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Improved separation of the 209 polychlorinated biphenyl congeners using comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry

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Abstract

The separation of the 209 polychlorinated biphenyl (PCB) congeners has been studied using comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC × GC–TOFMS). Four column combinations based on thermally stable phases, DB-1/HT-8, DB-XLB/HT-8, DB-XLB/BPX-50, and HT-8/BPX-50, have been investigated. The HT-8/BPX-50 set produced the best separation. The distribution of the 100 to 150 ms wide peaks was highly structured in the chromatographic space and based on the degree of *ortho*-substitution within each separated homologue series. A total of 192 congeners were resolved in 146 min (1.3 analyte per min) using this column set. Eight coelutions involved 17 congeners. Among them, seven congeners were present in Aroclors at levels >1.0 wt.% (CBs 33, 47, 48, 95, 97, 163, 187). Except for CBs 47 and 48, none of the major constituents of commercial mixtures were coeluting. CB 138 was well separated from CBs 163 and 164 in the second dimension. For all column sets, CBs 20, 33, and 109 always coeluted with other PCBs. The 12 toxic dioxin-like congeners (CBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189), and the seven European Union marker PCBs (CBs 28, 52, 101, 118, 138, 153, 180) were separated from any interfering congeners. This was not the case for the other investigated column sets.

Keywords: Resolution; Gas chromatography, comprehensive two-dimensional; Polychlorinated biphenyls

1. Introduction

The chromatographic separation of polychlorinated biphenyls (PCBs) has challenged analytical chemists since they were found in environmental samples more than 35 years ago [1]. PCBs are among the substances of anthropogenic origins that have been classified as persistent organic pollutants (POPs) by the United Nations Environment Programme (UNEP) under the Stockholm Convention on POPs in 1997 [2]. The 209 possible PCB congeners, can be grouped into 10 homologue groups containing 1–46 compounds, depending on their level of chlorination. The industrial PCB mixtures are known under the trade names of Aroclor, Kanechlor, Clophen, and Delor [3] which contain approximately 150 congeners that are the major congeners in environmental samples [4].

Despite the broad range of gas chromatography (GC) stationary phases available, none can separate all 209 PCB congeners from each other. The efficiency of a column, therefore, often is estimated by the number of PCBs that are not coeluting. In practice, the column phase selection depends on which congeners need to be separated for a specific application. Depending on their toxicity or occurrence in samples, some of the PCBs have been grouped in subsets. The resolution requirements for a chromatographic system can vary depending on the number of PCB congeners to be considered, the number of PCB congeners potentially present in samples, and the number of critical coelution to be avoided. Larsen [5] and, more recently, by Cochran and Frame [6] reviewed the high-resolution GC of PCBs.

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Many reports also have been published during the last two decades concerning the efficiency of many different column phases for the separation of the PCB congeners [7–21]. The aim of the present paper is to evaluate the use of an emerging technique based on the combination of commercially available GC columns to offer increased separation power.

Comprehensive two-dimensional GC (GC × GC) [22,23] is accomplished by the serial coupling of two GC columns using an interface called a "modulator". This modulator is responsible for efficiently and continuously sampling narrow bands (trapping and refocusing) of all the species eluting from the first column (first dimension [^{1}D]) and re-injecting them into the second column (second dimension [^{2}D]). By using a high-sampling rate (modulation frequency) at the modulator, the separation achieved in ^{1}D must be maintained through the entire separation process (conservation rule). The modulator acts on the secondary column as a pulsed on-column injector. The detector records the signal at the end of ^{2}D column, as it does for any classical one-dimensional GC separation, and creates high-speed two-dimensional chromatograms. Several recent review articles are available [24–27]. In contrast to selective heart-cutting 2DGC, all ^{1}D eluents undergo separation in ^{2}D. This technique is, therefore, characterized by an increased peak capacity and thus an increased separation power, which can be used to investigate complex mixtures of analytes such as those encountered in essential oil analysis, petroleum characterisation, and environmental monitoring [28–32]. More specifically, GC × GC also has been used to separate selected PCBs. Haglund et al. [33] reported the use of GC × GC–FID (flame ionization detector) based on a liquid crystal shape selective GC column phase (LC-50) coupled to a classical non-polar phase for the separation of toxic PCBs from other PCB congener present in technical mixtures. They also showed that the seven marker PCBs usually monitored were separated from other congeners. Korytár et al. [34] reported the use of HP-1/HT-8 and HP-1/SupelcoWax-101 column combination for the complete separation of the 12 priority PCBs from a mixture of 90 PCBs in a little bit more than 2 h. Ordered structures were obtained, mainly depending on the number and position of the chlorine atoms. The use of a DB-1MS/HT-8 column combination was further extended to the simultaneous separation of 38 prominent PCBs in human as well as environmentally relevant organochlorine pesticides and polybrominated diphenyl ethers [35]. Very recently, Harju et al. [36], reported the use of GC × GC–μECD (micro electron capture detector) to attempt the separation of the 209 PCB congeners. The best separations were achieved using DB-XLB/SP-2340 and DB-XLB/LC-50 column combinations but not all congeners were resolved. They were able to separate the toxic PCBs as well as the marker PCBs from others.

Considering chromatographic peak widths at baseline in the range of 50–200 ms, which characterize peaks produced during the high-speed separation process in ^{2}D, time-of-flight mass spectrometry (TOFMS) is the mass-selective detector of choice [37,38]. The comprehensive mass spectrometric analysis is accompanied by an accurate description of the chromatographic peaks resulting from the fast TOFMS spectral acquisition rate. Additionally, the absence of concentration skewing in the TOFMS instrument ensures spectral continuity and allows mass spectral deconvolution of coeluting chromatographic peaks characterized by different fragmentation patterns [39,40]. This capability allows the identification of different compounds if the peak apexes of coeluting analytes are at least separated by three scans and differ somewhat in their mass spectra. The use of deconvoluted ion current (DIC) makes the TOFMS almost like a third dimension for the separation system. Consequently, the GC × GC–TOFMS coupling is a powerful instrument combining improved chromatographic resolution of the GC × GC and the analytical resolving power of the TOFMS [41,42].

The present study evaluated the capability of a GC × GC–TOFMS system to improve the separation of the 209 PCB congeners using different ^{1}D/^{2}D column combinations.

2. Experimental

2.1. Chemicals

The PCB standard solutions were obtained from AccuStandard Inc. (New Haven, CT, USA). The nine multicongener solutions (C-CS-01 to C-CS-09), containing all native 209 PCB congeners at concentrations of 10 μg/mL in isooctane, were used. They were mixed to produce a solution containing all 209 congeners at a concentration of 1 ng/μL. The tetra-chlorobiphenyl CB 52 and the hepta-chlorobiphenyl CB 180 were used as retention time markers to calculate temperature-programmed relative retention times ($RRT_x = PCB_x/[CB_{52} + CB_{180}]$), and to use previously published RRT data for peak assignment [7].

To number the individual PCB congeners, we used the IUPAC numbering approach. It differs from both the modified numbering sytem proposed by Guitart et al. [43] and the original and modified numbering systems of Ballschmitter et al. [44,45]. The sensitive congeners are CB 107 (IUPAC 2,3,3′,4′,5), CB 108 (IUPAC 2,3,3′,4,5′), CB 109 (IUPAC 2,3,3′,4,6), CB 199 (IUPAC 2,2′,3,3′,4′,5,5′,6), CB 200 (IUPAC 2,2′,3,3′,4,5,6,6′), and CB 201 (IUPAC 2,2′,3,3′,4,5′,6,6′).

2.2. GC × GC–TOFMS analysis

The GC × GC–TOFMS instrument was the Pegasus 4D (Leco Corp., St Joseph, MI, USA). This system is based on a nonmoving quad-jet modulator made of two permanent cold nitrogen jets and two pulsed hot-air jets that are

responsible for trapping and refocusing of compounds eluting from the ^{1}D column. This modulator is mounted in an Agilent 6890 GC oven (Palo Alto, CA, USA) and liquid nitrogen is used to create the cold jets. Details regarding the system have been reported elsewhere [35]. The temperature of the modulator (the temperature of the heater for the hot jets) had an offset of 60 °C compared with the temperature of the primary GC oven. The primary GC oven was programmed as follows: 90 °C for 1 min, then to 150 °C at 30 °C/min, then to 300 °C at 1 °C/min. The ^{2}D column was coiled in the secondary oven that was 40 °C higher than the primary oven and operating in the iso-ramping mode. The modulator period was 3 s (0.33 Hz modulation frequency) with the hot-pulse duration set at 800 ms and the cool time between stages set at 700 ms. Pure GC-grade He, was used as carrier gas at a constant flow of 0.8 mL/min. The inlet temperature was 280 °C for splitless injections of 1 μL. The purge time was 120 s at a flow of 20 mL/min.

Four major different column sets were investigated. The first set used a DB-1 100% dimethylpolysiloxane (75 m × 0.25 mm I.D. × 0.25 μm film thickness) narrowbore capillary column (J&W Scientific, Folsom, CA, USA) as ^{1}D and a high-temperature HT-8 (8% phenyl)-polycarborane-siloxane (2.5 m × 0.10 mm i.d. × 0.10 μm film thickness) microbore capillary column (SGE, Austin, TX, USA) as ^{2}D. The second column set consisted of a DB-XLB (60 m × 0.25 mm i.d. × 0.25 μm film thickness) narrowbore capillary column (J&W Scientific) as ^{1}D and a HT-8 (2.5 m × 0.10 mm i.d. × 0.10 μm film thickness) microbore capillary column (SGE) as ^{2}D. The third column set was made of a DB-XLB (60 m × 0.25 mm i.d. × 0.25 μm film thickness) narrowbore capillary column (J&W Scientific) as ^{1}D and a BPX-50 (50% phenyl)-polysilphenylene-siloxane (2.5 m × 0.10 mm i.d. × 0.10 μm film thickness) microbore capillary column (SGE) as ^{2}D. The fourth column set was made of a HT-8 (50 m × 0.22 mm i.d. × 0.25 μm film thickness) narrowbore capillary column (SGE) as ^{1}D and a BPX-50 (2.5 m × 0.10 mm i.d. × 0.10 μm film thickness) microbore capillary column (SGE) as ^{2}D.

Deactivated universal presstight connectors from Restek Corp. (Bellefonte, PA, USA) were used for connecting narrowbore and microbore capillary columns. Leak-free connections were ensured by careful inspection of the column cuts and cleanup of the column ends using acetone to remove any finger grease. The connection was cured from 40 to 320 °C at a rate of 2 °C/min. and held at the final temperature for two additional hours.

The transfer line connecting the secondary column and the MS source was operated at a temperature of 250 °C. The source temperature was 250 °C with a filament bias voltage of −70 V. The data acquisition rate was 60 scans/s for a mass range of 100–550 amu. The detector voltage was 1800 V.

Data processing and display of the GC × GC chromatograms were achieved using the integrated Leco ChromaTOF^{TM} software. Peak apexes were found automatically and further manually corrected when required.

3. Results and Discussion

3.1. Data handling and peak assignments

Once the modulation process has occurred, an analyte is distributed in several slices characterized by slightly decreasing ^{2}D retention time values (e.g. ^2t_RX or ^2t_RY). With a modulation period, P_M, of 3 s, an average of five slices were produced for each analyte. Some 1100 slices (peaks) were identified and combined to describe the chromatographic profile. The combination of the slices corresponding to each analyte was carried out automatically, following pre-established match criteria (t_R, mass spectra reverse search). Such an exercise requires high-computing power. A mass range of 100–550 Da was acquired at a scanning frequency of 60 Hz during 140 min, yielding file sizes up to 500 Mb. The data processing time ranged from 0.5 to 2 h. The data still required manual review of to ensure reliability of the peak combinations.

After peak assignment, the chlorination level was the only data available, with no indication as to the substitution pattern. Congener assignment was carried out through the use of temperature-programmed RRTs to cross-compare the elution order with congener specific data available in the literature for the selected phases [15]. Some of the less complex mixtures of PCBs (C-CS-01 to C-CS-09) also were injected to double-check peak assignments.

3.2. Chromatographic distributions and wrap-around

The chromatographic distribution of each of the 209 PCBs into the retention plane differed markedly depending on the column set used (Fig. 1). The apex plots represent the ^{1}D and ^{2}D coordinates of peak apexes of ^{2}D peaks obtained after data processing.

All sets were based on columns made of thermally stable phases to perform the separation with a secondary oven temperature offset and have all compounds eluting during the temperature ramping stage. An offset temperature of 40 °C was maintained relatively to the primary oven and yieled to a final temperature of 340 °C for ^{2}D column. Performing the ^{2}D separation at high temperature gave ^{2}D peak widths at the base of 100–150 ms. It also reduced wrap-around ($^2t_R > P_M$), which was expected because of the short value of P_M selected to comply with the GC × GC conservation rule (e.g., the separation achieved in ^{1}D must be maintained through the entire separation process). A P_M value of 3 s was required to efficiently sample ^{1}D peaks that were 20 s wide, at the base. For all investigated column sets, one wrap-around was observed in the elution window but no coelutions between analytes issued from different modulation cycles were created and the separation profile was conserved. In Fig. 1, the apex plots have been "wrap-around corrected" by reducing ^2t_R values and correcting the ^2t_R of wrap-around compounds by the value of P_M (see Fig. 1).

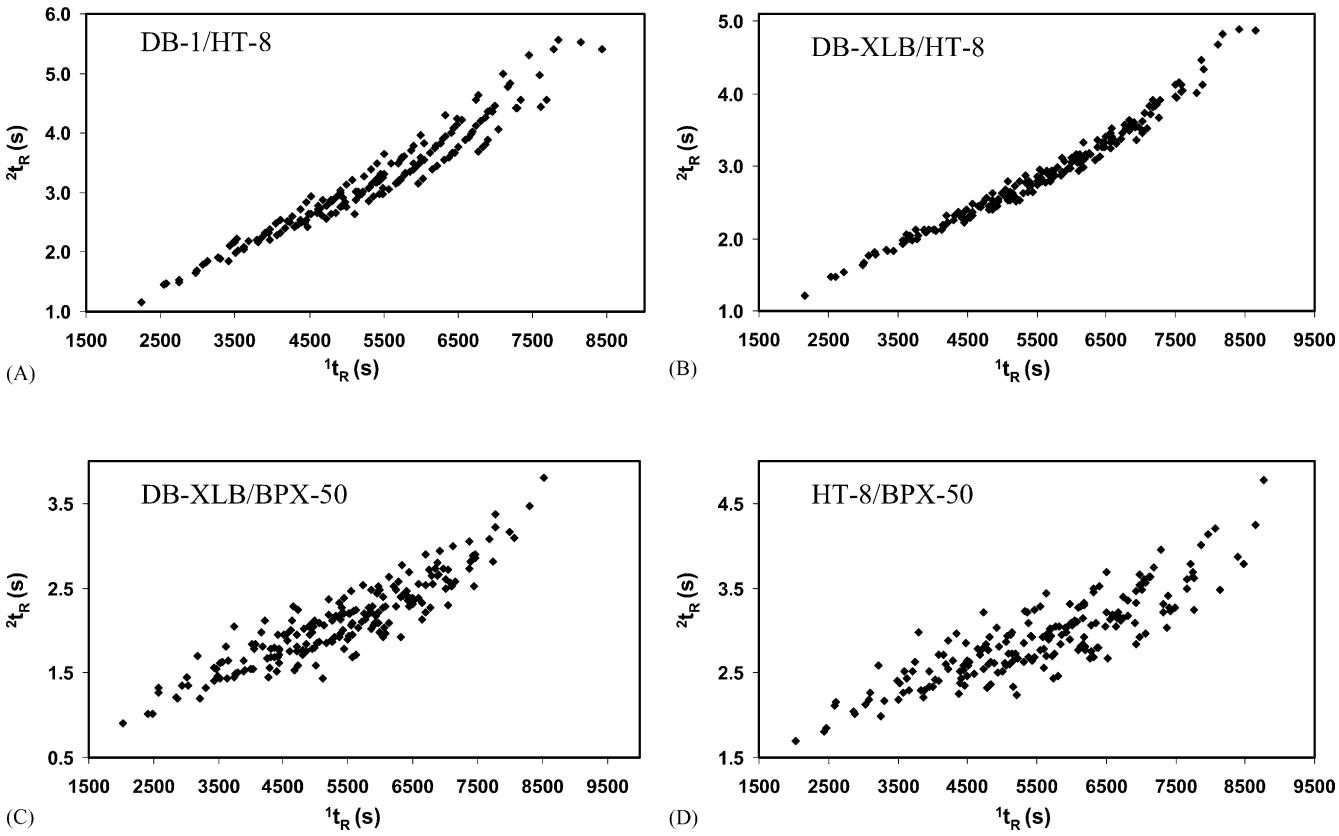

Fig. 1. GC × GC–TOFMS apex plots of a standard solution containing the 209 PCB congeners at a concentration of 1 ng/μL. The temperature of the modulator had an offset of 60 °C compared with the temperature of the primary GC oven. The primary GC oven was programmed as follows: 90 °C for 1 min, then to 150 °C at 30 °C/min, then to 300 °C at 1 °C/min. The ^{2}D column was coiled in the secondary oven, which was 40 °C higher than the primary oven (iso-ramping mode). The acquired mass range was 100–550 amu. The data acquisition rate was 60 Hz and the detector voltage was 1800 V. The modulation frequency was 0.33 Hz with a hot pulse duration of 800 ms. The distribution of the congeners in the separation spaces is shown for the DB-1/HT-8 (A), the DB-XLB/HT-8 (B), the DB-XLB/BPX-50 (C), and the HT-8/BPX-50 (D) column sets. ^2t_R that showed wrap-around (values higher than the modulation period P_M) were corrected by the P_M value (3 s) to simplify the display of the apex plots.

3.3. DB-1/HT-8 column set

The first column set was a DB-1/HT-8 combination because of our experience with it in PCB separation and the fairly good orthogonality from the phase combination. The characteristic distribution of the PCBs organized by homologue series (Fig. 2A; Table 1) was expected and in accordance with previous reports [34,35]. The nonpolar ^{1}D stationary phase generated ^1t_R values proportional to the vapor pressure of the congeners and to the degree of chlorination. For ^{2}D, the carborane group has reportedly higher affinity toward PCBs with a low degree of *ortho*-substitution [12]. In general, although a limited number of exceptions exists, within a homologue group, the higher the *ortho*-substitution, the shorter the retention time, for both dimensions. For example, the tri-CB homologue series gave the following elution order: the tri-*ortho*-CB (CB 19), then the di-*ortho*-CBs (CBs 30, 18, 17, 27, 24, 16/32), then the

Table 1
Selected masses used to build up the deconvoluted ion current (DIC) trace of the 209 PCBs

No. of chlorine atoms	No. of congeners	Selected TOFMS masses
1	3	188 + 190
2	12	222 + 224 + 226
3	24	186 + 188 + 256 + 258 + 260
4	42	220 + 222 + 255 + 257 + 290 + 292 + 294 + 296
5	46	254 + 256 + 291 + 324 + 326 + 328 + 330
6	42	288 + 290 + 292 + 358 + 360 + 362 + 364
7	24	322 + 324 + 326 + 392 + 394 + 396 + 398
8	12	356 + 358 + 360 + 362 + 426 + 428 + 430 + 432
9	3	390 + 392 + 394 + 396 + 398 + 460 + 462 + 464 + 466 + 468
10	1	424 + 426 + 428 + 430 + 432 + 494 + 496 + 498 + 500 + 502

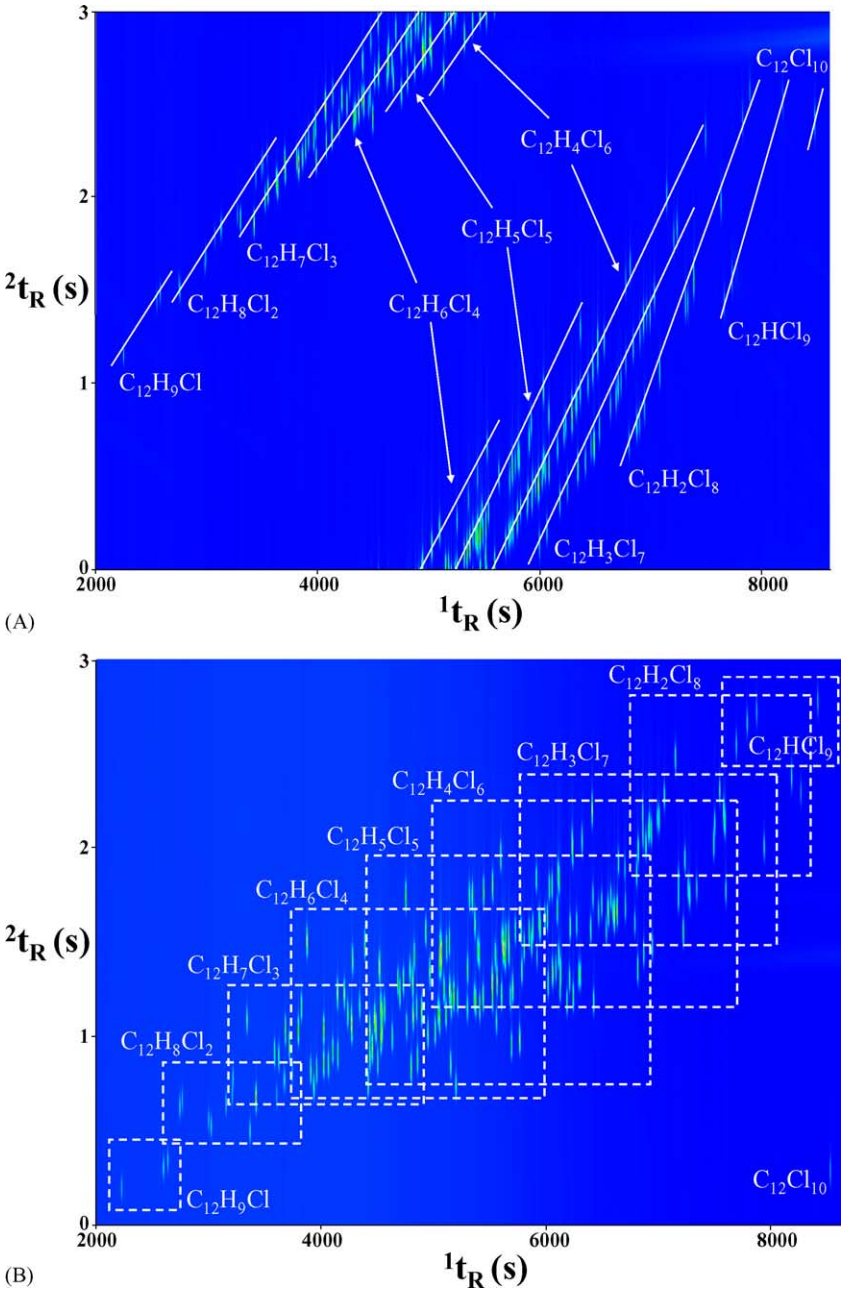

Fig. 2. GC × GC–TOFMS chromatogram of the 209 PCB congeners using the DB-1/HT-8 (A) and the HT-8/BPX-50 (B) column sets. The signal was reconstructed using the characteristic ions of each chlorination group (DIC traces) listed in Table 1. The same conditions as in Fig. 1 were used. For clarity, the ^{2}D scale was shifted by 1.5 s for the HT-8/BPX-50 data.

mono-*ortho*-CBs (CBs 34, 23, 19, 26, 25, 31, 28, 20/21/33, 22) and finally the non-*ortho*-CBs (CBs 36, 39, 38, 35, 37).

The separation of the homologue groups was so reliable that only one coelution between two congeners (CBs 23 and 54) resulted from two homologue series (tri- and tetra-substituted, respectively). The only other coelutions were for congeners within a homologous series. Among the 209 congeners, only 163 were chromatographically resolved in 140 min. In this particular case, because most the coeluting compounds were characterized by similar mass spectra, the deconvolution was not possible. No additional separation was therefore achieved for this column set, except for CBs 23 and 54, which separated 165 congeners. The added value of the TOFMS deconvolution capability was thus limited when using this particular column combination, regarding the use of micro electron capture detection (μECD). For comparison, Mullin et al. [46] reported a total of 187 PCB congeners potentially resolved using a one-dimensional separation based on a 50 m SE-54 5% diphenyl 1% vinyl dimethyl siloxane GC column. Recently, Korytár et al. [34], used GC × GC–μECD and a thermal sweeper modulator to study the separation of a mixture of 90 PCBs. The best

separation, in which 84 PCBs were solved (including the 12 WHO congeners) in 135 min, was achieved using a DB-1 equivalent phase as ^{1}D and a very polar polyethylene glycol (WAX) phase as ^{2}D. However, this particular column set did not offer the useful ordered structure available with the HT-8/BPX-50 set (and the DB-1/HT-8 set), and no data were reported regarding the remaining 119 congeners.

3.4. DB-XLB/HT-8 column set

We tested the DB-XLB/HT-8 column set because of the reported [12,20] PCB selectivity of these two phases. However, those phases can not separate all the 209 PCB congener when used separately in classical one-dimensional GC [15]. As illustrated by the apex plot in Fig. 1B, the congener distribution in the chromatographic space was not as good as when we used the DB-1/HT-8 combination. The separation mechanisms involved in the two dimensions of the DB-XLB/HT-8 set were not as different as for the DB-1/HT-8 set. This reduced the degree of orthogonality of the system (t_R in the two dimensions were not independent), and therefore, the dispersion of the peaks through the chromatographic space suffered. This resulted in a higher number of interhomologue series coelutions and a reduction of the chromatographic resolution power. Nevertheless, because mass spectral deconvolution of coeluting PCBs issued from different homologue groups was possible, 21 coelutions were further resolved that way and only 23 coeluting PCBs remain. This approach conducted to a total separation (chromatographically and analytically) of 186 congeners in 144 min.

This approach of combining the DB-XLB phase with MS detection to solve coelution issues was reported earlier as acceptable because, in most cases, the highly chlorinated compound is the minor component (low level in commercial mixtures) of the coeluting group and its dechlorination to a lower homologue group is negligible [15]. However, one should not encourage such an approach of reducing the chromatographic resolution of a system because of the potential for deconvolution of the MS signals. In fact, this might lead to identification and quantification problems in, for example, the situation in which a hexa-CB congener coelutes with a tetra-CB congener. The interfering fragmentation loss of Cl_2 from the hexa-CB produces a M-70 cluster of ions that correspond to the ion cluster of the tetra-CB and makes accurate identification impossible. Some other deconvolution limitations were reported in pesticide analysis [37], and those potential issues should be considered when performing coelutions. In conclusion, this phase combination is not recommended for accurately separating the 209 PCB congeners.

3.5. DB-XLB/BPX-50 column set

To improve the separation on the basis of a DB-XLB ^{1}D phase, we combined it with a more polar BPX-50 ^{2}D phase that is stable at high temperature and available in 0.10 mm I.D. × 0.10 μm film thickness. The separation was more efficient (Fig. 1C) than it was with the previous sets and conducted to the separation of 194 congeners after deconvolution of three coeluting congeners. Unfortunately, among the coeluting compounds, an unacceptable pair occurred between the tetra-chlorinated 77 and the hexa-chlorinated 144, reducing the appeal of the remaining separation. A recent study by Harju et al. [36] however reported the successful use of the DB-XLB phase as ^{1}D of several column sets. They separated 181 congeners with a DB-XLB/LC-50 (poly-50% liquid crystalline/50% dimethyl-siloxane phase) combination. None of the seven marker and WHO PCBs were among the coeluting congeners. They were using μECD detection and all the separation was achieved chromatographically. As far as we know, although its good shape-selectivity towards PCBs make it a phase of prime interest for PCB separation [33], the working temperature range of the LC-50 phase is quite limited and special care has to be taken to avoid excessive column bleeding.

3.6. HT-8/BPX-50 column set

The HT-8/BPX-50 column set was investigated to try to take advantage of a long ^{1}D based on the high-temperature HT-8 carborane phenylmethylsiloxane copolymer phase rather than the DB-XLB phase for the coupling with the much more polar BPX-50 phase. This resulted in a very good dispersion of the peaks into the separation space because the mechanisms involved in ^{1}D and ^{2}D clearly differed (Fig. 1D). Similarly to the homologue series separations achieved using the DB-1/HT-8 set, the chromatogram was structured (Fig. 2B).

A closer look at the elution order shows that, depending on the number of chlorines on the rings, up to five subseries were separated within the same homologue group. As expected, the carborane group of the HT-8 phase showed a high affinity toward PCBs with a low degree of *ortho*-substitution. Practically, this had the effect of splitting every homologue group across the ^{1}D retention line. In Fig. 3, the apex plots resulting from the separation of the 209 PCBs on the HT-8/BPX-50 column set are presented. The series defined by the dashed lines correspond to the *ortho*-substitution level of the analytes. From right to left, the *ortho*-substitution level increases from as low as non-*ortho*-CBs up to tetra-*ortho*-CBs. The congener distribution can be explained by the interaction of the carborane phase with PCB π–electrons, which is related to the degree of *ortho*-substitution and to the planarity of the molecule, as previously reported for PCBs [5,46–49]. The resulting ordered structure was, thus, different than the one from the DB-1/HT-8 set. The separation of homologue groups in subseries was valuable because it increased the spreading out of the congeners in the chromatographic space. This contributes to ease the peak identification and quantification, as well as the prediction of PCB retention data in complex mixtures. Chromatographic coelution problems were

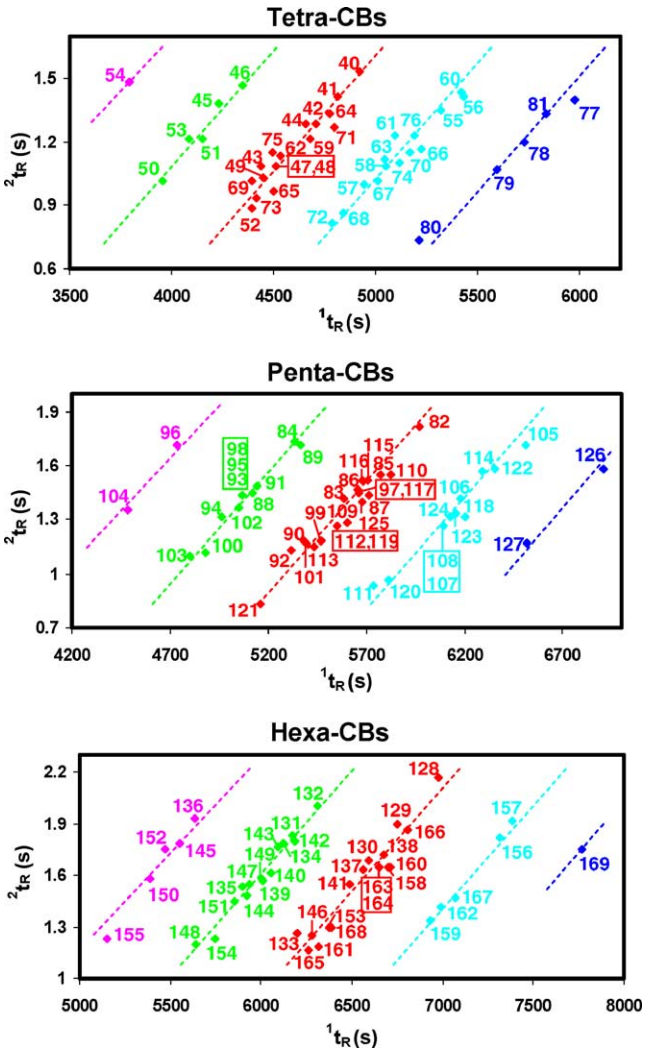

Fig. 3. GC × GC–TOFMS apex plots of the terat-, penta and hexa-CB homologue groups using the HT-8/BPX-50 column set (all parameters identical to Fig. 1). A separate apex plot is shown for each homologue group. Numbers correspond to individual PCBs following Guitart et al. numbering [43]. The *ortho*-substitution level is described as follow: Tetra-*ortho*-CBs are in pink, tri-*ortho*-CBs are in green, di-*ortho*-CBs are in red, mono-*ortho*-CBs are in light blue, and non-*ortho*-CBs are in dark blue. Boxes represent coeluting congeners.

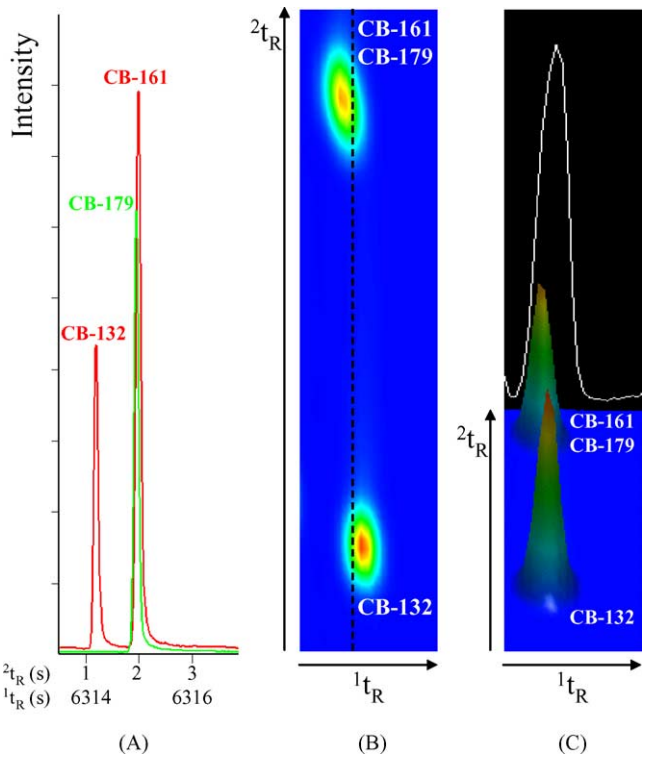

Fig. 4. GC × GC–TOFMS raw data (A), contour plot (B), and three-dimensional plot (C) for the chromatographic region where CBs 132, 179, and 161 were eluting using the HT-8/BPX-50 column set. (A) Only one cluster of peaks, corresponding to one modulation cycle at the time represented by the dashed line on B. The red (*m*/*z* 292 × 3) and the green (*m*/*z* 398) traces correspond to hexa- (CBs 132, 161) and hepta-CBs (CB 179), respectively. (B) Contour plots corresponding to the two peak units chromatographically separated. (C) Reconstructed 1DGC–TOFMS trace (white) based on the sum of the signals recorded in ^{2}D.

minimized and the need for mass deconvolution was reduced. Nevertheless, we can take advantage of the TOFMS deconvolution capability in some cases where no interfering ions are produced by the coeluting species. Fig. 4 illustrates such an example where three congeners (CBs 132, 179, 161) were separated, although only two were chromatographically separated in ^{2}D (Fig. 4). Fig. 4 illustrates that a one-dimensional GC separation would have peaked only once (the reconstructed trace in Fig. 4C), a GC × GC separation using a micro-electron-capture detector would have peaked twice (the contour plots in Fig. 4B), and the GC × GC–TOFMS permitted the identification of three separate analytes. Other examples of ^{1}D coelution problems chromatographically resolved in ^{2}D are illustrated in Fig. 2B. Among the 209 CB congeners, 188 were chromatographically separated and four (CB 132/CB 179 and CB 160/CB 175) required mass spectral deconvolution, conducting to a total of 192 congeners separated in 146 min. For comparison, Harju et al. [36] recently reported a 240 min separation of 194 congeners using GC × GC–μECD and a column set made of a 60 m DB-XLB/2.25 m BPX-70 (70% cyanopropyl polysilphenylene-siloxane).

Retention times (^1t_R and ^2t_R) are listed in Table 2. In the table, ^1t_R values were for the most intense peak (base peak) of the modulation cluster. Because there was no synchronization between the start of the first modulation and the start of the GC, slight shifts in ^1t_R had changed the place of the base peak in the cluster. Therefore, a ^1t_R shift equal to the value of P_M was sometimes observed in between runs. The ^1t_R values (Table 2) were the most systematically observed from run-to-run ($n = 5$). The ^2t_R values did not depend on the modulation phase and the standard deviation ranged from 0.01 to 0.03 s.

Eight coelutions involved 17 congeners. Among them, seven congeners were present in Aroclors at levels >1.0 wt.% (CBs 33, 47, 48, 95, 97, 163, 187) and co-eluted with

Table 2
Congener elution order (^1t_R, ^2t_R in seconds) using the HT-8/BPX-50 column set

Congener	Cl position	^1t_R	^2t_R	Congener	Cl position	^1t_R	^2t_R
1	2	2036	1.70	**136**	**2,2′,3,4′,5,6′**	**5633**	**0.43**
2	3	2432	1.80	148	2,2′,3,3′,6,6′	5642	2.70
3	4	2474	1.85	86	2,2′,3,4,5	5654	2.97
10	2,6	2585	2.12	**97**	**2,2′,3′,4,5**	**5660**	**2.95**
4	**2,2′**	**2609**	**2.15**	*117*	2,3,4′,5,6	5660	2.95
9	2,5	2861	2.05	125	2′,3,4,5,6′	5678	2.90
7	2,4	2885	2.02	116	2,3,4,5,6	5681	0.02
6	**2,3′**	**3026**	**2.13**	115	2,3,4,4′,6	5708	0.02
8	**2,4′**	**3086**	**2.18**	**87**	**2,2′,3,4,5′**	**5711**	**2.93**
5	2,3	3095	2.27	78	3,3′,4,5	5726	2.70
19	2,2′,6	3227	2.58	111	2,3,3′,5,5′	5735	2.43
14	3,5	3254	1.98	154	2,2,′,4,4′,5,6′	5747	2.73
30	2,4,6	3311	2.17	**85**	**2,2′,3,4,4′**	**5771**	**0.05**
18	**2,2′,5**	**3488**	**2.40**	120	2,3′,4,5,5′	5813	2.47
11	3,3′	3509	2.18	**110**	**2,3,3′,4′,6**	**5825**	**0.05**
17	**2,2′,4**	**3527**	**2.38**	81#	3,4,4′,5	5834	2.83
13	3,4′	3578	2.27	**151**	**2,2′,3,5,5′,6**	**5855**	**2.95**
12	3,4	3584	2.27	**135**	**2,2′,3,3′,5,6′**	**5900**	**0.03**
24	2,3,6	3593	2.52	144	2,2′,3,4,5′,6	5924	2.98
27	2,3′,6	3629	2.43	147	2,2′,3,4′,5,6	5936	0.05
15	**4,4′**	**3656**	**2.30**	**82**	**2,2′,3,3′,4**	**5972**	**0.32**
32	**2,4′,6**	**3713**	**2.52**	77#	3,3′,4,4′	5978	2.90
16	**2,2′,3**	**3743**	**2.63**	**149**	**2,2′,3,4′,5′,6**	**6002**	**0.08**
54	2,2′,6,6′	3794	2.98	139	2,2′,3,4,4′,6	6008	0.07
23	2,3,5	3830	2.30	140	2,2′,3,4,4′,6′	6053	0.12
34	2′,3,5	3860	2.22	188	2,2′,3,4′,5,6,6′	6077	0.10
29	2,4,5	3887	2.30	124	2′,3,4,5,5′	6089	2.77
26	**2,3′,5**	**3956**	**2.33**	143	2,2′,3,4,5,6′	6095	0.27
50	2,2′,4,6	3956	2.52	134	2,2′,3,3′,5,6	6122	0.28
25	2,3′,4	4001	2.33	108	2,3,3′,4,5′	6125	2.82
31	**2,4′,5**	**4040**	**2.42**	*107*	2,3,3′,4′,5	6125	2.82
53	2,2′,5,6′	4085	2.72	123#	2′,3,4,4′,5	6158	2.83
28*	**2,4,4′**	**4088**	**2.40**	184	2,2′,3,4,4′,6,6′	6170	0.15
51	2,2′,4,6′	4151	2.72	131	2,2′,3,3′,5,5′	6176	0.33
21	2,3,4	4181	2.60	106	2,3,3′,4,5	6182	2.92
33	**2′,3,4**	**4217**	**2.55**	142	2,2′,3,4,5,6	6188	0.30
20	2,3,3′	4217	2.55	133	2,2′,3,3′,4,6	6197	2.77
45	**2,2′,3,6**	**4229**	**2.88**	**118#***	**2,3′,4,4′,5**	**6203**	**2.82**
22	**2,3,4′**	**4295**	**2.65**	165	2,3,3′,5,5′,6	6263	2.67
46	2,2′,3,6′	4346	2.97	**146**	**2,2′,3,4′,5,5′**	**6281**	**2.75**
36	3,3′,5	4376	2.25	114#	2,3,4,4′,5	6290	0.07
69	2,3′,4,6	4391	2.52	**132**	**2,3,3′,4,5′,6**	**6311**	**0.50**
52*	**2,2′,5,5′**	**4394**	**2.38**	**179**	**2,2′,3,3′,5,6,6′**	**6314**	**0.45**
73	2,3′,5′,6	4415	2.43	161	2,2′,3,3′,4,6′	6320	2.68
43	2,2′,3,5	4439	2.58	122	2′,3,3′,4,5	6353	0.08
49	**2,2′,4,5′**	**4448**	**2.53**	**153***	**2,2′,4,4′,5,5′**	**6374**	**2.80**
39	3,4′,5	4466	2.35	168	2,3′,4,4′,5′,6	6389	2.80
104	2,2′,4,6,6′	4484	2.85	176	2,2′,3,3′,4,6,6′	6407	0.52
75	2,4,4′,6	4493	2.65	**141**	**2,2′,3,4,5,5′**	**6488**	**3.05**
65	2,3,5,6	4499	2.47	186	2,2′,3,4,5,6,6′	6503	0.68
47	**2,2′,4,4′**	**4508**	**2.58**	**105#**	**3,3′,4,5,5′**	**6509**	**0.22**
48	**2,2′,4,5**	**4508**	**2.58**	127	2,3,3′,4,4′	6515	2.67
62	2,3,4,6	4532	2.63	137	2,2′,3,4,4′,5	6563	0.13
38	3,4,5	4604	2.48	130	2,2′,3,3′,4,5′	6593	0.18
44	**2,2′,3,5′**	**4655**	**2.78**	178	2,2′,3,3′,5,5′,6	6635	0.05
59	2,3,3′,6	4676	2.72	**163**	**2,3,3′,4′,5,6**	**6653**	**0.15**
42	**2,2′,3,4′**	**4709**	**2.78**	*164*	2,3,3′,4′,5′,6	6653	0.15
96	2,2′,3,6,6′	4736	0.22	**138***	**2,2′,3,4,4′,5′**	**6677**	**0.22**
35	3,3′,4	4742	2.55	158	2,3,3′,4,4′,6	6698	0.15
64	**2,3,4′,6**	**4775**	**2.83**	160	2,3,3′,4,5,6	6713	0.15
72	2,3′,5,5′	4784	2.32	175	2,2′,3,3′,4,5′,6	6713	0.12
71	2,3′,4′,6	4799	2.77	182	2,2′,3,4,4′,5,6′	6737	0.15
103	2,2′,4,5′,6	4802	2.60	**187**	**2,2′,3,4′,5,5′,6**	**6737**	**0.15**

Table 2 (*Continued*)

Congener	Cl position	^1t_R	^2t_R	Congener	Cl position	^1t_R	^2t_R
41	2,2′,3,4′	4814	2.92	129	2,2′,3,3′,4,5	6749	0.40
37	**3,4,4′**	**4838**	**2.63**	166	2,3,4,4′,5,6	6809	0.36
68	2,3′,4,5′	4844	2.37	**183**	**2,2′,3,4,4′,5′,6**	**6815**	**0.17**
100	2,2′,4,4′,6	4883	2.62	126#	3,3′,4,4′,5	6908	0.08
40	2,2′,3,3′	4922	0.03	185	2,2′,3,4,5,5′,6	6926	0.33
57	2,3,3′,5	4943	2.50	159	2,3,3′,4,5,5′	6935	2.83
94	2,2′,3,5,6′	4961	2.82	202	2,2′,3,3′,5,5′,6,6′	6938	0.47
67	2,3′,4,5	5009	2.52	**128**	**2,3,3′,4′,5,5′**	**6980**	**0.67**
63	2,3,4,5′	5042	2.62	**174**	**2,2′,3,3′,4,5,6′**	**6983**	**0.53**
58	2,3,3′,5′	5051	2.58	162	2,2′,3,3′,4,4′	6989	2.92
102	2,2′,4,5,6′	5051	2.87	181	2,2′,3,4,4′,5,6	7010	0.48
98	2,2′,3′,4,6	5066	2.93	201	2,2′,3,3′,4,5′,6,6′	7037	0.57
95	**2,2′,3,5′,6**	**5066**	**2.93**	**177**	**2,2′,3,3′,4′,5,6**	**7043**	**0.60**
93	2,2′,3,5,6	5066	2.93	204	2,2′,3,4,4′,5,6,6′	7061	0.57
61	2,3,4,5	5093	2.73	167#	2,3′,4,4′,5,5′	7070	2.97
74	**2,4,4′,5**	**5114**	**2.60**	**171**	**2,2′,3,3′,4,4′,6**	**7121**	**0.63**
91	2,2′,3,4,6	5120	2.95	197	2,2′,3,3′,4,4′,6,6′	7136	0.63
121	2,3′,4,5′,6	5144	2.98	173	2,2′,3,3′,4,5,6	7184	0.75
155	2,2′,4,4′,6,6′	5150	2.73	200	2,2′,3,3′,4,5,6,6′	7292	0.95
88	2,2′,3,4′,6	5159	2.33	172	2,2′,3,3′,4,5,5′	7319	0.22
70	**2,3′,4′,5**	**5165**	**2.65**	**156#**	**2,3,3′,4,4′,5**	**7319**	**0.32**
76	2′,3,4,5	5189	2.73	192	2,3,3′,4,5,5′,6	7367	0.03
80	3,3′,5,5′	5210	2.23	157#	2,3,3′,4,4′,5′	7382	0.42
66	**2,3′,4,4′**	**5225**	**2.67**	**180***	**2,2′,3,4,4′,5,5′**	**7412**	**0.27**
92	2,2′,3,5,5′	5318	2.63	193	2,3,3′,4′,5,5′,6	7427	0.23
55	2,3,3′,4	5318	2.85	**191**	**2,3,3′,4,4′,5,6**	**7493**	**0.27**
84	**2,2′,3,3′,6**	**5336**	**0.23**	198	2,2′,3,3′,4,5,5′,6	7655	0.50
89	2,2′,3,4,6′	5363	0.22	**199**	**2,2′,3,3′,4,5,5′,6′**	**7667**	**0.60**
90	2,2′,3,4′,5	5384	2.68	**170**	**2,2′,3,3′,4,4′,5**	**7712**	**0.78**
150	2,2′,3,4′,6,6′	5387	0.08	196	2,2′,3,3′,4,4′,5′,6	7751	0.68
101*	**2,2′,4,5,5′**	**5396**	**2.67**	190	2,3,3′,4,4′,5,6	7754	0.63
60	**2,3,4,4′**	**5417**	**2.93**	**203**	**2,2′,3,4,4′,5,5′,6**	**7763**	**0.62**
56	**2,3,3′,4′**	**5429**	**2.92**	169#	3,3′,4,4′,5,5′	7769	0.25
113	2,3,3′,5′,6	5435	2.65	208	2,2′,3,3′,4,5,5′,6,6′	7868	1.02
99	**2,2′,4,4′,5**	**5468**	**2.68**	207	2,2′,3,3′,4,4′,5,6,6′	7973	1.13
152	2,2′,3,5,6,6′	5471	0.25	195	2,2′,3,3′,4,4′,5,6	8063	1.20
119	2,3′,4,4′,6	5552	2.77	189#	2,3,3′,4,4′,5,5′	8135	0.48
112	2,3,3′,5,6	5552	2.77	**194**	**2,2′,3,3′,4,4′,5,5′**	**8393**	**0.87**
145	2,2′,3,4,6,6′	5555	1.78	205	2,3,3′,4,4′,5,5′,6	8480	0.78
83	2,2′,3,3′,5	5585	2.92	206	2,2′,3,3′,4,4′,5,5′,6	8642	1.25
79	3,3′,4,5′	5594	2.57	209	2,2′,3,3′,4,4′,5,5′,6,6′	8762	1.78
109	2,3,3′,4,5′	5600	2.78				

Coeluting congeners are enclosed in a box. PCBs present in Aroclors 1242, 1254, and 1260 at levels >1.0 wt.% and <1.0 wt.% are in bold and italic, respectively. The other congeners are not present in Aroclor mixtures at levels >0.05 wt.%. Congeners characterized by a WHO TEF value are marked by a (#) sign, and the seven EU marker congeners are marked by a (∗) sign. These values are the raw numbers with no ^2t_R wrap-around correction or normalization.

congeners either present in Aroclors at levels <1.0 wt.% or not present at all in the Aroclor mixture. The only exceptions were CBs 47 and 48, which coeluted and were both at levels >1.0 wt.% in Aroclors. Independently of the column set used, three congeners always coelute with other PCBs (CBs 20, 33, 109) (Table 3). Commonly observed coelutions such as CBs 138 and 163 (a major congener in technical mixtures) were not present with this column set. CB 138 was well separated from CBs 163 and 164 in ^{2}D (Fig. 3). CBs 163 and 164 co-eluted but this is of little importance because CB 164 is not found in technical mixtures. Among the 38 PCB congeners that we routinely measure at the Centers for Disease Control and prevention (CDC) [36], only one coelution was present for CBs 187 and 182. However, CB 182 is unlikely to be present because of its absence in Aroclor mixture. All the dioxin-like World health Organization (WHO) congeners (CBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) [50], as well as the EU marker PCBs (CBs 28, 52, 101, 118, 138, 153, 180), were separated from any interfering congeners. This was not the case for the other column sets (Table 4).

As already mentioned earlier in the manuscript, only few studies have been carried out on the use of GC × GC for the separation of PCBs since the early report of Duinker et al. [51] who used 2DGC (heart-cutting) for the analysis of selected toxic congeners. Those studies were either carried out

Table 3
Co-eluting PCBs on each of the four investigated column sets

Congener	Column set			
	DB-1/HT-8	DB-XLB/HT-8	DB-XLB/BPX-50	HT-8/BPX-50
Resolved by mass				
Di-CBs/Tri-CBs	–	CB 11/18	–	–
	–	CB 13/27	–	–
Tri-CBs/Tetra-CBs	CB 23/57	CB 23/54	CB 38/47/62	–
	–	CB 36/69	–	–
Tri-CBs/Tetra-CBs/Penta-CBs	–	CB 37/68/103	–	–
Tetra-CBs/Penta-CBs	–	CB 72/96	–	–
	–	CB 60/113	–	–
	–	CB 78/116	–	–
	–	CB 47/104	–	–
Penta-CBs/Hexa-CBs	–	CB 119/152	–	–
Hexa-CBs/Hepta-C Bs	–	–	–	CB 132/179
	–	–	–	CB 160/175
Unresolved by mass				
Di-CBs	–	CB 4/10	–	–
Tri-CBs	CB 16/32	–	–	–
	CB 20/21/33	CB 20/21/33	CB 20/21/33	CB 20/33
Tetra-CBs	CB 52/69	CB 62/65	–	CB 47/48
	CB 43/49	CB 58/67	–	–
	CB 48/75	–	–	–
	CB 42/59	–	–	–
	CB 41/64	–	–	–
	CB 61/70	–	–	–
	CB 56/60	–	–	–
Tetra-CBs/Hexa-Cbs[a]	–	–	CB 66/155	–
	–	–	CB 77/144	–
Penta-CBs	CB 98/102	CB 84/89	CB 84/89	CB 93/95/98
	CB 88/91	CB 90/101	CB 90/101	CB 112/119
	CB 90/101	CB 86/125	CB 107/123	CB 97/117
	CB 83/112	CB 115/117	–	CB 108/107
	CB 115/116	CB 107/123	–	–
	CB 108/107	–	–	–
Hexa-CBs	CB 139/149	CB 153/168	CB 153/168	CB 163/164
	CB 134/143	–	–	–
	CB 146/165	–	–	–
	CB 138/163/164	–	–	–
Hepta-CBs	CB 182/187	CB 175/182	–	CB 182/187
Octa-CBs	CB 196/203	–	–	–
Number of separated congeners	165/209	186/209	194/209	192/209

[a] Those congeners can not be efficiently mass-separated because of the M-2Cl loss of the hexa-CB.

using a flame ionization detector (FID) or a μECD. As far as we know, the present study is the first attempt to resolve the 209 PCB congeners using GC × GC–TOFMS. A comparison with the study of Harju et al. [36], who considered the separation of the 209 PCBs using GC × GC–μECD, shows that the input from the use of TOFMS detection is quite limited and that most (if not all) the separation of the PCB congeners can be achieved chromatographically when suitable GC conditions and column sets are selected. Mass spectrometric detection, however, significantly improves peak identification and offers an extra level of accuracy through mass ratio check and library searching. This is ensured by the high quality of the mass spectra that are produced. Additionally, if we think beyond the PCB family and consider that many other organochlorine compounds expressing similar GC behavior might be present in PCB-containing extracts, mass spectral deconvolution might be requested to solve inter-family coelutions.

Concerning the sensitivity of the TOFMS instrument, we achieved instrument limit of detection (iLOD) of 0.5 pg/μL in a previous report on fast GC-IDTOFMS of PCBs [52]. The GC × GC–TOFMS iLOD in the present study ranged between 0.1 and 0.5 pg/μL injected at a scan rate of 60 scans/s with a signal to noise ratio greater than 3. This is in

Table 4
Resolution of the WHO and marker PCBs on the four investigated column sets

PCB congeners		Column set			
		DB-1/HT-8	DB-XLB/HT-8	DB-XLB/BPX-50	HT-8/BPX-50
Non-*ortho*	CB 77	s.	s.	c. (144)	s.
	CB 81	s.	s.	s.	s.
	CB 126	s.	s.	s.	s.
	CB 169	s.	s.	s.	s.
Mono-*ortho*	CB 105	s.	s.	s.	s.
	CB 114	s.	s.	s.	s.
	CB 118	s.	s.	s.	s.
	CB 123	s.	c. (107)	s.	s.
	CB 156	s.	s.	s.	s.
	CB 157	s.	s.	s.	s.
	CB 167	s.	s.	s.	s.
	CB 189	s.	s.	s.	s.
Marker	CB 28	s.	s.	s.	s.
	CB 52	c. (69)	s.	s.	s.
	CB 101	c. (90)	c. (90)	s.	s.
	CB 153	s.	c. (168)	c. (168)	s.
	CB 138	c. (164, 165)	s.	s.	s.
	CB 180	s.	s.	s.	s.

s.: single non-coeluting congener, c.: coeluting congener (coeluter).

agreement with the actual 10-fold signal enhancement we previously reported for PCBs when using GC × GC–TOFMS instead of classical GC–TOFMS [35]. The sensitivity of the TOFMS operating in electron impact (EI) mode is however lower than what has been reported for μECD [34], but it is acceptable for measurements of PCBs in most matrices at usual background levels. Additionally, as mentioned elsewhere [36], TOFMS produce less post-column band broadening than μECD. In the present study, classical peak widths at the base in ^{2}D ranged between 100–150 ms, which permitted easier peak identification when retention times were close.

4. Conclusions

Comprehensive GC × GC–TOFMS improved the separation of the 209 PCBs. The column set of choice is a combination of a carborane HT-8 phase as the first dimension ^{1}D and a 50% phenyl BPX-50 phase as the second dimension ^{2}D. This HT-8/BPX-50 set allows the separate identification of 192 congeners in 146 min (1.3 analyte/min). Among the investigated column sets, this is the only one that simultaneously resolves both the 12 WHO and the seven EU marker PCB congeners. The use of thermally stable phases allows the operation of ^{2}D at high temperature, producing 100–150 ms peak widths and reducing wrap-around. The expected separation into homologous series is also accompanied by a further subfractionation depending on the *ortho*-substitution of the phenyl rings. The structure of the dispersion of the peaks in the chromatographic space is highly ordered, which combined with the RTs for the two dimensions, greatly facilitates peak identification. This report definitely bring us a step closer to the "Holy Grail" of the 209 congener-specific PCB analysis in one run, as described by Frame [53].

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