25/25	60
I.D. (mm)	0.25	0.18	0.25	0.25/0.25	0.25
Film (µm)	0.50	0.18	0.25	0.25/0.10	0.25
Carrier Gas	He	H ₂	He	H ₂	H ₂
Pressure (psi)	9.0	0.8ml/min	20.5	24.7	24.7
Flow (cm/s)	28.6	51.3	20.3	35.2	42.7
Flow Temp (°C)	225	205	225	202.5	202.5
Temp. Prog.					
Start (°C)	72	72	75	90	90
Hold (min)	2	2	2	2	2
Ramp 1 (°/min)	15	15	15	20	20
Stop (°C)	150	150	150	130	130
Ramp 2 (°/min)	2.5	2.0	1.5	2.0	2.0
Stop (°C)	300	260	300	275	275
Hold (min)	0	0	0	5	5
PCB209 (min)	65.9	60.3	102.0	67.8	75.6
Detector	MS-SIM	MS-SIM	MS-IT	ECD	ECD
Model	HP 5971	HP-GCD	Saturn	HP 5890	Dual ECD
Cost (~\$)	\$70,000	\$50,000	\$60,000	\$40,000	\$40,000

2.4 Calculation of Aroclor Congener Distributions

For **Systems 1 and 3** (**System 2** Aroclor data not calculated for incorporation into the summary distribution), the response factors relative to 2F-BP IS (RRFs) were calculated from peak areas in chromatograms of the 9 calibration mixtures. Only PCBs 37 and 103 in one mixture coeluted on the DB-XLB columns. The (M + 2)⁺ response for 103 could be measured without interference, but a separate standard containing PCB 37 and the IS needed to be injected to determine its M⁺ RRF. Concentrations of each congener were calculated by multiplying the ratio of the sample peak's RRF to the corresponding standard peak's RRF by the standard's concentration of 1 µg/ml; *i.e.* a simple single point calibration. Contributions to a congener's M⁺ peak area from single chlorine loss fragments from a coeluting next higher homolog congener were minor in all cases and were not compensated for. Only the major two-chlorine-loss signal contribution to PCB 77 values from coelution with PCB 144 required its subtraction to correct the PCB 77 values in the Aroclor 1254s.

The series-coupled HP5/HT5 column (**System 4A**) was not included in the original retention database study [12]. Therefore, the 30 mixtures totaling all 209 congeners used in that study were

initially employed to determine the elution order and coelutions of PCBs on this column and the parallel DB-17 (**System 4B**) column as well as the RRFs to decachlorobiphenyl IS. There were several congener coelutions on both it and the parallel DB-17 column when the 9 calibration mixtures used in this study were injected on **System 4**. In order to provide RRFs for congeners undergoing such coelutions, the RRF values obtained from the completely separated 30 mixtures runs were listed in order of increasing value. The RRF (obtained during the 9 mixture calibration) of a measurable (*i.e.* no coelution in one of the 9 calibration mixtures) congener with the value closest (usually $< \pm 2\%$) to that of each of the congeners suffering coelution in the calibration mix was selected from the ordered list to substitute for the latter. In many cases an interfering calibration mix congener would not appear at significant levels in an Aroclor, so the level of the desired congener could be measured on at least one of the columns of **System 4**. There were 6 categories of calculation from the combined data of the **System 4** columns (**4A** and **4B**). These employed the same single point RRF ratio formula used with systems 1 and 3, and they enabled quantitation of 132 values; namely:

- 41 PCBs as the *mean* of unique elutions on both **4A** and **4B**
- 47 PCBs eluting uniquely only on **4A**
- 33 PCBs eluting uniquely only on **4B**
- 5 PCBs as sum value on **4A** minus value of coeluter measured uniquely on **4B**
- 3 PCBs as sum value on **4B** minus value of coeluter measured uniquely on **4A**
- 6 PCBs measured as 3 sums of coeluting pairs on either of **4A** or **4B**

These categories are defined for congeners significantly present in Aroclors (*i.e.* above ~ 0.05 weight%) as determined in the earlier Aroclor distribution study [13] and confirmed by the data in **Table 4** of this study.

3 Results and Discussion

3.1 PCB Congener Nomenclature

Column 1 of **Table 4** lists the 209 possible PCB congeners in order of their IUPAC number. Their presence in any of Aroclors 1242, 1254 or 1260 [13] as a major congener (>1.0 Wt%) is indicated by **Bold Underline**, as a minor congener (between 0.05 and 1.0 Wt%) by **Boldface**, and as a trace or undetected congener (<0.05 Wt%) by *italic* font. The numbers for congeners 107, 108, 109, 199, 200, and 201 in this paper are derived according to Guitart *et al.* [19], and they differ from the corresponding numbers assigned by Ballschmiter and Zell [20] as 108, 109, 107, 201, 199, and 200, respectively. Column 2 of **Table 4** displays the pairs of individual single phenyl-ring chlorine-substitution patterns according to the convention: 234-245 = 2,2',3,4,4',5'-hexachlorobiphenyl, where the hyphen represents the bond between the two phenyl rings. This permits easy visualization of the chlorination pattern on each ring and assists evaluation of the relative proportions of each pattern produced by the Aroclor synthesis process. Chlorines in the 2 or 6, the 3 or 5, and the 4

positions are described as *ortho*-, *meta*-, and *para*- substituted, respectively.

3.2 Comparisons of HRGC Systems Aroclor PCB Resolution Performance

Table 2A displays all Aroclor congener (*i.e.* **Bold** numbers in **Table 4**) coelutions in each system by the convention X @ Y, where X is the minor component of the pair coeluting with Y.

Table 2A. Comparison of HRGC systems' performance.

System 1 29.6m DB-XLB 0.25mm x 0.5µm Helium	System 2 28m DB-XLB 0.18mm x 0.18µm Hydrogen	System 3 60m DB-XLB 0.25mm x 0.25µm Helium	System 4 HP5/HT5 + DB17 25/25m + 60m Hydrogen
Isomer Coelutions of Aroclor Congeners (>0.05% in 1242, 1254 or 1260)			
	Wt%	Wt%	Wt%
10@4	T	10@4	T
20@33	5.7	20@33	5.7
59@42	2.0	59@42	2.0
43@52	T		
48@49	5.7		
76@63	0.3	76@63	0.3
89@84	T	89@84	T
115@85	2.2	115@85	2.2
119@83	0.6	119@83	0.6
123@109	0.8	123@109	0.8
129@158	1.2	129@163	1.2
131@133	0.3		
132@153	12.3	132@153	12.3
163@138	9.0		
147@149	T		
193@180	T		
196@203	2.5		
198@199	T		
SUM =	42.6	12.8	10.4
			17.4
			41 NQ
			56@60
			70 NQ
			92@84
			196@203

Table 2B. Additional classes of coelutions in System 3 (60m DB-XLB).

Different Chlorine Number ECD Unresolvable	Non-Aroclor PCB Coelution @ Aroclor PCB (Isomers)
11@18	T
13@27	0.7
53@31	8.1
91@66	7.1
84@56	4.3
117@136	0.7
139@124	0.5
141@105	6.1
128@185	1.1
201@171	1.4
198@170	T
207@195	T
SUM =	30.0
	21@33/20
	62@75
	68@40
	58@67
	88@74
	90@101
	120@110
	143@139
	168@153
	182@175
	162@128
	169@196

XXX@YY = minor congener XXX coelutes with major congener YY.

NQ = Not quantifiable by dual-column difference calculation (categories 4 or 5).

T = 1st congener is trace component not quantifiable, but increases major component value by less than 10%.

Wt% is sum of largest mean weight percents for pair of coeluters in any of Aroclors 1242, 1248, 1254, or 1260.

Major congener coelutions are underlined.

The following comparisons and observations are made from these data:

1. Doubling the length of the DB-XLB column in **System 3** versus that in **System 1** doubled theoretical plates for n-tetradecane with hydrogen carrier from 124,000 to 249,000 (J&W test data). As a consequence, the number of Aroclor congener coelutions dropped from 17 to 6, and major coeluting pairs 48@49, 163@138, and 196@203 could be resolved. **Table 2B** shows additional different homolog (congeners of different chlorine number) coelutions on **System 3**, measurable by MS but not ECD, as well as those non-Aroclor congeners not measurable in the presence of some Aroclors.
2. The 28m narrow-bore, thin-film DB-XLB column used with hydrogen carrier (**System 2**, measured by J&W to have 170,000 theoretical plates) retained most of the above resolution improvements, and most importantly, achieved baseline resolution of the important 132/153 pair and also allowed measurement of PCB 138 without interference. Using longer, narrow-bore, thin-film DB-XLB capillaries both J&W and J. Cochran's labs [21] have also succeeded in resolving these pairs with *helium* carrier gas. Critical resolution comparisons between **Systems 1 and 2** are displayed in **Figure 1**. Note in the **System 2** segments of this figure that there is an enhancement of $(M - 1Cl)^+$ fragmentation responses when hydrogen was used in **System 2**. This resulted both in several-fold lower signals at M^+ and larger one-chlorine-loss fragment interferences in cases of coeluting homologs. Such alteration of PCB fragmentation patterns was not observed when hydrogen was employed as GC carrier gas with the Varian Saturn ion-trap MS. Its higher capacity turbomolecular pumps may achieve a lower ion-source hydrogen pressure than the diffusion pump of the HP-GCD. An elucidation of the mechanism of the fragmentation pattern alteration by hydrogen requires further study. Analysts requiring hydrogen carrier to achieve critical congener resolutions in GC-MS-SIM CQCS PCB analyses should check their systems for the possible presence of this behavior.
3. Column 4 of **Table 2A** shows that the **System 4** combination of GC columns **4A** and **4B** yields the most complete Aroclor congener profile. In practice PCBs 41 and 70 could not be accurately measured in some Aroclors as required by the calculation categories 4 and 5 described in Section 2.4 above, and there remained 3 pairs of Aroclor congeners not resolved on either column. Fortunately **System 4** could quantify all congeners not measurable by **Systems 1 or 3**, thus enabling complete Aroclor congener distributions to be obtained. The multiple categories of measurement in more comprehensive **System 4** made reduction of data from it much more complex and time consuming than from **Systems 1 and 3**.

3.3 Comparison of Systems Quantitation Performance

The first 3 data columns of **Table 3** display the number of congeners measured in each Aroclor lot by **Systems 1, 3, and 4**.

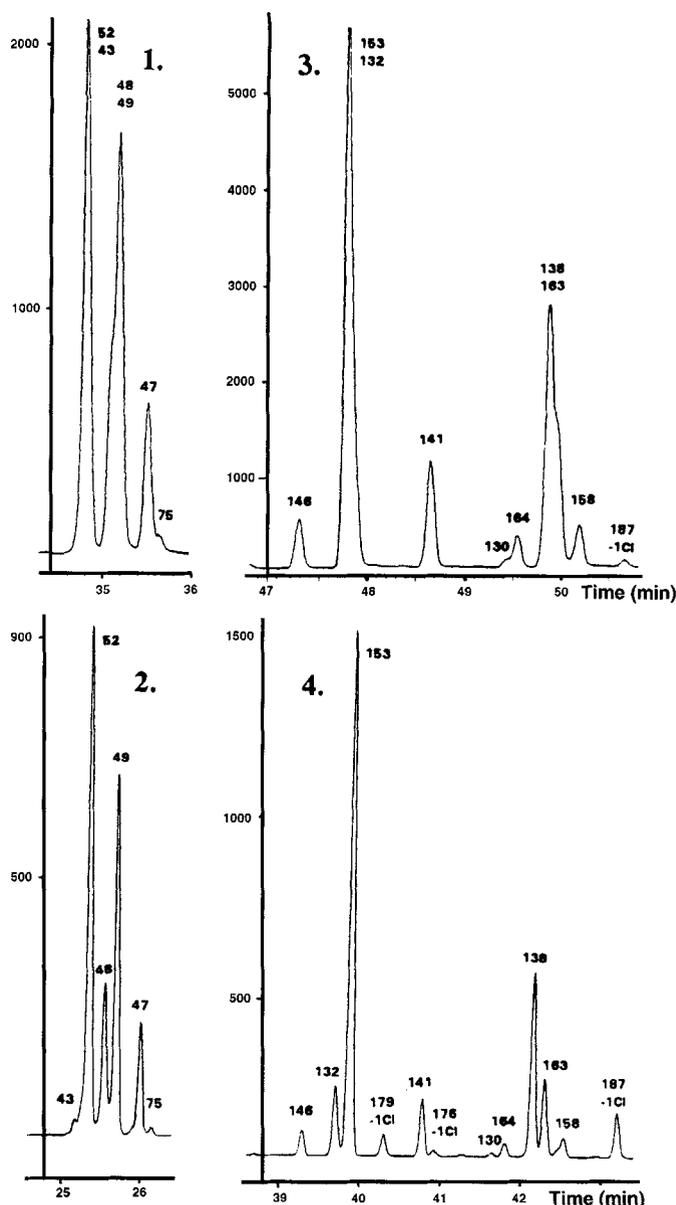


Figure 1. Critical congener resolution comparisons between GC-MS systems 1 and 2.

1. **System 1**, G3 Aroclor 1242, Mass = 291.9 (4-Cl M^+)
2. **System 2**, G3 Aroclor 1242, Mass = 291.9 (4-Cl M^+)
3. **System 1**, G5 Aroclor 1260, Mass = 359.8 (6-Cl M^+)
4. **System 2**, G5 Aroclor 1260, Mass = 359.8 (6-Cl M^+).

Note that dual-column ECD **System 4** employed 16-fold diluted standards and samples to reduce the effect of non-linearity of detector response. Assuming a near equal split to each column, the effective concentrations sampled by each ECD were 1.25 or 0.03 $\mu\text{g/ml}$ for Aroclors or individual congener standards, respectively, compared to 40.0 or 1.0 $\mu\text{g/ml}$ for the MS detectors. As in the predecessor study [13], where single point calibration was also employed, the individual calculated ECD congener concentrations ranged higher than the corresponding MS values; with the differences being inversely proportional to the absolute concentrations. Despite the effective 32-fold dilution, single point calibration was still clearly insufficient for accurate ECD measurements over portions of the concentration range due to non-

Table 3. No. of congeners measured by each system. Similarity of Aroclor congener distributions.

Aroclor	Lot	No. of Congeners Measured			Sum of % Diffs. ^{a)}	
		Sys 1	Sys 3	Sys 4 ^{b)}	Lots 1&2 Lots 2&3	Lots 1&3
1221	A1	59	63	45		
1232	A1.5	77	93	81	1.9	
1232	G1.5	75	91	88		
1016	A2	58	71	52	1.1	
1016	S2	58	70	54		
1242	A3	82	95	75	9.3	
1242	G3	79	93	76		6.3
1242	S3B	81	95	78	12.3	
1248	A3.5	92+	95+	88	19.8	
1248	G3.5	92+	95+	92		
1254	A4	92+	95+	81	52.5	
1254	G4	92+	95+	97		
1260	A5	89	93	67	1.7	
1260	S5	89	93	73		7.2
1260	G5	84	82	65	6.4	
1262	A6	91	95	78	10.3	
1262	G6	91	92	74		

"+" – additional trace congeners detected, not reported.

a) The absolute differences in Wt% of pairwise comparisons are summed for all congeners for pairs of Aroclor lots using **Table 4** values.

b) The number of measured PCBs is reduced because of the 16-fold dilution needed to place the range of PCB congeners in a more linear region of the ECD response curve when using single-level calibration.

linearity of the detector response over the range from the lower Aroclor congener concentrations to the much higher level of the IS. A linearity study of **System 1** responses for 39 congeners covering all levels of chlorination (except decachlorobiphenyl) revealed concentration/response ratios constant to $\pm 10\%$ over the range equivalent to 0.1 to 10.0 Wt% of 1.0 μL of the 40 $\mu\text{g}/\text{ml}$ Aroclor solutions injected. This suggests that the single point calibration was adequate over this range *for this particular GC-MS-SIM system*. More than 90% of the full-scan ion-trap **System 3** Aroclor congener weight% values were within $\pm 10\%$ of the corresponding **System 1** values over this range. The two GC-MS systems displayed similar sensitivity; the greater congener count of **System 3** in **Table 3** being primarily due to greater congener resolution, as outlined in **Table 2A**. Conversely, the even more comprehensive congener measurement capability of dual-column ECD **System 4** was offset by the need to analyze more dilute samples. This resulted in fewer detections of minor congeners; especially less chlorinated ones having lower ECD RRFs. **System 4** was incorporated in this study after solutions had been prepared for and analyzed only by **Systems 1 and 3**. Its quantitative accuracy would surely have improved in a study design employing multilevel calibration and use of a lower decachlorobiphenyl IS concentration requiring less dilution. With some extracts of environmental samples standard cleanup procedures [7] may be able to remove much higher levels of non-PCB contaminants which degrade either the chromatographic separation or the MS quantitation of PCBs in GC-MS systems.

If the contaminant levels are low enough or can be reduced sufficiently to allow concentration of the extracts to attain the PCB levels measured in this study, then the GC-MS methods may provide better analyte selectivity and more facile quantitation than the more complex multicolumn analysis and multilevel calibration required for full CQCS implementation of **System 4**. On the other hand, the latter provides more comprehensive congener coverage at slightly lower equipment cost (**Table 1**), and provides dual chromatographic confirmation capability instead of mass spectrometric confirmation.

Figure 2 illustrates the remarkably sensitive detection by **System 1**, without further isolation and concentration, of only 1.4 picograms injected of critical coplanar PCB 126 from lot G4 Aroclor 1254 at 40 $\mu\text{g}/\text{ml}$. Note the much elevated level of this congener in lot A4, which is discussed further in Section 3.6. PCB 159 coelutes with PCB 126 on some DB-XLB columns, but its absence was demonstrated by the absence of its $(M+2)^+$ ion one chlorine isotope mass above that of PCB 126. **Figure 3** illustrates the library-searchable full-scan mass spectrum obtained by **System 3** on the trace level (only 15 picograms injected) of PCB 138 measured in Aroclor 1232. The ability of the Ion-Trap MS to provide full-scan spectra of even minor Aroclor components provides more complete MS confirmation of PCB peaks than do the several masses usually monitored in MS-SIM methods. Additionally, in the event of contaminant interferences at the molecular ion cluster masses routinely monitored, one may be able to employ other fragment masses from the full-scan sample and standard data files to quantify the PCB content of a peak.

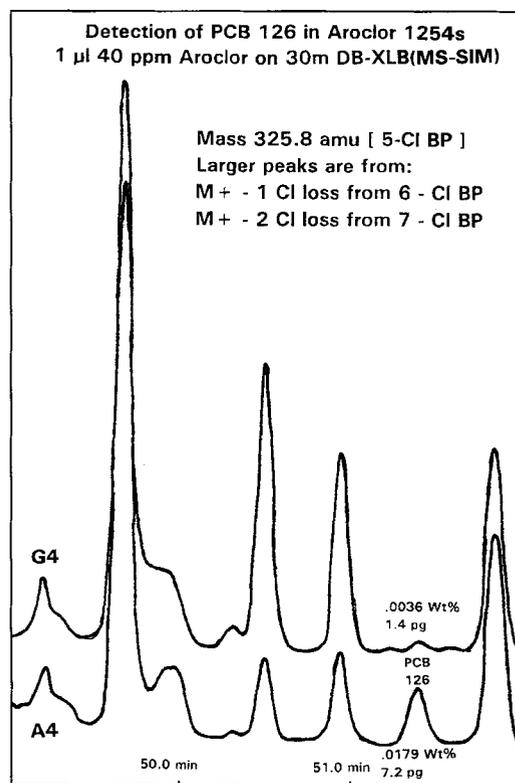


Figure 2. **System 1**, GC-MS-SIM detection of PCB 126 in A4 and G4 Aroclor 1254s.

Table 4A. Summary weight% PCB congener distributions in Aroclors compiled from data from HRGC Systems 1, 3, and 4.

IUP AC#	Aroclor - Structure Cl Pos.	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17	
		A1 1221	A1.5 1232	G1.5 1232	A2 1016	S2 1016	A3 1242	G3 1242	S3B 1242	A3.5 1248	G3.5 1248	A4 1254	G4 1254	A5 1260	S5 1260	G5 1260	A6 1262	G6 1262																	
1	2	35.80	15.21	15.84	.52	.54	.51	.34	.78	.05	.02	.02	.03	.03	.01	.02	.03																		
2	3	3.81	1.98	1.94	.02	.03	.02	.02	.05																										
3	4	20.44	10.36	10.20	.15	.16	.15	.11	.27	.01			.00				.01																		
4	2-2 +10	6.19	5.32	5.38	3.62	3.66	3.11	2.71	3.41	.32	.04	.02	.06	.03	.03	.00	.07	.04																	
5	23	.74	.49	.50	.17	.15	.13	.11	.19	.00			.00																						
6	2-3	3.82	3.02	3.00	1.64	1.69	1.42	1.24	1.63	.13	.00	.00	.02	.01	.01		.03	.02																	
7	24	1.70	1.12	1.09	.29	.30	.26	.18	.34	.02																									
8	2-4	12.34	10.71	10.72	8.29	8.31	6.99	6.48	7.68	.81	.26	.05	.13	.06	.06	.00	.15	.08																	
9	25	1.74	1.25	1.29	.58	.59	.50	.40	.60	.04								.00																	
10	26	.80	.60	.58	.23	.23	.20	0.14	.25																										
11	3-3	.16																																	
12	34	.59	.35	.35	.07	.07	.06	.04	.09																										
13	3-4	1.12	.73	.72	.24	.25	.20	.17	.27	.02																									
14	35	.00	.00	.02																															
15	4-4	4.18	3.24	3.19	2.40	2.49	1.98	1.95	2.39	.22	.06	.01	.03	.00	.02		.03	.02																	
16	23-2	.31	1.79	1.79	3.88	3.88	3.03	3.44	2.94	1.04	.71	.02	.09	.02	.02	.00	.07	.03																	
17	24-2	.34	1.83	1.82	3.98	3.98	3.14	3.29	2.97	1.05	.93	.02	.08	.02	.02	.00	.07	.03																	
18	25-2	.78	4.89	4.83	10.86	10.75	8.53	9.14	7.93	4.29	3.29	.08	.25	.07	.07	.00	.19	.10																	
19	26-2	.08	.46	.47	.99	1.01	.79	.84	.75	.22	.14			.00			.02																		
20	23-3	.07	.42	.42	.88	.89	.68	.77	.71	.14	.08																								
21	234	NM	NM	NM	NM	NM	NM	NM	NM																										
22	23-4	.26	1.62	1.62	3.50	3.51	2.71	3.08	2.73	1.33	1.38	.02	.04	.02	.02	.00	.06	.03																	
23	235	.00	.00	.00	.01	.02	.01	.01	.01	.00																									
24	236	.02	.08	.08	.16	.17	.13	.13	.14	.00																									
25	24-3	.09	.37	.37	.72	.72	.57	.61	.60	.11	.04						.00	.00																	
26	25-3	.13	.75	.74	1.57	1.59	1.21	1.38	1.24	.40	.23	.00	.03	.00	.00	.00	.03	.01																	
27	26-3	.05	.12	.12	.51	.50	.40	.44	.39	.12	.07						.00	.00																	
28	24-4	.62	3.92	3.89	8.50	8.57	6.68	7.31	6.60	3.59	5.57	.06	.19	.05	.05	.00	.15	.08																	
29	245	.01	.05	.05	.10	.10	.08	.08	.09	.00	.00																								
30	246				.00	.00																													
31	25-4	.60	4.17	4.11	9.32	9.26	7.18	7.82	7.01	5.07	5.47	.11	.28	.06	.05	.00	.16	.08																	
32	26-4	.17	1.08	1.07	2.37	2.37	1.85	2.05	1.79	.88	.93	.01	.05	.01	.01	.00	.05	.02																	
33	34-2 + 20	.48	2.84	2.88	6.21	6.19	4.85	5.35	4.82	2.23	2.21	.05	.16	.04	.04	.00	.13	.07																	
34	35-2		.01	.01	.03	.03	.02	.02	.03	.00	.00																								
35	34-3	.00	.06	.05	.05	.06	.07	.07	.09	.00																									
36	35-3																																		
37	34-4	.19	1.15	1.12	1.02	1.01	1.86	2.19	2.05	.79	.95	.01	.07	.01	.00	.00	.04	.02																	
38	345																																		
39	35-4																																		
40	23-23	.04	.40	.36	.58	.58	.77	.79	.72	1.13	.92	.15	.12	.00	.00		.00	.00																	
41	234-2	.03	.36	.35	.76	.76	.69	.69	.65	.77	.75	.02	.01	.00	.00		.00	.00																	
42	23-24 + 59	.09	.66	.69	1.59	1.59	1.13	1.25	1.17	1.67	1.79	.09	.15	.00	.00	.00	.03	.01																	
43	235-2		.12	.09	.28	.25	.18	.19	.16	.30	.19																								
44	23-25	.21	1.81	1.81	4.47	4.48	3.60	3.63	3.42	6.31	5.09	.67	2.31	.04	.04	.03	.10	.05																	
45	236-2	.04	.47	.45	1.23	1.22	.93	.91	.84	1.09	.91	.02	.05	.00	.00		.00	.00																	
46	23-26	.02	.19	.19	.49	.48	.37	.38	.33	.47	.39			.00			.00	.00																	
47	24-24	.05	.49	.49	1.26	1.24	.97	.92	.91	1.49	2.41	.07	.14	.00	.00	.00	.01	.00																	
48	245-2	.06	.61	.62	1.61	1.59	1.18	1.17	1.19	1.66	1.54	.05	.12	.00	.00		.01	.00																	
49	24-25 + 48	.15	1.37	1.36	3.35	3.40	2.59	2.60	2.38	4.12	4.17	.26	1.10	.01	.02	.01	.07	.04																	
50	246-2				.01	.01	.00	.00	.00																										
51	24-26	.00	.12	.13	.32	.32	.25	.23	.22	.30	.31																								
52	25-25 + 43	.22	1.83	1.86	4.63	4.61	3.64	3.47	3.47	6.93	5.58	.83	5.38	.27	.25	.21	.17	.11																	
53	25-26	.04	.37	.37	.95	.94	.75	.71	.68	1.05	.88	.04	.12	.00	.00	.00	.00	.00																	
54	26-26		.00	.00	.01	.02	.00	.00	.01	.00																									
55	234-3		.05	.05			.09	.11	.10	.06	.05																								
56	23-34	.12	.93	.92	.07	.06	1.80	1.85	1.80	3.16	3.19	1.70	.55	.02	.02	.00	.04	.02																	
57	235-3		.00	.01	.01	.01	.02	.00	.03	.02	.02																								
58	23-35																																		
59	236-3	.01	.20	.15	.41	.38	.37	.32	.27	.37	.23	.00	.02				.00																		
60	234-4	.07	.61	.60	.04	.03	1.17	1.17	1.19	1.85	2.67	.95	.18	.04	.04	.03	.02	.02																	
61	2345																																		
62	2346																																		
63	235-4 + 76	.00	.10	.10	.06	.05	.13	.11	.12	.17	.19	.07	.02																						
64	236-4	.10	.87	.87	1.87	1.84	1.76	1.68	1.67	3.01	3.32	.36	.59	.01	.01	.00	.04	.02																	
65	2356																																		
66	24-34	.21	1.74	1.71	.39	.36	3.38	3.38	3.40	5.84	7.22	3.56	1.01	.03	.03	.01	.08	.05																	
67	245-3	.00	.09	.08	.06	.06	.15	.17	.16	.13	.10	.00																							
68	24-35																																		
69	246-3				.00	.00																													
70	25-34	.24	1.90	1.90	.59	.56	3.76	3.70	3.73	7.28	7.39	6.83	3.49	.04	.04	.05	.12	.07																	

Table 4B. Summary weight% PCB congener distributions in Aroclors compiled from data from HRGC Systems 1, 3, and 4.

IUP AC#	Aroclor - Structure CI Pos.	1 A1 1221	2 A1.5 1232	3 G1.5 1232	4 A2 1016	5 S2 1016	6 A3 1242	7 G3 1242	8 S3B 1242	9 A3.5 1248	10 G3.5 1248	11 A4 1254	12 G4 1254	13 A5 1260	14 S5 1260	15 G5 1260	16 A6 1262	17 G6 1262
71	26-34	.06	.54	.54	1.16	1.17	1.04	1.06	1.00	1.67	1.86	.11	.15	.00	.00	.00	.02	.00
72	25-35		.00		.00	.00	.01	.01	.01	.02	.01							
73	26-35				.00	.00		.00										
74	245-4	.12	.92	.92	.33	.33	1.83	1.76	1.84	3.14	4.67	2.19	.84	.05	.05	.04	.06	.04
75	246-4		.02	.02	.06	.06	.05	.03	.04	.08	.08							
76	345-2	.00					.08	.08	.09	.13	.13	.03	.02					
77	34-34	.01	.17	.16			.27	.33	.33	.41	.52	.20	.03					
78	345-3																	
79	34-35																	
80	35-35																	
81	345-4		.00				.00	.01	.01	.01	.02	.00						
82	234-23	.00	.12	.12			.29	.22	.28	.81	.62	1.53	1.11					
83	235-23 + 119		.05	.04			.12	.09	.12	.26	.20	.56	.48	.00	.00	.00	.00	.00
84	236-23 + 89	.02	.20	.18	.05	.05	.46	.35	.43	1.26	.91	1.58	2.32	.11	.12	.10	.05	.03
85	234-24 + 115	.03	.17	.17	.00		.36	.24	.32	.98	1.14	2.49	1.28	.00	.00	.02	.03	.01
86	2345-2		.01	.01			.03		.04	.11	.09	.10	.06					
87	234-25	.04	.22	.22			.52	.38	.49	1.45	1.11	3.41	3.99	.44	.42	.36	.11	.11
88	2346-2						.00	.00		.02	.02							
89	234-26		.05	.05			.10	.07	.09	.20	.17	.11	.09					
90	235-24									NM	NM	NM	NM					
91	236-24		.10	.10	.06	.06	.24	.17	.23	.63	.56	.53	.93	.00	.00	.01	.01	.00
92	235-25	.02	.05	.05			.06	.09	.13	.38	.25	.57	1.29	.34	.32	.25	.07	.09
93	2356-2							.00	.00	.04	.03							
94	235-26					.00	.00	.00	.01	.03	.02	.00	.02					
95	236-25	.05	.30	.30	.31	.30	.68	.51	.64	1.96	1.43	1.84	6.25	2.56	2.54	2.27	.87	.99
96	236-26		.01	.01	.04	.04	.03	.02	.03	.08	.06	.01	.04					
97	245-23	.03	.18	.17	.00	.04	.43	.31	.41	1.22	.97	2.78	2.62	.10	.09	.08	.06	.03
98	246-23					.00												
99	245-24	.04	.21	.21	.01	.01	.53	.36	.49	1.47	1.81	4.53	3.02	.03	.04	.06	.06	.03
100	246-24																	
101	245-25	.07	.33	.32	.04	.03	.78	.57	.71	2.22	1.89	5.49	8.02	3.23	3.18	2.99	1.03	1.23
102	245-26		.03	.03	.04	.04	.08	.05	.07	.19	.17	.09	.15					
103	246-25									.02	.00		.03					
104	246-26																	
105	234-34	.05	.22	.21	.00		.52	.37	.52	1.60	1.45	7.37	2.99	.22	.21	.23	.18	
106	2345-3																	
107	234-35																	
108	2346-3																	
109	235-34 + 123		.03	.03			.08	.04	.06	.18	.13	.78	.37	.00	.00	.00	.00	.00
110	236-34	.05	.38	.38			.94	.68	.88	2.97	2.55	8.42	9.29	1.38	1.36	1.25	.36	.42
111	235-35																	
112	2356-3						.00											
113	236-35											.01		.00				
114	2345-4		.02	.01			.05	.03	.05	.12	.12	.50	.18	.00		.00		
115	2346-4		.01	.01			.04	.03	.05	.11	.11	.37	.20			.00		
116	23456																	
117	2356-4		.01	.00			.03	.02	.04	.09	.10	.19	.23					
118	245-34	.08	.29	.28			.78	.51	.69	2.29	2.35	13.59	7.35	.51	.50	.45	.17	.14
119	246-34									.06	.06	.12	.08					
120	245-35																	
121	246-35																	
122	345-23						.01	.00	.02	.06	.05	.25	.10					
123	345-24						.03	.02	.03	.07	.08	.32	.15					
124	345-25		.00				.03	.02	.03	.10	.07	.47	.29	.00	.00	.00	.00	.00
125	345-26		.00	.00			.02	.02	.02	.04	.03	.03	.02					
126	345-34									.00	.00	.02	.00					
127	345-35																	
128	234-234						.04	.00	.02	.12	.08	1.71	1.42	.56	.55	.50	.17	.20
129	2345-23							.00		.02		.39	.38	.15	.14	.12	.03	.04
130	234-235									.04	.01	.50	.60	.23	.22	.21	.03	.06
131	2346-23											.14	.19	.08	.07	.05		
132	234-236		.02	.02			.05	.03	.04	.15	.14	1.50	2.29	2.84	2.96	2.91	1.07	1.35
133	235-235 + 131												.11	.08	.06	.06	.03	.05
134	2356-23									.04	.01	.20	.37	.36	.36	.31	.11	.14
135	235-236									.28	.61	1.14	1.09	1.02	1.02	1.02	.67	.65
136	236-236			.00					.00	.05	.06	.24	.70	1.48	1.45	1.44	1.02	.99
137	2345-24									.03	.02	.52	.42	.02	.02	.02	.01	.00
138	234-245 + 163		.06	.05			.16	.05	.10	.38	.41	5.95	5.80	6.47	6.41	6.73	2.33	3.14
139	2346-24											.14	.15					
140	234-246																	

Table 4C. Summary weight% PCB congener distributions in Aroclors compiled from data from HRGC Systems 1, 3, and 4.

IUP AC#	Aroclor - Structure CI Pos.	1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17						
		A1 1221	A1.5 1232	G1.5 1232	A2 1016	S2 1016	A3 1242	G3 1242	S3B 1242	A3.5 1248	G3.5 1248	A4 1254	G4 1254	A5 1260	S5 1260	G5 1260	A6 1262	G6 1262	A4 1254	G4 1254	A5 1260	S5 1260	G5 1260	A6 1262	G6 1262	A4 1254	G4 1254	A5 1260	S5 1260	G5 1260	A6 1262	G6 1262	A4 1254	G4 1254	A5 1260	S5 1260	G5 1260	A6 1262	G6 1262	
141	2345-25									.01	.00	.00	.07	.09				.69	.98	2.62	2.68	2.57	1.63	1.69																
142	23456-2																																							
143	2345-26																																							
144	2346-25																					.01	.12	.24	.61	.61	.61	.41	.41											
145	2346-26																																							
146	235-245													.04	.05				.45	.67	1.17	1.16	1.11	.57	.61															
147	2356-24																	.02	.10																					
148	235-246																																							
149	236-245 + 147			.05	.05					.07	.04	.06	.24	.33	1.82	3.65	8.74	8.78	8.73	6.36	6.44																			
150	236-246																																							
151	2356-25			.01	.00							.00	.04	.08	.22	.69	3.04	3.04	3.03	3.14	2.81																			
152	2356-26																																							
153	245-245 + 132	.00	.05	.05						.09	.04	.05	.23	.43	3.29	3.77	9.09	9.17	9.91	6.78	7.42																			
154	245-246																.02	.04																						
155	246-246																																							
156	2345-34									.02			.06	.04	1.13	.82	.53	.54	.50	.14	.18																			
157	234-345												.00	.00	.30	.19	.02	.02	.02	.00	.00																			
158	2346-34 + 129									.02		.01	.04	.04	.90	.81	.57	.58	.60	.18	.21																			
159	2345-35																																							
160	23456-3																																							
161	2346-35																																							
162	235-345																																							
163	2356-34		.02	.02						.00	.02	.00	.06	.08	.70	1.03	2.41	2.43	2.44	1.50	1.55																			
164	236-345									.00			.02	.03	.31	.40	.72	.70	.66	.23	.30																			
165	2356-35																																							
166	23456-4														.05	.05																								
167	245-345												.00	.00	.35	.27	.20	.20	.17	.02	.05																			
168	246-345																																							
169	345-345																																							
170	2345-234													.08	.35	.52	3.97	4.01	4.36	3.05	3.47																			
171	2346-234														.08	.14	1.09	1.08	1.17	.85	.89																			
172	2345-235														.03	.07	.71	.70	.69	.63	.62																			
173	23456-23																.11	.09	.09	.03	.05																			
174	2345-236														.08	.14	4.92	4.96	4.99	6.56	6.10																			
175	2346-235																.18	.18	.17	.19	.16																			
176	2346-236														.00	.04	.59	.58	.59	.73	.66																			
177	2356-234													.03	.08	.20	2.54	2.52	2.64	2.82	2.73																			
178	2356-235															.03	.86	.84	.79	1.31	1.10																			
179	2356-236													.02	.02	.10	2.05	2.04	1.99	3.64	3.01																			
180	2345-245 + 193		.02	.00								.00	.02	.21	.42	.67	10.90	11.20	12.05	13.72	14.53																			
181	23456-24																.00	.00	.00																					
182	2345-246																																							
183	2346-245														.06	.09	.18	2.33	2.35	2.56	2.89	2.86																		
184	2346-246																																							
185	23456-25																.56	.56	.53	.93	.81																			
186	23456-26																																							
187	2356-245		.01	.00											.09	.09	5.44	5.37	5.39	9.55	8.76																			
188	2356-246																																							
189	2345-345															.00	.01	.08	.11	.12	.03	.04																		
190	23456-34														.05	.07	.82	.80	.85	.74	.77																			
191	2346-345																.16	.17	.17	.13	.13																			
192	23456-35																																							
193	2356-345																.03	.54	.49	.57	.67	.65																		
194	2345-2345															.01	2.11	2.06	2.03	3.79	4.32																			
195	23456-234																.86	.81	.85	1.39	1.46																			
196	2345-2346																1.02	1.03	1.21	2.41	2.12																			
197	2346-2346																.07	.07	.07	.14	.13																			
198	23456-235																.10	.11	.09	.24	.22																			
199	2345-2356+198																.01	1.87	1.86	1.60	4.91	4.57																		

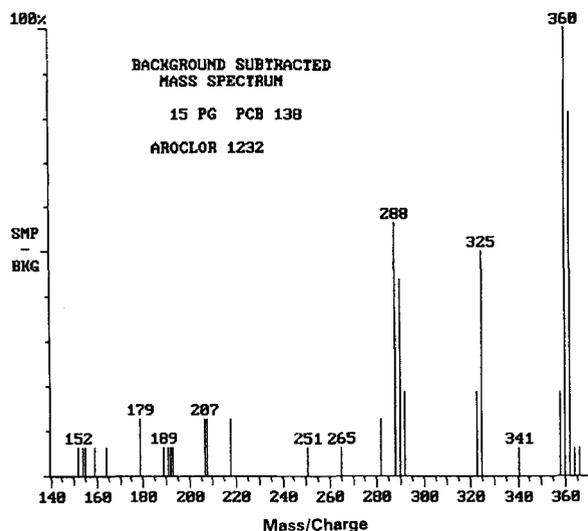


Figure 3. System 3, GC-Ion-trap MS, full-scan spectrum of PCB 138 in Aroclor 1232.

3.4 Aroclor Congener Weight% Distributions

Weight percentages for each congener in 17 Aroclor lots were calculated against the sum of all congener concentrations found in each Aroclor and are displayed in the 3 pages of **Table 4**. Since Aroclors 1221 and 1232 contain ~12% and ~6% unmeasured unchlorinated biphenyl [17], the reported weight percents should be adjusted by factors of 0.88 and 0.94 before using their distributions as a secondary calibration standard. Concentrations of individual PCB congeners were calculated in **Systems 1, 3, and 4** by single point calibration as described in Section 2.4. The values used to calculate the weight% in **Table 4** were compiled in three ways:

1. MS detection does not enable separate quantitation of coeluting *isomers* (congeners of the same chlorine number). In cases where specific Aroclor *isomers* were not party to coelutions in either **Systems 1 and 3**, the calculated concentrations on each system agreed within $\pm 10\%$ more than 90% of the time, and the mean of the concentrations on each system was used.
2. **System 3** resolved more isomer pairs than **System 1** (**Table 2A**). Isomer coelutions on **System 1** are designated in weight% **Table 4** by adding the IUPAC number of the minor component of the pair to the major component structure designation in the Cl-position column. Such combinations are underlined for cases where **System 3** could resolve the pair, and in those cases the **System 3** concentration was used for each of the congeners coeluting on **System 1**.
3. In cases where neither **Systems 1 or 3** could resolve significant isomer coelutions (non-underlined), the average of the **System 1 and 3** concentrations measured using the major component's GC-MS RRF was calculated, and that value was apportioned between the two congener components according to the relative amounts measured on columns **4A** and/or **4B** of the dual-column ECD system. Congener weight% calculated by this procedure are enclosed by out-

lines in **Table 4**. This method of calculation was chosen in order to base all congener quantitation in **Table 4** on the more linear MS responses.

Values below 0.05 Wt% are trace levels with poor quantitative accuracy due to difficulties of integrating small peaks close to background noise level. They are also more than 50-fold lower than the single standards, and 200-fold lower than the internal standard levels. As pointed out by Hess *et al.* [7], even with the greater linearity of the MS detector's responses, this is too great a span for accurate quantitation by single point calibration. The values are retained in **Table 4** as very rough approximations of the trace levels detected. Values calculated between 0.015 and 0.005 are rounded to .01 and those below 0.005 are displayed as .00. NM (not measurable) designates congeners verified elsewhere at trace levels in some Aroclors but not measurable because of coelutions with either other Aroclor congeners, or with the IS in the case of PCB 209. Contributions to the PCB 206 and 208 peaks from traces of these congeners in the PCB 209 IS were measured and subtracted to calculate the values displayed in **Table 4**.

3.5 Systematics of Chlorine Substitution in Aroclors

The weight% data of **Table 4** were converted to mole percents of each of 20 possible single phenyl-ring chlorine-substitution patterns and displayed for 5 biphenyl chlorination levels in **Table 5A**. The results are consistent with the theory of electrophilic substitution reactions on aromatic rings:

1. 246- and 35-substituted rings are highly suppressed (<0.1 mole% in any Aroclor). Their formation requires 2 unfavored substitutions *meta*- to either the other ring or prior chlorines, and once formed these ring substitution patterns direct rapid, strongly favored additional chlorination at positions *ortho*- or *para*- to multiple chlorine atoms.
2. 26-, 235-, and 345-substituted rings are less common (<3 mole% in any Aroclor) as a result of the same factors in 1. above, but in these cases they act with lesser force.
3. 25-substitution occurs extensively and relatively rapidly, and it persists once formed; 24-substitution also occurs relatively rapidly but is then also rapidly removed by further chlorination above the percentages in Aroclor 1248; 34-substitution is initially slower but persists longer in higher Aroclors.

The 52 congeners listed in **Table 5B** were not detected above 0.01 Wt% in any Aroclor. All but PCB 182 should be observable without Aroclor congener coelution in at least one of **Systems 1, 3, 4A or 4B**. All 52 either possess one or more of the unfavored phenyl ring chlorination patterns described in 1. or 2. above, or display strong imbalance in the number of chlorines on each ring, (*e.g.* PCBs 38, 61, 62, 116, 142, 181), which is another feature unlikely to accumulate significantly. Measurable traces of PCBs 21 and 90 are anticipated on the basis of these correlations, but these PCBs suffer Aroclor congener coelutions on all systems of this study. The former has been detected in Aroclor mixtures on an HT8 column [11], and the latter has been reported in Aroclor 1254 by de Boer and Dao [22] and Frame [13] at levels considerable lower than those reported by Schulz *et al.* [14] in Aroclors 1242, 1254, and 1260.

Table 5A. Mole percents of PCB phenyl ring substitutions.

Lot → Aroclor- Ring Cl Pattern	A1 1221	Mean(3) 1242	Mean(2) 1248	G4 1254	Mean(3) 1260	Mean of all 5
none	34.89	1.33	.06		.02	7.26
2	33.12	21.01	7.05	.71	.18	12.41
3	4.59	2.85	63	.05	.00	1.63
4	21.78	20.00	12.83	1.80	.19	11.32
23	.78	7.82	9.24	5.67	.51	4.80
24	1.40	10.18	12.94	4.62	.12	5.85
25	1.81	17.84	22.99	21.24	7.57	14.29
26	.52	2.86	2.61	.35	.01	1.27
34	.82	9.32	14.64	14.46	3.48	8.54
35	.00	.02	.00	.00	.00	.00
234	.07	1.60	3.98	10.56	10.03	5.25
235	.00	.30	.65	2.11	2.37	1.09
236	.10	2.27	5.24	13.86	14.43	7.18
245	.14	2.49	6.66	19.84	30.26	11.88
246		.02	.07	.07		.03
345	.00	.04	.14	.69	.90	.35
2345		.03	.23	2.01	15.04	3.46
2346		.02	.09	.88	3.43	0.88
2356		.02	.14	1.38	9.61	2.23
23456				.07	2.15	.45
SUM	100.05	100.03	100.19	100.37	100.29	100.19

Table 5B. Chlorine substitution patterns of PCBs not detected in Aroclors above 0.01 weight%.

PCB No.	Cl Pattern	Cl Diff.	PCB No.	Cl Pattern	Cl Diff.
14	35		116	23456	5
30	246	3	120	245 - 35	
36	35 - 3		121	246 - 35	
38	345	3	127	345 - 35	
39	35 - 4		140	234 - 246	
50	246 - 2		142	23456 - 2	4
58	23 - 35		143	2345 - 26	2
61	2345	4	145	2346 - 26	2
62	2346	4	148	235 - 246	
65	2356	4	150	236 - 246	
68	24 - 35		152	2356 - 26	2
69	246 - 3		155	246 - 246	
72	25 - 35		159	2345 - 35	2
73	26 - 35		160	23456 - 3	4
78	345 - 3		161	2346 - 35	2
79	34 - 35		162	235 - 345	
80	35 - 35		165	2356 - 35	2
98	246 - 23		168	246 - 345	
100	246 - 24		169	345 - 345	
104	246 - 26		181	23456 - 24	3
106	2345 - 3	3	182	2345 - 246	
107	234 - 35		184	2346 - 246	
108	2346 - 3	3	186	23456 - 26	3
111	235 - 35		188	2356 - 246	
112	2356 - 3	3	192	23456 - 35	
113	236 - 35	3	204	23456 - 246	

BOLD indicates "suppressed" ring substitution.

italic indicates "less common" ring substitution.

3.6 Comparison of Aroclor Lots

The last 2 columns of **Table 3** display pairwise comparisons of the congener distributions of different lots of the same numbered Aroclors as the sum of all the individual congener weight% differences calculated from the values in **Table 4**. The sums for

pairs of Aroclors 1016s, 1232s, and one pair of 1260s are less than 2%. These pairs likely represent the same manufacturer's lot, and pairwise comparisons of the individual congener weight% between these in **Table 4** may therefore provide an indication of the precision (*i.e.* the repeatability) of this study's analytical quantitation. Sums for pairs of 1242s, 1262s and an additional 1260 differ by 6 to 12%; values probably representing small lot-to-lot differences for these Aroclors. The sums for the pair of 1248s differ by 20% and for the pair of 1254s by 53%! Aroclors 1248 and 1254 are representative of the midpoint of the chlorination process for biphenyls. A number of tetra-, penta- and hexa- chloro-substituted PCBs are being rapidly created and destroyed in this range, so one might expect to find greater lot-to-lot variations among these.

A close examination of the differences between the AccuStandard (A4) and General Electric (G4) Aroclor 1254s reveals remarkable differences with respect to *ortho*-chlorine (2,6) substitution. When the G4/A4 ratio of weight% is calculated for 11 non- or mono-*ortho*- substituted congeners (77, 126; 56, 60, 66, 74, 105, 114, 118, 122, 123) the ratios range from 0.15 to 0.54; while for 11 di-, tri- or tetra-*ortho*- chloro-substituted congeners (44, 49, 52, 92, 95; 135, 144, 149, 151, 187; 136) the ratios range from 2.00 to 6.72. A ratio of 1.00 would indicate that the proportions of a congener in each lot were the same. This striking difference suggests a rationale for many of the major differences in congener weight% displayed between this pair of Aroclor 1254s in **Table 4**. The chlorination process for synthesis of the AccuStandard A4 lot (perhaps using an atypical chlorination catalyst or reaction conditions) may have been less favorable for *ortho*-chlorination than the one used for most other lots. Thus non- or mono- *ortho*- chloro-substituted congeners could build up, while further *ortho*-chlorination to produce di-, tri-, and tetra-*ortho*-chloro-substituted congeners was suppressed. By contrast the differences between the Aroclor 1248 lots do not display this *ortho*-substitution effect. The G4 Aroclor 1254 distribution is closer to that reported by Schulz *et al.* [14] and to the majority of other lots of Aroclor 1254 we have observed when simple comparisons of ECD or MS-SIM chromatographic patterns are made. The atypical A4 Aroclor 1254 lot is no longer distributed by AccuStandard.

4 Conclusion

The substantial differences between the Aroclor 1248 and 1254 lots emphasize the need to obtain the appropriate lots when using Aroclor mixtures as secondary standards for calibrating CQCS PCB analyses. All lots of Aroclors of the same chlorination level do NOT have similar congener distributions! The comprehensive Aroclor congener distributions in **Table 4** are considered to be more complete (especially for trace components) and accurate than those presented in earlier comprehensive studies [13, 14]. However, the shortcomings of the single level calibration which was employed indicate that the $\pm 10\%$ accuracy desirable for Aroclor-calibrated CQCS analysis has certainly not been achieved for all major and minor congeners over the full range of concentrations. **Table 6** compares our weight percentages for several minor mono-*ortho*- PCBs with the values accurately determined in other lots of 4 Aroclors by both 2D-GC-ECD and serial-coupled column GC-ECD [23]. The generally good agree-

Table 6. Wt% Comparisons of minor mono-*ortho*-substituted congeners.

PCB	A1242	A1248	A1254	A1260	Lab
74	2.30	4.10	1.30	.09	a
	2.10	4.00	1.10	.02	b
	1.81	3.91	.84	.05	c
114	.04	.13	.19	.03	a
	.04	.14	.25	<.01	b
	.04	.12	.18	<.01	c
123	<.02	.09	.14	<.03	a
	.04	.09	.25	<.01	b
	.03	.08	.15	<.01	c
157	<.01	<.01	.24	.08	a
	<.01	.02	.30	.15	b
	<.01	<.01	.19	.02	c
167	<.03	.03	.45	.18	a
	<.01	.03	.39	.13	b
	<.01	<.01	.27	.19	c
189	<.01	<.01	.04	.14	a
	<.01	<.01	.04	.10	b
	<.01	<.01	.01	.10	c

a = Data produced by 2D-GC-ECD [22] Netherlands Institute for Fisheries Research

b = Data produced by serial coupled GC-ECD [22] CEC Joint Research Center.

c = Data produced by GC-MS and GC-ECD from

Tables 4 B, C: This paper, means for each Aroclor, except A1254 is lot G4 only.

ment for most components, even at low levels one or more orders of magnitude less than the concentrations of the single point standards and IS, supports the claim of semi-quantitative accuracy for our weight% distributions. There remains a need for a set of *individual* Aroclor CQCS secondary standards (minimally including Aroclors 1221, 1242, a characteristic 1254, and 1262) to cover all Aroclor congeners at measurable levels. These need to have all congeners carefully quantified against multilevel certified primary standards on suitable HRGC columns, such as those employed in this study, and must be available to the PCB analytical community indefinitely. The best, readily available, documented Aroclor secondary standard for CQCS PCB analysis is presently that of Mullin's "Green Bay Method" [18], comprising a *single* mixture of Aroclors 1232 (itself a 50:50 blend of Aroclors 1221 and 1242): 1248: 1262 in proportions of 25:18:18. Aroclor 1262 is probably preferable to 1260 for this purpose, since it enhances the amounts of some of the most heavily chlorinated congeners. However, inspection of Table 4 reveals that the chlorination-level gap between Aroclors 1248 and 1262 in the "Green Bay Standard" results in barely measurable levels of minor pentachlorobiphenyls 83, 109, 117, 122, 123, 124, and hexachlorobiphenyls 128, 129, 130, 131, 134, 137, 139, 147, 156, and 167 by comparison with the coverage obtained using an Aroclor 1242/1254 pair.

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