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Review

Recent developments in the high-resolution gas chromatography of polychlorinated biphenyls

Jack W. Cochran[a,*], George M. Frame[b]

[a]*Waste Management and Research Center, One East Hazelwood Drive, Champaign, IL 61820, USA*
[b]*Full Spectrum Analytical, 46 Deer Run Hollow, Clifton Park, NY 12065, USA*

Abstract

The capillary gas chromatography of polychlorinated biphenyls (PCBs) is reviewed. Focus is on the most recent developments in the separation and detection of PCBs rather than sample preparation methods. Included are a comprehensive look at stationary phases that have been used to separate PCBs and the relatively new work on chiral separations of PCBs. Mass spectrometry and atomic emission are presented as selective detection techniques. Suggestions for additional research are proposed where appropriate.

Keywords: Reviews; Atropisomers; Retention indices; Aroclors; Polychlorinated biphenyls

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*Corresponding author.

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1. Introduction

The interest in improving the gas chromatographic analysis of polychlorinated biphenyls (PCBs) continues for several reasons. Unfortunately, one of the reasons is because they are extremely persistent and widespread environmental contaminants that require monitoring because of their potential health impacts on a wide variety of biota, including humans. PCBs continue to be detected in remote locations in the Arctic [1] and Antarctic [2], in wildlife ranging from insects [3–5] to frogs [6] to fish [7–9] to birds [10–13] to marine mammals [14], and in human tissues [15,16] and breast milk [17,18]. PCBs have received attention as endocrine disruptors and environmental estrogens [19]. Most wildlife exposure is a result of transport up the food chain where PCBs tend to concentrate in organisms that have higher lipid contents (e.g. fish, fish-eating birds). The primary sources of this ongoing PCB contamination to living organisms are sediments, soils, waters, and air, which received their initial inputs from the improper and careless disposal practices, or accidental discharges, of technical mixes of PCBs (e.g. Aroclors) that were previously used in industry.

The complexity of the PCB chromatographic separation problem is defined by the number of possible congeners (209) and their chemical and physical similarities. For this reason, it could be that no other environmental analysis has benefitted as much from the development of capillary gas chromatography (GC) as the analysis of PCBs. Capillary GC introduced the possibility of congener-specific analysis while simultaneously revealing how much work needed to be done to make it routine [20]. Whereas previously with packed column PCB separations the complaint could be ‘‘lack of resolution’’, now we had too much resolution; in high efficiency systems over 100 peaks could be present. This, coupled with a focused (or even regulatory) interest on the most toxic and/or environmentally significant congeners, has led to the development of short lists of PCBs for monitoring purposes (Appendix C).

The unambiguous separation of only a few select PCBs is problematic even with high efficiency capillary GC. Eventually when it was understood that certain critical separations would not be possible by column efficiency alone, much research and development (or sometimes trial and error?) started on new stationary phases for PCB analysis [20,21]. Interestingly most of this work preceded by years the first report (1995) of the preparation of commercially available individual standards for all 209 congeners [22].

While we consider the congener-specific analysis of PCBs to be very challenging, it perhaps is not as tough as attempting to: (1) introduce the most valuable contributions to PCB analysis in the past; and (2) provide a comprehensive review of the most recent and important reports on PCB separations. While we plan to meet the second issue head-on and hopefully fulfill the obligation with this report, the first item can be partially avoided, resulting in a more manageable bibliography, by citing some thorough PCB review papers from the recent past, and by mentioning that Erickson’s second book on the analytical chemistry of PCBs was published in 1997 [23].

Creaser and Krokos [24] reviewed analytical methods for non-*ortho*-substituted PCBs, considered to be the most toxic congeners. Since these congeners are almost always at trace levels, they are subject to measurement bias because of interferences, including from other PCBs that may exist at

much higher concentrations. These authors put special emphasis on the off-line column chromatography methods that are available to isolate non-*ortho*-PCBs and provided a discussion on GC and detectors. Hess et al. [25] proposed to review the analysis of non- and mono-*ortho*-PCBs, including discussions on matrix, sample preparation and extraction, cleanup, fractionation, chromatographic separations, and detection. In reality their paper was even more comprehensive (thankfully), noting GC separations for PCBs other than non- and mono-*ortho*. Especially valuable were their suggestions for quality assurance techniques to be used for PCB work.

V. Lang's review was titled, ''Polychlorinated biphenyls in the environment'', but much of the content was devoted to the analytical chemistry of PCBs, including sample preparation and gas chromatography [26]. The use of mass spectrometry (MS) for PCB analysis was reviewed by Facchetti [27]. Larsen's 1995 review [21] concentrated on the congener-specific PCB GC issue, demonstrating how proper choice of stationary phase and/or multi-column configurations could ultimately produce the necessary critical separations.

Hansen's 1998 review [28], while centering on assessing PCB congener toxicities, should be of great interest to the PCB analytical community. He suggests that the data sets for environmental risk assessments may be incomplete when only a limited number of congeners are monitored, and proposes a comprehensive ''short list'' (!) of 79 PCBs (Appendix C). He echoes the comments of Hess et al. [25] who said that reporting only planar PCB data ''is an unfortunate and retrograde step since a balanced data set of a wider selection of CBs which have different biological activity would be intrinsically more useful . . . ''. If there is any movement in this direction, additional critical separations will challenge the PCB chromatographer.

This review will focus on the notable capillary GC separation and detection methods for PCBs that have occurred since 1994. Emphasis is high on new or recently characterized stationary phases, and on improvements in the detection of PCBs by MS. Injector studies (or even discussions) [29] and techniques such as pressure programming [30], while potentially very important, were almost nonexistent in the literature and will not be treated as a separate topic. The GC separations of PCB atropisomers are thoroughly covered. Sample preparation, extraction, and cleanup issues will not be discussed. Most of the citations originated from an on-line search of *Current Contents*. We apologize in advance for any significant report that has been left out.

2. Polychlorinated biphenyl nomenclature

Appendix A lists all PCB congeners and their structure according to a simple convention of single-ring chlorine substitution patterns (e.g. 234–245= 2,2′,3,4,4′,5′-hexachlorobiphenyl). PCBs are listed in the order of their IUPAC number. The numbers for congeners 107, 108, 109, 199, 200, and 201 are derived according to Guitart et al. [31], and differ from the numbers assigned by Ballschmiter and Zell [32] as 108, 109, 107, 201, 199, and 200, respectively. Where appropriate, mainly in tables showing coeluting congeners, we have used a convention that classifies congeners according to their significance in Aroclors 1242, 1254, or 1260 [33]:

Bold Underline=congener>1.0% (w/w).
Boldface=congener between 0.05 and 1.0% (w/w).
Italic=trace or undetected congener.

3. Separations

3.1. Stationary phases

The state-of-the-art in congener-specific PCB analysis is gas chromatography with fused-silica capillary columns coated with chemically bonded phases that range from apolar to highly polar (Appendix B). An efficient separation of a sample that may have over 100 chemically similar compounds demands attention to details. These details include, but are not limited to: (1) proper injection to minimize analyte band broadening; (2) choice of carrier gas–hydrogen may be operated at higher flow rates than helium without a loss in column efficiency; (3) optimized carrier gas velocity; (4) GC oven programming; (5) column dimensions–length, inside diameter, film thickness, number of plates; and (6) the type of column stationary phase. While it is not the authors'

intent to minimize the role that the first five items play in PCB analysis (and in fact, sometimes these parameters are approached rather casually), certain critical congener separations are only achievable by selecting the proper stationary phase. A phase that exhibits the selectivity for the desired separations tends to make the analysis more forgiving, i.e. a slight shift in PCB retentions due to less than perfect injection parameters or higher than optimum carrier velocities should not necessarily cause coelution of critical PCBs.

The mechanisms for separations/molecular interactions for PCBs on stationary phases were covered nicely by Larsen [21] in his 1995 review. In summary, dispersion, dipole-induced, and shape/size interactions are the governing forces behind PCB separations with capillary GC. At the same time Larsen detailed recognized orders for separations within PCB homolog groups for alkyl, phenyl, and cyanopropyl phases. And it is well defined that on nonpolar stationary phases, PCBs within a homolog group elute according to their number of *ortho* chlorines:

$$4 < 3 < 2 < 1 < 0$$

In general, structured orders to PCB separations tend to become more convoluted with an increase in stationary phase polarity. Vetter et al. [34,35] noted trends in the elution orders of 245-substituted PCBs depending upon the stationary phase used and suggested the term ''selectivity order'' to define the pattern of 245 elution on a particular column.

The classic paper of Mullin et al. [36] used SE-54 for a capillary column, congener-specific separation of PCBs, and led to 5% phenyl columns (e.g. SE-54, DB-5) being used as the standard for PCB analysis. A number of potential coelutions on 5% phenyl (Table 1), especially those that involve a toxic or regulated congener, has led researchers to explore alternative phases for PCB separations. Unfortunately, due to a lack of individual congener standards, even as recently as 1995 only Bolgar et al. [22], and Vetter and Luckas [37] listed elution orders for all PCBs on phases other than SE-54, although there has been extensive reporting on the retention characteristics of PCBs found in technical mixes on a variety of phases [38–45]. The recent paper documenting relative retention times of all PCBs on 20 different

Table 1
Significant PCB coelutions on 5% phenyl phases[a]

Classification		Coeluting PCBs				
		A	**4**	**10**		
		a	**9**	**7**		
		a	**12**	**13**		
		A	**17**	**15**		
		a	**27**	**24**		
		A	**32**	**16**		
	E	A	**28**	**31**		
		A	**33**	**20**	**53**	
McF&C		A	**43**	**49**		
		A	**47**	**75**	**48**	
McF&C		A	**44**	**59**		
McF&C		A	**37**	**42**		
		A	**71**	**41**	**64**	
		A	**66**	**95**		
		A	**56**	**60**		
McF&C	E	A	**84**	**89**	**101**	*90*
McF&C		A	**117**	**87**	**115**	
McF&C		A	**77**	**110**		
		A	**135**	**144**	**124**	
		a	**147**	**109**		
McF&C	E	A	**123**	**139**	**149**	**118**
McF&C		a	**114**	**133**		
		a	**131**	**122**		
McF&C	E	A	**153**	**132**	**105**	
		a	**176**	**130**		
McF&C	E	A	**164**	**163**	**138**	
McF&C		A	**158**	**129**		
		a	**175**	**166**		
McF&C		a	**173**	**157**	**201**	
McF&C		A	**170**	**190**		
McF&C		A	**198**	**199**		
		A	**203**	**196**		

[a] Classification is noted if at least one coeluting congener is in the group.
McF&C = McFarland and Clarke congener [52].
E = European indicator congener [53–55].
A = major Aroclor congener [33].
a = minor Aroclor congener [33].

stationary phases [46], the subsequent widespread distribution of congener standards used for that work, and the introduction of a reasonably priced standard set containing all 209 PCBs [47] have led to additional characterization of stationary phases for PCB analysis [48–51]. Most of these papers focused on key separations. The value of [46] was that the relative retention time data for such a wide variety of phases facilitates selection of a phase to achieve critical congener separations. In particular a DB-XLB phase showed a low number of Aroclor con-

gener coelutions and in many cases those coelutions could be resolved by MS. A representative chromatogram of a mixture of Aroclors 1232, 1248, and 1262 on a DB-XLB column is shown in Fig. 1. As previously noted by Larsen [45], an HT8 column performed well on critical congener separations including the resolution of PCBs 153/132 and 163/138. It is probably worth noting again that no stationary phase available today is capable of the unambiguous, chromatographic separation of all 209 PCBs, the 135+ Aroclor PCBs [33], the 36 McFarland and Clarke PCBs [52], or even the seven European indicator PCBs [53–55]!

Carborane backbone phases were developed for their high temperature stability but have been reported to have selectivity for PCB analysis [56]. An HT5 carborane column was used for separating PCBs in Clophen A40 and found to be better than DB-5 [57]. This phase was suggested to be shape selective for mono-*ortho* and non-*ortho* (coplanar) PCBs, which aided the separation of important pairs such as 110/77, 149/118, and 132/105 that tend to coelute on 5% phenyl columns. A 60 m×0.25 mm, 0.25 μm HT8 carborane column, when combined with a DB-17 column in a parallel GC–electron-capture detection (ECD) system, separated a total of 106 Aroclor congeners [45]. When MS was used as the detection means, 138 congeners were analyzed without interference. The HT8 column allowed a near baseline separation of congeners 138 and 163. A 0.15 μm version of the HT8 column was used for a 13 min (!) screening analysis for the seven indicator congeners.

A bonded and crosslinked nonpolar phase with a high molecular weight similar to squalane (CP-Select for PCBs) was described for PCB analysis and showed a high degree of retention for coplanar congeners [58]. The separation of congeners 28/31, and 153/132/105 was reported on this phase, although different (and significant) coelutions might prohibit the unbiased measurement of congeners 28 and 105. The first reported separation of congeners 164/163/138 permitted their measurement in Aroclors 1242, 1254, 1260, and 1262 [59]. A shortcoming of CP-Select is its relatively low temperature limit of 270°C.

Although they are not commercially available, cyanobiphenyl phases have been used for several studies on PCB analysis [60–63]. A comparison of selectivities for six different cyanobiphenyl phases demonstrated that PCB retentions were dependent on both dispersion and congener shape (planar versus nonplanar) [61]. The favorable properties of *p,p*-cyanobiphenyl included the interference-free elution of coplanar PCBs 77, 126, and 169, and the separation of PCBs 138/163/164 [60,61]. The *p,p*-cyanobiphenyl column was used to quantitate PCBs in standard reference materials including cod liver oil, whale blubber, and mackerel oil [62], with emphasis on producing separate concentration values for PCBs 138/163/164, 170/190, 187/182, 110/77, and 66/95, coelutions typical on 5% phenyl phases. The *p,p*-cyanobiphenyl phase was employed with MS to measure 133 congeners in Aroclors 1242, 1254, and 1260 [63]. The GC–MS setup reportedly allows resolution for 33 of 36 McFarland and Clarke congeners.

Elution orders of all PCBs were reported for a novel 50% methyl–50% phenyl polysiloxane (Thermocap A) column prepared by using an in situ process [50]. This phase has excellent thermal stability and a selectivity for PCBs that is significantly different from other 50% phenyl phases. In contrast to a variety of phases ranging from nonpolar to polar that eluted 245 hexachlorobiphenyls in the order:

$$246 < 236 < 235 < 245 < 234 < 345,$$

the Thermocap A phase eluted those PCBs in the order:

$$246 < 235 < 236 < 245 < 234 < 345.$$

PCB 133 (235–235) eluted prior to PCB 136 (236–236) on Thermocap A, which was not reported for any of the 20 stationary phases tested in the Frame study [46].

Shape selectivity can be very important in PCB separations, especially when one considers that the most toxic PCBs (those that can assume a planar configuration) are the ones likely to experience increased retention afforded from a shape selective mechanism. For GC though, this does not seem to be a very active research area, notwithstanding the earlier mentioned papers on the cyanobiphenyl phase. In one of those studies, cyanobiphenyl phases were compared to a smectic liquid crystalline phase

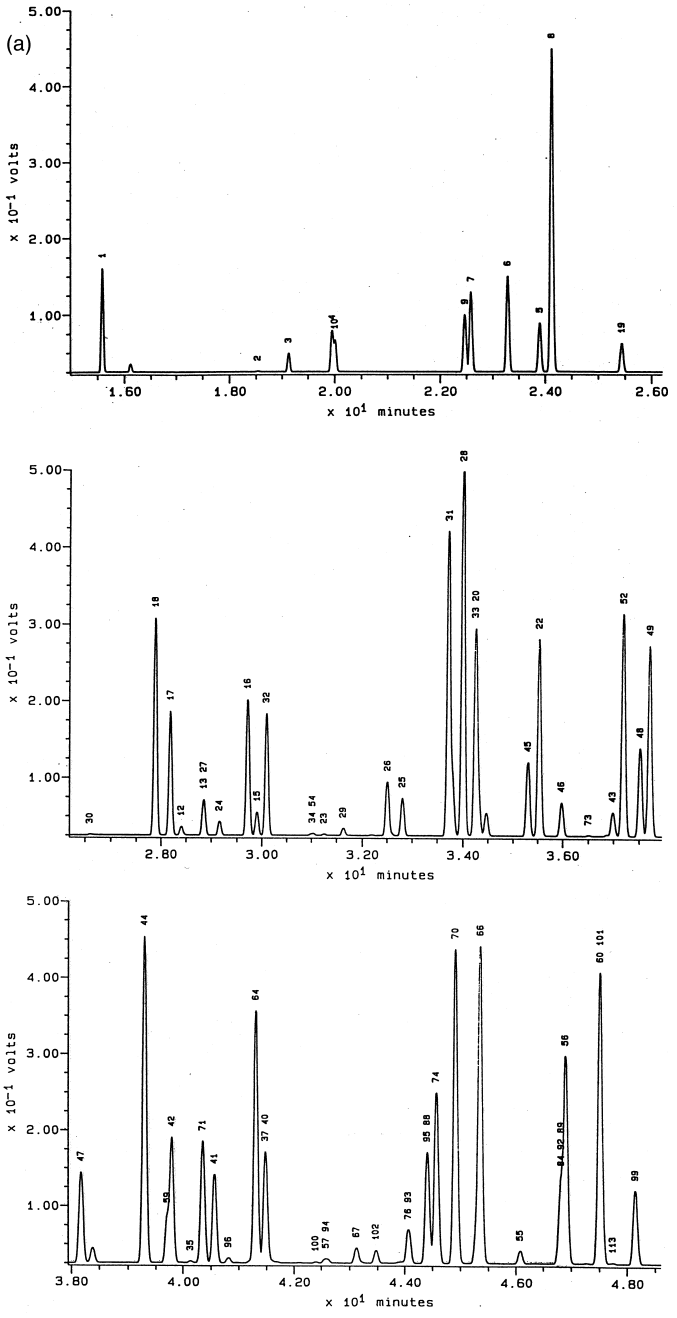


Fig. 1. Chromatogram of PCBs on a 60 m×0.18 mm, 0.18 μm DB-XLB column (J&W Scientific) using hydrogen carrier and ECD. (Courtesy of Academic Press from the book Analytical Gas Chromatography.)

[61] and found to have some shape-selective characteristics, though not nearly as strong as the smectic phase. A smectic phase was used to record retention times for a few *ortho*-substituted PCBs, coplanar PCBs, and the seven indicator PCBs but lack of retention data for other PCBs did not rule out

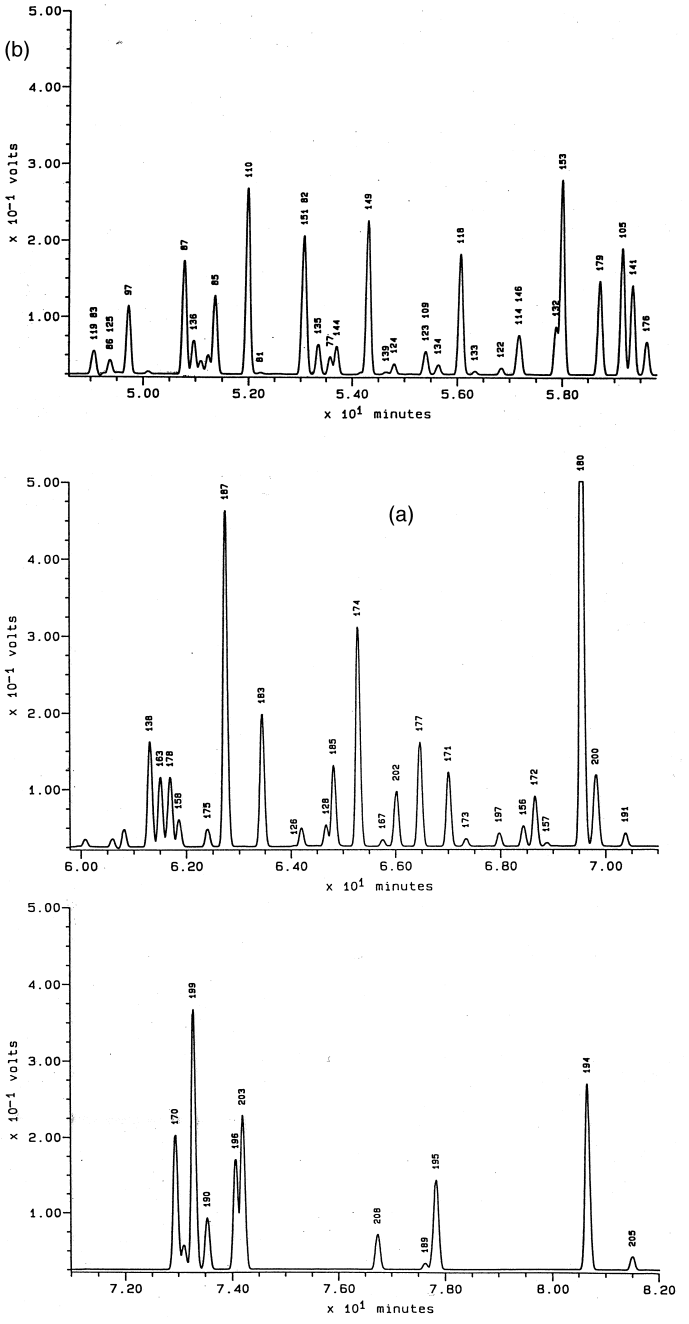
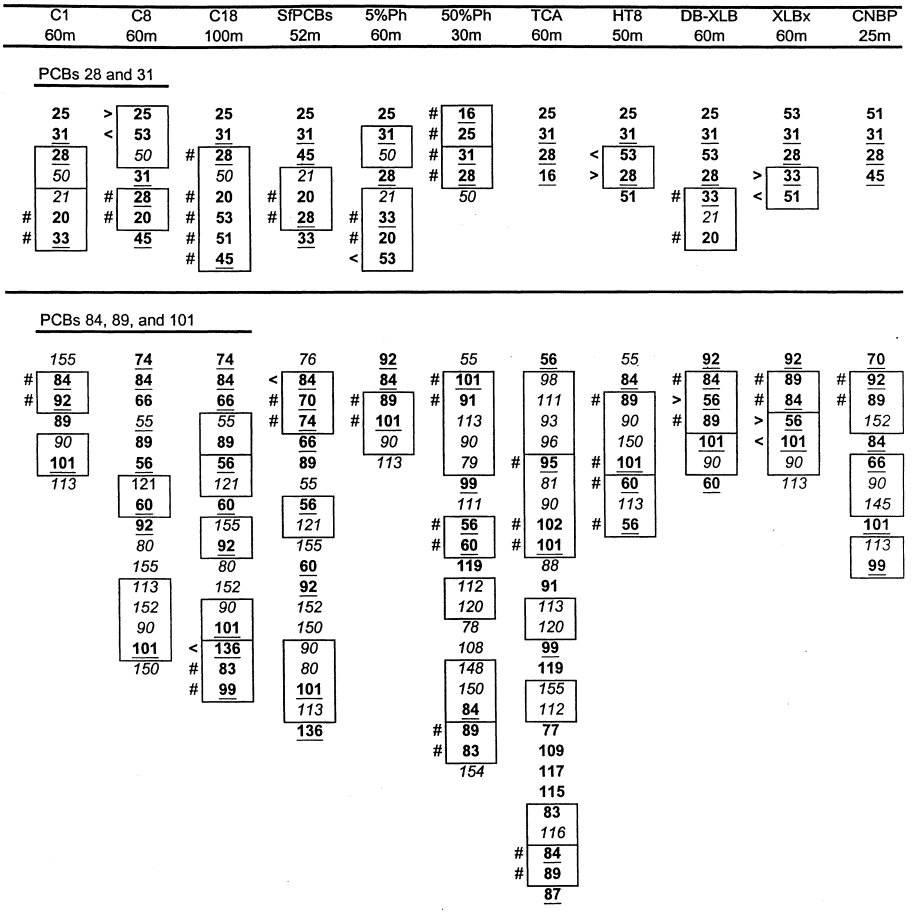


Fig. 1. (*continued*)

coelutions [64]. Harju et al. [51] have reported relative retention times for all 209 PCBs on a liquid crystalline phase. This work dramatically demonstrates the high selectivity of this type of phase for planar PCBs. PCB 37, a trichlorobiphenyl (34-4), elutes after PCB 186, a heptachlorobiphenyl (23456-26)! And PCB 77 (34-34), a tetrachlorobiphenyl, is one of the last eluting congeners. Recently a C_{60}

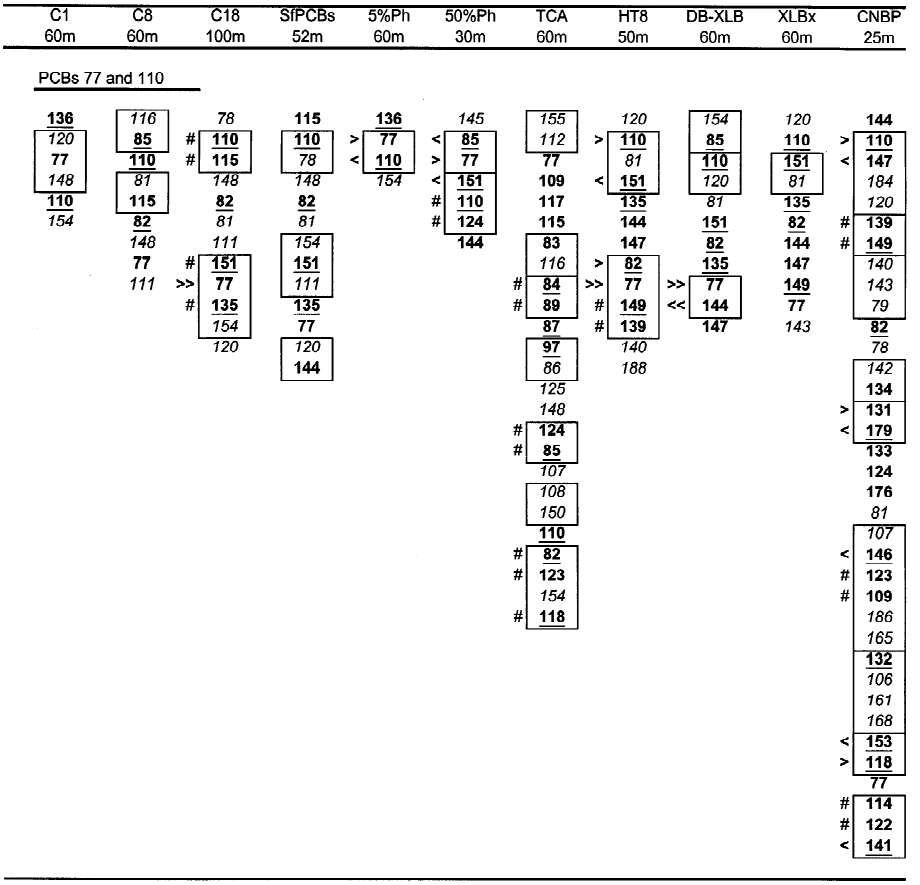
Table 2
Elution orders and coelutions for significant PCB congeners on a variety of stationary phases[a]



fullerene phase was synthesized and used to determine the retention behavior of a group of hexachlorobiphenyls [65]. As expected, increased retention was observed for planar PCBs. The lack of use of shape selective phases by most analysts is probably due to their low temperature limit, high bleed, and poor peak shapes, although some applications note their value as a second column in multidimensional GC (MDGC) analysis of PCBs [41,66].

The driving force behind an analyst's decision to use a particular phase for PCB analysis is, of course, his particular separation. That said, the commercial development of a PCB stationary phase would seem to rest on its ability to resolve environmentally significant PCBs, perhaps best described as those that exist in Aroclors, or those that are regulated and/or those that have some toxic effect to humans or other biota. Some select PCB congener separations based on these criteria are listed for a variety of phases in Table 2. All of this data was pulled from current literature and demonstrates a very important point: no one column phase can resolve these few select PCBs without interference from another PCB. Even eliminating consideration of PCBs that are not present in Aroclors, or that can be uniquely identified using MS, does not produce one column that can resolve the PCBs in Table 2. Therefore, continued evaluation of new phases for their suitability in resolving critical congeners is worth pursuing. Either by design, or more likely by good fortune, new phases may be found, which when evaluated for their potential as parts of parallel dual column systems

Table 2 (*continued*)



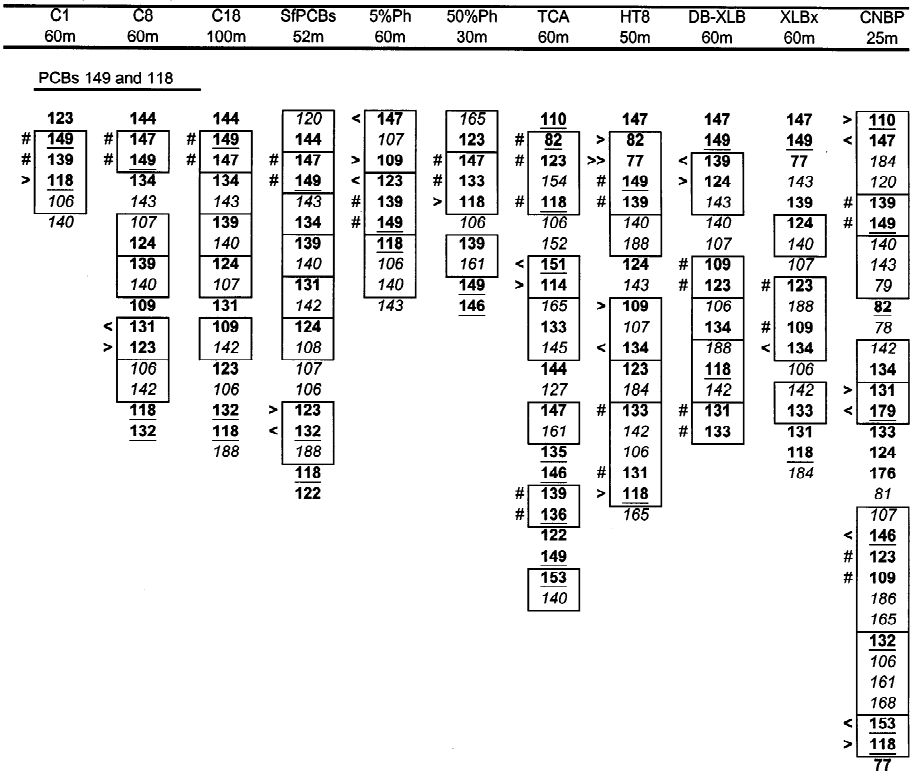
using ECD or when coupled with MS detection, may more closely approach the ''Holy Grail'' of a system which can measure all significant congeners with a single injection. The value of such a discovery is that it could lead to a single procedure and appropriate calibration standard which could be recommended for all purposes requiring comprehensive, quantitative, congener-specific PCB analysis.

3.1.1. Retention indices

The recently published profiles of Aroclors on a wide variety of capillary column phases [46] opens the door on their potential use as qualitative standards for PCB analysis. While MS is invaluable as a qualitative identification tool, it cannot distinguish between PCBs within the same homolog group in most cases, and may lack the sensitivity necessary for trace level PCB work. Mass spectrometry may also be outside the cost range for some laboratories engaged in PCB analysis. The expense involved in purchasing individual, primary standards for retention time mapping may also be prohibitive. Prediction of retention times based on structure, or assignment of PCB names to GC peaks through the use of retention indices or other calculations, is therefore an attractive alternative.

Retention indices (*I*) have been used for qualitative work for numerous years. The classical Kovats *I* system [67], based on using *n*-alkanes as retention markers, is impractical for determining PCB indices because the ECD used for PCB analysis does not respond well to the alkanes. Attempts to adapt (or improve upon) Kovats indices for PCBs include splitting of GC column effluent to flame ionization detection (FID) and ECD systems (for alkane and PCB identification, respectively) [68], and the use of

Table 2 (*continued*)

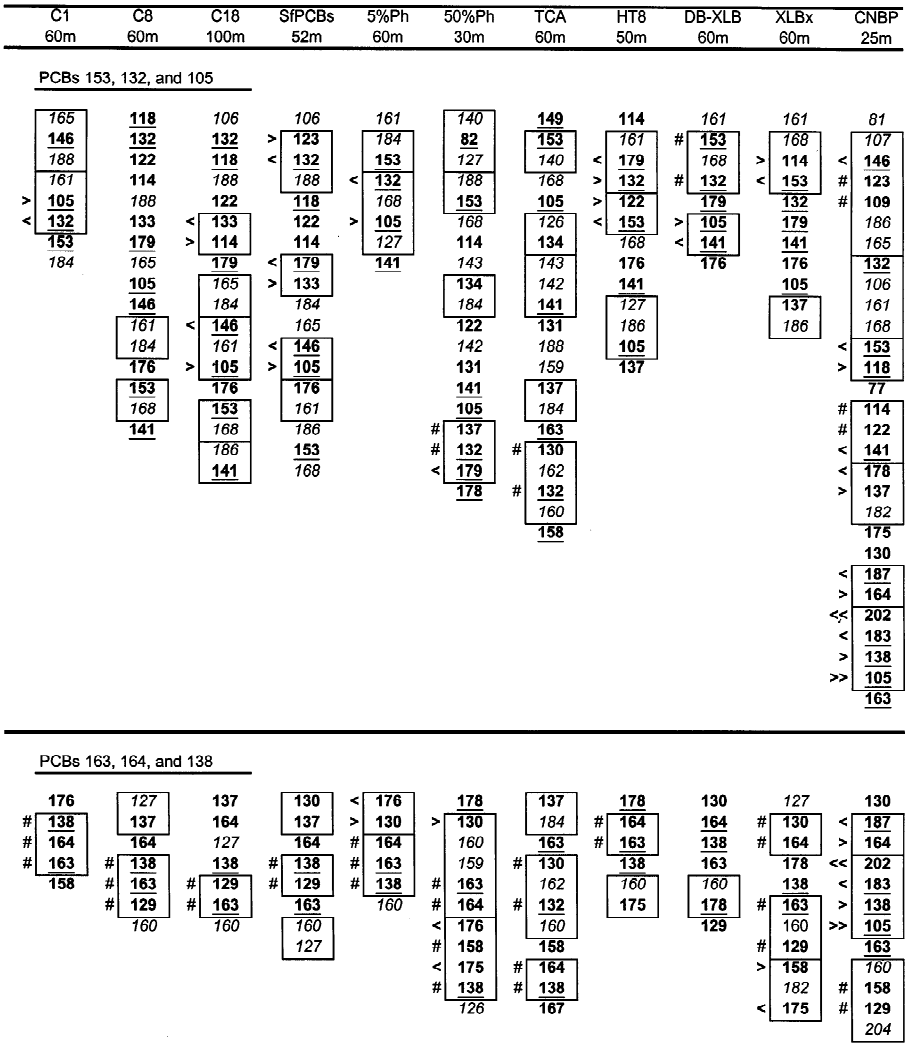


homologous series of compounds of electrophilic nature (e.g. *n*-alkyl iodides [68], *n*-alkyltrichloroacetates [69–71], and *n*-alkyl-bis(trifluoromethyl)-phosphines [72]) that give a good response on ECD. In addition to good ECD response, a reference series of compounds for PCB *I* values should approximate the PCBs in retention characteristics and have similar retention time increments between members of the reference series. Designating standards that are commercially available facilitates the adoption of an *I* system. These criteria have lead some researchers to use PCBs as the reference series for an index system [68,73,74].

Morosoni and Ballschmiter [75] used a homologous series of eight 2,4,6-trichlorophenyl alkyl ethers (TCPEs) to plot *I* values for 28 PCBs with GC–ECD on a 5% phenyl-methylpolysiloxane column. The TCPEs ranged from the ethyl to the hexadecyl ether and appear to bracket all 209 PCBs. The TCPEs were chosen to approximate the retention characteristics of halogenated aromatic hydrocarbons, including PCBs, and because of their good response when using ECD. The authors noted some problems when using the slightly polar TCPEs, as opposed to the classical *n*-alkanes, for *I* calculations under temperature programming conditions. They recommended that any PCB *I* values calculated using TCPEs be accompanied by the oven program used for their analysis. Differences in the TCPE *I* values for PCBs (for different program conditions) were explained by a change in the TCPEs' interactions with the stationary phase due to their content of polar and non-polar moieties.

Chu et al. [73] proposed an *I* system for PCBs using congeners 8, 31, 44, 101, 138, 180, and 194. A simple linear model was developed that regressed the chlorine number of the marker PCBs versus their retention times on a SE-54 column. The congeners that were selected in this approach occur in many environmental samples and technical PCB mixes

Table 2 (*continued*)



Columns: C_1 = Rtx-1; C_8 = SPB-Octyl; C_{18} = CP-Sil 5/C_{18}; SfPCBs = CP-Select for PCBs; 5%Ph = Rtx-5; 50%Ph = DB-17; TCA = Thermocap A; XLBx = modified DB-XLB; CNBP = *p,p*-cyanobiphenyl; □ = coeluting congeners; # = coeluting congeners with same no. of chlorines, not separately measurable by MS detection; < or > = more or less chlorinated congeners differing by one chlorine, measurable in coelutions by MS detection; << or >> = more or less chlorinated congeners differing by two chlorines, NOT measurable in coelutions by MS detection. References for experimental conditions: C_1, C_8, C_{18}, 5%Ph, 50%Ph, HT8, CNBP [46]; SfPCBs [58]; TCA [50]; DB-XLB, XLBx [49].

(e.g. Aroclors, Clophens) which means that a sample could have a resident reference series for qualitative analysis.

One of the most interesting papers on using PCBs as retention markers is from Castello and Testini [74] which built upon their earlier work [68] using the Dry Color Manufacturer's Association (DCMA) test mix as a reference series for *I* values. The DCMA mix, composed of congeners 1, 11, 29, 47, 121, 136, 185, 194, 206, and 209, did not exhibit linear retention time behavior as a function of congener chlorine number. This led the authors to propose congeners 1, 9, 27, 69, 121, 151, 178, 200, 207, and 209 as a reference series. The plot of retention values

Table 3
Retention indices calculated on different methylpolysiloxane columns[a]

PCB No.	Structure Cl Pos.	Rtx-1 *I*	CP-Sil 5 *I*	Difference
81	345-4	560.08	558.99	1.09
77	34-34	573.40	572.09	1.31
123	345-24	611.49	611.53	−0.04
118	245-34	615.37	614.78	0.59
114	2345-4	628.01	627.71	0.30
105	234-34	647.09	644.70	2.39
126	345-34	692.61	691.39	1.22
167	245-345	724.79	725.00	−0.21
156	2345-34	753.92	753.39	0.53
157	234-345	760.33	759.30	1.03
169	345-345	809.62	809.85	−0.23
189	2345-345	863.60	863.67	−0.07

Rtx-1 data from Ref. [46].
CP-Sil 5 data from Ref. [74].

versus the number of chlorine atoms for these chosen congeners was linear for an amazing variety of stationary phases. The authors then used a modified Van den Dool and Kratz equation [76] to plot *I* values for the PCBs. A comparison of some of the index values from Castello and Testini, and values calculated from Frame [46] using a similar phase, is shown in Table 3. The results are in reasonable agreement.

When one considers applying the work of Castello and Testini to the retention data from Frame [46], which covers all 209 PCBs on 20 GC stationary phases, it would appear that a valuable index system could be constructed. A drawback to their proposed series is that some of the congeners will be absent from environmental samples and technical mixes. This leads to the complication of spiking a reference mix into samples or standardizing retention times based on analysis of the reference mixture in the sample queue. To minimize errors in the indices calculations, the authors recommended using a relatively low, initial GC oven temperature to help maintain linearity of the reference series. It would seem to follow that a slower oven program rate would be necessary, not only to promote PCB separation, but also to ensure that the PCBs elute while the oven is ramping and not during a final hold time. By design, the Frame data meet these criteria.

Based upon our knowledge of the composition of PCB technical mixes we propose a hybrid Chu et al./Castello and Testini *I* system containing PCBs 1, 8, 31, 44, 101, 138, 180, 203, and 206. PCBs 1 and 206 elute first and last (excluding PCB 209), respectively, on almost every column tested in the Frame study referenced above, thus bracketing all significant PCBs. PCB 209 becomes unnecessary as a marker. Furthermore, PCB 206 is the major nonachlorobiphenyl in technical mixes. 203 is substituted for 194 (Chu et al.) because it strengthens the linearity plot on a *n*-octyl column while maintaining the desire to include in the reference series, PCBs that are present in technical mixes. A summary comparing the correlation coefficients of linear plots for a variety of columns, using the authors' proposed system versus the published systems of Chu et al., and Castello and Testini, is presented in Table 4. While it is obvious that the Castello and Testini PCB references are superior for producing linear plots, our proposed hybrid system may be easier to use since the likelihood exists for samples/technical mixes to contain the marker series.

Although the paper was not aimed specifically at PCBs, a novel additive scheme for calculating *I* values for hydroxylated PCBs (OH-PCBs) makes an interesting addition to the literature [77]. There are

Table 4
Correlation coefficients for several proposed PCB reference series as a linear function of retention time versus chlorine number on different stationary phases[a]

Retention Index System	Rtx-1	SPB-Octyl	DB-XLB	DB-XLBx
Chu et al. [73]	0.9913	0.9869	0.9929	0.9928
Castello and Testini [74]	0.9976	0.9952	0.9999	0.9997
Cochran and Frame	0.9952	0.9915	0.9933	0.9915

[a] See text for PCBs in index systems. x = experimental.

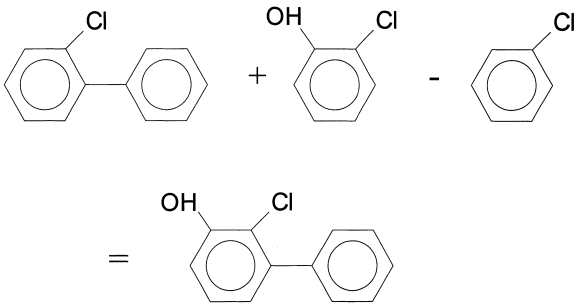


Fig. 2. The retention index for 2-chloro-3-hydroxy biphenyl can be calculated from the additive scheme shown above if retention indices are known (or measured) for the simple structural analogs.

839 possible compounds in this class, an almost overwhelming number to consider for preparation of standards and mapping of retention times. The additive scheme allows calculation of *I* values for OH-PCBs from simple structural analog *I* values by addition and subtraction. An example for 2-chloro-3-hydroxy biphenyl is shown in Fig. 2. Standards (and perhaps even *I* values) for the simple structures in this example are widely available. A number of possible paths to a structure can produce several *I* values and these can be averaged to give a mean index and estimate of the error associated with the calculated *I*. To minimize errors, an important consideration when using this approach is that the precursors must reflect the main features of a compound under characterization (i.e. at least one additive precursor must contain a similar steric situation to the product compound). *I* values were determined experimentally for the precursor hydroxybiphenyls and a group of PCBs (also precursors) ranging from dichloro- to heptachlorobiphenyl. Then the additive scheme was used to generate *I* values from the precursor *I* values. A synthesized mix of OH-PCBs, and *n*-alkane retention markers were analyzed by GC–MS to provide experimental *I* values for the OH-PCBs. Comparisons were performed for experimental and calculated *I* values for select OH-PCBs and found to be in reasonable agreement.

The use of *I* values may enable a chromatographer to perform qualitative PCB analysis without a large number of congener standards, but it comes at the cost of greater complexity in the method, due to the potential need for incorporating and measuring a suitable series of reference compounds and the additional data reduction required. It is inherently less definite than calibration and assignment of congeners to peaks by using congener standards. *I* systems were valuable prior to the ready availability of calibration sets of all PCBs, and will continue to have great value in supporting congener-specific work on PCB metabolites, for which few standards are currently available.

3.1.2. Structure–retention relationships

The retention of PCBs on a particular chromatography phase is very simply described as being dependent on their boiling point and structure, i.e. the chlorine substitution pattern. However, one only has to look in the literature at the number of molecular descriptors used to model structure–retention relationships (SRRs) for PCBs [78,79] to realize the complexity of predicting retention behavior for 209 compounds. Larsen [21] provided a good background discussion on SRRs, or quantitative structure–activity relationships as they are also named. In summary, the models he developed were excellent at explaining retention characteristics of PCBs on non-polar columns, but the models were less successful at describing PCB retention on polar columns.

Prior to the commercial availability of all 209 PCB congeners, SRRs had a practical use for assigning PCB names to GC peaks in complex chromatograms [80,81]. It may be that defining SRRs for PCBs at this point is only an interesting theoretical exercise, although Larsen suggested that column manufacturers could use SRRs to design new stationary phases for PCBs [21]. One area that warrants further research is the possibility that SRRs derived from chromatographic models could be used to describe the behavior of PCBs in biological or other environmental systems.

One of the most important criteria for producing good SRR models is accurate and reproducible GC retention data for all PCBs. A rich database for creating SRR models has recently been provided by Frame [46] when he published relative retention times for all PCBs on 20 different GC phases. To our

knowledge these data have not yet been used to model SRRs. Still, there were a few papers located in our literature search that describe SRR models for PCBs.

Gankin et al. [79] explored SRRs for 209 PCBs based upon a dual column analysis of 85 congeners using DB-5 and DB-17 phases. An SRR model was derived from molecular descriptors and the retention data. The model was then used to identify the PCBs in a harbor sediment extract. In most cases the dual column model suggested 1 or 2 PCBs for each GC peak. Mass spectrometry was employed to further assist in peak assignments and validate the model. The dual column model was described as being very efficient for correct assignment of PCB congeners in a complex environmental sample.

A less complex method of considering PCB SRRs involves keeping one phenyl ring substitution constant and looking at the impact of the other substituted ring on the retention of PCBs [80,81,32]. Kurz and Ballschmiter [82] used this ''single-ring'' method to describe PCB elution sequences on CP-Sil $8/C_{18}$, SE-54, and SP-2331 columns. The orders for all three phases were:

$2 < 3 < 4$

$26 < 25 < 24 < 23 < 35 < 34$

$246 < 236 < 235 < 245 < 234 < 345$

$2356 < 2346 < 2345$

A series of papers on using simple, single-ring retention indices for predicting retention behavior of PCBs has been produced by Vetter and Luckas [37,83,84]. Their first algorithm [37], similar to the work of Sissons and Welti [80], was developed by establishing time increments for 20 symmetrically substituted PCB isomers representing every possible chlorine substitution pattern on one ring. Time increments are defined as the measured retention times of the chosen PCB divided by two. Any PCB retention time (t_R) can be calculated by simple addition of two time increments representing two single-ring chlorine substitutions. An example from their paper would be for PCB 138 (234-245): 29 min for 234 ($1/2$ t_R for PCB 128) and 27 min for 245 ($1/2$ t_R for PCB 153) would equal 56 min as the calculated retention time. The algorithm was tested on a CP-Select for PCBs column and calculated retention times were noted to be accurate within 2% of measured retention times. The value of the method seems to be for predicting elution orders and coelutions. A strong influence of the GC oven temperature program was noted; the authors recommended a rapid heating to 140–160°C followed by a rate of 1–2°C/min to elute all PCBs.

Larsen [21] used a similar method to create single-ring indices, but then normalized them to PCB 16 (=0) and PCB 180 (=100). His table of single-ring indices, for a variety of stationary phases ranging from apolar to highly polar, provides a convenient overview of PCB SRRs.

A variation of the above work described a calculation mode for retention times of all PCBs by analyzing the 245 substituted PCBs [83,84]. A time increment was defined as the measured retention time of one of the 20 245 substituted congeners minus $1/2$ the measured retention time of PCB 153 (245-245). This allowed a time increment to be calculated for each possible ring substitution. For example, the retention time of PCB 105 (234-34) on CP-Select for PCBs would be calculated as 53.22, the sum of: t_R of PCB 138 (**234**-245) minus $1/2$ t_R PCB 153 and t_R of PCB 118 (245-**34**) minus $1/2$ t_R PCB 153, under the prevailing GC oven program. Good agreements between calculated and measured retention times were claimed for the apolar CP-Select for PCBs column, a 14% cyanopropylphenyl column, and a 20% octadecyl column. The results for a very polar cyanopropyl column were significantly worse. The congeners with the greatest deviations between calculated and measured retention times were the same on all of the tested columns.

Further work with 245 PCBs by Vetter et al. [35] led to an indices system normalized to PCB 29 (245) at zero and PCB 203 (23456-245) at 100. The authors defined the elution order of 245 PCBs on a particular stationary phase as the ''selectivity order'' and noted distinct elution trends for the 245 congeners on stationary phases covering a range of polarity.

We used the systems of Vetter [37,84] to calculate

Table 5
Single-ring retention indices for symmetrically substituted PCBs on a methylpolysiloxane column[a]

PCB No.	Structure Cl Pos.	t_R (min)	I	Cl-Ring
4	2-2	22.15	11.08	2
11	3-3	28.70	14.35	3
15	4-4	29.67	14.83	4
40	23-23	42.13	21.07	23
47	24-24	38.73	19.37	24
52	25-25	38.00	19.00	25
54	26-26	32.53	16.27	26
77	34-34	51.47	25.73	34
80	35-35	45.18	22.59	35
128	234-234	63.35	31.68	234
133	235-235	56.37	28.18	235
136	236-236	51.33	25.67	236
153	245-245	57.80	28.90	245
155	246-246	47.03	23.52	246
169	345-345	70.93	35.47	345
194	2345-2345	79.35	39.68	2345
197	2346-2346	68.53	34.27	2346
202	2356-2356	66.90	33.45	2356
209	23456-23456	87.30	43.65	23456

[a] $I = t_R/2$. Experimental conditions given in [46].

Table 6
Single-ring retention indices for 245-substituted PCBs on a methylpolysiloxane column[a]

PCB No.	Structure Cl Pos.	t_R (min)	I	Cl-Ring
29	245	32.97	4.07	0
48	245-2	38.92	10.02	2
67	245-3	43.20	14.30	3
74	245-4	44.17	15.27	4
97	245-23	50.07	21.17	23
99	245-24	48.40	19.50	24
101	245-25	47.88	18.98	25
102	245-26	44.88	15.98	26
118	245-34	54.85	25.95	34
120	245-35	51.45	22.55	35
138	234-245	60.60	31.70	234
146	235-245	57.08	28.18	235
149	236-245	54.77	25.87	236
153	245-245	57.80	28.90	245
154	245-246	52.47	23.57	246
167	245-345	64.10	35.20	345
180	2345-245	68.85	39.95	2345
183	2346-245	63.58	34.68	2346
187	2356-245	63.02	34.12	2356
203	23456-245	73.93	45.03	23456

[a] $I = t_R$-PCB 153 $t_R/2$. Experimental conditions given in [46].

retention times for a suite of PCBs chromatographed on a 60 m×0.25 mm, 0.25 μm Rtx-1 column (methylpolysiloxane). The PCBs used for the symmetrical and 245 single-ring indices algorithms are shown with their measured retention times in Tables 5 and 6, respectively. Table 7 compares the calculated retention times to the measured retention times. In some cases the model predictions are close to the measured values, and both algorithms correctly predicted the coelution of PCBs 132 and 105 on the methyl column. But while the symmetry model accurately forecast the coelution of PCBs 149 and 118, it did not include PCB 139. Both models failed to predict the coelution of PCBs 138/164/163 on the methyl column.

Castello and Testini [85,86] correlated PCB retention times from Mullin et al. [36] with a class system of 19 parent compounds (from single-ring chlorine substitution). Each series of compounds in a class was obtained by changing the number and position of chlorines on the second ring while holding the parent ring chlorine constant. The difference in retention times for a parent and its other class members followed a trend based upon the number of chlorines and their structure. This trend can be used to tentatively identify a PCB as follows: (1) select PCBs with retention times within a given range of the unknown PCB; (2) find the difference in retention time between the unknown and the parents with smaller retention times; (3) compare these values with the retention differences (parent minus class member) for compounds in their respective classes, which should narrow the list to a few likely candidates [85]. This method was further developed to use linear regression to predict retention times for PCBs [86].

It should be noted that there are distinct hazards associated with using models to assign (not predict!) PCBs to peaks generated from the analysis of complex environmental samples. SRRs might be an elegant way to perform qualitative PCB work but they are no substitute for experience and other more authoritative techniques such as MS. Perhaps most importantly, the commercial availability of all 209 PCB congeners now allows an analyst a primary way to map retention times for congeners where peak assignments may be in question.

Table 7
Retention times calculated from single-ring indices compared to measured retention times on a methylpolysiloxane column[a]

PCB No.	Structure Cl Pos.	Measured t_R (min)	Symmetry Calculated t_R (min)	Difference	245 Calculated t_R (min)	Difference
77	34-34	51.47	51.47	0.00	51.90	-0.43
148	235-246	51.52	51.70	-0.18	51.75	-0.23
110	236-34	51.77	51.40	0.37	51.82	-0.05
154	245-246	52.47	52.42	0.05	52.47	0.00
82	234-23	52.77	52.74	0.03	52.87	-0.10
151	2356-25	53.53	52.45	1.08	53.10	0.43
135	235-236	53.93	53.85	0.08	54.05	-0.12
124	345-25	54.00	54.47	-0.47	54.18	-0.18
144	2346-25	54.10	53.27	0.83	53.67	0.43
107	234-35	54.18	54.27	-0.08	54.25	-0.07
109	235-34	54.27	53.92	0.35	54.13	0.13
147	2356-24	54.33	52.82	1.52	53.62	0.72
123	345-24	54.52	54.83	-0.32	54.70	-0.18
149	236-245	54.77	54.57	0.20	54.77	0.00
139	2346-24	54.82	53.63	1.18	54.18	0.63
118	245-34	54.85	54.63	0.22	54.85	0.00
106	2345-3	54.90	54.03	0.87	54.25	0.65
140	234-246	55.10	55.19	-0.09	55.27	-0.17
143	2345-26	55.82	55.94	-0.12	55.93	-0.12
134	2356-23	55.87	54.52	1.35	55.28	0.58
114	2345-4	55.93	54.51	1.42	55.22	0.72
122	345-23	56.18	56.53	-0.35	56.37	-0.18
131	2346-23	56.35	55.33	1.02	55.85	0.50
133	235-235	56.37	56.37	0.00	56.37	0.00
142	23456-2	56.60	54.72	1.88	55.05	1.55
165	2356-35	57.02	56.04	0.98	56.67	0.35
146	235-245	57.08	57.08	-0.00	57.08	0.00
188	2356-246	57.10	56.97	0.13	57.68	-0.58
161	2346-35	57.42	56.86	0.56	57.23	0.18
132	234-236	57.55	57.34	0.21	57.57	-0.02
105	234-34	57.57	57.41	0.16	57.65	-0.08
153	245-245	57.80	57.80	0.00	57.80	0.00
184	2346-246	57.90	57.78	0.12	58.25	-0.35
127	345-35	58.12	58.06	0.06	57.75	0.37
168	246-345	58.25	58.98	-0.73	58.77	-0.52
141	2345-25	59.15	58.68	0.47	58.93	0.22
179	2356-236	59.32	59.12	0.20	59.98	-0.67
137	2345-24	59.82	59.04	0.78	59.45	0.37
130	234-235	60.00	59.86	0.14	59.88	0.12
176	2346-236	60.13	59.93	0.20	60.55	-0.42
138	234-245	60.60	60.58	0.02	60.60	0.00
164	236-345	60.67	61.13	-0.47	61.07	-0.40
163	2356-34	60.68	59.18	1.50	60.07	0.62
158	2346-34	61.02	60.00	1.02	60.63	0.38

[a] □ = coeluting congeners.

3.2. Column configurations/operation

3.2.1. Parallel dual column GC

The application of using two dissimilar GC stationary phases in parallel for the analysis of PCBs is a valuable technique [87–90]. PCB coelutions that occur on one column may be resolved on a second column, permitting an accurate, congener-specific measurement approach. Even in cases where a PCB is resolved on both columns, the dual column system assists in determining positive bias resulting from other interferences (e.g. organochlorine pesticides) that occur when analyzing complex samples. A dual column method can consist of two separate GC–ECD or GC–MS systems, or a combination, but the most functional (and least costly) system is one that uses a single injector split to two columns that end in two ECD systems [87–89]. Obviously with the single GC system, the drawbacks are that both columns must be approximately the same inside diameter and length, and both columns are bound to use the same oven programming conditions to effect elution of the PCBs. However, the possibility of building a single-run system is a very attractive benefit.

The single-run, dual column system of Larsen et al. [91] used a 60 m×0.25 mm, 0.25 μm DB-17 column, and a series column of 25 m×0.25 mm, 0.25 μm CP-Sil 8 and 25 m×0.22 mm, 0.1 μm HT5, to measure PCBs in Mediterranean fish. This system was reported to be the most powerful setup for resolving environmentally significant PCBs (104 resolved) and organochlorine pesticides (OCPs). This same dual column combination later provided the most complete congener profiles in a study that characterized a series of Aroclors [33]. The only Aroclor congeners for which quantities could not be estimated with this system were 41, 56/60, 70, 92/84, and 196/203.

Other dual column systems were used recently to analyze PCBs in mineral oil and powdered milk [92], fish oil and human fat [93], marine sediment and mussel tissue [94], and, human body fluids and tissues [95]. All of these systems were geared towards resolving important congeners such as 118/149, 163/138, and 153/132/105, which tend to coelute on 5% phenyl columns typically used for PCB analysis. Hajslova et al. [93] reported the unbiased determination of the seven indicator congeners with a parallel system of 60 m×0.25 mm, 0.25 μm DB-5 and DB-17 columns, and recommended a system using 50 m×0.2 mm, 0.1 μm Ultra 2 and NB-1701 columns for toxic coplanar PCB analysis.

Larsen et al. [91] designed their dual column system based on the characterization of several stationary phases for separating PCBs and OCPs. Using their work and the recent publication of relative retention times for all 209 PCBs on a variety of GC stationary phases [46], an analyst should be able to construct a dual column system that provides interference-free measurement of the PCBs that are of most concern for the sample type. In environmental analysis, regulatory bodies and researchers have published lists of certain important congeners (Appendix C). The seven BCR indicator congeners are widely used by European countries. An analysis of the most recent literature shows that these congeners have still not been reported to be unambiguously resolved from other PCBs on any single GC stationary phase [21,45,46,50,57,58] although Larsen [45] described their unbiased measurement using an HT8 column and MS. Employing a parallel combination of columns may be the most simple chromatographic solution to this problem.

In an attempt to provide an estimate of what might be achievable with single-run, dual column ECD systems, the authors present here an analysis based upon relative retention time data for PCBs on a number of stationary phases [46,96]. Table 8 describes the number of PCBs that could be resolved using a dual column system if experimental conditions were essentially the same as those in a previous study [46]. Although the goal of the study was to have similar analysis conditions for similar dimension columns, in reality the carrier gas linear velocities and GC oven programming were slightly different. Therefore the most accurate use of the data would be for double-run, dual column systems only. A quick inspection of the data indicates the complexity of the PCB chromatographic problem. Only a few dual column systems shown here (when using ECD) would allow resolution of all seven indicator congeners. And in this case the definition of ''resolved'' includes a criterion for eliminating consideration of coeluting congeners that either are not present or

Table 8
Dual column combinations and PCB resolutions[a]

Column 1	Column 2	Length (m)	Number of PCBs resolved				
			All	Aroclor	Aroclor (tr)[b]	Eur[c]	McF&C[d]
DB-1	SPB-Octyl	30	144	96	119	6	23
DB-1	SPB-Octyl	60	164	108	126	6	26
DB-1	HT8	60/50	164	95	106	6	22
DB-1	DB-17	30	144	94	103	6	25
DB-1	CNBP	60	121	85	112	5	23
DB-1	HP-1301	60	149	99	118	6	22
Rtx-5	HP-1301	60	137	88	109	6	24
DB-1	DB-XLB	60	153	102	119	7	26
Rtx-5	DB-XLB	60	140	90	108	7	25
HP-1301	DB-XLB	60	144	97	114	7	26
Total PCBs in group>>>			209	136		7	36

[a] See [46] for experimental conditions.
[b] Aroclor (tr)=Congener is considered resolved when it only coelutes with a congener(s) that exists at less than 0.05% in any Aroclor.
[c] Eur=European indicator congeners [53–55].
[d] McF&C=McFarland and Clarke [52] congeners with 163 substituted for 168 per Larsen [45].

only exist at trace levels in technical mixes. Although it is only capable of resolving 6 of the indicator congeners, one of the most powerful systems consists of DB-1 (methylpolysiloxane) and SPB-Octyl columns [46,97,98]. One hundred and twenty six of 136 Aroclor congeners>0.05% (w/w) in Aroclors 1242, 1254, or 1260 [98] are resolved when using this setup. In fact, the US Environmental Protection Agency (EPA) recommends the use of these columns in their draft Method 1668 for analysis of toxic PCBs [99] and makes the claim that this pair is ''capable of resolving all 209 PCB congeners.'' While we have not found that to be true, the methyl and octyl column combination is certainly useful.

3.2.2. Multidimensional GC

Multidimensional GC is a powerful, two column technique for PCB analysis whereby coeluting congeners on a precolumn are transferred via a heart cutting technique to a second column of different selectivity [100–108]. If the separating power of the second column (analytical column) is strong enough then unambiguous measurement of PCBs is possible. Historically the precolumn uses a relatively nonpolar stationary phase and the analytical column is a more polar, or even shape-selective phase. Pressure or valve control at the midpoint of a tandem column system can be switched to either cause effluent from the precolumn to travel to a monitor detector, or to the analytical column (a heart cut) and its detector. Commercial systems are available for performing MDGC. The Siemens Sichromat GC has a ''live-T piece'' to enable heart cutting, and two independently controlled ovens for maximum flexibility in resolving analytes on both precolumn and analytical column. The SGE MDS-2000 is an add-on system that is generally utilized in a single GC oven. Cryogenic cooling at the midpoint of this system permits refocusing of heart cut fractions prior to their injection to the analytical column. Most of the recent literature in MDGC PCB analysis concerns these two systems. A Carlo Erba dual oven system based on the ''IfC cross'' of Kaiser [109,110] is also available, but only in Germany [111].

Larsen [21] listed the problems associated with MDGC, including lack of PCB retention data on a wide variety of stationary phases, retention time variability on the precolumn, poor accuracy of heart cuts, long run times, and difficulty of using internal standard quantitation. Nevertheless, in the absence of one column to perform all critical PCB separations,

MDGC remains a viable option for PCB analysis in the hands of skilled operators [112,113]. In fact, until very recently the most comprehensive congener distribution and amount data in technical mixes was obtained by MDGC [114]. Sippola et al. [115] increased the accuracy of heart cutting by using computer control based upon PCB retention indices generated on-the-fly, with alkane references chromatographed on a precolumn to an FID system. Electronic pressure control was used at the injector and midpoint of the SGE MDGC system for very narrow and reproducible heart cuts. Midpoint pressure programming also allowed a closer to optimum carrier flow in the precolumn. Quantitation of coplanar PCBs was performed on a polycarbonate analytical column and the results were compared to previously published values.

MDGC was used to quantify the toxic mono-*ortho*-PCBs 60, 74, 114, 123, 157, 167, and 189 in Aroclor mixes and aquatic organisms [116]. Most of these congeners exist only at trace levels in technical mixes and environmental samples so it is a challenge to provide an unbiased measurement. A Siemens double-oven GC with Ultra 2 and FFAP columns used nitrogen as the carrier gas, which was described as permitting more precise heart cuts. The FFAP column was selected because of increased retention of mono-*ortho*-PCBs. It was not possible to include the heart cuts of all seven fractions in one GC run since peaks included in a particular heart cut fraction sometimes interfered with the determination of a mono-*ortho*-PCB on the FFAP column. PCBs 56 and 60 coeluted on both columns. The MDGC results for mono-*ortho*-PCBs in Aroclors and eels were generally lower than single column results for the same samples, an indication of interferences for the single column method. The MDGC Aroclor results were found to be in good agreement (mean difference 20%) with those produced by Larsen's DB-17 and CP-Sil 8/HT5 parallel column system. The repeatability as determined by five replicate analyses of an eel extract gave RSDs ranging from 8 to 23% for congeners 74, 114, 157, and 167. Detection limits were between 5 and 10 pg.

The group of Kinghorn [117–119] used the SGE MDGC system to attack the separation problem of the seven indicator congeners (28, 52, 101, 118, 138, 153, 180). Their one-oven apparatus consisted of BPX5 and HT8 columns. Liquid carbon dioxide was used as a cryogenic coolant to refocus heart cut PCB fractions from the BPX5 column prior to their injection onto the HT8 column [117,118]. Multidimensional GC with the chosen columns allowed determination of the indicator PCBs but 138 proved to be a difficult resolution due to neighboring congeners (both columns) 158, 160, 163, and 164. The run time of 134 min, in part due to the negative temperature ramp to cool the HT8 column in the one-oven system, limited the practicality of this method. A later paper [119] used phase ratio focusing, instead of cryogenic cooling, to reduce the overall run time to less than one hour. Phase ratio focusing preserved chromatographic integrity of heart cut solutes, permitting them to be efficiently separated on the analytical column while the GC oven continued to heat.

Comprehensive, two-dimensional GC is a powerful separation technique researched by Phillips et al. [120,121]. In this method a serial nonpolar/more polar column configuration is separated by a thermal desorption modulator [121,122]. The columns are short length and narrow bore (e.g. 2 m$\times$250 μm and 80 cm$\times$100 μm [121]). The modulator ''chops'' (concentrates and reinjects) column 1 effluent to column 2 to generate a series of high speed chromatograms. All of the sample is subjected to the separation process, and plotting of the results generates a chromatogram that is a retention plane (column 1 time$\times$column 2 time). Recently comprehensive, two-dimensional GC was evaluated for PCBs [123,124] by using the retention data from Frame [46] to construct predicted two-dimensional chromatograms. Congener distribution across the retention plane of the chromatograms was ordered with respect to chlorine-number groups. Experimental data confirmed the computer model for several stationary phase combinations. De Geus et al. [125] designed an improved thermal desorption modulator and demonstrated its application to semi-comprehensive MDGC of PCBs. The marriage of comprehensive, two-dimensional GC with high resolution mass spectrometry looks to be a very promising and highly selective methodology for PCB, and chlorinated dioxan and furan analysis [126].

One of the most active research fields in MDGC concerns the analysis of atropisomers, the enantiomers of PCBs that occur as a result of restricted rotation around the central C–C bond of biphenyl. Enantiomer separations are important since bioaccumulation and biodegradation of PCBs may be enantioselective. When one considers that there are 19 possible stable atropisomers, it is easy to see why MDGC is used for complex samples (e.g. Aroclors) that may already contain 100 or more PCBs. Almost all of the reported methods for MDGC utilize two-oven systems with an achiral precolumn and a chiral analytical column of modified cyclodextrin (e.g. Chirasil-Dex) for enantiomer separation. PCBs 84, 91, 95, 132, and 149 are the most commonly analyzed atropisomers. Atropisomers have been determined in Clophens [127], human milk [128], river sediments [129–131], and shark liver [132] by MDGC. MDGC has also been used to calculate enantiomerization barriers for atropisomers 95, 132, 136, and 149 [133].

3.2.3. High-speed GC

High-speed gas chromatography is characterized by narrow bore columns and high carrier gas velocities. The benefits of high speed GC are substantial, and include fast analyses, low detection limits, and high separation efficiencies. However, the limitations of commercially available GC systems have slowed the development of high-speed GC as a routine approach [134]. Generally most injectors and detectors are considered incompatible with columns less than 100 μm inside diameter because of their contribution to band broadening, which defeats any efficiency that could be gained by using a narrow bore column. Even the inlet pressure control of many commercial instruments is inadequate for the increased carrier flows necessary for narrow bore columns. Although split injections can provide the narrow input bands required for high-speed GC, they are not preferred due to the tradeoff loss of sensitivity. Many recent high-speed GC injection techniques rely on cryofocusing/thermal desorption to improve sample introduction [135–137].

The speed advantage of high-speed GC may be insignificant for PCB analyses when one considers that sample preparations dominate the time scale. It is hardly practical to apply a system that requires such stringent attention to details and achieve a low min separation, although admittedly a beautiful technical achievement, when sample extraction and cleanup may have taken a day or more. This seemingly simple observation is almost never addressed in high-speed GC literature, although Bertsch pointed it out in a recent editorial [138]. Nevertheless, high-speed GC PCB applications have been reported [139–146], mainly as separations of standards or Aroclors.

The group of Cramers has used high-speed GC for PCBs with ECD [139,140] and MS [141,142]. The GC injector was modified with the addition of a high pressure regulator to allow operation with a 5 m×50 μm column. They used split (0.5 μl) and splitless (0.3 μl) injections. Split ratios were very high, as much as 1200/1. Splitless valve times of 3 min were used to allow full introduction of analytes to the column under the low flow conditions (0.4 to 0.5 ml/min) of the narrow bore column. A 1 mm inside diameter liner also sped sample transfer. The end times of temperature programmed Aroclor chromatograms were less than 15 min. The most promising part of their work was the demonstration that proper cold trapping and solvent refocusing allowed the use of ''conventional'' hot splitless injection with narrow bore columns [140].

The detector in high-speed GC must have a fast time constant to record very narrow peaks. When MS is used, fast scanning is necessary. High-speed GC PCB applications have been demonstrated for quadrupole [143] and magnetic sector instruments [141,142,145]. In the case of an ECD it is preferable to have a limited detector volume so that resolution of the narrow bore column is maintained. Alternatively, high ECD makeup flows were found to preserve the narrow band widths from a high-speed GC PCB analysis [139,140].

The application of the specialty high-speed technique of comprehensive, two-dimensional GC for PCBs has already been covered in the multidimensional GC section of this review.

If high-speed GC analysis of PCBs is ever to transcend the academic world, sample preparation techniques must be dramatically shortened. Otherwise, we envision that the value of high-speed GC

for PCBs will be greatest for screening techniques (where sample preparation is minimized, e.g. in the field) or for applications where the absolute lowest detection limits are required. Low detection limits and the low ng capacities of narrow bore columns are complementary anyway. High-speed GC PCB analysis would also be valuable to a central chromatography lab that receives a heavy load of sample extracts [145], or to allow an increase in the number of calibration or sample replications, thus improving data quality [146]. Method translation computer programs that calculate optimum GC parameters for high-speed GC will assist the transition [147].

3.3. Specific separation examples

3.3.1. Aroclors or technical mixes

Although all 209 PCB congeners are now commercially available as primary standards, the use of Aroclors or other technical PCB mixes, such as Clophens or Kanechlors, as calibration standards [97,148–150] continues. This reliance on secondary standards is mainly due to the high cost associated with purchasing individual, primary standards. Also, even though technical mixes undergo alteration in the environment through a multitude of physicochemical and biological processes, an individual Aroclor or mix of Aroclors is more likely to match the congener distributions in environmental PCB extracts. Therefore, an Aroclor standard contains more appropriate calibration levels for strongly and weakly represented congeners as opposed to a primary standard mix that contains all congeners at equal concentration values.

A congener-specific capillary GC method employing quantitative calibration against technical mixtures has three main requirements. **First**, all congeners eluting in each identifiable peak in the chromatogram must be correctly assigned. **Second**, the total weight percent in the technical mixture of all the congeners eluting in each identifiable peak must be accurately known or measured. For GC–MS methods separate values for each set of homologs, i.e. congeners with the same number chlorine atoms must be provided for each peak. **Third**, the calibration mixture, or calibrated Aroclor lots from which various mixtures might be formulated must be available to analysts.

One of the best such systems in the authors' opinion is Mullin's ''Green Bay Calibration Mixture'', which is calibrated for use with a DB-5 capillary column, and whose origin is discussed in references [97,150]. It has been widely used in the USA for congener-specific PCB studies in and around the Great Lakes. While its originator supplies the mixture together with all necessary information fulfilling the three criteria above, these details have not yet appeared in the peer-reviewed literature. One of us (Frame) has employed the most definitive PCB retention [46] and Aroclor congener distribution databases [33] to check the values supplied by Mullin against predictions from the databases, and finds reasonably close quantitative agreement for all but a few congeners, and the absence of only expected PCB 179 in the listing.

In 1996 Frame et al. [150], described another such system, in use for over a decade, colloquially referred to as the ''General Electric 118-peak system'', which is based on separate congener distributions for individual Aroclors 1221, 1232, 1242, 1016, 1248, 1254, 1260, and 1262, enabling formulation of a wide range of mixtures to best match the congener distributions being analyzed. That paper evaluates and critically discusses prior publications of systems based on calibration against technical mixtures. Electrolytic conductivity detection (ELCD), whose response is proportional to the chlorination level of congeners eluting from a DB-1 column, was calibrated by a subset of congeners covering all chlorination levels. Mass spectrometric detection was used to determine proportions of congeners of different chlorination levels eluting within each peak. Due to sensitivity limitations of the early model ELCD system used, only Aroclor congeners present at greater than 0.5% (w/w) were quantitated, although those between 0.05 and 0.5% (w/w) were identified and assigned to the peaks in which they eluted. The eight lots of calibrated Aroclors are now in very limited supply and not readily available to all analysts.

Some analysts [148,149] attempt comprehensive congener-specific PCB analysis by calibration against technical mixtures, using published values of their % (w/w) distributions. For most of the current decade, the most comprehensive such listing came

from the landmark 1989 paper by Schulz et al. [114], who characterized Aroclors 1016, 1242, 1254, and 1260 plus Clophens A30, A40, A50, and A60 by MDGC, using a primary SE-54 column and secondary OV-210 or non-polar C_{87} columns. As observed by Larsen [21] in his 1995 review, the difficulties in making the heart cuts or insufficient resolution of the secondary columns, appear to have resulted in overlooking of some significant congeners in the technical mixtures. Frame [98] employed data acquired by various collaborators using 8 GC–ECD and 8 GC–MS systems to characterize other lots of the same four numbered Aroclors as well as Aroclors 1221, 1232, 1248, and 1262. The results from that study identified the same omissions noted by Larsen, as well as additional ones. These included minor percentages (less than 0.2%, w/w) of PCBs 4, 12, 102, 139, 147, and more significant omissions of PCBs 2, 13, 43, 71, 114, 124, 144, 157, 163, and 164. Additionally there were major quantitative discrepancies (2-fold or more) for a number of other congeners. Many, but not all of these latter discrepancies were for the Aroclor 1254s.

In a followup study Frame et al. [33] used three carefully chosen, complementary, optimized sets of chromatographic systems, and calibration with primary standard mixtures of all 209 congeners to characterize multiple lots of the full range of Aroclors 1221 through 1262. This revealed that there were two radically different types of Aroclor 1254, and that the one profiled in Frame's original study [98] was a lot with an abnormal congener distribution, thus accounting for some, but not all of the quantitative discrepancies with Schulz et al.'s [114] values.

The existence and nature of the abnormal Aroclor 1254 lots deserve comment. As discussed in [33], the abnormal lot has elevated levels of congeners with none or only one chlorine substituted in the position *ortho* to the other phenyl ring, i.e. the 2 or 6 position. Such congeners have less steric hinderance to rotation about the bond between the rings, resulting in easier attainment of a ''coplanar'' conformation. Some such coplanar congeners are considered to have potential for Dioxin-like toxicity, and contribute to the TEQ (PCB toxic equivalency), and they generally have higher boiling points and longer GC retention times than congeners of the same chlorine number with more *ortho*-substituted chlorines. A recent comparison of the congener distributions of many more lots of Aroclor 1254, using more careful quantitative calibration; namely, 6-level inclusive calibration with primary standard mixtures, and full correction for MS detector fragmentation interferences [151] confirms the dichotomy of Aroclor 1254s into two distinct, highly uniform types. The abnormal Aroclor 1254 lots represent less than 1% of total Aroclor 1254 production. They were produced during the last few years of Aroclor production when Aroclor 1016 was made by distillation of Aroclor 1242 to leave behind small amounts of more bioaccumulable 4, 5, and 6 chlorine PCBs. This residue, which was highly enriched in the coplanar 3 and 4 chlorine congeners from Aroclor 1242 was then chlorinated approximately 5 to 6% more to 54% (w/w) chlorine and distributed as another form of Aroclor 1254. Because the abnormal lots were current at the end of Aroclor production, they were disproportionately distributed to standards suppliers and have sometimes been inadvertently selected for use in biological research. Researchers undertaking to perform biological or toxicological experiments with Aroclor 1254, or analysts who persist in using Aroclors to calibrate congener-specific PCB analyses, need to determine which form is most appropriate for their experiments, and have their material carefully analyzed to ensure that they know for certain which one they have!

The two lots of Aroclor 1248 profiled by Frame et al. [33] displayed significantly different quantitative proportions of some congeners, but in this case there was no correlation with substitution pattern to suggest an alternate synthetic route. There was smaller lot-to-lot variability among Aroclors 1242 and 1260 studied. It will be emphasized by the authors again here that the distributions in [98] and especially the more comprehensive ones in [33] were determined by single-level calibration at levels close to those of the major congeners present, but several orders of magnitude above the trace level congeners. Therefore the quantitative values for low level congeners likely lack sufficient absolute accuracy to enable them to be used to calibrate a congener-specific method. They are believed by the authors to be more

complete than those of earlier publications, and to contain no significant omissions. They are recommended as the most accurate and comprehensive depiction of Aroclor compositions, and as suitable for comparative purposes to identify congener omissions or gross quantitative errors in other comprehensive congener-specific PCB analysis methods. When the values are compared to the relative levels anticipated from the theory of electrophilic chlorine substitution on a phenyl-substituted benzene ring [33,97] there is great consistency between the amounts anticipated and those observed in these studies. This provides a degree of confidence in both the correct identification of the primary standards used and in the measurements and peak assignments made in these large, multiple capillary GC system studies.

Given the variability of congener distributions among same-numbered lots of technical mixtures, the difficulty in reliably and completely measuring and certifying the levels of all congeners over as much as three orders of magnitude of mass percentage (e.g. 10% to 0.01%), the lack of calibration information on the approximately 50 non-Aroclor (i.e. $<0.01\%$) congeners, and the absence of available certified Aroclor lots, and finally the present commercial availability of sets of all 209 primary standards formulated for calibration purposes, the authors concur with Hess et al. [25] that the future development of comprehensive congener-specific PCB analyses should avoid secondary calibration with technical mixtures. This should not exclude continued use of such analytical methods in studies where well-defined procedures, such as the Green Bay Calibration Mix applied to Great Lakes Studies, or the General Electric 118-Peak Method applied to Hudson River samples, have resulted in the accumulation of valuable databases of thousands of analyses over many years. In such cases any deficiencies in absolute quantitation are outweighed by the value of maintaining a consistent data set where significant changes may be more reliably detected.

Table 9
Stable PCB atropisomers[a]

236 PCB No.	Structure Cl Pos.	2346 PCB No.	Structure Cl Pos.
45	236-2	*88*	2346-2
84	236-23	**131**	2346-23
91	236-24	**139**	2346-24
95	236-25	**144**	2346-25
132	234-236	**171**	2346-234
135	235-236	**175**	2346-235
136	236-236	**176**	2346-236
149	236-245	**183**	2346-245
174	2345-236	**196**	2345-2346
176	2346-236	**197**	2346-2346

[a] PCB 176 is listed twice.

3.3.2. Atropisomers

Atropisomers are stereoisomers that are chiral as a result of hindered rotation surrounding a single bond. Out of 209 possible PCBs, 78 show axial chirality if viewed in non-planar configurations. Kaiser [152] predicted that 19 of these PCBs, containing three or four *ortho* chlorines, would exist as stable atropisomers at ambient or physiological temperatures due to restricted rotation about the central C–C bond of biphenyl. All 19 are either 236 or 2346 chlorine substituted (Table 9). Eleven of the 19 are found in significant concentrations in technical mixes (e.g. Aroclors) and another 7 have been detected in technical mixes as relatively minor components [33].

Atropisomeric PCBs have been introduced into the environment as racemates from improper storage and disposal practices, or accidental releases, of commercial technical mixes such as Aroclors, Clophens, etc. In principle, the individual enantiomers of a racemic pair can have different toxicities and metabolic pathways, including their ability to be biodegraded. Robertson et al. [153–155] have studied the toxicity/chirality connection for PCBs. But relatively little research has been done on monitoring the environment for enantioselective degradation processes or enantiomer enrichment in biota [127–132,156–162].

Part of the reason for this lack of information on environmental enantiomer concentrations of PCBs is that the separation science of chiral PCBs is still in its infancy. The complexity of PCB analysis is well-defined; the separation of over 100 components is tough. Adding another 11 peaks, if only the major atropisomers are considered, to any separation would only increase the possibility for interferences to occur. For this reason, the baseline system used by many current researchers for ''real world'' samples,

is MDGC with an achiral–chiral column combination [127–132,162]. The elution order of PCB enantiomers is still being defined on a variety of chiral column phases, currently limited to those consisting of modified cyclodextrins (i.e. mixes of cyclodextrin derivatives and polysiloxane polymers).

Interestingly, whereas one would have to reach back into the 1970s to cite the first reports of capillary GC separations of PCB congeners, the first reports of PCB atropisomer separations by GC were in 1993 by Konig et al. [163] and Schurig and Glausch [164]. Konig separated PCBs 45, 95, and 139 into their enantiomers on a capillary coated with octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin. Schurig and Glausch achieved that same separation and additionally, separated atropisomeric PCBs 91, 95, 132, 136, and 149 on immobilized Chirasil-Dex, a bonded and crosslinked commercial column available from Chrompack that has since been proven to be most efficient at resolving the 236 substituted atropisomers of PCBs [165].

Table 10
Modified cyclodextrin phases and their enantiomeric PCB resolutions

PCB No.	Structure	Cyclodextrin phase					
	Cl Pos.	[A]	[B]	[C]	[D]	[E]	[F]
236 substitution							
45	236-2	R	NR			R	
84	236-23		R			R	R
91	236-24		R			R	
95	236-25	R	R		NR	R	NR
132	234-236	R	R		R		R
135	235-236		R	R			
136	236-236		R			R	
149	236-245		R		R	R	R
174	2345-236		R			R	R
176	2346-236		R			R	
2346 substitution							
88	2346-2	R	NR				
131	2346-23		NR		R	R	
139	2346-24	R	NR				
144	2346-25		NR				R
171	2346-234		NR				R
175	2346-235		NR			R	
176	2346-236		R			R	
183	2346-245		NR			R	R
196	2345-2346		NR				
197	2346-2346		NR				

[A] octakis(2,6-di-*O*-methyl-3-*O*-pentyl)-γ-cyclodextrin [156,163].
[B] heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (Chirasil-Dex) [165].
[C] heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin [156].
[D] heptakis(6-*O*-*tert*.-butyldimethylsilyl-2,3-di-*O*-methyl)-β-cyclodextrin [156].
[E] heptakis(2,3-di-*O*-methyl-6-*O*-*tert*.-hexyldimethylsilyl)-β-cyclodextrin [156].
[F] *tert*.-butyldimethylsilylated-β-cyclodextrin [166].
R = resolved into enantiomers.
NR = not resolved into enantiomers.

Further studies on the enantiomeric separation of PCBs have focused mainly on two areas: exploring other cyclodextrin phases that can separate a broad spectrum of atropisomeric PCBs [156,158–161,165,166] and, reporting enantiomeric ratios for PCBs found in environmental samples [127–132,157–161]. Table 10 summarizes the separation experiments. It should be made clear that literature reports do not always indicate if a pair of enantiomers is unresolved on a particular phase; the emphasis is on resolved peaks. Also, substantially different isothermal temperatures or temperature programs are sometimes necessary to effect resolution for different atropisomeric pairs on the same phase, leading to multiple analyses. As mentioned above, Chirasil-Dex, heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin, is efficient at resolving 236 substituted congeners into enantiomers, although there is no report that we could find in the literature of PCB 45 (236-2) resolution. Conversely, Chirasil-Dex does not resolve any of the 2346 substituted congeners, except for PCB 176 (2346-236) which is also 236 substituted. The phase that had the most resolutions by number, and crossed 236 and 2346 substitution lines, was heptakis(2,3-di-*O*-methyl-6-*O*-*tert*.-hexyldimethylsilyl)-β-cyclodextrin [156]. Vetter et al. [166] suggested that the key to separation of the 2346 substituted atropisomers ''might be the modification of all terminal hydroxyl groups of the cyclodextrin with bulky substituents'' (e.g. *tert*.-butyl- or *tert*.-hexyl-dimethylsilyl).

One of the most recent and comprehensive studies on chiral stationary phases for PCB analysis comes from Wong and Garrison [161]. Without employing MDGC, they used a suite of modified cyclodextrin phases, all commercially available, to quantify PCB

Table 11
PCB atropisomer elution orders on achiral phases[a]

SPB-Octyl		DB-5MS		DB-XLB		SPB-Octyl		DB-5MS		DB-XLB	
PCB No.	RRT	PCB No.	RRT	PCB No.	RRT	PCB No.	RRT	PCB No.	RRT	PCB No.	RRT
PCB 45						**PCB 149**					
28	0.3349	51	0.4133	33	0.4105	144	0.5005	124	0.5455	144	0.5389
20	0.3365	22	0.4159	21	0.4108	147	0.5051	107	0.5466	147	0.5419
45	0.3378	45	0.4188	20	0.4109	149	0.5060	109	0.5475	149	0.5428
51	0.3379	36	0.4225	51	0.4120	134	0.5096	139	0.5481	139	0.5449
21	0.3380	46	0.4251	45	0.4181	143	0.5109	149	0.5482	124	0.5454
33	0.3390			22	0.4198			123	0.5486	143	0.5458
46	0.3428			46	0.4232			140	0.5506	140	0.5472
								106	0.5508		
								118	0.5517		
PCB 84						**PCB 171**					
61	0.4235	56	0.4955	80	0.4911	202	0.6005	177	0.6222	202	0.6139
88	0.4242	60	0.4962	55	0.4912	177	0.6009	202	0.6245	177	0.6164
74	0.4260	92	0.4973	92	0.4951	167	0.6050	171	0.6262	201	0.6198
91	0.4261	84	0.4989	84	0.4961	181	0.6050	156	0.6284	171	0.6199
70	0.4261	89	0.5006	56	0.4963	171	0.6093	173	0.6299	204	0.6204
76	0.4261	90	0.5010	89	0.4968	173	0.6094	201	0.6306	173	0.6224
66	0.4306	101	0.5021	90	0.4998	201	0.6127			197	0.6259
84	0.4311	113	0.5029	101	0.4999	204	0.6209				
55	0.4335			60	0.5003						
89	0.4371			113	0.5013						
PCB 95						**PCB 174**					
94	0.4082	98	0.4791	98	0.4772	185	0.5923	167	0.6118	126	0.6027
57	0.4110	76	0.4793	63	0.4780	159	0.5941	185	0.6132	159	0.6031
100	0.4146	102	0.4795	93	0.4781	174	0.5949	174	0.6186	128	0.6065
95	0.4150	93	0.4805	76	0.4784	162	0.5984	181	0.6194	185	0.6066
58	0.4152	70	0.4811	95	0.4801	202	0.6005	177	0.6222	162	0.6067
67	0.4168	95	0.4823	88	0.4807	177	0.6009	202	0.6245	174	0.6093
93	0.4174	66	0.4830	74	0.4812					167	0.6118
102	0.4188	121	0.4831	121	0.4830					181	0.6130
98	0.4195	88	0.4836	70	0.4838						
		80	0.4842								
		91	0.4873								
		55	0.4890								

atropisomers in Aroclors, sediments, and biotic tissue. By choosing the proper chiral column combination they separated all 19 atropisomers.

Chiral GC has been used to measure PCB enantiomeric ratios in human milk [127–129], doe liver and eel [127], blue mussels [156,157], technical mixes [127,131], river sediments [130,131], shark livers [132], seal blubber [158,159], bass and barn swal-

Table 11 (*continued*)

SPB-Octyl		DB-5MS		DB-XLB		SPB-Octyl		DB-5MS		DB-XLB	
PCB No.	RRT	PCB No.	RRT	PCB No.	RRT	PCB No.	RRT	PCB No.	RRT	PCB No.	RRT
PCB 132						**PCB 183**					
106	0.5189	*161*	0.5632	**114**	0.5609	**166**	0.5810	**187**	0.6008	**175**	0.5918
142	0.5196	**146**	0.5636	*161*	0.5618	**187**	0.5816	*182*	0.6008	*182*	0.5921
118	0.5218	*184*	0.5671	**153**	0.5646	*126*	0.5819	*159*	0.6029	**187**	0.5938
132	0.5251	**153**	0.5687	*168*	0.5647	*182*	0.5839	**183**	0.6049	**183**	0.5980
188	0.5265	*168*	0.5690	**132**	0.5649	**128**	0.5841	*162*	0.6073	**166**	0.5989
122	0.5278	**132**	0.5695	**179**	0.5701	**183**	0.5897	**128**	0.6090	*126*	0.6027
		105	0.5711	**105**	0.5727	**185**	0.5923			*159*	0.6031
		127	0.5729			*159*	0.5941				
PCB 135						**PCB 196**					
111	0.4889	**82**	0.5378	**151**	0.5350	**190**	0.6650	**198**	0.6647	**199**	0.6567
77	0.4923	**151**	0.5389	**82**	0.5361	**198**	0.6650	**199**	0.6671	**190**	0.6591
151	0.4930	**135**	0.5418	**135**	0.5367	**199**	0.6660	**203**	0.6716	*169*	0.6613
135	0.4944	**144**	0.5428	**77**	0.5383	*169*	0.6667	**196**	0.6718	**196**	0.6614
154	0.4946	**147**	0.5445	**144**	0.5389	**196**	0.6748	**189**	0.6841	**203**	0.6621
120	0.4951					**203**	0.6773	**208**	0.6916	**208**	0.6776
144	0.5005					**208**	0.6914				
147	0.5051										

Phase	# Significant Coelutions
SPB-Octyl	1
DB-5MS	3
DB-XLB	2

PCB 136

150	0.4552	**85**	0.5253	*116*	0.5192
99	0.4605	*120*	0.5265	*78*	0.5210
83	0.4611	**136**	0.5274	**87**	0.5210
136	0.4626	**110**	0.5298	**136**	0.5222
112	0.4629	*154*	0.5301	**117**	0.5230
145	0.4651	**77**	0.5319	**115**	0.5239
119	0.4672			*111*	0.5241
108	0.4674				

[a] Data from [46]. RRT = PCB t_R/(PCB 52 t_R + PCB 180 t_R). □ = coeluting congeners.

lows [160], and, striped dolphin liver and blubber [162] . Most of the work was performed with MDGC systems consisting of an achiral precolumn and a chiral main column [127–132,162]. Heart cuts (from the precolumn) containing the atropisomer of interest, and inevitably, other PCBs or interferences, are directed towards the chiral column. ECD, or MS for added selectivity, is used for detection. Benicka et al. [131] noted the importance of choosing a selective precolumn, since any heart cut of multiple peaks can compromise the chiral separation. The recent paper of Frame [46] provides a convenient way to select an achiral precolumn that minimizes this concern. Although the authors realize that different chromatographic parameters (e.g. carrier velocity, oven temperature program, etc.) do not allow absolute predic-

tions of interferences, Table 11 at least provides a consideration of the possibilities. Only the most significant atropisomeric congeners, as defined by their presence in technical mixes, are listed in this table. Also, since most chiral columns have maximum lengths of 25 m, only 30 m columns have been considered as precolumns for MDGC in this example. After precolumn selectivity considerations, MDGC analysis of PCB atropisomers might be further improved by increasing the accuracy of the heart cut technique. Using the MDGC system described by Sippola et al. [115] with electronic pressure control, on-the-fly retention indices monitoring, and computer-controlled heart cutting should improve the data quality for atropisomers measured in complex, ''real world'' samples.

Additional quality control techniques for PCB atropisomer separations in biological samples were listed by Vetter et al. [159] and include (1) using individual enantiomer standards where available, (2) the sum of the measured enantiomer levels should match the measured level of the racemic PCB on an achiral column, and (3) internal standard quantitation is recommended.

In a pioneering work that addressed the standards concern, Haglund [167] obtained mg quantities of pure enantiomers for PCBs 84, 131, 132, 135, 136, 174, 175, 176, and 196 by HPLC on permethylated β-cyclodextrin [168], and characterized their optical properties. Subsequently he was able to determine their (+/−) GC elution sequences on Chirasil-Dex [165].

Chiral GC has also been used to determine the interconversion (or rotation) barriers of select atropisomeric PCBs [133,169]. Values were compared to those calculated by quantum chemistry methods. Recently Andersson et al. [170] used a semi-empirical method to calculate rotation barriers for all 209 PCBs. Nezel et al. [171], in addition to PCBs, used quantum methods to calculate interconversion barriers for methylthio and methylsulfonyl PCBs. One of the most technically elegant techniques for estimating interconversion barriers for PCBs is the stopped-flow MDGC system of Reich and Schurig [133]. First the racemates were separated on a chiral phase with one enantiomer transferred (cut) to an uncoated, deactivated fused-silica column. Flow is stopped in this reactor column, heat is applied (up to 320°C), and enantiomerization is allowed to occur. After a defined time the reactor column is cooled and the enantiomers are transferred to and separated in another chiral column. The barrier can be calculated from the enantiomer ratio, and the reaction time and temperature.

A few other references bear mentioning for this topic. The first may only be of sideline interest to gas chromatographers, but demonstrates the impressive enantiomer separation of PCBs 45, 84, 88, 91, 95, 132, 136, 139, 149, 171, 183, and 196 by micellar electrokinetic chromatography (MEKC) [172]. Mixtures of beta- and gamma-cyclodextrins were used with sodium dodecyl sulfate micelles. A mixture of PCBs 45, 88, 91, 95, 136, 139, 149, and 196 was separated into all 16 enantiomers in approximately 35 min. The poor sensitivity of the detection method (240 nm) was seen as a serious drawback to applying this method to routine sample analysis, but chiral PCB separations by MEKC continue to be researched [173–175].

A very recent report describes the relative retention times for all 209 PCBs on Chirasil-Dex [51]. Interestingly no mention is made of enantiomer separations! While it is unlikely that this highly polar column with relatively low temperature stability will ever find favor in routine congener-specific PCB analysis, those researchers that are interested in chiral PCB separations should find the relative retention time table helpful. Another reference that we found relatively late as this paper was being compiled is the work of Benicka et al. [176]. They studied the separation of 15 chiral PCBs on a series of modified cyclodextrin phases with different types of polysiloxanes. Unfortunately we only had access to the abstract of this paper so we can not comment further.

Enantiomeric separations of chiral methylsulfonyl PCBs have been reported by GC with modified cyclodextrin phases [177,178].

Finally, an important work is the recent review on enantioselective determination of chiral organochlorine compounds by Vetter and Schurig [179]. Although we have duplicated most of their PCB atropisomer reference base in this review, their paper is far superior in its detail, and it includes a wealth of

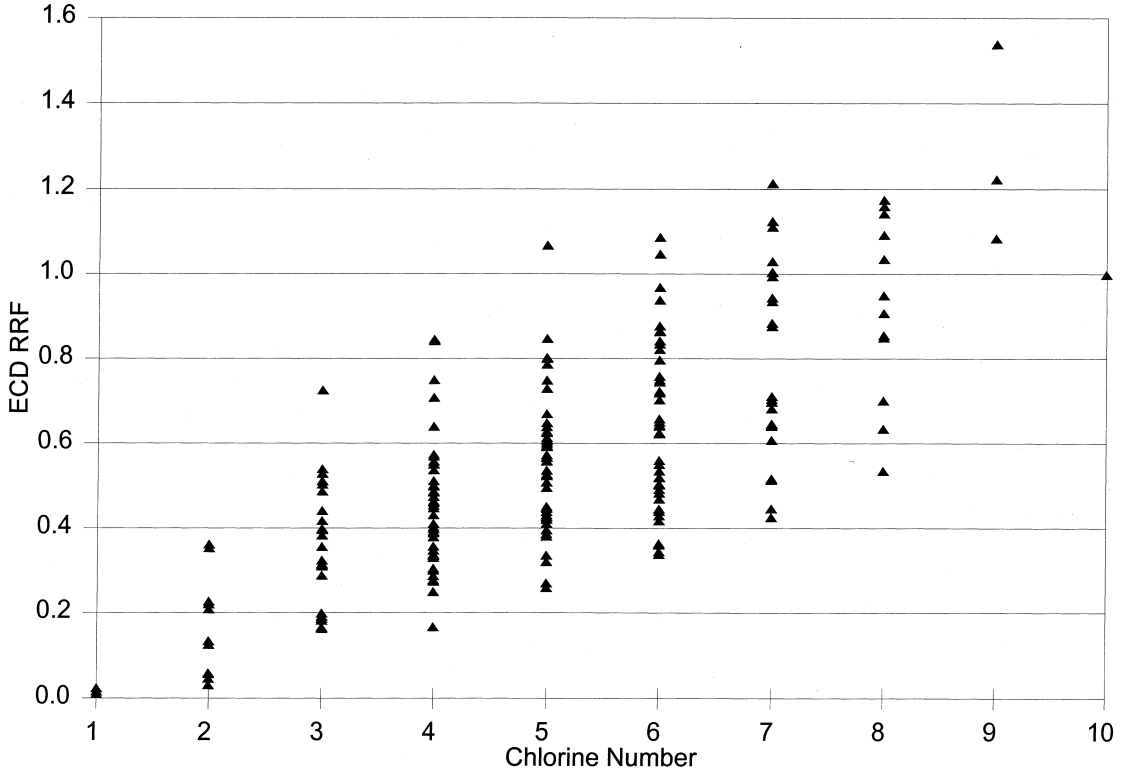


Fig. 3. Plot of ECD relative response factors versus chlorine number for all 209 PCBs.

information on chiral organochlorine pesticides and their GC separations on modified cyclodextrins.

4. Detectors

4.1. Electron-capture detector

ECD is the most utilized detection method for trace PCB analysis due to its sensitivity and selectivity towards polyhalogenated compounds. However, ECD, as used for PCB analysis, suffers from two major problems: nonlinear response behavior across a relatively narrow amount range, and wide variation in response within a PCB homolog group. Nonlinear response leads analysts to: (1) reanalyze samples to put PCB amounts into the linear range of the ECD (complicated by the fact that congeners exist in a wide concentration range in the same sample), and/or (2) use nonlinear functions to calibrate the ECD [180]. The fitting of nonlinear functions presumes that several standards covering the concentration range of interest have been analyzed (multi-point calibration). Even if nonlinear functions are not used, single-point ECD calibration should be considered poor laboratory practice. Because of the variability associated with ECD relative response factors (RRFs), attempts at using one RRF for a homolog group, or using published RRF data instead of measuring RRFs, can lead to serious errors in quantitation. Numerous publications on ECD RRFs demonstrate this point [36,181–183]. Attempts to correlate ECD RRFs, within a homolog group, with a PCB's structure have also been reported [184].

Fig. 3 is a plot of ECD RRFs recently acquired for

Table 12
Normalized ECD relative response factors for pentachlorobiphenyls[a]

PCB No.	Structure Cl Pos.	RRFs normalized to PCB 101							AVG	RSD
		DCB [185]	DCB [183]	DCN [181]	TCN [181]	OCN [181]	MBB [181]	TBB [181]		
82	234-23	1.46	1.19	2.18	2.27	1.49	1.42	1.42	1.63	24
83	235-23	1.15	1.18	1.02	1.06	1.02	1.22	1.18	1.12	7
84	236-23	1.04	0.83	0.86	0.96	1.02	1.22	1.18	1.01	13
85	234-24	1.48	1.33	1.02	1.14	1.39	1.44	1.50	1.33	13
86	2345-2	1.55	1.49	1.22	0.98	1.72	1.51	1.49	1.42	16
87	234-25	1.50	1.74	1.48	1.56	1.98	1.69	1.66	1.66	10
88	2346-2	1.32	1.33	1.09	1.07	1.48	1.38	1.36	1.29	11
89	234-26	1.02	1.32	2.73	3.02	2.23	2.33	2.40	2.15	31
90	235-24	1.18	1.32	0.84	0.89	0.80	1.74	0.97	1.10	28
91	236-24	0.88	1.16	0.81	0.90	1.01	1.05	1.09	0.99	12
92	235-25	1.04	1.48	0.71	0.70	1.03	1.00	0.96	0.99	25
93	2356-2	0.99	1.32	0.96	0.84	1.07	1.40	1.34	1.13	18
94	235-26	0.78	1.31	0.73	0.60	0.60	0.89	0.88	0.83	27
95	236-25	0.90	1.33	0.77	0.85	1.12	0.89	0.88	0.96	19
96	236-26	0.63	1.16	0.65	0.64	0.88	0.82	0.81	0.80	22
97	245-23	1.05	1.04	1.02	1.06	1.14	1.27	1.25	1.12	9
98	246-23	0.95	0.80	1.03	0.98	1.39	1.22	1.22	1.09	17
99	245-24	0.99	1.20	0.93	0.98	0.80	1.74	0.97	1.09	26
100	246-24	0.98	0.94	1.15	0.92	1.29	1.40	1.42	1.16	17
101	245-25	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0
102	245-26	0.74	1.09	0.73	0.60	0.60	0.89	0.88	0.79	21
103	246-25	0.92	1.17	0.96	0.94	1.39	1.21	1.24	1.12	15
104	246-26	0.60	0.94	0.71	0.68	0.50	0.50	0.51	0.64	23
105	234-34	1.86	1.59	1.04	0.99	1.44	1.28	1.28	1.35	21
106	2345-3	1.86	1.50	1.25	1.21	1.75	1.51	1.51	1.51	15
107	234-35	1.69	1.51	1.17	1.18	1.62	1.34	1.34	1.41	13
108	2346-3	1.74	1.35	1.57	1.46	1.98	1.89	1.87	1.69	13
109	235-34	1.39	1.34	1.09	1.08	1.80	NR	NR	1.34	20
110	236-34	1.41	0.99	1.03	1.02	1.70	NR	NR	1.23	23
111	235-35	1.40	1.50	1.03	1.03	1.43	1.18	1.19	1.25	14
112	2356-3	1.42	1.34	1.21	1.20	1.66	1.43	1.45	1.39	11
113	236-35	1.29	1.34	1.45	1.39	1.82	1.53	1.54	1.48	11
114	2345-4	1.97	1.64	1.22	1.15	1.95	1.99	2.14	1.72	21
115	2346-4	1.82	1.14	1.34	1.16	1.48	1.92	1.85	1.53	20
116	23456	2.48	1.65	2.55	2.64	3.62	3.08	3.07	2.73	21
117	2356-4	1.46	1.48	1.21	1.19	1.71	1.82	1.53	1.49	15
118	245-34	1.15	0.97	1.14	1.09	1.49	1.27	1.27	1.20	13
119	246-34	1.38	1.34	1.10	1.24	1.45	1.49	1.56	1.37	11
120	245-35	1.30	1.27	1.03	1.03	1.43	1.18	1.19	1.20	11
121	246-35	1.37	0.92	1.16	1.09	1.45	1.42	1.40	1.26	15
122	345-23	1.31	0.80	0.80	0.65	1.12	0.98	0.97	0.95	22
123	345-24	1.33	1.11	1.08	1.06	1.55	1.40	1.41	1.28	14
124	345-25	1.24	0.68	1.32	1.26	1.71	1.63	1.61	1.35	24
125	345-26	1.22	0.94	1.13	1.25	2.45	2.33	2.40	1.67	38
126	345-34	1.21	0.96	0.54	0.53	0.74	0.70	0.69	0.77	29
127	345-35	1.45	1.31	1.17	1.18	1.62	1.34	1.34	1.34	11

[a] RRF = peak area PCB/peak area internal standard. Internal Standard List: DCB = decachlorobiphenyl, DCN = dichloronaphthalene, TCN = tetrachloronaphthalene, OCN = octachloronaphthalene, MBB = monobromobiphenyl, TBB = tetrabromobiphenyl, NR = not reported, [ ] = reference number.

all 209 PCBs [185] and vividly shows the wide range of response, even within a homolog group. When viewing these data in table form, we could not find any obvious relationship between PCB structure and ECD response, other than the trend for greater response with increasing chlorine number. And the data were sometimes in contrast to what has been previously reported. That is, the relative magnitudes of RRFs did not correlate within a homolog group among different ECD systems. Table 12 lists normalized ECD RRFs for all pentachlorobiphenyls from several different ECD systems. This manipulation allows a quick visual confirmation of whether different ECD systems are responding similarly, relatively speaking, within a homolog group. The table provides the conclusion that the range of RRFs can not be predicted among different ECD systems. Possible explanations for the differences include different detector design, oxygen in the carrier or makeup gas, makeup gas flow rates, and ECD temperature. Ciganek et al. [186] conducted a detailed study on some of these parameters for a select group of PCBs using two different ECD systems. Detector temperature had a strong influence on PCB responses for one detector, with maxima for some PCBs noted at much lower detector temperatures (180–200°C) than are normally used by chromatographers for PCB analysis. Differing oxygen contents of the ECD makeup gas were also shown to contribute significantly to changes in the ECD response. The authors again noted the hazards of attempting to use published relative congener responses for PCB ECD work.

In a recent publication, Booij et al. [187] studied ECD response for a suite of 21 PCBs. ECD was nonlinear over a very narrow amount range. They showed that the definition of apparent linear range, from a plot of response factor versus amount, depends upon the largest amount considered. PCB 118 could have the following apparent linear ranges: 160–360, 80–180, or 40–90 pg, when a slope sensitivity of no greater than 10% was tolerated for the response factor. These authors suggested using power fits, or log or linear interpolations, to obtain better calibration functions for ECD.

The group of Cramers [139,140] was concerned with the ECD makeup gas flow because their application involved high-speed GC with 50 μm columns. ECD cell volumes have been considered to be too large to be compatible with high-speed GC. However, with high makeup flow the detector contribution to band broadening can be minimized or eliminated. In this work the analysis of PCBs on a 50 μm column required a makeup flow of 400 ml/min through a 450 μl ECD cell. Interestingly, even though the ECD system is described as a concentration sensitive detector (as opposed to a mass flow sensitive detector), the detection limits were actually enhanced at the higher flow rates. High-speed chromatograms of Aroclors and an extract of PCBs from sediment were less than 20 min long and showed good resolution.

The problems associated with ECD systems have led Hewlett-Packard researchers to investigate an alternative design [188–190]. Their new ''micro-ECD'' cell size is only 150 μl, 1/10 the size of previous models. The detector uses a hidden anode to reduce the influence of contamination on detector response. A fused-silica insert/column stop helps create a turbulent mixing zone for column effluent and makeup gas. This reportedly improves linearity of response. An application note [189] describes the analysis of a series of standards (2–200 ppb) containing 20 PCBs from dichloro- to decachlorobiphenyl. Correlation coefficients were at least 0.9996 for every PCB studied. The RSDs for response factors ranged from 0.55 to 12.5%. In another study, decachlorobiphenyl as a test probe gave correlation coefficients of 0.996 and 0.998 for 15 point (0.2–64000 pg) and 10 point (2–3200 pg) calibrations, respectively [190]. A chromatogram of a PCB mix at 50 ppt each congener (50 fg/1 μl injection) showed easily detectable peaks [189]. Although this type of sensitivity is highly desirable for trace level PCB work, it places stringent demands on the cleanliness of the chromatographic system, not to mention the purity of solvents and the handling requirements for samples. The small cell size of the new detector and its variable sampling rate from 5–50 Hz also make it suitable for high-speed GC.

4.2. Atomic emission detector

One of the best ways to accurately monitor for PCBs, especially in complex environmental samples, is to use highly specific detectors. While ECD is selective towards PCBs and other halogenated com-

pounds of environmental concern, for some samples the high levels of non-halogenated coextractives can confound the measurement of PCBs. The MS analysis of PCBs, when using selected ion recording (SIR) techniques, can also suffer when interferences are present in samples. Full scan MS improves the specificity of PCB analysis but the trade-off loss of sensitivity may not permit the trace measurement of PCBs so often necessary in environmental analysis.

Atomic emission detection (AED) is an element-selective technique that uses a plasma to disintegrate GC-eluted compounds into excited atoms, followed by the photodiode array detection of characteristic emitted light from these atoms. Most of the recent PCB AED work has been performed on commercial systems with microwave induced plasmas, available from Hewlett-Packard (HP) since 1989 [191–195]. The attractiveness of using GC–AED for PCBs is twofold. First, AED operated in chlorine-selective mode is highly selective for PCBs (and other chlorinated compounds). Second, element detection offers the possibility of determining empirical formulas and performing universal or compound-independent calibration [196]. The obvious value here is the potential for qualitative identification of PCBs and their quantitative determination, with only a few standards. In practice, the second benefit has only been partially realized due to some variability in AED response, depending on a compound's structure or GC elution temperature [196].

Recently (1996) in an excellent review on environmental applications of GC–AED, Pedersen-Bjergaard and Greibrokk [197] discussed PCB analysis by GC–AED. In the interest of completeness, the applications they noted from 1994–1996 will be mentioned again in this paper. Somewhat surprisingly the literature search for our review turned up only one new paper on PCB analysis using AED [198]. As Pedersen-Bjergaard and Greibrokk pointed out, the high detection limits (chlorine) of AED systems may limit their use for PCB applications.

Hajslova et al. [192] used GC–AED to monitor the seven European indicator PCBs in biological matrices, including beef tallow and fish oil. The AED response for chlorine was poor and the detection limit for PCB 28 in fat was almost three orders of magnitude higher than that for ECD. These authors suggested using pressure-pulse injections of up to 6 μl to overcome the detection limit problem. They added the caveat: avoid overloading the GC column with other coextractables. The selectivity of AED versus ECD was high for the samples used in this study. Compound-independent calibration was employed. Sum totals of the seven PCBs were compared to ECD and found to be in good agreement.

A series of papers by Pedersen-Bjergaard, Greibrokk et al. [193–195,198] define the current state-of-the-art in PCB analysis by GC–AED. GC–AED, because of its selectivity, was found to be superior to ECD, low-resolution MS (LRMS), and high-resolution MS (HRMS) in the analysis of marine sediments for PCBs [193,195]. The chromatograms for ECD and LRMS–SIR were seriously compromised by coextractives even after sulfuric acid treatment and gel permeation chromatography (GPC) cleanup of the extracts. Using 8000 resolving power and MS–SIR significantly improved the situation but there were still interferences with the 2-, 3-, and 4-chlorine SIR channels. PCB detectability for AED versus the other detectors was relatively poor with minimum levels in the range of: ECD 0.009–0.035 pg, LRMS–SIR 0.4–5.6 pg, HRMS–SIR 0.4–48 pg, AED 300–1100 pg, for a group of PCBs from mono- to nonachlorobiphenyl. Sulfur, a common coextractive for sediment samples, interfered with the chlorine channel of the AED, mandating its removal from the extracts by GPC prior to AED analysis.

Interest exists in compound-independent, or universal calibration for PCBs using AED [192,194,195,198], most likely due to the expense of acquiring individual congener standards. Chlorine response factors differed by less than 10% for select PCBs and thus made it possible to use only PCB 53 for calibration purposes [194]. GC–AED results for seven PCBs in sediments and fish, using one-congener calibration, were within 15% of the results obtained by GC–ECD and individual congener calibration plots. A study on a laboratory-built AED with an on-column plasma demonstrated chlorine response factors that ranged within 17% for 25 PCB congeners at the 500 pg/μl level [198]. A high level of background components from chimney soot was found to thwart quantitation of PCBs, most likely due to a plasma quenching effect.

The biggest obstacle to exploiting element-selec-

tive detection for PCB analysis is the poor response for chlorine. These sensitivity limitations have been addressed by HP, and researchers using the HP systems [191] and a laboratory-built AED with an on-column plasma [198]. Janak et al. [191] modified a first-generation HP AED to reduce peak tailing associated with plasma wall effects and to minimize other problems associated with incomplete decomposition and overloading in the plasma. Their supply of additional makeup gas flow through a reduced exit diameter, transfer line capillary improved chlorine detector response to approximately 20 pg minimum. The second-generation HP AED system has been reported to have 10 times better detection limits [197]. The on-column plasma system gave PCB detection limits of around 10 pg [198]. The promise of AED for PCB analysis should be fully realized when it is possible to routinely monitor congener amounts in a range between what is achievable with ECD and MS.

Although it is slightly outside the scope of a review on PCB analysis, GC–AED work has been performed on methylsulfonyl PCBs [191,196,199,200], an important class of PCB metabolites that are bioaccumulable. The sulfur channel of the AED was used to distinguish the methylsulfonyl metabolites in the presence of PCBs, in gray seal tissue [199,200]. The issues of universal calibration, detection limits, and plasma quenching were discussed and were similar to those for PCBs.

4.3. Mass spectrometer

Capillary GC–MS is a powerful multidimensional tool for PCB analysis. Improvements in the design of MS systems, including the introduction of low cost, bench top units, make them highly usable to chromatographers as routine detectors in electron ionization (EI) mode. Selected ion recording and the use of ion traps enable PCB detection limits approaching the level of ECD. Flexibility of analysis is increased by chemical ionization (CI) techniques that produce both positive and negative ions for mass analysis.

4.3.1. Electron ionization

The electron ionization of PCBs produces molecular ion isotope patterns that are used for qualitative and quantitative purposes (Table 13). A PCB RRF study by Buthe and Denker [201] relied on a standard quadrupole MS and EI. Using 8 trichloro-, 10 tetrachloro-, 12 pentachloro-, 13 hexachloro-, 9 heptachloro-, and 6 octachlorobiphenyls, they realized RRF patterns by $M+/\text{sum}<M+$ ratios and proposed a qualitative/quantitative standard containing only 14 PCBs of environmental significance (PCBs 18, 28, 52, 66, 92, 101, 118, 126, 138, 153, 155, 180, 189, and 194). The patterns came from a PCB's ability to produce a stable molecular ion. PCBs, grouped according to their chlorine substitution patterns, were stable in the order:

non-*ortho* > *mono-ortho* > 26 > 26-26 > 26-2 > 2-2.

para-Chlorines stabilized a molecular ion and so did an equal distribution of an even number of chlorines on both rings. A symmetrical distribution of chlorines also stabilized a molecular ion. For PCBs up to pentachlorobiphenyl, a hydrogen-bonded carbon between two chlorines stabilized the molecular ion. Combinations of these parameters lead to increased molecular ion production. Although some significant PCBs were not measured experimentally, presumably they could be classified according to the above principles. The standard does not cover mono-, di-, and nonachlorobiphenyls.

A more ambitious work by Haglund and Harju [202] recorded EI response factors for all 209 PCBs. They noted that the molecular ion response generally decreased with increasing chlorine number. Their PCB MS fragmentation data also confirmed the Buthe and Denker [201] molecular ion stability rules. Bolgar et al. [22] provided an in-depth discussion of EI mass spectra of PCBs after they collected response factor data for all 209 congeners. Their observations were similar to Buthe and Denker [201] concerning relative intensities of M^+, $(M-Cl)^+$, and $(M-Cl_2)^+$ ions of PCBs; they related these observations to steric hindrance and resonance stabilization of parent and fragment ions.

4.3.2. Electron-capture negative ionization

Negative ions are produced when PCBs capture low energy electrons generated in the source of the MS from a buffer gas such as methane. The gas also acts to stabilize negative ions so they do not dissociate prior to their mass analysis and, as a result, PCB negative ion mass spectra are dominated by

Table 13
Mass spectrometry molecular ion isotope patterns for PCBs

Cl No.	Formula	Exact Mass	Nominal Mass	Abundance	^{35}Cl	^{37}Cl
1	$C_{12}H_9Cl$	188.0393	188	100	1	0
		190.0363	190	33	0	1
2	$C_{12}H_8Cl_2$	222.0003	222	100	2	0
		223.9974	224	65	1	1
		225.9944	226	11	0	2
3	$C_{12}H_7Cl_3$	255.9613	256	100	3	0
		257.9584	258	97	2	1
		259.9554	260	31	1	2
		261.9525	262	4	0	3
4	$C_{12}H_6Cl_4$	289.9224	290	78	4	0
		291.9194	292	100	3	1
		293.9165	294	48	2	2
		295.9135	296	11	1	3
		297.9106	298	1	0	4
5	$C_{12}H_5Cl_5$	323.8834	324	62	5	0
		325.8804	326	100	4	1
		327.8775	328	64	3	2
		329.8745	330	21	2	3
		331.8716	332	3	1	4
6	$C_{12}H_4Cl_6$	357.8444	358	52	6	0
		359.8415	360	100	5	1
		361.8385	362	80	4	2
		363.8356	364	35	3	3
		365.8326	366	8	2	4
		367.8297	368	1	1	5
7	$C_{12}H_3Cl_7$	391.8054	392	45	7	0
		393.8025	394	100	6	1
		395.7995	396	96	5	2
		397.7966	398	52	4	3
		399.7936	400	17	3	4
		401.7907	402	3	2	5
8	$C_{12}H_2Cl_8$	425.7665	426	35	8	0
		427.7635	428	89	7	1
		429.7606	430	100	6	2
		431.7576	432	64	5	3
		433.7547	434	26	4	4
		435.7517	436	7	3	5
		437.7488	438	1	2	6
9	$C_{12}HCl_9$	459.7275	460	27	9	0
		461.7245	462	78	8	1
		463.7216	464	100	7	2
		465.7186	466	75	6	3
		467.7157	468	36	5	4
		469.7127	470	12	4	5
		471.7098	472	3	3	6
10	$C_{12}Cl_{10}$	493.6885	494	22	10	0
		495.6856	496	69	9	1
		497.6826	498	100	8	2
		499.6797	500	86	7	3
		501.6767	502	48	6	4
		503.6738	504	19	5	5
		505.6708	506	5	4	6
		507.6679	508	1	3	7

molecular ion isotope patterns. Sensitivity is enhanced and the technique is selective since polyhalogenated compounds preferentially form negative ions. The electron-capture negative ionization (ECNI) of PCBs has been studied by Stemmler et al. [203,204] and, Ma and Bayne [205].

Recently ECNI was used by Wells and Echarri [206] to measure PCBs in fish and sea mammals. Hydrogen was used as the buffer gas but no information was given on selectivity or detection limits. A study by Raverdino et al. [207] compared ECNI with EI for measuring the coplanar PCBs 77, 126, and 169 in sewage sludge. At a source temperature of 250°C and methane gas pressure of 1.2 Pa, the ECNI mass spectra of PCBs consisted mainly of molecular ion isotope patterns. Quantitative results for a group of sludge samples compared favorably for the two methods but ECNI provided lower detection limits, around 100 fg, versus EI that had detection limits of about 1 pg. SIR was used for mass analysis.

ECNI has been used to increase sensitivity for PCBs in the analysis of fish and waters [208–210]. Ten percent methane/argon was used as the buffer gas and the ECNI detection limits were lower than what could be achieved with EI. When using large volume injection (up to 500 μl to the GC) and ECNI, direct pg/l measurements of select PCB congeners in water were possible [209,210].

Methylsulfonyl PCBs ($MeSO_2$-PCBs) are prime candidates for analysis by ECNI [211,212]. A detailed investigation by Letcher and Norstrom [213] documented the differences in $MeSO_2$-PCB mass spectra when experimental parameters such as source temperature and methane gas pressure were varied. At a gas source pressure of 0.5 mbar and a source temperature of 140°C, M^- ions dominated for the tetrachloro- to heptachloro-$MeSO_2$-PCBs. An increase in source temperature increased fragmentation, and abundance of all ions decreased. A reduction of the gas pressure to 0.05 mbar decreased the sensitivity by an order of magnitude. Possibly this could be attributed to higher energy electrons in the source and/or a decrease in the probability for collisional stabilization of negative ions.

The first report of monobrominated PCBs (Br-PCBs) in a biological sample was produced by using ECNI–MS [214] . The base peak of a monobromopentachlorobipenyl was Br^- with other significant ions M^-, $(M-Br+H)^-$ and $(M-Br-Cl+2H)^-$. Monobromotetrachloro- and monobromopentachlorobiphenyls were the most abundant homologs in a seal blubber sample. A technical PCB mix, Clophen A50, was also found to contain Br-PCBs.

A novel approach to electron production for ECNI, without using a buffer gas, was recently demonstrated by Laramee and Deinzer [215] through their use of a trochoidal electron monochromator [216]. In the monochromator, a magnetic field confines low energy electrons emitted from a rhenium filament. Crossed electric and magnetic fields disperse the electrons and a series of lenses is used to inject the electrons into the source of a MS. Electron energies can be narrowly focused and tuned, so there is the potential for isomer differentiation, since electron energies for producing stable negative ions are different for different molecules. The system was demonstrated by analyzing Aroclor 1254 and monitoring the Cl^- ion or total ion current. The elimination of problems associated with the use of gas for electron production and the possibility of performing electron energy/mass scans for qualitative analysis were mentioned as benefits for this technique. More research is needed on the effect of not having a buffer gas for collisional stabilization of negative ions.

Negative ion mass spectrometry has been shown to be a sensitive and selective technique for PCB analysis but is still underutilized. Poor gas pressure reproducibility, instrument-to-instrument variability, and the cost of negative ion instruments are conspiring to prohibit its routine use. Hardware modifications to permit electronic measurement and reproducible control of gas pressures are suggested to instrument vendors as a way to further acceptance of this technique. Additional studies on source design are also necessary. The recent introduction of a negative ion-capable bench top mass spectrometer from Finnigan may contribute to increased use of ECNI for PCB analysis.

4.3.3. Ion trap mass spectrometer

The ion trap mass spectrometry (ITMS) systems is a three-dimensional quadrupole mass analysis device. Ions are manufactured, stored in an electric field, and then destabilized/ejected according to

mass, to a detector. Because it is an ion storage device the ITMS is inherently more sensitive than pass-through mass filters such as quadrupole rods and sector instruments. Full scan ITMS data can be acquired at analyte levels (pg) that would only be possible through SIR on traditional mass spectrometers. Two vendors, Varian and Finnigan, offer ITMS systems in bench top versions and this, coupled with their sensitivity and ability to perform MS–MS experiments, has led to the exploration of their use for PCB analysis [40,217]. These two instruments differ slightly in ionization design. Varian ionizes compounds internal to the ion trap; Finnigan ionizes compounds externally and ''injects'' them into the ion trap for mass analysis.

In ion trap mass spectrometry the presence of coeluting interferences, even if they are not the same mass as PCBs, can reduce PCB sensitivity. This is because the ion trap can store only a limited number of ions efficiently, this limited number being achieved by varying the ionization time on-the-fly via the operating software. An example of this problem is the analysis of PCBs in waste oil. Usually the PCBs are at trace level in the oil and any reduced ionization time as a result of coelution of oil peaks and PCBs will result in fewer PCB ions being available for mass analysis and detection. Fortunately the oil peaks are mostly of lower mass/charge ratio than the PCB molecular ions. Using limited mass range scanning (e.g. 120 to 520 u) and increasing the radio frequency storage voltage so that the lower mass ions are not stored, helps decrease the severity of this problem [218,219].

Although it is generally taken that coeluting PCB congeners which differ by one chlorine can be resolved by EI–MS, the statement is rigidly true only if the higher mass PCB is not substantially greater in concentration than the lower mass PCB. A ''real world'' example occurs with PCBs 110 and 77 which tend to coelute on 5% phenyl columns. PCB 77's high toxicity relative to other congeners, mandates its accurate quantitation but its concentration in environmental samples may be several orders of magnitude lower than that of PCB 110. Lausevic et al. [220] studied positive ion CI of PCBs 110 and 77 using a variety of reagent gases (Table 14) and ITMS to determine if a selective approach to the analysis of PCB 77 was possible. The beauty of using an ion trap for CI is that a particular reagent ion can be selected (from the many that are formed upon gas ionization) for the ion/molecule reaction (e.g. $C_2H_5^+$/PCB 77). The time allowed for a reaction can also be controlled using ITMS. Subsequent to CI, the ion trap is scanned and product ions are recorded. Lausevic's work indicated that methane/$C_2H_5^+$ promoted mainly $(M+H)^+$ ions for the PCBs, with little fragmentation, a desirable outcome for the interference-free measurement of these coeluting congeners. $C_2H_5^+$ ionization efficiencies were similar for PCBs 110 and 77. Benzene may be valuable as a selective reagent gas in the charge exchange mode, due to its greater efficiency at ionizing PCB 77 versus 110.

Table 14
Reagent gases for chemical ionization of PCBs 77 and 110[a]

Reagent	Reagent Ions		
Methane	$C_2H_3^+$	$C_2H_5^+$	$C_3H_5^+$
Ethylene	$C_2H_4^+$	$C_3H_5^+$	
Isobutane	$C_4H_9^+$		
Benzene	$C_6H_5^+$		
Toluene	$C_7H_8^+$		
Carbon dioxide	CO_2^+		

[a] Ref. [220].

In a followup study, Lausevic et al. [221] determined ITMS responses for 60 PCBs using selected ion monitoring with EI and CI ($C_2H_5^+$). Detection limits for PCB 153 were 0.76 pg and 30 pg for EI and CI, respectively, compared to 70 fg for ECD.

MS–MS is a highly selective technique that is used for trace PCB analysis when the chemical background of a sample is high [222]. MS–MS with an ion trap can be said to occur in time, not space, as with conventional tandem mass spectrometers that use gas-filled quadrupole rods as collision cells to induce dissociation of ions in flight as they pass through to a mass analysis region. Simply described, MS–MS in an ion trap proceeds as follows: (1) an ion for reaction is mass selected, (2) excitation voltage is applied to the ion trap end cap electrodes, (3) energized ions dissociate, and (4) product ions are mass analyzed. Recent ion trap MS–MS PCB experiments have focused on the more toxic coplanar and mono-*ortho* congeners. Leonards et al. [223] used MS–MS methods to analyze PCBs 77, 126, and 169 in mussels, sediments, and fish. MS and MS–

Table 15
PCB average relative response factors for an ion trap mass spectrometer[a]

Cl No.	No. of PCBs	Quantitation ions			RRF	RSD (%)
1	3	188	190		0.233	15
2	12	222	224		0.249	14
3	24	256	258	260	0.254	11
4	42	290	292	294	0.232	13
5	46	324	326	328	0.211	13
6	42	358	360	362	0.188	16
7	24	394	396	398	0.168	15
8	12	428	430	432	0.165	20
9	3	462	464	466	0.161	19
10	1	Total ions			1.000	

[a] Experimental conditions given in [185].

MS quantitation results were similar although the detection limits for MS–MS were lower due to the reduction in chemical noise. Detection limits were 60, 300, and 200 fg, for PCBs 77, 126, and 169, respectively. Lausevic et al. [224] found that a defined excitation voltage caused selective fragmentation for di-*ortho*-PCBs. Di-*ortho*-tetrachloro-PCB molecular ions were almost completely decomposed while 70+% of mono- and non-*ortho*-tetrachloro-PCB molecular ions stayed intact. It remains to be seen if this can be exploited for quantitation in a situation where there are coelutions of the toxic congeners with other (e.g. di-*ortho*) congeners.

In another PCB study using the ITMS under EI conditions, RRFs were generated for all 209 PCBs versus decachlorobiphenyl [185]. The range of RRFs within a homolog set was relatively narrow (Table 15) and could be further restricted by grouping PCBs according to their *ortho*-chlorine substitution patterns (Table 16). It was suggested that by using a well-characterized GC column, as few as 23 PCBs could be used in a calibration standard to provide semi-quantitative data for Cl_1 to Cl_{10} PCBs.

ITMS has been used for the determination of hydroxylated PCBs [225]. MS–MS of the trifluoroacetyl derivatives was found to provide a highly selective analysis for a chicken egg sample.

4.3.4. High-resolution mass spectrometer

The advantage of high-resolution mass spectrometry with an iron-core magnet is its ability to resolve beyond nominal mass units. This allows for a substantial increase in the reliability of a quantitative measurement that is based on SIR. Another element that was recently exploited by Van Ysacker et al.

Table 16
PCB average relative response factors grouped by *ortho*-chlorines for an ion trap mass spectrometer[a]

Cl No.	26-26			2-2			All others		
	No. of PCBs	RRF	RSD (%)	No. of PCBs	RRF	RSD (%)	No. of PCBs	RRF	RSD (%)
1	0			0			3	0.233	15
2	0			1	0.211		11	0.252	14
3	0			4	0.220	10	20	0.261	9
4	1	0.312		14	0.211	13	27	0.239	9
5	2	0.279	12	21	0.194	11	23	0.221	6
6	5	0.253	5	23	0.168	9	14	0.196	6
7	5	0.208	8	14	0.152	9	5	0.173	6
8	5	0.201	6	6	0.137	5	1	0.153	
9	2	0.179	1	1	0.125		0		

[a] 2-2 includes 26-2 and 2-26 congeners. Experimental conditions given in [185].

[142] is high-speed scanning. They used fast GC on a 5 m×50 μm DB-1 column and a double focusing MS with a small magnet to analyze Aroclor 1242 in waste oil. When MS resolving power was 2000, a highly selective SIR analysis was possible that showed none of the interfering oil peaks that were seen at a resolution of 300. The MS duty cycle for analyzing a group of 5 PCB molecular ions from di- to hexachlorobiphenyl, including a lock mass peak, was 245 ms, thus accommodating the narrow peaks produced under high-speed GC conditions. A single ion can be monitored in as little as 35 ms. Detection limits were around 5 to 50 fg using SIR but a split injection of 0.5 μl with a split ratio of 1/1200 was necessary to produce the narrow input band required by the microcolumn. The total analysis time was around 6 min!

The EPA is developing analytical methods for PCBs by GC–HRMS. Their draft Method 1668 [99] focuses on the analysis of 13 toxic congeners using SIR and a minimum resolving power of 10 000. Isotope dilution is used for quantitation. This method is currently being expanded to include the analysis of all 209 congeners [226]. HRMS not only enables high specificity in the presence of coextractives but also permits quantitation of the lower PCB in a coeluting pair where the PCBs differ by two chlorines. In a nominal mass instrument, resolution is not possible because the higher PCB's fragment ions, from the loss of Cl_2, are indistinguishable from the lower PCB's molecular ions (e.g. hexachlorobiphenyl 360 to 290 interferes with the 290 molecular ion of tetrachlorobiphenyl). The exact masses of the ions in this example are 289.9038 (hexachlorobiphenyl-Cl_2) and 289.9224 (tetrachlorobiphenyl). A resolving power of around 15 000 would permit unbiased measurement of both ions.

4.3.5. Tandem mass spectrometer

Tandem mass spectrometers perform MS–MS experiments. They typically consist of two mass analysis areas separated by a field-free collision cell. Several tandems are available but the most common are triple quadrupole instruments and magnet-quadrupole hybrids. A MS–MS (reaction monitoring) scan with a tandem MS is conducted by: (1) ionizing the compound, (2) mass selecting a parent ion (in the case of a PCB, a molecular ion), (3) passing the parent into a gas-filled collision cell where dissociation into fragment ions occurs, (4) selecting a particular fragment ion for detection with the next mass analyzer (for PCBs, typically M–Cl or M–Cl_2). Since these scans can be conducted on the ms time scale they are very compatible with capillary GC. Although the selectivity of these instruments can be greater than high resolution mass spectrometers they are not routinely used for PCB analysis, probably due to their cost and complexity. In a demonstration of the utility of a tandem MS, Zupancic-Kralj et al. [227] used a magnet-quadrupole hybrid to analyze PCBs in pine needles and paraffin oils, and to resolve PCBs in the presence of toxaphene and polychlorinated naphthalenes. Nitrogen was used as the collision cell gas. Selectivity was excellent against interferences.

4.3.6. Resonance-enhanced multiphoton ionization time-of-flight MS

Zimmerman et al. [228] combined laser induced, resonance-enhanced multiphoton ionization (REMPI) and time-of-flight (TOF)-MS with a post-GC column hydrodechlorination reactor to measure PCBs. The MPI technique involves excitation and ionization of target compounds by the absorption of laser photons. A supersonic molecular beam source was developed for the TOF-MS. A supersonic jet is formed by expanding a gas effluent through a narrow orifice, so that during expansion, molecules cool and their internal motions are dampened. These jet-cooled molecules exhibit narrow spectroscopic features and can be ionized selectively by a tuned laser. To overcome the incompatibility of this high flow technique with the vacuum requirements of the MS, a gated gas pulse system was developed to introduce cooled compounds to the MS source region for laser ionization. The highly specific technique could be valuable for target compound analysis but could be disadvantageous if numerous compounds are to be analyzed comprehensively. Even isomers may not be ionized with only one laser wavelength. This problem was solved for PCBs by using a post-GC column hydrodechlorination reactor with a palladium catalyst and hydrogen reagent gas to create biphenyl from every PCB, thus allowing a one-wavelength laser ionization. The main advantage is high selectivity against interferences, including other chlorinated

compounds. Disadvantages are associated with maintaining the catalytic converter, and include catalyst poisoning and degradation.

4.3.7. Compound-specific isotope analysis

In a very interesting application the compound-specific isotope analysis (CSIA) of PCBs in Aroclors and other technical mixes was performed by GC–MS [229]. CSIA uses a combustion interface to produce CO_2 and H_2O from GC eluted peaks and then measures the ^{12}C and ^{13}C content by isotope ratio MS. PCBs showed increased depletion in ^{13}C with increasing chlorine content. Values for congeners within technical mixtures showed a wide range of $^{12}C/^{13}C$ ratios. And the mixtures (Aroclor, Clophen, Kanechlor, Phenoclor) themselves showed different ratios, even though their chlorine content was the same. Further work will use this technique on ''real world'' samples in an attempt to determine sources of PCB introduction into the environment.

4.3.8. High-speed GC–time-of-flight MS

We were disappointed that our literature search did not reveal any reports of PCB analysis by the fast GC–TOF-MS systems that have been used for other applications [230,231]. Using TOF-MS it is possible to record hundreds of mass spectra per second, an ideal situation for high-speed GC. The possibility also exists of using such a fast recording detector as an extra dimension for separation of closely eluting PCB congeners. We hope that PCB research can begin on these instruments.

The power of mass spectrometry is its ability to perform as a universal detector and a specific detector. As a confirmational device for capillary GC, it has no equal. The numerous operation modes that enhance its specificity (SIR, CI, MS–MS, etc.) make it an extremely flexible tool for PCB analysis. Bench top systems have put this power in the hands of the chromatographer and this should result in improved PCB data quality.

5. Conclusions

It is relatively easy from looking at the literature on PCB analysis to mentally plot a curve describing the development of GC techniques over the years. An oversimplification of the start and current end points would be packed column/ECD/technical mix reporting of data, to congener-specific/MS analysis with primary standards. What is somewhat hard to determine is what the slope of the curve is from 1994 until the present, i.e. has PCB analysis by GC reached a plateau where developments are coming more slowly? Perhaps, but there are still worthwhile gains to be made in the development of stationary phases for PCBs. Even if the ''Holy Grail'' column is never manufactured that will resolve all 209 congeners, a wider variety of phases will permit the construction of tunable parallel dual column or multidimensional GC systems that will surely be of value to the gas chromatographer. The field of chiral GC for PCBs could also benefit from further characterization of stationary phases, including combinations of achiral–chiral phases that allow interference-free enantiomer measurements while using multi-dimensional GC.

The challenge for detectors may be more wide open. If the GC column is not going to provide the selectivity necessary then mass spectrometry may be the answer. For the most trace level measurements an improvement in MS sensitivity is desirable. Ion trap mass spectrometry may be best positioned to provide this sensitivity; its ability to perform MS–MS experiments should improve selectivity. High-speed GC–TOF-MS for PCB analysis should be tested as soon as possible. The atomic emission detector has promise as a selective detector, especially for samples that have high levels of matrix components that would typically interfere with ECD or MS.

Although it deserves more than the casual mention we have chosen for this conclusion, better columns and selective detectors are no substitute for proper sample extraction and cleanup. Interferences that have the potential to seriously alter data quality or degrade chromatographic systems should always be removed, if possible, prior to their introduction to the GC column.

Acknowledgements

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Appendix A. Polychlorinated biphenyls listed by IUPAC No. and chlorine structure[a]

PCB No.	Structure Cl Pos.	PCB No.	Structure Cl Pos.	PCB No.	Structure Cl Pos.
Monochlorobiphenyls		Pentachlorobiphenyls		Heptachlorobiphenyls	
1	**2**	82	**2**34-**2**3	170	**2**345-**2**34
2	3	83	**2**35-**2**3	171	**2**34**6**-**2**34
3	4	84	**2**3**6**-**2**3	172	**2**345-**2**35
		85	**2**34-**2**4	173	**2**345**6**-**2**3
Dichlorobiphenyls		86	**2**345-**2**	174	**2**345-**2**3**6**
4	**2**-**2**	87	**2**34-**2**5	175	**2**34**6**-**2**35
5	**2**3	88	**2**34**6**-**2**	176	**2**34**6**-**2**3**6**
6	**2**-3	89	**2**34-**26**	177	**2**35**6**-**2**34
7	**2**4	90	**2**35-**2**4	178	**2**35**6**-**2**35
8	**2**-4	91	**2**3**6**-**2**4	179	**2**35**6**-**2**3**6**
9	**2**5	92	**2**35-**2**5	180	**2**345-**2**45
10	**26**	93	**2**35**6**-**2**	181	**2**345**6**-**2**4
11	3-3	94	**2**35-**26**	182	**2**345-**2**4**6**
12	34	95	**2**3**6**-**2**5	183	**2**34**6**-**2**45
13	3-4	96	**2**3**6**-**26**	184	**2**34**6**-**2**4**6**
14	35	97	**2**45-**2**3	185	**2**345**6**-**2**5
15	4-4	98	**2**4**6**-**2**3	186	**2**345**6**-**26**
		99	**2**45-**2**4	187	**2**35**6**-**2**45
Trichlorobiphenyls		100	**2**4**6**-**2**4	188	**2**35**6**-**2**4**6**
16	**2**3-**2**	101	**2**45-**2**5	189	**2**345-345
17	**2**4-**2**	102	**2**45-**26**	190	**2**345**6**-34
18	**2**5-**2**	103	**2**4**6**-**2**5	191	**2**34**6**-345
19	**26**-**2**	104	**2**4**6**-**26**	192	**2**345**6**-35
20	**2**3-3	105	**2**34-34	193	**2**35**6**-345
21	**2**34	106	**2**345-3		
22	**2**3-4	107	**2**34-35	Octachlorobiphenyls	
23	**2**35	108	**2**34**6**-3	194	**2**345-**2**345
24	**2**3**6**	109	**2**35-34	195	**2**345**6**-**2**34
25	**2**4-3	110	**2**3**6**-34	196	**2**345-**2**34**6**
26	**2**5-3	111	**2**35-35	197	**2**34**6**-**2**34**6**
27	**26**-3	112	**2**35**6**-3	198	**2**345**6**-**2**35
28	**2**4-4	113	**2**3**6**-35	199	**2**345-**2**35**6**
29	**2**45	114	**2**345-4	200	**2**345**6**-**2**3**6**
30	**2**4**6**	115	**2**34**6**-4	201	**2**34**6**-**2**35**6**
31	**2**5-4	116	**2**345**6**	202	**2**35**6**-**2**35**6**
32	**26**-4	117	**2**35**6**-4	203	**2**345**6**-**2**45
33	34-**2**	118	**2**45-34	204	**2**345**6**-**2**4**6**
34	35-**2**	119	**2**4**6**-34	205	**2**345**6**-345
35	34-3	120	**2**45-35		
36	35-3	121	**2**4**6**-35	Nonachlorobiphenyls	
37	34-4	122	345-**2**3	206	**2**345**6**-**2**345
38	345	123	345-**2**4	207	**2**345**6**-**2**34**6**
39	35-4	124	345-**2**5	208	**2**345**6**-**2**35**6**
		125	345-**26**		

Appendix A (*continued*)

PCB No.	Structure Cl Pos.	PCB No.	Structure Cl Pos.	PCB No.	Structure Cl Pos.
Tetrachlorobiphenyls		126	345-34	Decachlorobiphenyl	
40	**2**3-**2**3	127	345-35	209	**2**345**6**-**2**345**6**
41	**2**34-**2**				
42	**2**3-24	Hexachlorobiphenyls			
43	**2**35-**2**	128	**2**34-**2**34		
44	**2**3-**2**5	129	**2**345-**2**3		
45	**2**3**6**-**2**	130	**2**34-**2**35		
46	**2**3-**26**	131	**2**34**6**-**2**3		
47	**2**4-**2**4	132	**2**34-**2**3**6**		
48	**2**45-**2**	133	**2**35-**2**35		
49	**2**4-**2**5	134	**2**35**6**-**2**3		
50	**2**4**6**-**2**	135	**2**35-**2**3**6**		
51	**2**4-**26**	136	**2**3**6**-**2**3**6**		
52	**2**5-**2**5	137	**2**345-24		
53	**2**5-**26**	138	**2**34-245		
54	**26**-**26**	139	**2**34**6**-24		
55	**2**34-3	140	**2**34-24**6**		
56	**2**3-34	141	**2**345-**2**5		
57	**2**35-3	142	**2**345**6**-**2**		
58	**2**3-35	143	**2**345-**26**		
59	**2**3**6**-3	144	**2**34**6**-**2**5		
60	**2**34-4	145	**2**34**6**-**26**		
61	**2**345	146	**2**35-**2**45		
62	**2**34**6**	147	**2**35**6**-24		
63	**2**35-4	148	**2**35-24**6**		
64	**2**3**6**-4	149	**2**3**6**-**2**45		
65	**2**35**6**	150	**2**3**6**-24**6**		
66	**2**4-34	151	**2**35**6**-**2**5		
67	**2**45-3	152	**2**35**6**-**26**		
68	**2**4-35	153	**2**45-**2**45		
69	**2**4**6**-3	154	**2**45-24**6**		
70	**2**5-34	155	**24**6-24**6**		
71	**26**-34	156	**2**345-34		
72	**2**5-35	157	**2**34-345		
73	**26**-35	158	**2**34**6**-34		
74	**2**45-4	159	**2**345-35		
75	**2**4**6**-4	160	**2**345**6**-3		
76	345-**2**	161	**2**34**6**-35		
77	34-34	162	**2**35-345		
78	345-3	163	**2**35**6**-34		
79	34-35	164	**2**3**6**-345		
80	35-35	165	**2**35**6**-35		
81	345-4	166	**2**345**6**-4		
		167	**2**45-345		
		168	**24**6-345		
		169	345-345		

[a] Any **2** or **6** value in the Structure Cl Pos. column represents an *ortho* chlorine.

Appendix B. Stationary phases recently tested for PCB analysis[a]

Company	Trade Name	Composition	Ref.
Chrompack			
	Chirasil-Dex	β-cyclodextrin methylpolysiloxane	[51]
	CP-Sil 5	100% methylpolysiloxane	[74]
	CP-Sil 8	5% phenyl-methylpolysiloxane	[33,91]
	CP-Sil 19	14% cyanopropyl-phenyl-methylpolysiloxane	[84]
	CP-Sil 88	100% cyanopropyl polysiloxane	[84]
	CP-Sil 5/C_{18}	50% octadecyl-methylpolysiloxane	[46]
	CP-Sil 8/C_{18}	4% phenyl-10% octadecyl-methylpolysiloxane	[84]
	CP-Select for PCBs	high mol. mass hydrocarbon similar to squalane	[37]
	Thermocap A	50% phenyl-methylpolysiloxane	[50]
Hewlett-Packard			
	Ultra 2	5% phenyl-methylpolysiloxane (silphenylene)	[93,116]
	HP-1301	6% cyanopropyl-phenyl-methylpolysiloxane	[46]
	HP-FFAP	nitroterephthalic acid modified-polyethylene glycol	[116]
J&K Environmental Ltd.			
	LC-50	50% liquid crystalline-methylpolysiloxane	[51]
J&W Scientific			
	DB-1	100% methylpolysiloxane	[46,150]
	DB-5	5% phenyl-methylpolysiloxane	[51]
	DB-5MS	5% phenyl-methylpolysiloxane (silphenylene)	[46]
	DB-17	50% phenyl-methylpolysiloxane	[46]
	DB-XLB	proprietary	[46,49]
	DB-XLBx	propietary	[49]
Nordion			
	NB-1701	14% cyanopropyl-phenyl-methylpolysiloxane	[93]
Quadrex			
	007-17	50% phenyl-methylpolysiloxane	[22]
	007-ODP	15% phenyl-40% octadecyl-methylpolysiloxane	[22,46]
Restek			
	Rtx-1	100% methylpolysiloxane	[46]
	Rtx-5	5% phenyl-methylpolysiloxane	[46]
SGE			
	BPX5	5% phenyl-methylpolysiloxane (silphenylene)	[118]
	HT5	5% phenyl-methylpolysiloxane (carborane)	[57]
	HT8	8% phenyl-methylpolysiloxane (carborane)	[45,46]
Supelco			
	SPB-Octyl	50% octyl-methylpolysiloxane	[46]
Not commercially available			
	p,p-cyanobiphenyl	25% *p*-cyanobiphenyl, *p*-allyoxy-methylpolysiloxane	[46,63]
		C_{60} fullerene-aminopropyl-methylpolysiloxane	[65]
		polycarbonate	[115]

[a] This list is not meant to be comprehensive. Only the most recent references with the greatest number of reported congeners are listed. For extensive PCB stationary phase references especially see work of: Ballschmiter [38,39,42]; Larsen [40,43,45]; and Vetter [37,50].

Appendix C. PCB short lists based on toxicity and environmental significance[a]

EPA Method 1668 [99]																			
77	105	114	118	123	126	156	157	167	169	170	180	189							
Community Bureau of Reference (BCR) [53–55]																			
28	52	101	118	138	153	180													
National Research Council Canada																			
15	18	31	40	44	49	52	54	60	77	86	87	101	103	105	114	118	121	128	129
137	138	141	143	151	153	154	156	159	170	171	173	180	182	183	185	187	189	191	194
195	196	199	201	202	203	205	206	207	208	209									
McFarland and Clarke [52]																			
18	37	44	49	52	70	74	77	81	87	99	101	105	114	118	119	123	126	128	138
151	153	156	157	158	167	168	169	170	177	180	183	187	189	194	199				
QUASIMEME [97]																			
28	31	44	47	49	52	56	66	74	85	87	97	99	101	105	110	118	128	137	138
141	149	151	153	156	170	180	187	194	202	206									
NOAA [97]																			
8	18	28	44	52	66	77	101	105	118	126	128	138	153	170	180	187	195	206	209
Hansen [28]																			
1	3	4	6	8	10	15	16	17	18	19	22	24	25	26	28	31	32	33	37
40	42	44	45	46	47	48	49	52	56	60	66	70	71	74	77	81	82	84	85
87	91	92	95	97	99	101	105	110	114	118	119	126	128	136	138	141	149	151	153
156	157	163	167	169	170	171	174	177	179	180	183	187	189	194	196	199	203	206	

[a] QUASIMEME = Quality Assurance of Information for Marine Environmental Monitoring in Europe. NOAA = National Oceanic and Atmospheric Administration.

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