

GROUP SEPARATION OF ORGANOHALOGENATED CONTAMINANTS BY GCxGC

Peter Korytar¹, Jordi Parera², Pim Leonards¹, Jacob de Boer¹, Udo Brinkman³

¹Netherlands Institute for Fisheries Research, IJmuiden

²Universitat de Barcelona, Barcelona

³Free University, Amsterdam

Introduction

The congener specific analysis of organohalogenated compounds is challenging, because of a large number of possibly interfering compounds not only within the compound class but also from congeners of other compound classes. Therefore, analytical procedures usually include complicated and time-consuming multi-step sample pre-treatment and/or selective detection (e.g. HRMS, MS/MS) in the consequent gas chromatographic analysis, what makes the procedures laborious and expensive. One way how to improve the situation would be to considerably increase the separation efficiency of the gas chromatographic analysis by replacing conventional GC by so-called comprehensive two-dimensional gas chromatography (GCxGC). As is explained in, e.g., ref. ¹, in GCxGC two independent separations are applied to an entire sample which effects a considerably enhanced overall resolution and also, because of the analyte refocusing during modulation, an improved analyte detectability. One further aspect which makes GCxGC especially attractive is the ordered structure of the two-dimensional chromatograms, which is observed when mixtures of related compounds, homologues or congeners are analysed. One good example are the bands of alkanes, naphthenes and aromatics present in 2D chromatogram when petrochemical samples are analysed². The ordered structure was reported also within the compound class of some organohalogenated contaminants, more precisely, of polychlorinated biphenyls^{3,4} and toxaphenes⁵ (ordering to number of chlorine atoms on the skeleton). However, to date, no study of separation among the different compound classes has been reported. In the present paper, this topic will be studied for the most common contaminants (cf. Table 1). While the principle aim is the group type separation, some attention will be devoted also to

within the class separation (e.g., for polychlorinated diphenylethers and polychlorinated alkanes).

Methods and Materials

The GC×GC system was built from an HP6890 (Agilent Technologies) gas chromatograph equipped with a loop-type carbon dioxide jet modulator (KT2002 CO₂ system; Zoex). Principles, working characteristics and optimisation of parameters are extensively described in ref. ⁶. The hot air pulse duration was 200 ms, hot jet temperature 400°C, and the modulation period was 8 s for DB-1×LC-50 and 9 s for DB-1×007-65HT column combination. At the start of each run, the CO₂ 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 with a purity of 99.999% was used as carrier gas. A micro-ECD was operated at 300°C, with 99.999% pure nitrogen as make-up gas at a flow-rate of 150 ml/min. The data acquisition rate was 50 Hz. 1-μl samples were injected manually into a split/splitless inlet port operated in the splitless mode at 280°C with split opening 2 min after injection. A 30 m × 0.25 mm × 0.25 μm DB-1 (100% methylpolysiloxane) fused-silica column was used as first-dimension column. Two columns were used as the second-dimension columns: 1 m × 0.1 mm × 0.1 μm LC-50 (50% liquid crystalline-methylpolysiloxane) and 1 m × 0.1 mm × 0.1 μm 007-65HT (65% phenyl-methylpolysiloxane). The columns were coupled via a 1.5 m × 0.1 mm I.D. uncoated fused-silica deactivated column, which serves as the modulator loop. Mini press-fits were used for the connections.

A standard mixture of each compound class was prepared either from individual congeners or from technical mixtures. The list of the studied compound classes with the composition of each of them is given in Table 1. The congener concentration varied between 1 to 100 pg/μl.

Table 1. Composition of studied compound classes

Compound class	Composition (list of congeners / name of technical mixture)
Polybrominated diphenyl ethers (PBDEs)	1,2,3,4,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,22,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,42,46,47,48,49,50,51,53,55,58,62,66,67,68,69,71,72,72,74,75,76,77,78,79,80,81,85,86,87,88,97,98,99,100,101,102,103,104,105,106,108,109,114,115,116,118,119,120,121,123,124,125,126,127,128,131,138,139,140,141,142,144,153,154,155,156,158,159,160,161,166,167,168,173,181,182,183,184,185,190,191,192,198,203,204, 205,206,207,208,209
Polychlorinated diphenyl ethers (PCDEs)	17,28,33,74,66,77,99,118,126,105,156,128,170, 194,209
Polybrominated biphenyls (PBBs)	15,52,49,101,153,169
Polychlorinated biphenyls (PCBs)	4,5,7,10,11,12,16,24,26,28,29,31,33,37,40,44,47,49,50,52,53,54,56,60,61,65,66,69,70,72,74,75,77,78,80,81,82,84,85,87,88,92,95,97,99,101,103,105,110,114,116,118,119,121,123,124,126,128,129,136,137,138,140,141,149,151,153,154,155,156,157,163,167,169,170,171,173,180,183,185,187,189,194,195, 198,201,202,206, 207,208
Polychlorinated naphthalenes (PCNs)	Technical mix Hallowax 1014
Polychlorinated dibenzothiophenes (PCDTs)	Technical mixture
Polychlorinated dibenzo-p-dioxins (PCDDs)	Seven 2,3,7,8-substituted congeners
Polychlorinated dibenzofurans (PCDFs)	Ten 2,3,7,8-substituted congeners
Organohalogenated pesticides (OCPs)	QCB, a-HCH, b-HCH, g-HCH, d-HCH, e-HCH, HCB, heptachlor, a-chlordeen, g-chlordene, aldrin, b-hepo, cis-hepo, a-hepo, t-hepo, OCS, oxychloordaan, g-chloordaan, op-DDE, a-chloordaan, t-nonachlor, endosulfan, pp-DDE, dieldrin, op-DDD, endrin, b-endosulfan, pp-DDD, op-DDT, pp-DDT
Toxaphene	11,12,15,21,25,26,31,32,38,39,40,41,42a,42b,44,50,51,56,58,59,62,63,69
Toxaphene	Technical mix Toxaphene
Polychlorinated terphenyls (PCTs)	Technical mix Hallowax 5041
Polychlorinated alkanes (PCAs)	Technical mix PCA-60

Results and Discussion

DB-1×LC-50: An overlaid chromatogram of the studied compound classes is shown in Figure 1. LC-50 column shows planarity selectivity⁴, resulting in much stronger retention of the planar compounds – PCDD/Fs, PCDTs and PCNs. LC-50 column combined with DB-XLB was shown to provide comparable quantitative results in dioxin analysis with results achieved with HRMS technique⁷. Figure 1 confirms this, because all commonly interfering compounds in HRMS determination – PCNs and PCDEs – are completely separated from PCDD/Fs. However, special attention has to be paid to PCDTs, which are the possible co-elutants to some congeners. This column combination is excellent also for PCNs determination, which are completely separated from other classes. PCDD/Fs and PCNs determination are often present in one fraction after typical dioxin pre-separation, and this column combination allows the determination of both classes in one run.

DB-1×007-65HT: A Figure 2 shows, this column combination is excellent for the determination of PBDEs and PCAs. PBDEs are retained much stronger than any other class, and also congener separation is excellent – only 15 out of 126 BDE congeners were not separated. PCAs are, on the other hand, retained the least of all the classes resulting in their separation from common interferences when ECD detection is used – toxaphene and BDE congeners. In addition, an ordered structure is observed for PCAs, which gives hope for more detailed description of technical mixtures. The extreme separation power of this column combination is further demonstrated in Figure 3. In one GC×GC run is possible to separate three technical mixtures – PCTs, PCAs and Toxaphenes. Moreover, in the same run is possible to perform a semiquantification of toxaphene and possibly also of PCA technical mixture, since they show the ordered structure.

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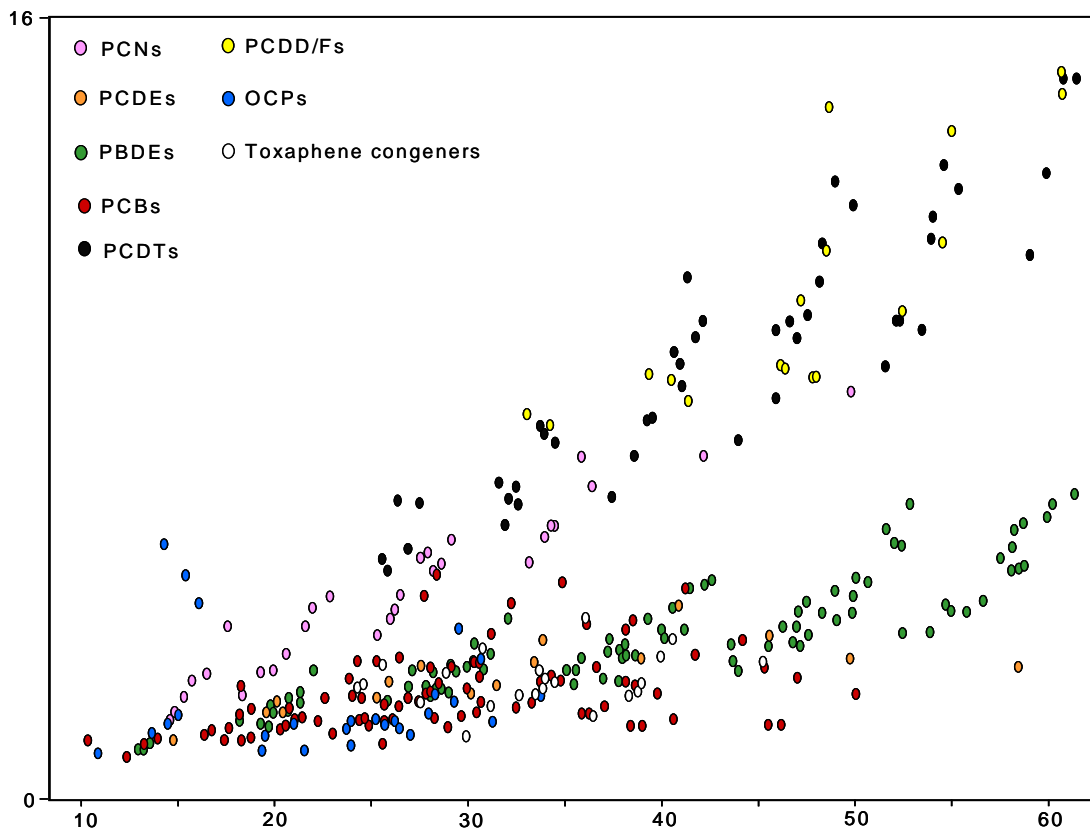


Figure 1 Overlaid GCxGC-ECD chromatograms of the studied compound classes as is indicated in the frames with DB-1 \times LC-50 column combination.

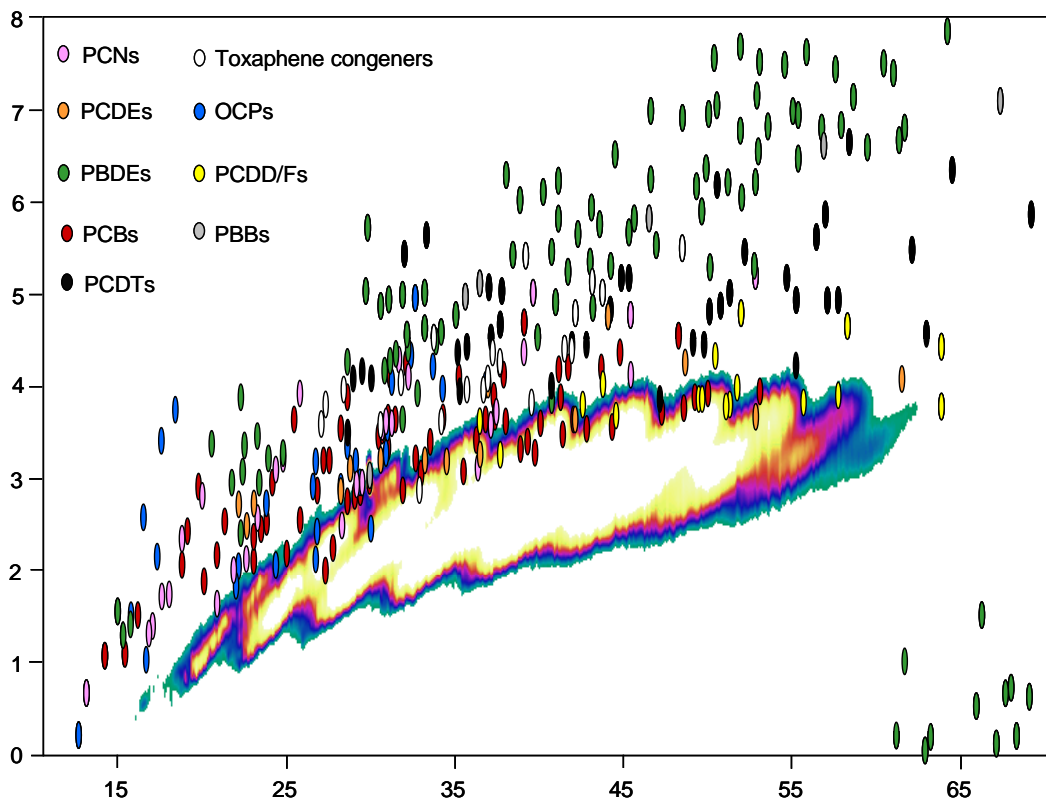


Figure 2 Overlaid GCxGC–ECD chromatograms of the studied compound classes as is indicated in the frames with DB-1 × 007-65HT column combination.

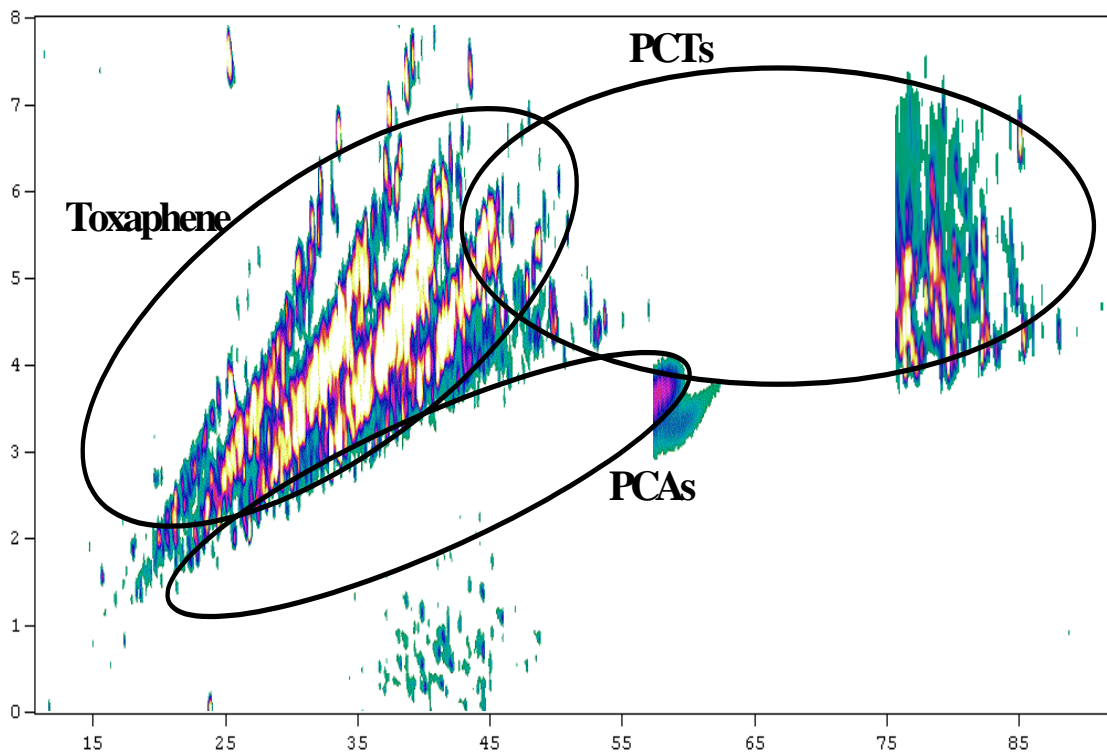


Figure 3 Overlaid GC×GC–ECD chromatograms of the technical mixtures of Toxaphenes, PCTs and PCAs with DB-1 × 007-65HT column combination.