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Group separation of organohalogenated compounds by means of comprehensive two-dimensional gas chromatography

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Abstract

Separations of 12 compound classes, polychlorinated biphenyls (PCBs), diphenyl ethers (PCDEs), naphthalenes (PCNs), dibenzothiophenes (PCDTs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), terphenyls (PCTs) and alkanes (PCAs), toxaphene, organohalogenated pesticides (OCPs), and polybrominated biphenyls (PBBs) and diphenyl ethers (PBDEs) by comprehensive two-dimensional gas chromatography were evaluated. Five column combinations, DB-1 × 007-210, DB-1 × HT-8, DB-1 × LC-50, DB-1 × 007-65HT and DB-1 × VF-23ms were used to study, primarily, group-type separations, but attention was devoted also to within-class separation, especially for those classes which were not addressed in much detail before, the PCNs, OCPs, PBBs and PCTs. The DB-1 × 007-210 column set did not offer any extra separation compared to one-dimensional GC. For the DB-1 × HT-8 column combination, the useful principle of congener separation on the basis of number of halogen substituents in a molecule was confirmed (PCBs, toxaphene) and extended (PCTs, PBDEs). No practically useful group-type separation was observed for this column combination. The DB-1 × LC-50 set provides group separation based on planarity: planar compounds such as PCDDs, PCDFs, PCDTs and PCNs are much more retained than, and therefore separated from, non-planar analytes. Within the classes of PCBs, PBBs and PCTs highly useful separation of planar from non-planar compounds was also observed. The DB-1 × 007-65HT column set effectively separates PCAs and PBDEs from all other compound classes, and provides a good separation of brominated and chlorinated analogue classes from each other. This column set was the most efficient one for within-class separation of OCPs and PCNs. Finally, DB-1 × VF-23ms yields excellent within-class separations, especially of non-aromatic compounds, viz. OCPs, toxaphene and PCAs. No group separation was observed here. The applicability of the approach was demonstrated for a sediment extract and a dust extract. In the sediment extract, PCDDs, PCDFs, PCAs and PCNs were identified and their efficient separation was achieved. In the dust sample, separation of PCAs and PBDEs was achieved and several new PBDE congeners were identified.

Keywords: Comprehensive two-dimensional gas chromatography; Organochlorine compounds; Organobromine compounds; Polychlorinated biphenyls; Polychlorinated diphenyl ethers; Polychlorinated naphthalenes; Polychlorinated dibenzothiophenes; Polychlorinated dibenzo-*p*-dioxins; Polychlorinated dibenzofurans; Polychlorinated terphenyls; Polychlorinated alkanes; Toxaphene; Organohalogenated pesticides; Polybrominated biphenyls; Polybrominated diphenyl ethers

1. Introduction

The congener-specific analysis of most classes of organohalogenated compounds is a challenging task, because of (i) the closely similar characteristics of the congeners and isomers within a single class, (ii) mutual interferences by related classes of organohalogens, and (iii) in real-life analysis, interferences caused by matrix constituents. Therefore, analytical procedures usually have to include complicated and time-consuming multi-step sample pre-treatment, because even state-of-the-art (one-dimensional) gas chromatography (1D-GC), combined with selective mass spectrometric detection often cannot solve the problem. One way to improve the situation is to considerably increase the separation efficiency of the GC analysis by replacing 1D-GC by so-called comprehensive two-dimensional gas chromatography (GC × GC). In GC × GC, two independent separations are applied to an entire sample – within the run time of the first-dimension separation – which effects a much enhanced

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overall resolution [1,2]. Another aspect that makes GC × GC attractive is the ordered structure, which is observed in the 2D plane for structurally related compounds. Such ordering often allows the classification and preliminary identification of unknown peaks based on their position in the GC × GC chromatogram, and is an efficient tool for screening purposes. The best-known early example are the bands of, e.g. paraffins, naphthenes and mono- and di-aromatics in 2D chromatograms of petrochemical samples [3,4]. More recently, ordered structures have been reported for polychlorinated biphenyls (PCBs) [5,6], polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) [5,7] and toxaphene [8]. On-going work in the field of polychlorinated alkanes (PCAs) [9,10] also appears to be successful. However, despite the wide-ranging interest in the use of GC × GC for organohalogen analysis [5–13], only limited attention has been devoted to the separation of the various compound classes of interest from each other. In the present paper, this interesting problem will be studied for the five classes of organohalogens mentioned above, and also for polybrominated and polychlorinated diphenyl ethers (PBDEs and PCDEs, respectively), polychlorinated naphthalenes (PCNs), polychlorinated dibenzothiophenes (PCDTs), polychlorinated terphenyls (PCTs), organochlorine pesticides (OCPs) and polybrominated biphenyls (PBBs). For each class of interest, a representative set of individual congeners-plus-isomers and/or technical mixtures will be studied. While the main aim is the group-type separation, some attention will also be devoted to within-class separations, especially for those groups which were not addressed in much detail before (PCNs, OCPs, PBBs and PCTs). The applicability of the approach will be demonstrated for a sediment extract (PCDD/Fs) and a dust extract (PBDEs and PCAs).

2. Experimental

2.1. Samples and chemicals

A standard mixture of each compound class was prepared either from individual congeners or from technical mixtures. The list of the compound classes and their detailed composition is given in Table 1. The congener concentrations varied between 1 and 100 ng/ml. Each solution was spiked with CB 40 (Promochem, Wesel, Germany) as internal standard to a final concentration of 50 ng/ml in order to check the retention-time stability.

The sediment sample was prepared by the Institut Químic de Sarrià (Barcelona, Spain) according to a method validated for PCDD/F determination by GC–HRMS. A brief summary is as follows: 8 g of sediment of marine origin (Western Scheldt) collected in the Netherlands were Soxhlet-extracted with toluene during 12 h. The extract was purified on a multilayer silica column (containing from top to bottom layers of anhydrous sodium sulphate, sulphuric acid–silica, activated silica, sodium hydroxide–silica, activated silica, silver nitrate–silica, and glass wool). The purified extract was transferred with *n*-hexane to a SPE carbon tube (Supelclean ENVI-Carb, 3 ml, 0.25 g, Supelco, Bellefonte, PA, USA). The first fraction, which contained the PCBs, was eluted with *n*-hexane and *n*-hexane–toluene (72:25, v/v) and the second fraction, which contained the PCDD/Fs, in the back-flush mode with toluene. The PCDD/F fraction was purified on a Florisil column (Florisil PR, 60/100 mesh; Supelco) and finally on a column containing layers of anhydrous sodium sulphate, activated silica, sulphuric acid–silica and glass wool. The sample was finally concentrated to 25 μl.

The dust sample was prepared according to a method validated for PCA and PBDE determination by GC–ECNI-MS. A brief summary is as follows: 2 g of dust of indoor origin collected in a Spanish (Madrid) household were extracted with Soxhlet for 12 h with 160 ml *n*-hexane–acetone (3:1, v/v) at 70 °C. After the addition of CB 112 and [^{13}C]-BDE 209 as internal standards, the extract was concentrated on a rotary evaporator, and demineralized water (adjusted to pH 2) was added and the organic layer collected. The aqueous phase was extracted two more times with isooctane. The organic extracts were combined and concentrated in 2 ml of dichloromethane. The extract was cleaned by gel permeation chromatography over two Polymer Labs. (Church Stretton, UK) gel (polystyrene–divinylbenzene) columns (300 mm × 25 mm; pore size, 10 μm) connected in series, using dichloromethane at 10 ml/min. The collected fraction (18–23 min) was concentrated under nitrogen, dissolved in isooctane and further purified by shaking with conc. sulphuric acid. Finally, the pentane–isooctane mixture was concentrated under nitrogen to 2 ml (isooctane) and purified on a silica column (deactivated with 2% water) with 11 ml isooctane and, next, 10 ml diethylether–isooctane (15:85, v/v). The latter fraction contained the PBDEs and PCAs and was concentrated to 1 ml (isooctane).

2.2. GC × GC–μECD

The GC × GC system was built from an HP6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph equipped with a loop-type carbon dioxide jet modulator (KT2002 CO_2 system; Zoex, Lincoln, NE, USA). The principles and operation of the KT2002 modulator are described in [16]. The hot air pulse duration was 200 ms, the hot jet temperature was 400 °C, and the modulation period varied between 8 and 9 s, depending on the column combination used (see Table 2 below). At the start of each run, the CO_2 flow was adjusted by using a needle valve to keep the cold-jet temperature at 0–10 °C, at an initial oven temperature of 90 °C. Helium gas (Hoek Loos, Schiedam, The Netherlands) with a purity of 99.999% was used as carrier gas at a constant flow of 1.2 ml/min. A micro-ECD (Agilent) was operated at 280 °C, with 99.999% pure nitrogen (Hoek Loos) as make-up gas at a flow-rate of 150 ml/min. The data acquisition rate was 50 Hz. One microliter samples were

Table 1
List of compound classes

Compound class	Composition	Manufacturer
PBDEs	126 congeners, see [14]	AccuStandard (New Haven, CT, USA)
PCDEs	17,28,33,74,66,77,99,118,126,105,156,128,170,194,209	CIL (Andover, MA, USA)
PBBs	15,52,49,101,153,169	Wellington (Guelph, Canada)
PCBs	91 congeners, see [5]	Promochem (Wesel, Germany)
PCNs	Technical mix Halowax 1014	Koppers Chemical (Pittsburgh, PA, USA)
PCDTs	Technical mixture; for composition see [15]	Prof. dr. J.T. Andersson, Münster, Germany
PCDDs	Seven 2,3,7,8-substituted congeners, see [7]	Wellington (Guelph, Canada)
PCDFs	Ten 2,3,7,8-substituted congeners, see [7]	Wellington (Guelph, Canada)
OCPs	28 compounds; see Fig. 6	Promochem (Wesel, Germany)
Toxaphene	23 congeners, see [8]	Dr. Ehrenstorfer (Augsburg, Germany)
Toxaphene	Technical mix Toxaphene	Polyscience (Warrington, PA, USA)
PCTs	Technical mix Aroclors 5442 + 5460 (1:1)	Promochem (Wesel, Germany)
PCAs	Technical mix PCA-60	Dover Chemical (Dover, OH, USA)

injected manually into a split/splitless inlet port operated in the splitless mode at 280 °C with the split opening 2 min after injection. A 30 m × 0.25 mm × 0.25 μm DB-1 (100% methylpolysiloxane) and a 30 m × 0.25 mm × 0.25 μm DB-XLB (proprietary) fused-silica column were used as first-dimension columns. The six fused-silica columns used in the second dimension are listed in Table 2. The columns were coupled to each other via a 1.5 m × 0.1 mm I.D. uncoated fused-silica deactivated column (BGB Analytik, Aldiswil, Switzerland), which served as the modulator loop. Mini press-fits (Techrom, Purmerend, The Netherlands) were used for the connections. The temperature programme was essentially the same for all column combinations; only the final temperature and the final hold time varied depending on the temperature limit of the second column (Table 2).

HP Chemstation software (Agilent) was used to control the GC instruments and to acquire data. Raw data files were imported into HyperChrom software (ThermoElectron, Milan, Italy) used for GC × GC data processing, evaluation and visualization. The first- and second-dimension retention times of the peaks were subsequently imported into Microsoft Excel (Microsoft, Redmond, WA, USA) for apex visualization. Colour contour plots were produced by Transform software (Fortner Research, Sterling, VA, USA).

2.3. GC × GC–TOF-MS

The GC × GC–TOF-MS system was built from a TRACE 2D (ThermoElectron, Milan, Italy) gas chromatograph coupled to a TEMPUS time-of-flight mass spectrometer (ThermoElectron, Austin, TX, USA). A 30 m × 0.25 mm × 0.25 μm DB-1 (100% methylpolysiloxane) fused-silica column was used as first-dimension column. The HT-8 column (for specification see Table 2) with dimensions of 1 m × 0.1 mm × 0.1 μm was used as second-dimension column. One end of the second-dimension column was coupled directly to the first-dimension column and the other end to the 30 cm × 0.1 mm retention gap mounted in the GC–MS interface. Mini press-fits (Techrom) were used for the connections. Modulation was performed at the beginning of the second column with a modulation period of 8 s. Helium gas (Hoek Loos) with a purity of 99.999% was used as carrier gas at a constant flow of 1.2 ml/min. One microliter samples were injected manually into a PTV inlet port operated in constant-temperature splitless mode at 280 °C with the split opening 2 min after injection. The mass spectrometer was tuned and calibrated in the electron ionisation (EI) and electron-capture negative ionisation (ECNI) mode using heptacosafluorotributylamine (Fluka, Buchs, Switzerland) as the reference gas according

Table 2
Second-dimension columns and experimental conditions used in GC × GC–μECD

Second-dimension column			Temperature programme[b]		Modulation period (s)
Commercial code[a]	Stationary phase	Dimensions (m × mm × μm)	Final temperature (°C)	Final hold (min)	
LC-50	50% liquid crystalline-methylpolysiloxane	0.8 × 0.1, 0.1	285	40	9
007-65HT	65% phenyl-methylpolysiloxane	1.0 × 0.1,0.1	335	10	8
VF-23ms	Proprietary (high cyano containing polymer; with absolute cyano content 70–90%)	1.5 × 0.1, 0.1	290	40	8
007-210	50% trifluoropropyl-methylpolysiloxane	2.0 × 0.1, 0.1	290	40	8
HT-8	8% phenyl-methylpolysiloxane (carborane)	1.0 × 0.1,0.1	325	20	8
SupelcoWax-10	Polyethylene glycol	1.0 × 0.1, 0.1	280	40	8

[a] LC-50 (J&K Environmental, Sydney, Canada), 007-65 HT and 007-210 (Quadrex, New Haven, CT, USA), VF-23 ms (Varian, Middelburg, the Netherlands), HT-8 (SGE International, Ringwood, Australia) and SupelcoWax-10 (Supelco, Bellefonte, PA, USA).
[b] 90 °C (2 min), then at 20 °C/min to 170 °C, then at 2 °C/min to final temperature (final hold).

to the recommendations of the manufacturer. In the ECNI mode, methane (2.5 ml/min) was used as an ionisation gas. The source temperature was 200 °C in both modes. The mass range of 50–750 Da was acquired at a data acquisition rate of 40 Hz. The temperature of the GC–MS transfer line was 325 °C for the EI mode and 300 °C for the ECNI mode. Xcalibur software (ThermoElectron) was used to control the GC × GC–TOF-MS instrument and to acquire data. Raw data files were imported into HyperChrom software (ThermoElectron) used for GC × GC data processing, evaluation and visualization. Colour contour plots were produced by Transform software (Fortner Research, Sterling, VA, USA).

3. Results and discussion

Six column combinations (cf. Table 2) were tested for the analysis of the twelve classes of organochlorinated and organobrominated compounds selected for the present study. For the first-dimension separation, a DB-1 column, which contains a non-polar 100% methylpolysiloxane stationary phase, was invariably used. This phase was selected because it separates exclusively on the basis of volatility, which is a generally recommended approach for the first dimension to build a truly orthogonal system that can deliver chemically meaningful structured chromatograms [1]. Six stationary phases were initially evaluated for the second dimension. They were selected, because of (i) their commercial availability with dimensions as are typically required for GC × GC, with an internal diameter of 0.1 mm and a film thickness of 0.1 μm, and (ii) their widely different retention mechanism compared with that of the 100% methylpolysiloxane first-dimension phase. Preliminary experiments carried out to select a proper temperature programme showed that the polyethylene glycol phase, SupelcoWax-10, caused the decomposition of some of the test compounds, i.e. the higher chlorinated PCDFs and the higher brominated PBDEs. Therefore, this phase was not included in any further work.

The preliminary tests also showed the need to use an internal standard to check the retention-time stability from one run to the next, because a small leak was sometimes found to occur in the press-fit connections after a few runs which may affect the retention times. In such a case, the overlays of the GC × GC chromatograms, which are discussed in the next sections for the five selected column combinations, would give erroneous information about the separation and/or co-elution of closely contiguous compounds. Each standard solution was, therefore, spiked with CB 40 and its retention time was checked for all overlays. Under these conditions, the variation of the first-dimension retention times for each column combination, calculated as the RSD for 10 consecutive injections, was always less than 0.5% and the variation of the second-dimension retention times less than 1.5%.

3.1. DB-1 × 007-210

The overlaid GC × GC chromatograms for the DB-1 × 007-210 column combination which are displayed in Fig. 1, show that all aromatic compounds show up in a very narrow band with a maximum width of 0.5 s in the central part of the chromatogram, despite the use of a 2-m instead of 1-m long second-dimension column. This indicates that the 50% trifluoropropyl-methylpolysiloxane stationary phase has little or no selectivity for these compounds. This is rather surprising, because it is well known that the trifluoropropyl groups act as strong electron acceptors and provide an increased retention for oxygenated compounds in the order ether < hydroxy < ester < keto. Therefore, increased retention of the PBDEs and PCDEs was expected. On the other hand, some selectivity was observed for the non-aromatic OCPs, PCAs and toxaphene. They are retained more strongly than the aromatic compounds and a within-group separation can also be observed. For the OCPs this can be seen in Fig. 1A and for the PCAs in Fig. 1B, which simultaneously illustrates the complexity and – certainly in 1D-GC – seriously interfering nature of the PCAs; the latter aspect will be discussed in more detail in subsequent sections. Fig. 1C clearly demonstrates how the general picture is further complicated when the toxaphene mixture is added to the list. The distinct ordered structure of technical toxaphene is similar to that earlier reported by us for a DB-1 × HT-8 column set [8]. The ordering is based on the number of chlorine substituents of the individual constituents, which are mainly bornanes and camphenes. In addition, a cluster of unknown compounds was found for the first time, which is separated from the bulk of the toxaphene constituents, as is indicated by a white circle in Fig. 1C, and will further be discussed in Section 3.2. Finally, it is worthwhile to note that the sudden break in the ordered structures of the PBDEs and PCTs at about 65 min does not reflect a change in physicochemical properties of the compounds involved, but indicates where the temperature gradient ends and the final isothermal run begins. This also causes the wrap-around of the higher boiling PCTs, which is visible from about 90 min in Fig. 1B.

The above information clearly shows that the DB-1 × 007-210 column combination has little or no practical use for the analysis of mixtures of organohalogenated compounds. However, even so does the combined experimental evidence indicate which aspects will be especially relevant when studying the other column combinations.

3.2. DB-1 × HT-8

Fig. 2A shows the overlaid GC × GC chromatograms obtained with the DB-1 × HT-8 combination. As with the previous column set, all classes of aromatic compounds show up as a band. However, in this case it is distinctly wider, i.e. 3 s, and has a more or less diagonal orientation. The increased bandwidth indicates that the HT-8 column creates more additional selectivity. The diagonal orientation of the general

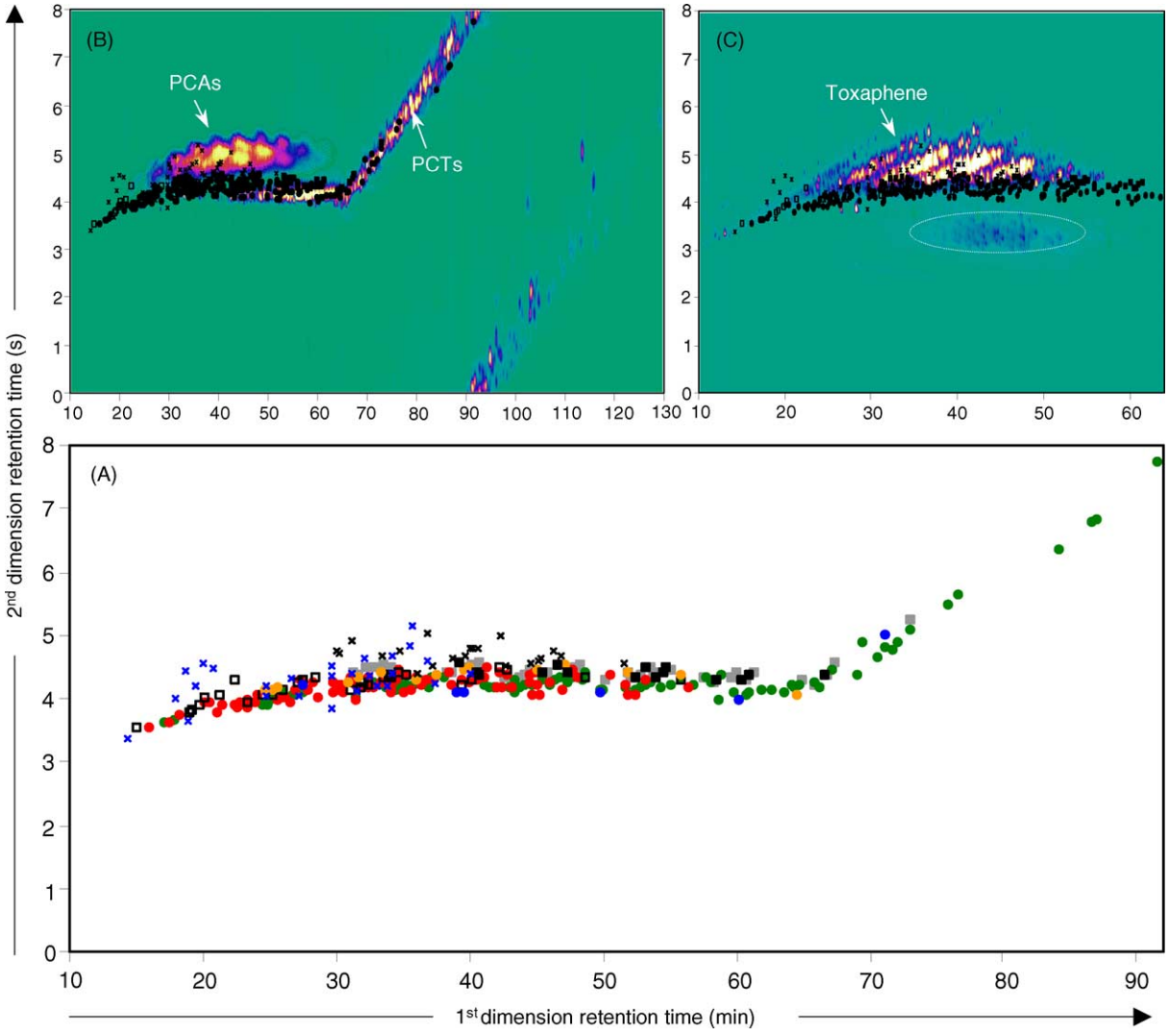


Fig. 1. Overlaid GC × GC–μECD chromatograms on DB-1 × 007-210 column combination of: (A) ● PCBs, ● PBBs, ● PCDEs, ● PBDEs, ■ PCDTs, □ PCNs, ■ PCDD/Fs, ✖ OCPs, ✖ individual toxaphene standards; (B) PCTs (Aroclors 5442 + 5460) and PCAs (PCA-60) as colour contour plot, and other classes as black dots; (C) toxaphene technical mixture as colour contour plot and other classes (except PCAs and PCTs) as black dots. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 290 °C (40 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

elution profile in the 2D plane indicates that, as with the first-dimension separation, analyte volatility plays a dominant role in the second-dimension separation. Finally, Fig. 2B and D vividly demonstrates the strongly disturbing role of the PCAs and toxaphene, respectively, for essential all other classes of organohalogens.

Earlier studies already showed that the DB-1 × HT-8 column set provides clearly ordered structures for both PCBs and toxaphene (Fig. 2D) based on the number of chlorine substituents of the individual congeners and isomers [5,6,8]. Fig. 2C shows that ordering also occurs with the PCTs. There is a distinct separation of the constituents of Aroclor 5442 from those of Aroclor 5460 and band structures are visible in both cases. The structure is more apparent for Aroclor 5460 than for Aroclor 5442 because in order to obtain a structured chromatogram the second-dimension separation has to be performed at a rather low temperature compared to boiling point of analytes and under the present conditions this is achieved better for Aroclor 5460. To obtain a similar result for Aroclor 5442, one should use a slower temperature programme, which would result in a lower temperature of the second-dimension separation. ToF MS detection was used to confirm that the same structuring principle prevails as for the PCBs and toxaphene. However, as is demonstrated in Fig. 3A and B, the bands with the same number of chlorine substituents are relatively broad and, consequently, overlap. This is due to the presence of three PCT sub-classes, with *ortho*-, *meta*- and *para*-terphenyl skeletons, which have slightly different retention characteristics. The congener distribution within each homologue band could not be determined, since the *ortho*, *meta* and *para* congeners have very similar mass spectra and no individual standards were available to us. Some sub-structuring of homologue bands can be discerned in Fig. 3B. Based on published GC data for 14 indi-

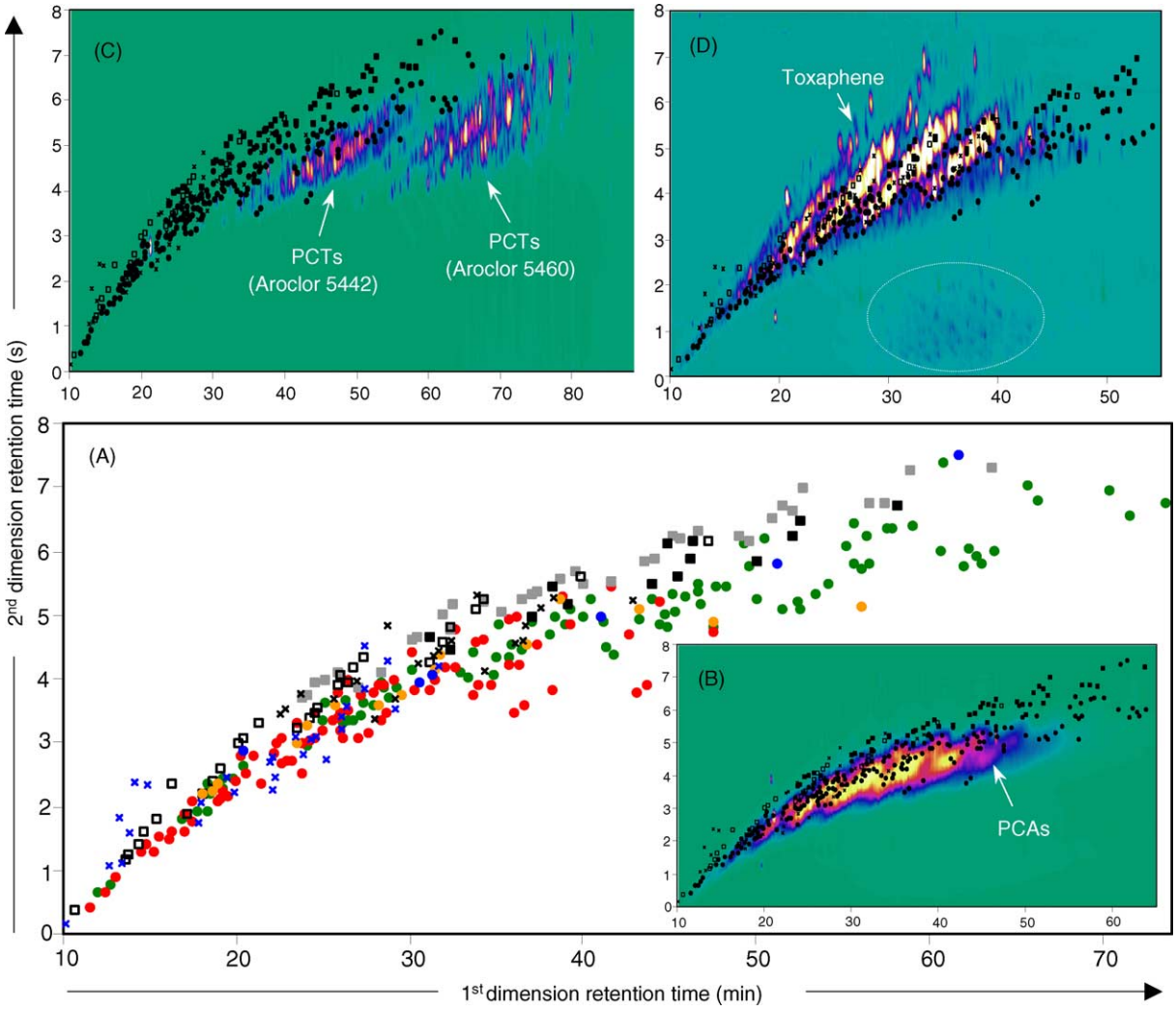


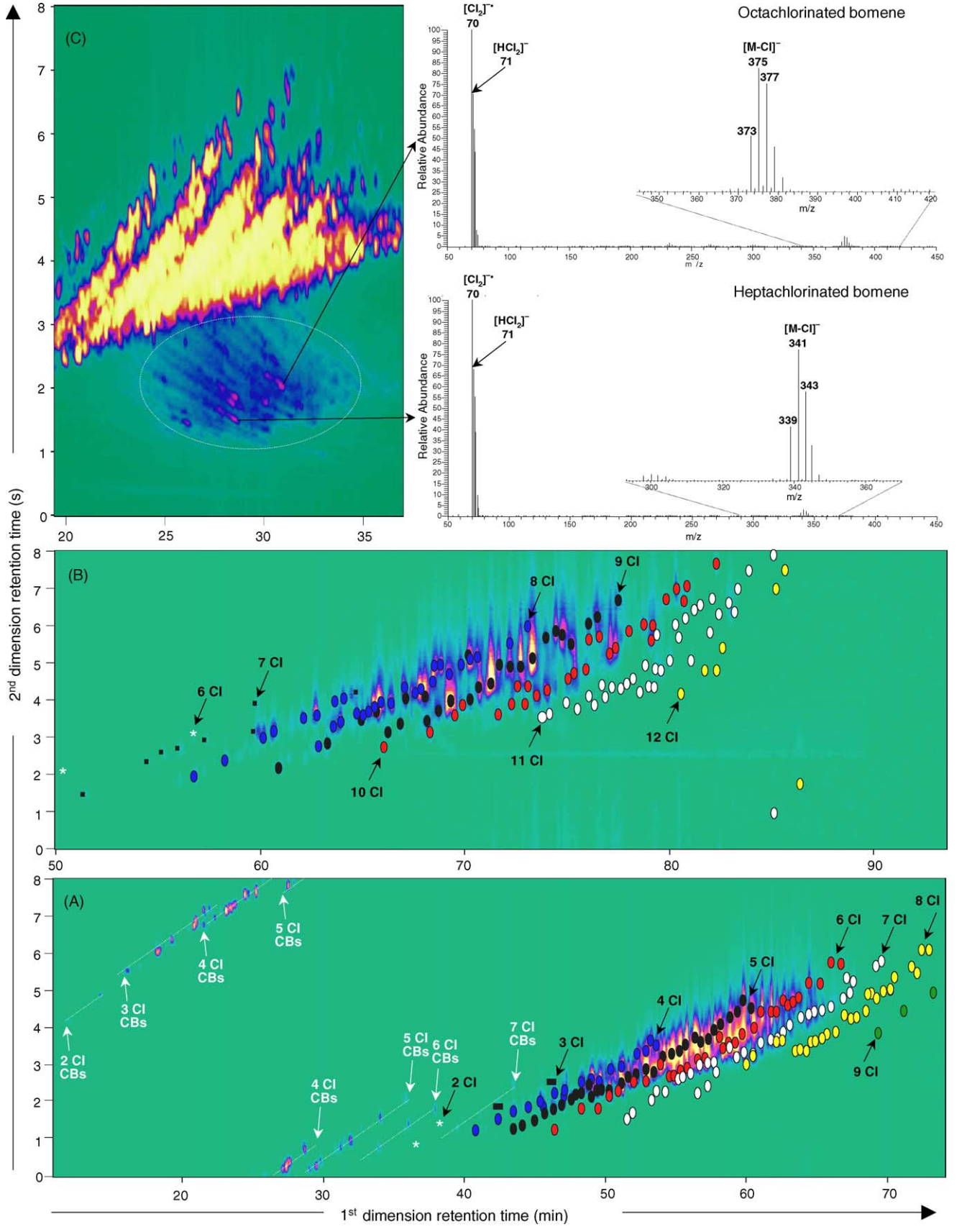
Fig. 2. Overlaid GC × GC–μECD chromatograms on DB-1 × HT-8 column combination of: (A) ● PCBs, ● PBBs, ● PCDEs, ● PBDEs, ■ PCDTs, □ PCNs, ■ PCDD/Fs, ✖ OCPs, ✖ individual toxaphene standards; (B) PCAs (PCA-60) as colour contour plot and other classes as black dots; (C) PCTs (Aroclors 5442 + 5460) as colour contour plot, and other classes (except PCAs) as black dots; (D) toxaphene technical mixture as colour contour plot and other classes (except PCAs and PCTs) as black dots. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 325 °C (20 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

vidual congeners [17], the *ortho*-PCTs can be expected to be the sub-structure appearing in the lower left-hand part of each homologue band, with the *meta*-PCT congeners showing up in the centre part of the band and the *para*-PCT congeners appearing in the upper right-hand part. It will be clear that further work in this area is indicated.

ToF MS-based detection of the composition of the two Aroclor mixtures confirms, and extends, previously published 1D-GC-based information regarding Aroclor 5460 [18]. Fig. 3B shows that the octa-, nona-, and deca-substituted congeners are the dominant constituents, with hexa-, hepta-, undeca- and dodeca-PCTs as minor components. In Aroclor 5442, tetra-, penta-, hexa- and hepta-substituted congeners were found to be the major, and di-, tri-, octa- and nona-substituted congeners the minor constituents. In addition, in the latter mixture several PCBs were found to be present. They are visible in the ordered structure in the left-hand part of the chromatogram of Fig. 3A and will be further discussed in Section 3.3.

The cluster of unknown compounds in technical toxaphene, which was mentioned in Section 3.1, was detected also with the present column combination (cf. circled area

Fig. 3. (A and B) Total-ion GC × GC–EI-ToF MS chromatograms on DB-1 × HT-8 column combination of (A) Aroclor 5442 and (B) Aroclor 5460 as contour plots with apices coded by colour according to the number of chlorine substituents. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 325 °C (10 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min. (C) Total-ion GC × GC–ECNI-TOF-MS chromatogram on DB-1 × HT-8 column combination of technical toxaphene with the mass spectra of two peaks as indicated. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 4 °C/min to 320 °C. Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.


(C)
(B)
(A)
Octachlorinated bomene
Heptachlorinated bomene
[Cl2]-•
70
[HCl2]-
71
[M-Cl]-
375
377
373
341
343
339
Relative Abundance
m/z
2nd dimension retention time (s)
1st dimension retention time (min)
6 Cl
7 Cl
8 Cl
9 Cl
10 Cl
11 Cl
12 Cl
2 Cl CBs
3 Cl CBs
4 Cl CBs
5 Cl CBs
6 Cl CBs
7 Cl CBs
2 Cl
3 Cl
4 Cl
5 Cl

in Figs. 2D and 3C). This group of compounds was not reported in our previous study [8], because the temperature programme then used was much slower. This caused much more spreading of the toxaphene congeners in the 2D plane: wrap-around occurred which led to co-elution with the unknown compounds. The nature of the unknown compounds was studied with MS detection. In order to achieve sufficient response of the unknown group and good-quality spectra, a concentrated sample of technical toxaphene (40 mg/ml) was analysed and the ECNI ionisation mode was used to avoid the extreme fragmentation typical of EI spectra. The total-ion GC × GC–ECNI-TOF-MS chromatogram is shown in Fig. 3C. It is obvious that the group has a 'hump shape' and individual peaks can hardly be distinguished. Moreover, the orientation of the bands differs markedly, i.e. by some 90°, from that of the main constituents, and the bands have increasing intensities with increasing elution time until their rather sudden termination. These GC × GC observations suggest that the group of unknowns contains first-dimension decomposition products. This is supported by published information on the thermal degradation of some chlorobornanes into chlorobornenes via HCl elimination during splitless injection [19]. The use of ECNI-MS detection allowed us to confirm the presence of bands of hexa- up to nona-chlorinated bornenes, probably formed by HCl elimination from hepta- up to deca-chlorinated bornanes, respectively. As an example, Fig. 3C shows the ECNI mass spectra for the two most intense peaks, which were a hepta- and an octa-chlorinated bornene.

Finally, comparison of Figs. 2A and 1A clearly shows the superiority of the DB-1 × HT-8 over the DB-1 × 007-210 combination: the 2D plane is used much more efficiently in the former case. This agrees with the information briefly referred to above that several successful studies on PCBs and toxaphene were carried out on the DB-1 × HT-8 column set. In all these instances – and also for the PCTs discussed above – the ordered structures are found to be based on the degree of halogen substitution. A disadvantage of the column combination is that the between-class separations are rather incomplete, specifically for the aromatics. This can easily create co-elution problems in real-life analyses.

3.3. DB-1 × LC-50

Relevant GC × GC separations obtained on the DB-1 × LC-50 column combination are shown in Fig. 4. The apex distribution of Fig. 4A convincingly demonstrates that a much larger part of the 2D plane is used than with the previous two column combinations—which is a good indication of its orthogonal performance. It is well known that liquid crystalline stationary phases separate on the basis of planarity [20]. Consequently, planar compounds such as the PCDD/Fs, PCDTs and PCNs, are retained much more strongly than the other classes of compounds and show up in the upper part of the chromatogram. In addition Fig. 4A shows that the liquid crystalline phase retains planar compounds with three-ring structures more than those with two-ring structures. This is evident from the stronger retention of PCDD/Fs and PCDTs compared to the PCNs—as a consequence, there is an excellent separation in the second dimension. As for within-group separations, LC-50 columns are known [11] for their effective separation of PCBs on the basis of the number of *ortho* substituents or, in other words, by distinguishing planar and non-planar PCBs. This is visualized in Fig. 4D with its widely divergent second-dimension retention times for the various CB congeners, and with the non-*ortho* congeners (see CBs 81, 77, 126 and 169) at the top, followed by mono- (e.g. CBs 123, 105, 167, 157 and 189), di- (e.g. CBs 52, 49, 101 and 153), tri- (e.g. CBs 151, 183, 195 and 206) and tetra-*ortho* (e.g. CBs 155, 201 and 207) CBs. Unfortunately, we had only six brominated analogues of the PCBs available; these PBBs are included in Fig. 4D. Not unexpectedly, the separation pattern of both groups is closely similar: the non-*ortho* congeners BB 15 and BB 169 are much stronger retained than the other BBs, which all have two *ortho* substituents, and the BB 49/52 pair is as closely together as is the CB 49/52 pair.

The PCDEs and PBDEs are another paired class of compounds. However, in this instance planar structures are not easily formed because the two free electron pairs of the oxygen atom linking the two rings do not allow rotation. Consequently, as Fig. 4E shows, there is much less congener separation within these classes than with the PCBs and PBBs. On the other hand, the close analogy of the GC × GC patterns of the brominated and chlorinated diphenyl ethers is readily seen for, e.g. the tri-substituted 17/28/33, the tetra-substituted 74/66/77, and the penta-substituted 99/105/118/126 pairs.

Fig. 4C shows the separation of the PCTs. The LC-50 column obviously is not really suitable for their analysis, because of its low maximum operating temperature. As a consequence, the Aroclor 5460 congeners elute under isothermal conditions which causes an enormous spread of the congeners starting at about 65 min, which next leads to wrap-around, as is visible from about 80 min. The LC-50 column is, nevertheless, a useful tool for the identification of a dioxin-like toxicity of the technical PCT mixtures, because all planar compounds are strongly retained by the liquid crystalline phase. One such contribution can originate from dioxin-like PCBs, because several PCBs were found to be present in Aroclor 5442 (cf. Section 3.2). By overlaying chromatograms of Aroclor 5442 with those of 12 dioxin-like PCBs for all four column combinations of interest, the non- and mono-*ortho* CBs 77, 118, 114, 105, 167, 156, 157 and 189 were indeed identified. Dioxin-like toxicity can also originate from PCTs, especially from *para*-PCTs with no chlorine substituents in the various *ortho* positions, which probably can have a planar conformation. Such congeners will be retained much stronger on the LC-50 column than the other PCTs. Fig. 4C shows that there are indeed several peaks present in the upper part of the chromatogram (indicated by white arrows); these may well be planar *para*-PCTs. It is interesting to add that a recent DR-CALUX receptor gene assay study showed Aroclor 5442 to

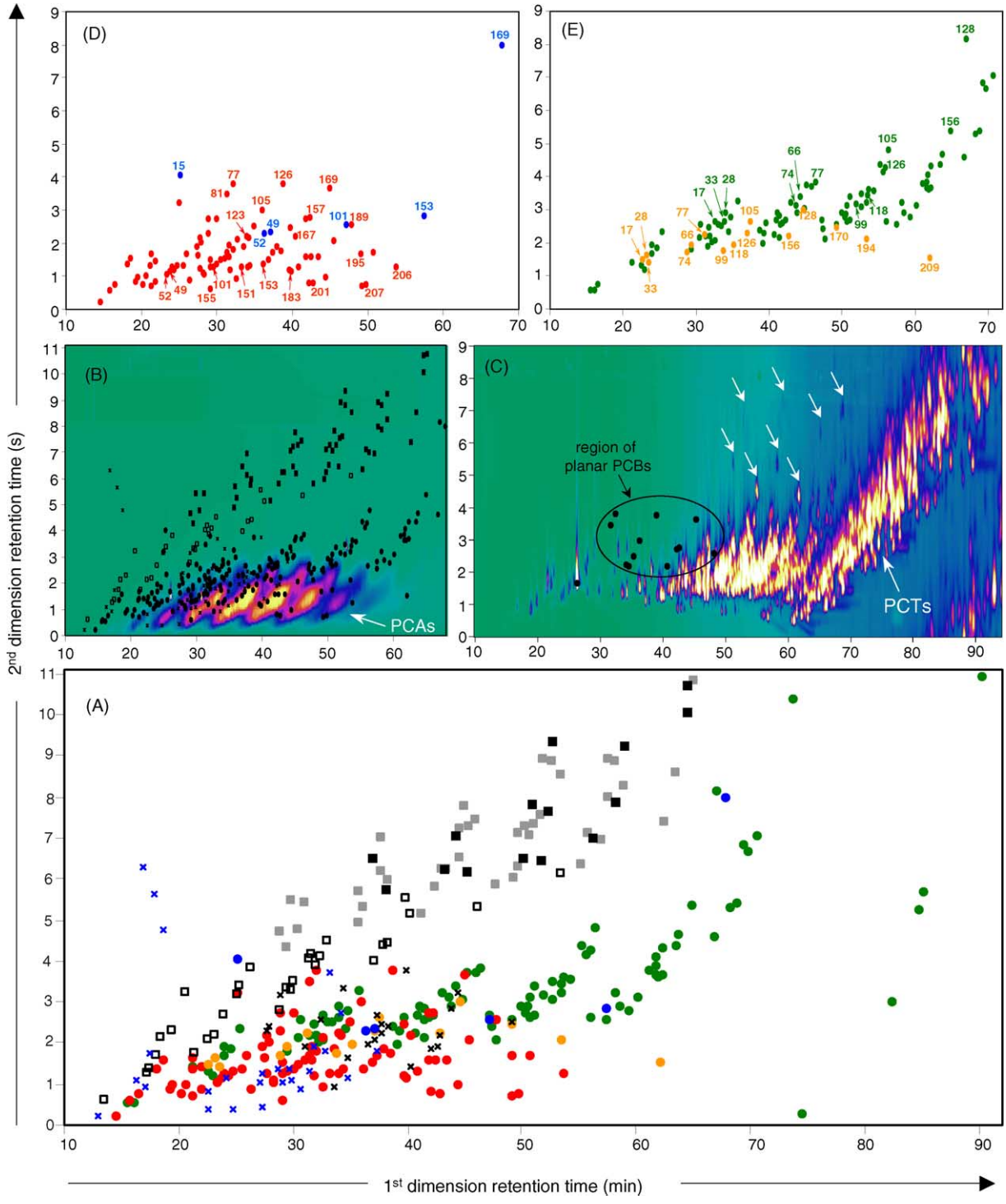


Fig. 4. Overlaid GC × GC–μECD chromatograms on DB-1 × LC-50 column combination of: (A) ● PCBs, ● PBBs, ● PCDEs, ● PBDEs, ■ PCDTs, □ PCNs, ■ PCDD/Fs, ✖ OCPs, ✖ individual toxaphene standards; (B) PCAs (PCA-60) as colour contour plot and other classes as black dots; (C) PCTs (Aroclors 5442+5460) as colour contour plot and visualized position of dioxin-like PCBs (black dots) and planar PCTs (white arrows); (D) ● PCBs and ● PBBs; (E) ● PBDEs and ● PCDEs. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 285 °C (40 min). Modulation period, 9 s; constant flow of helium carrier gas, 1.2 ml/min.

have a dioxin-like activity [21]. In that study, Aroclor 5442 was found to give a similar response as Halowax 1014 and a response even higher than those of the PCB mixtures, Aroclor 1242, 1254 and 1260. Obviously, further studies with individual standards of possibly planar PCTs are required to decide whether the dioxin-like toxicity of Aroclor 5442 is mainly caused by the dioxin-like PCBs or by the planar PCTs.

One final remark is that the DB-XLB × LC-50 column set was earlier selected for the separation and quantification of PCDD/Fs by GC × GC [7,12]. However, co-elution problems were encountered in a few instances. Fig. 4A convincingly demonstrates that the common interferences of (one-dimensional) GC–HRMS methods, the PCNs and PCDEs, are satisfactorily separated from the target analytes if GC × GC is used. However, if PCDTs are present in the samples, then ECD-based detection can easily yield too high results.

3.4. DB-1 × 007-65HT

Fig. 5 shows the overlaid chromatograms obtained with the DB-1 × 007-65HT column combination. On the 65% diphenyl-methylpolysiloxane stationary phase, the PBDEs are the strongest retained compounds in the second dimension and show up at the top of the chromatogram, while the PCAs clearly are the least retained class of organohalogens. Actually, the distribution of the various classes of compounds in the 2D plane indicates that the present column combination is highly promising for the determination of PCAs and PBDEs, especially because they are usually present in the same fraction after standard clean-up procedures [22,23]. In addition, the PCA fraction usually contains toxaphene congeners and/or some OCPs [24,25], since it is difficult to separate these during sample clean-up. Due to such co-elution, the determination of short-chain PCAs with ECD is not accurate. Fig. 5A shows that this problem is essentially solved when using the present column combination.

Fig. 5C shows the positions of the PCDD/Fs and PCDTs test sets in the GC × GC chromatogram. The stronger retention of the latter group in the second dimension effects a clear-cut separation. It is worthwhile to note that the DB-1 × 007-65HT column set was the only one delivering such a distinct separation. Admittedly, this conclusion is based on the behaviour of a limited number of PCDD/Fs. Should the present conclusion be confirmed for a larger set of PCDD/Fs, then the DB-1 × 007-65HT column combination may become a promising tool for the determination of PCDTs in real-life samples, because the two compound classes often end up in the same fraction after clean-up and fractionation, and, in 1D-GC, HRMS is then required to distinguish PCDDs from PCDTs. The retention of the Br-substituted compounds is somewhat stronger than of the corresponding Cl-containing compounds. This was also observed for the DB-1 × LC-50 column combination, but for the present column set the difference is more pronounced. It can be observed for PBBs versus PCBs (Fig. 5A) and PBDEs versus PCDEs (Fig. 5D).

Finally, Fig. 5B displays the overlay of the four technical mixtures—toxaphene, PCA-60 and a mixture of Aroclors 5442 and 5460. What shows up in the 2D plane can be interpreted in two rather different ways. One is to emphasize that the presence of these four mixtures in any real-life sample will virtually obscure all other classes of organohalogens included in our work, even in GC × GC analysis. On the other hand, it is also interesting to note that a striking separation of the three compound classes of interest – PCAs, PCTs and toxaphene constituents – is observed, inclusive of the cluster of degradation products of toxaphene congeners (^1t_R 35–45 min; ^2t_R 0–2 s) referred to above. In addition, clearly ordered structures are observed for toxaphene and PCAs. One more observation should be made here. The toxaphene structuring is based on the number of chlorine substituents in the molecule. Recently, the same separation principle was confirmed also for PCAs [9], but in that study only PCAs with a C10 chain were analysed. In the present paper, however, the PCA-60 mixture subjected to analysis contains congeners with C10–13 chain lengths. In other words, now both the number of substituents and the length of the carbon skeleton vary. Therefore, the bands in Fig. 5A and B contain congeners with different length of the skeleton and also with a different number of chlorine substituents. Further unravelling of the composition of these bands is beyond the scope of this paper and will be addressed in a subsequent study [10].

The DB-1 × 007-65HT combination was also found to provide a highly rewarding separation of the OCP test set (Fig. 6A) and the PCNs present in Halowax 1014 (Fig. 6B). In the latter case, ordering based on the number of substituents is very distinct. Actually, the selectivity is rather strong, which results in additional separation of, e.g. CNs 73 and 74. The OCPs were identified by injecting the individual standards, and the CN congeners by combining ToF MS information and retention data published for 1D-GC systems [26,27].

3.5. DB-1 × VF-23ms

The overlaid chromatograms of the last column combination tested, DB-1 × VF-23ms, are displayed in Fig. 7A. Careful examination of the figure shows that this combination, similarly to DB-1 × 007-210 and DB-1 × HT-8, does not yield much separation of one class of organohalogens from another. On the other hand, it is extremely powerful in within-class separation: compounds are very well spread in the second dimension. This is true for all classes of aromatics (Fig. 7A and D), and especially for non-aromatics such as PCAs, OCPs and toxaphene (Fig. 7A–C); actually, toxaphene and – even more so – the PCAs cover the entire chromatographic plane. Some congeners even show wrap-around, as is visible at the bottom of the chromatograms shown in Fig. 7B and C. Compared with the other column combinations, DB-1 × VF-23ms is certainly the most powerful in term of congener separation and is, therefore, a proper choice if unravelling of the composition of the complex mixtures of non-aromatic compounds, i.e. visualizing the maximum number of individual congeners, is the goal. Then number of toxaphene congeners resolved with this column combination is expected to be higher than the 1010 reported in our previous study with the DB-1 × HT-8 column combination. A direct comparison, however, cannot be made here, because rather different chromatographic conditions were used (temperature programmes, modulators used).

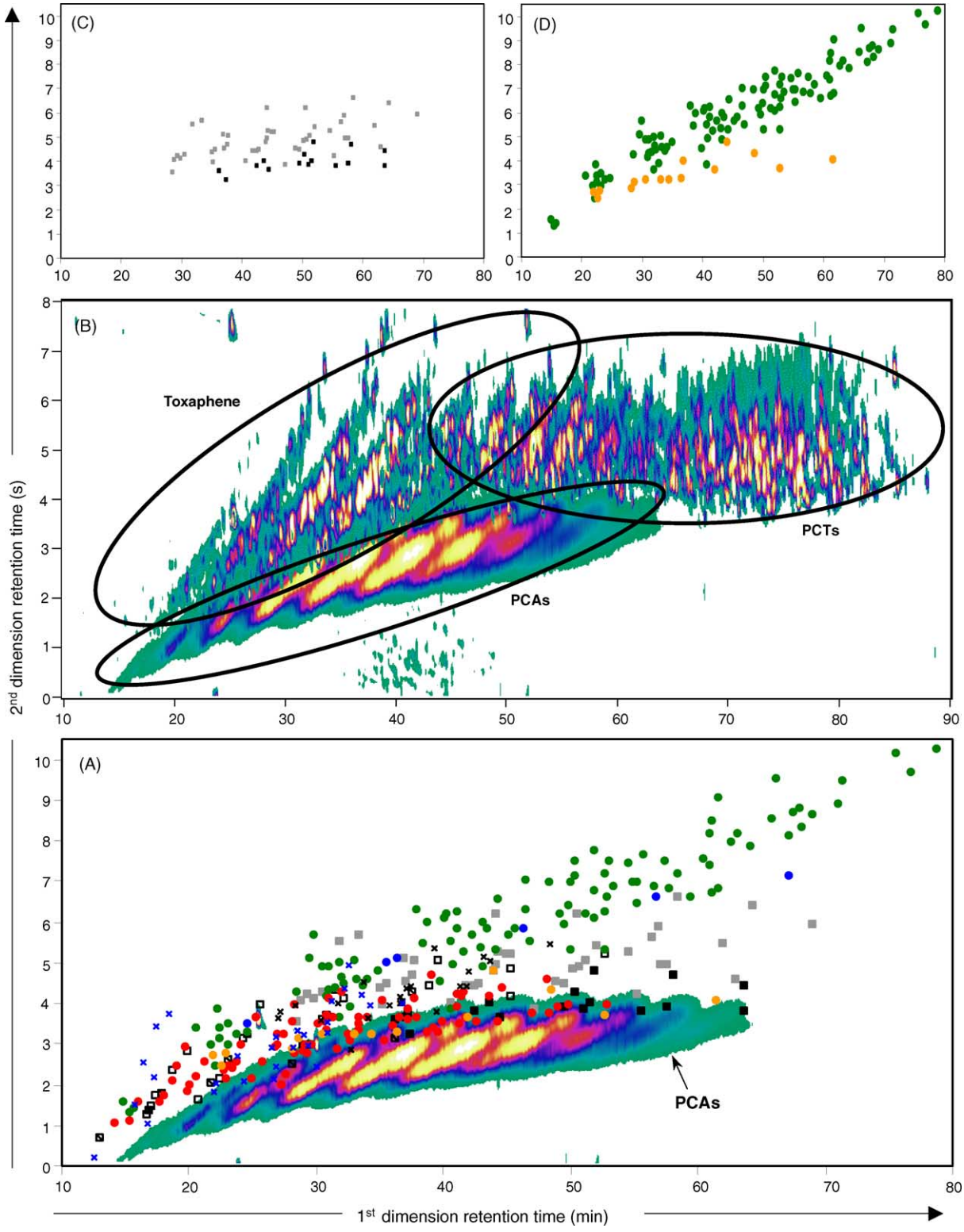


Fig. 5. Overlaid GC × GC–μECD chromatograms on DB-1 × 007-65HT column combination of: (A) ● PCBs, ● PBBs, ● PCDEs, ● PBDEs, ■ PCDTs, □ PCNs, ■ PCDD/Fs, ✕ OCPs, ✕ individual toxaphene standards and PCAs (PCA-60); (B) PCAs (PCA-60), PCTs (Aroclors 5442 + 5460) and toxaphene technical mixture; (C) ■ PCDTs and ■ PCDD/Fs; (D) ● PCDEs and ● PBDEs. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 335 °C (10 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

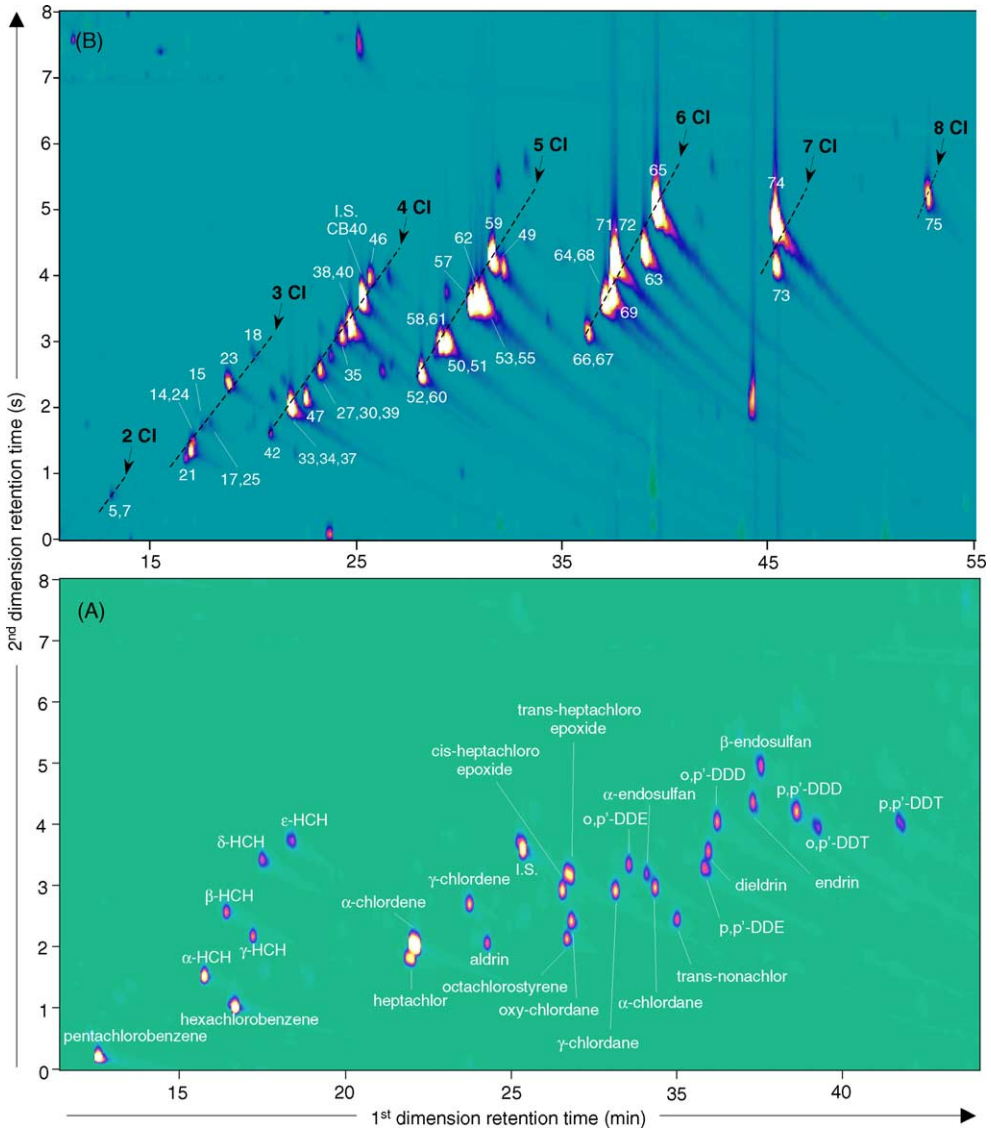


Fig. 6. GC × GC–μECD chromatograms of (A) OCPs and (B) PCNs in Halowax 1014 on DB-1 × 007-65HT column combination. For IUPAC numbering of CN congeners, see [28]. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 335 °C (10 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

Finally, with the OCPs an excellent distribution in the 2D plane was observed. However, in this instance one should preferably use the DB-1 × 007-65HT column set because one pair of analytes, *cis*- and *trans*-heptachlor-epoxide, which was clearly separated on the latter combination (cf. Fig. 6A), co-eluted on the present set (data not shown).

3.6. Applications

One interesting application is shown in Fig. 8A. It shows the GC × GC–μECD chromatogram of the PCDD/F fraction of a sediment sample obtained after the extract had been fractionated on a SPE carbon tube (Supelclean ENVI-Carb) into two fractions—one containing the mono- and non-*ortho* PCBs and the other, the PCDD/Fs. The chromatogram was obtained as part of the quantification evaluation of GC × GC–μECD for dioxin analysis [29]. Since the DB-XLB × LC-50 column combination is known to have excellent selectivity for the analytes of interest [7], it was used in this study. From the point of view of the compound distribution in the GC × GC plane, it is closely similar to the DB-1 × LC-50 combination—one merely has to expect a slightly different first-dimension separation.

The chromatogram shows the complexity of the sediment extract despite the extensive clean-up used (cf. Section 2.1). Next to the priority analytes, indicated by acronyms in black (for the exception, 1,2,3,4,6,7,9-HpCDD, see below), which all show up in the upper part of the chromatogram, many other peaks are present in the GC × GC plane. Without any doubt, the eye-catching region is the lower part of the chromatogram,

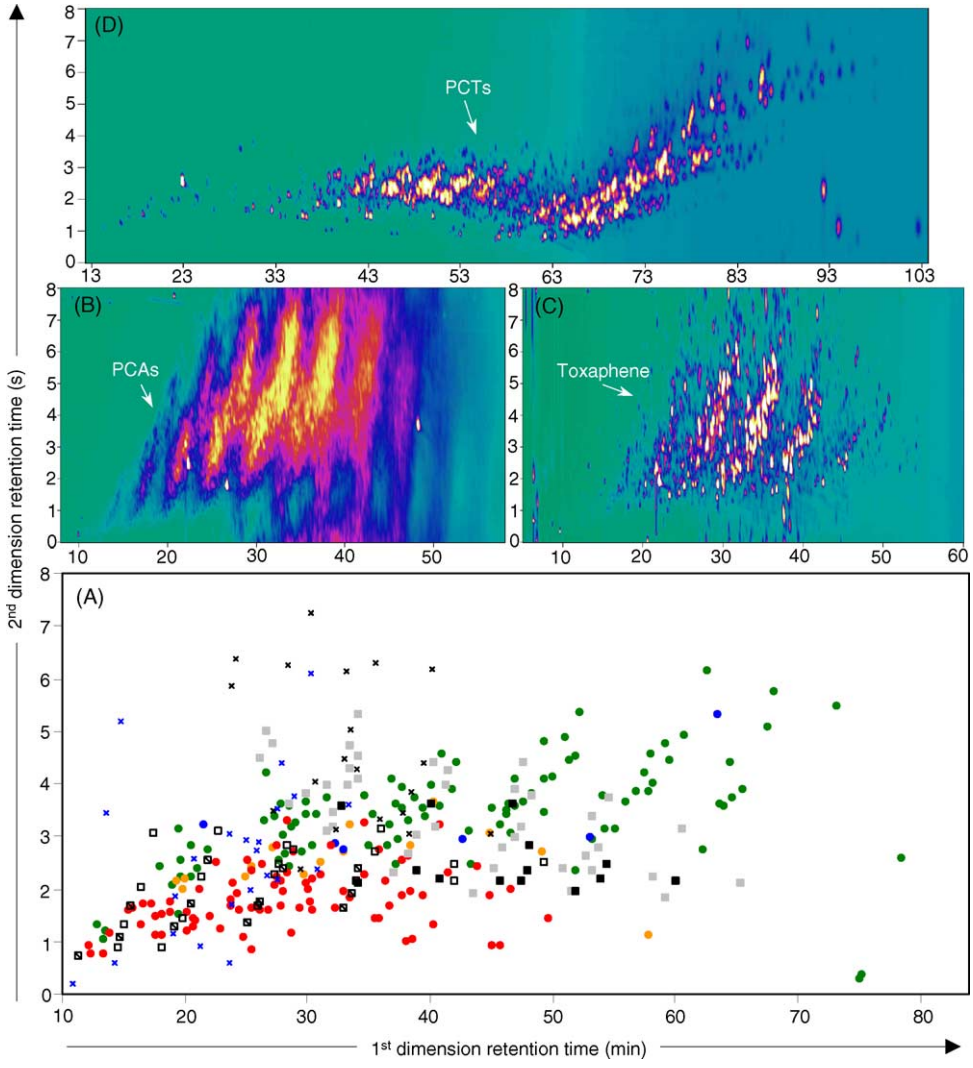


Fig. 7. Overlaid GC × GC–μECD chromatograms on DB-1 × VF-23ms column combination of: (A) ● PCBs, ● PBBs, ● PCDEs, ● PBDEs, ■ PCDTs, □ PCNs, ■ PCDD/Fs, ✖ OCPs, ✖ individual toxaphene standards; (B) PCAs (PCA-60); (C) toxaphene technical mixture; (D) PCTs (Aroclors 5442 + 5460). Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 290 °C (40 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

where a highly intense (white-yellow) band is present along the whole length of the first-dimension run. When zoom-out visualization is used, it readily becomes clear that the band is composed of several sub-structures (Fig. 8B). And, when the result is compared with the DB-1 × LC-50 chromatogram of Fig. 4B, it is obvious that this band mainly contains PCAs. The sudden drop of the position of the PCA band, i.e. of its second-dimension retention time range at about 52 min is due to an acceleration of the temperature programme, used to speed up the elution of the hepta- and octa-chlorinated dioxins and furans. The presence of the PCAs in the 'planar' PCDD/F fraction is rather surprising. One explanation is that the compounds originate from the clean-up process, for instance from the carbon-containing plastic tubes. Another explanation is that they are present in the sediment in very high concentrations. This may cause overloading of the carbon column and, consequently, a partial co-elution with the PCDD/Fs. Apparently, further study is required but, whatever the outcome, this will not detract from the aim of the present work—that is, to illustrate the group-type separation of the various classes of organohalogens in the 2D plane and its practical usefulness.

Another interesting observation is that there are, in Fig. 8A, many other peaks in the close vicinity of the target compounds. One of these is octachloronaphthalene (OCN), which was added as a syringe internal standard. By careful evaluation of the GC × GC chromatogram and injecting the technical PCN mixture, Halowax 1014, the presence of two heptachloronaphthalenes, CNs 73 and 74, was confirmed. Somewhat unexpected, further study revealed that they are contaminants present in the OCN standard. Another rather intense peak could be attributed to 1,2,3,4,6,7,9-HpCDD, a non-2,3,7,8-substituted congener which was also added as an internal standard. Since it shows up right in the middle of the

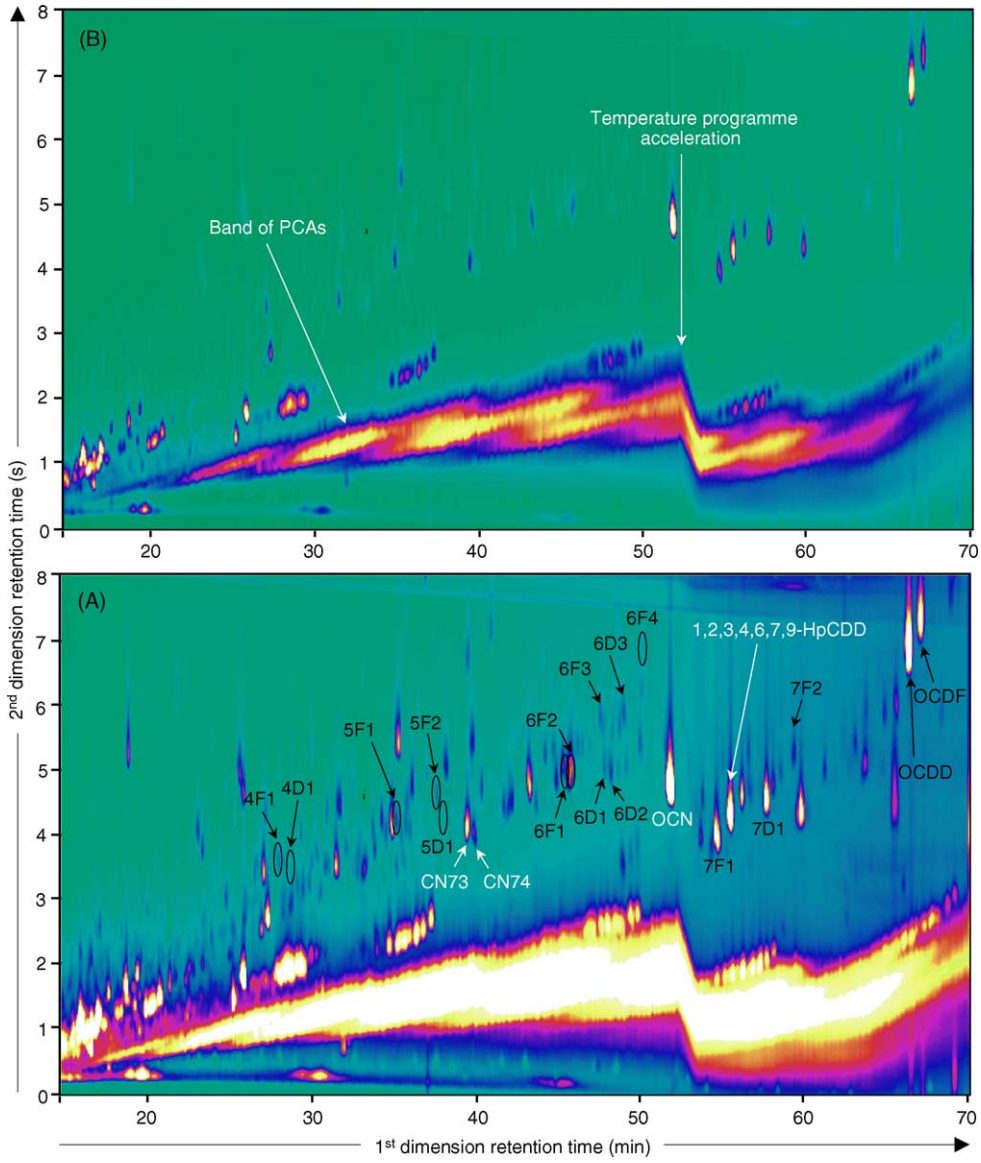


Fig. 8. GC × GC–μECD chromatogram of the PCDD/F fraction of a sediment extract on DB-XLB × LC-50 column combination, and visualized at two different colour intensity scales (A and B). Temperature programme: 90 °C (2 min), at 30 °C/min to 220 °C, then at 1 °C/min to 266 °C, then at 10 °C/min to 277 °C, and finally at 1 °C/min to 287 °C (10 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

2,3,7,8-substituted congeners, the other peaks present in this region probably also are non-2,3,7,8-substituted PCDD/Fs. The same may well be true for the unknowns visible in the region of the hexa- and penta-substituted PCDD/Fs. Another possibility is that some of these peaks are PCDTs, which also have very similar retention characteristics, as was shown in Section 3.3. In conclusion, the present application shows the potential of GC × GC which, if properly tuned, can accommodate a very high number of compounds in the 2D plane, and can separate target analytes from co-extractants even if the latter are present in much higher concentration. Moreover, once the positions of a variety of analyte classes in that plane are known, rapid preliminary identification is possible even with non-selective, but highly sensitive, μECD detection.

Another application, with the DB-1 × 007-65HT column combination, is shown in Fig. 9. A dust extract was analysed to detect both PCAs and PBDEs; after clean-up, these are present in the same fraction. As with the previous application, the band of PCAs occupies the lower part of the chromatogram. However, the present column combination is more selective for PCAs and well structured PCA bands show up in the 2D plane. Comparison of these bands, especially when zoom-out visualization is used (insert of Fig. 9), with those of the PCA-60 standard in Fig. 5A, reveals a clearly different pattern. The explanation is that in the real-life sample also medium- and long-chain PCAs are present, while PCA-60 is comprised of only short-chain PCAs. The strong retention of the PBDE congeners creates a fully satisfactory

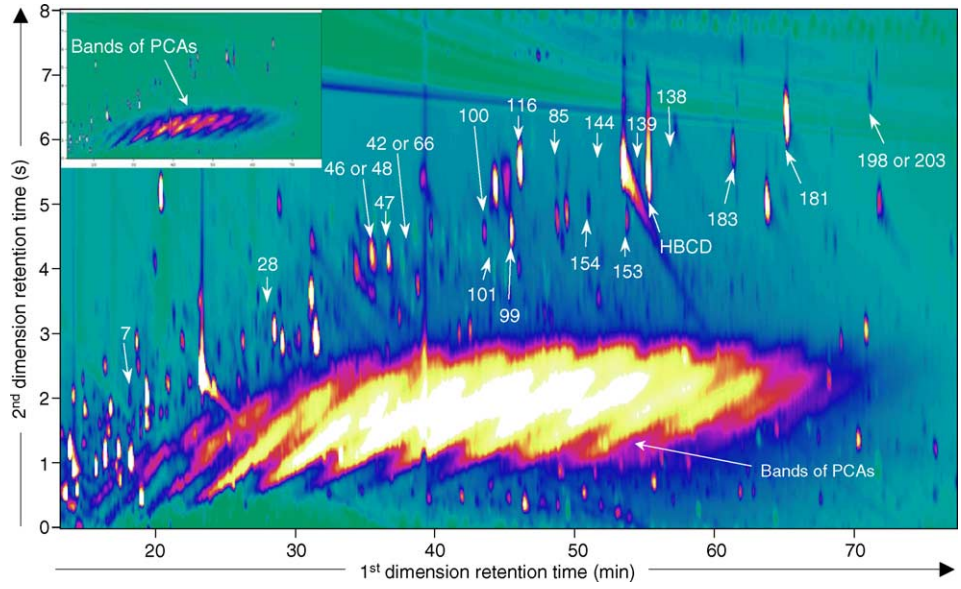


Fig. 9. GC × GC–μECD chromatogram of a dust extract on DB-1 × 007-65HT column combination for PCA and PBDE determination. Insert shows visualization with zoom-out *z*-scale. Temperature programme: 90 °C (2 min), at 20 °C/min to 170 °C, then at 2 °C/min to 335 °C (10 min). Modulation period, 8 s; constant flow of helium carrier gas, 1.2 ml/min.

separation from the PCAs. By using the standard mixture of 124 PBDE congeners, 18 congeners could be identified in the sample and are indicated in Fig. 9. This figure further shows that the area between PCAs and PBDEs contains many other peaks. As Fig. 5A shows, it is the area of other organohalogenated compounds. In conclusion, the present exercise demonstrates the potential of this column combination for PCA and PBDE determination.

4. Conclusions

The present paper demonstrates that both the between- and within-group GC × GC separations of the twelve classes of organohalogens included in the study, are strongly dependent on the column combination used. For rather obvious reasons, an essentially non-polar stationary phase is preferred for the first-dimension separation. In other words, it is the selection of the second-dimension phase that has to be highlighted. Our experimental findings show that each of the five phases studied has unique characteristics and, consequently, can or cannot be used for specific purposes. Some typical examples are as follows.

(1) The 50% trifluoropropyl-methylpolysiloxane (007-210) phase provides no added selectivity compared with the non-polar first-dimension phase (DB-1) and has, therefore, no practical value in the present context. However, it may be of interest to test this phase in future studies for the selective retentions of, e.g. the hydroxy or methoxy metabolites of the organohalogens, because it is selective towards ether, hydroxyl, ester and keto functional groups.

(2) The 8% phenyl-methylpolysiloxane on carborane (HT-8) phase does not yield much separation between the various groups. On the other hand, valuable within-group separations are created which are based on the number of halogen substituents in a molecule. Examples include PCBs, but also toxaphene and PCTs with which – different from PCBs – several different, but mutually rather similar, carbon skeletons are present. It will be of interest to determine whether this selectivity derives from the 8% diphenyl functional groups, the polycarborane base or their combined effect.

(3) The 50% liquid crystalline-methylpolysiloxane stationary phase (LC-50) offers shape – more specifically, planarity – selectivity. Three distinct groups of analyte classes can now be distinguished. Three-ring planar compounds such as PCDD/Fs, PCDTs and planar PCTs are most strongly retained. Next in line are two-ring planar compounds such as PCNs and planar PCBs. Non-planar analytes show least retention. As for within-group separation, the column combination is recommended for use with analyte classes such as PCBs, PBBs and PCTs, whose congeners differ widely in planarity (and, as is well-known, in dioxin-type toxicity).

(4) The 65% phenyl-methylpolysiloxane (007-65HT) phase displays a high retention for PBDEs, and very little for PCAs—with all other classes more or less in between. The practicability of the PBDE versus PCA separation was demonstrated by analysing a dust extract. Further, the column combination efficiently separates chlorinated from brominated analogues (PCBs/PBBs and PCDEs/PBDEs), and it is the best combination for within-class separations of OCPs and PCNs.

(5) The cyano-containing VF-23ms phase should not be used for separation of the various groups, but it is extremely effective in within-class separations. Especially non-aromatic compound classes such as the PCAs, toxaphene and the OCPs, cover the entire 2D plane. This column set should therefore be preferred when unravelling the composition of, specifically, toxaphene and the PCAs, is the main aim of a study.

In summary, GC × GC–μECD – if properly optimised as regards the stationary-phase combination and relevant experimental conditions – is a powerful technique to separate a large variety of organohalogen compounds and compound classes. Two examples, the determination of PBDEs next to PCAs in a sediment, and of PCDD/Fs in a fractionated dust extract seriously contaminated with PCAs, illustrate the practical usefulness of the approach. However, one should also consider that in these same sample extracts, many non-target-analyte peaks are visible. Some of these could be provisionally identified by using the available information on all organohalogen classes included in the study. However, an even larger number remained unidentified. Obviously, GC × GC–ECNI-TOF-MS, which combines the selectivity of the GC × GC system with the selectivity and high sensitivity of the recently introduced ECNI-TOF-MS instrument will be needed for a wider-ranging and unambiguous identification of the several hundreds and, occasionally, even thousands of analyte peaks now being displayed in the GC × GC plane(s).

Acknowledgements

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