COMPREHENSIVE TWO-DIMENSIONAL GASCHROMATOGRAPHY

The state-of-separation-arts

Part II: Applications Environment

JAN BEENS

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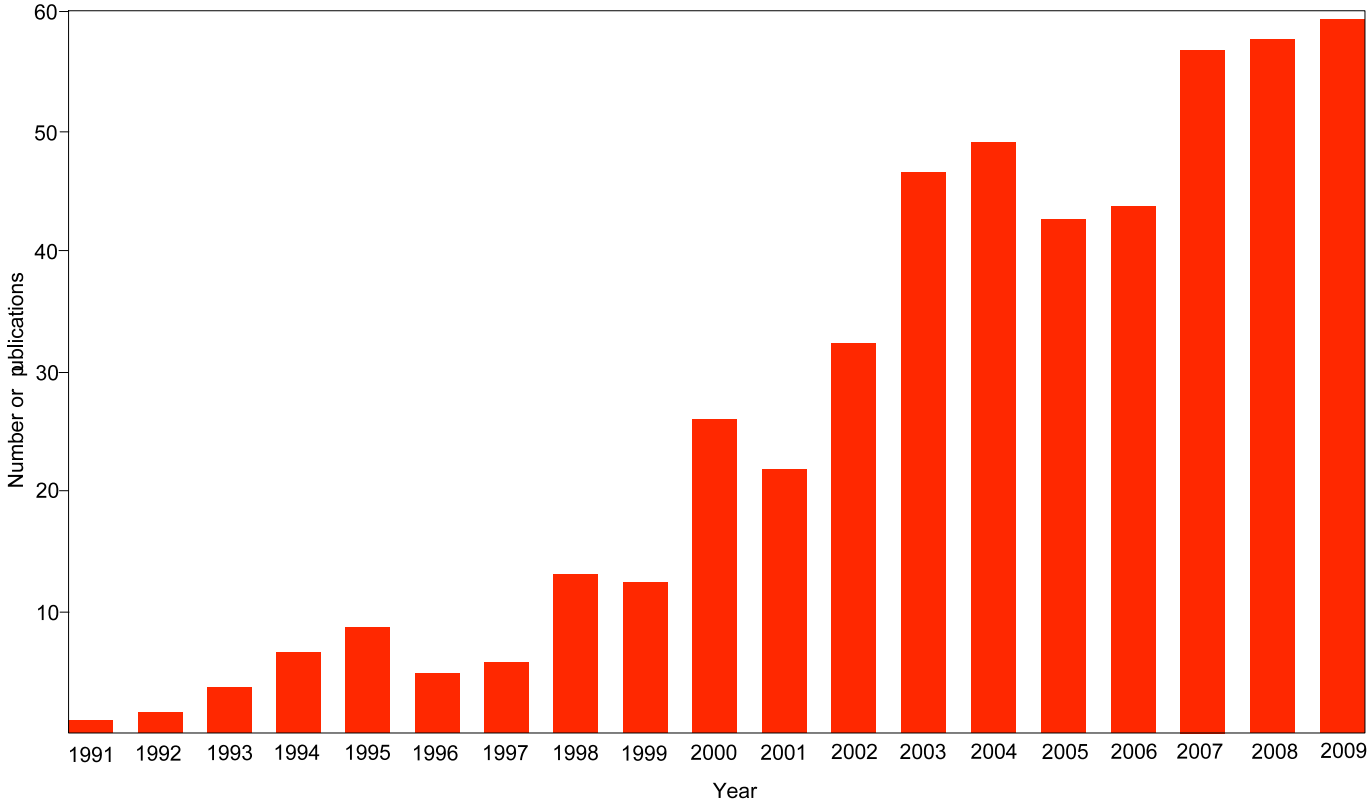
PART II

—APPLICATIONS—
Environmental



The number of published papers on GC×GC.

From the very first publication of the technique of GC×GC by Liu and Phillips on, it was clear that interesting separations, containing hundreds to thousands of separated peaks, suddenly became possible.

During the decade following this publication a steadily increasing number of papers have been published about GC×GC, of which the majority demonstrates a specific application. The figure above depicts the growth in interest in this technique quite nicely by the growth of the number of published papers.

In this Part II (referred to as chapter 12), other applications that have been demonstrated and reported so far and not yet covered in previous chapters are collected and depicted. On first page the sample and the GC×GC conditions through which these separations have been derived are presented. On the next page the colour or contour plot of the separated sample appears.

The areas in which GC×GC successfully has been applied have been reviewed in a number of papers [1-5]. The applications that are described in this chapter are listed below.

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PCBs Standards (209) and Aroclor 1248

M. Harju, C. Danielsson, P.J. Haglund, *Comprehensive two-dimensional gas chromatography of the 209 PCBs*, Chromatogr. A 1019 (2003), 111-126

Instrumental conditions:

***Columns*:**
First: 60 m × 0.18 mm ID, 0.180µm DB-XLB
Second: a) 2 m × 0.15 mm ID, 0.1µm LC-50
b) 3 m × 0.1 mm ID, 0.1µm SP-2340
Modulation cap.:

Carrier gas: hydrogen @ 438 kPa

***Temperatures*:**
Main oven: 80°C (2 min), 30°C/min → 140°C, 1.5°C/min → 270ºC (5 min)
Second oven:

Injector: splitless
Temperature: 250°C
Injection volume: 1 µL

Modulator: LMCS

Modulation time: 5 s

Detector: µECD
Temperature: 280ºC
Make up gas flow: 150 mL/min

Data acquisition: 50 Hz

Sample description and separation:
The DB-XLB stationary phase separates more congeners than any other GC phase currently available. When combined with a biscyanopropyl siloxane (SP-2340 or BPX70) or smectic liquid crystal (LC-50) second-dimension column, many additional CBs can be separated. In total, 176 and 181 of the 209 congeners were separated ($R_s \geq 0.5$) on the column combinations DB-XLB/SP-2340 and DB-XLB/LC-50, respectively. Of the 136 CBs present in any Aroclor mixture at concentrations above 0.05% (w/w), 126 were resolved using either of these two column combinations. The seven frequently measured CBs 28, 52, 101, 118, 138, 153, 180, and the WHO-PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189 were all separated from Aroclor CBs on the DB-XLB/LC-50 column set, whereas CBs 118 and 131 co-eluted on the DB-XLB/SP-2340 column set.

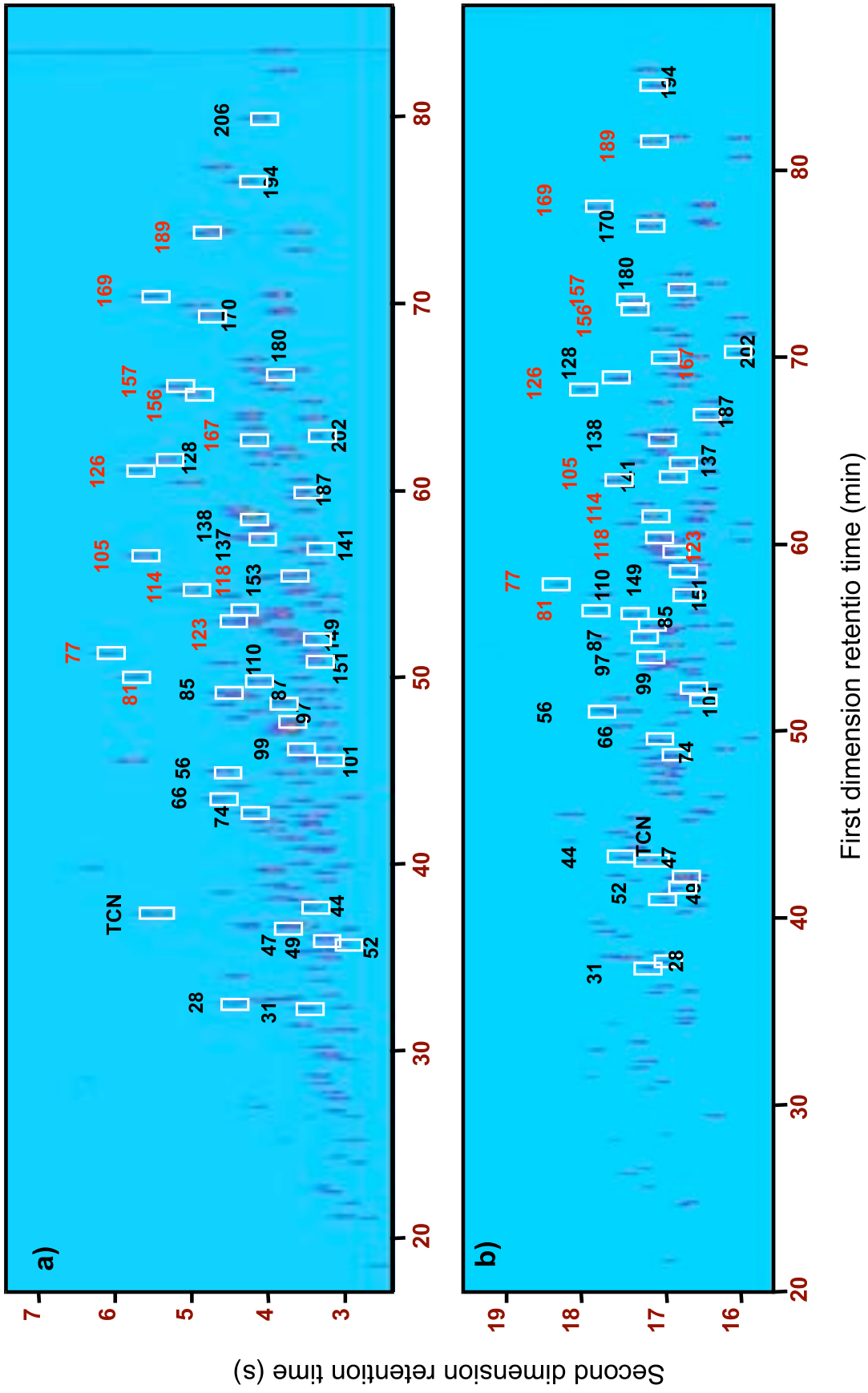

Figure 12.28. GC×GC colour plots of the separation of 209 CBs.
The numbers refer to IUPAC numbering

Clophen A50 fortified with PCBs and PCDD/Fs

M. Harju, C. Danielson, P.J. Haglund, University of Umeå, Sweden, *unpublished results*

Instrumental conditions:

***Columns*:**

First:	30 m × 0.25 mm ID, 0.25 µm, DB-XLB
Second:	0.9 m × 0.15 mm ID, 0.10 µm, LC-50
Modulation cap.:	0.15 m × 0.10 mm ID, 0.10 µm, Quadrex 007-1

Carrier gas: helium, constant pressure @ 344.74 kPa

***Temperatures*:**

Main oven:	80°C (2 min), 30°C /min →180°C, 3°C /min → 270°C (30 min)
Second oven:	80°C (2 min), 10°C/min →170°C, 5°C/min →175°C, 2°C/min →211°C, 30°C/min →270°C

Injector:	PTV, splitless
Temperature:	280°C
Injection volume:	1 µL

Modulator: Sweeper

Modulation time: 6 s

Detector:	µECD
Temperature:	300°C
Make up gas flow:	150 mL/min

Data acquisition: 100 Hz

Sample description and separation.

Clophen A50 has been fortified with PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189 and 2,3,7,8- PCDD/Fs. The following congeners co-elute: 1,2,3,4,7,8-HxCDF/1,2,3,6,7,8-HxCDF and 1,2,3,4,7,8HxCDD/1,2,3,6,7,8-HxCDD.

All 17 2,3,7,8-substituted PCDD/Fs and the 12 WHO-PCBs were almost completely separated from each other and from other CBs in the mixture. The two 1,2,3,4,7,8- and 1,2,3,6,7,8-substituted congener pairs overlapped in the first dimension, however they have the same TEF values. Whilst the 2,3,7,8-TCDD and PCB 126 are co-eluted in the first dimension but were separated in the second due to the difference in planarity. 2,3,7,8-TCDD is more planar than PCB 126 and is therefore retained more by the LC-50 column. Notably, there is almost no separation at all between PCDD/Fs in the second dimension, which indicates similar planarity.

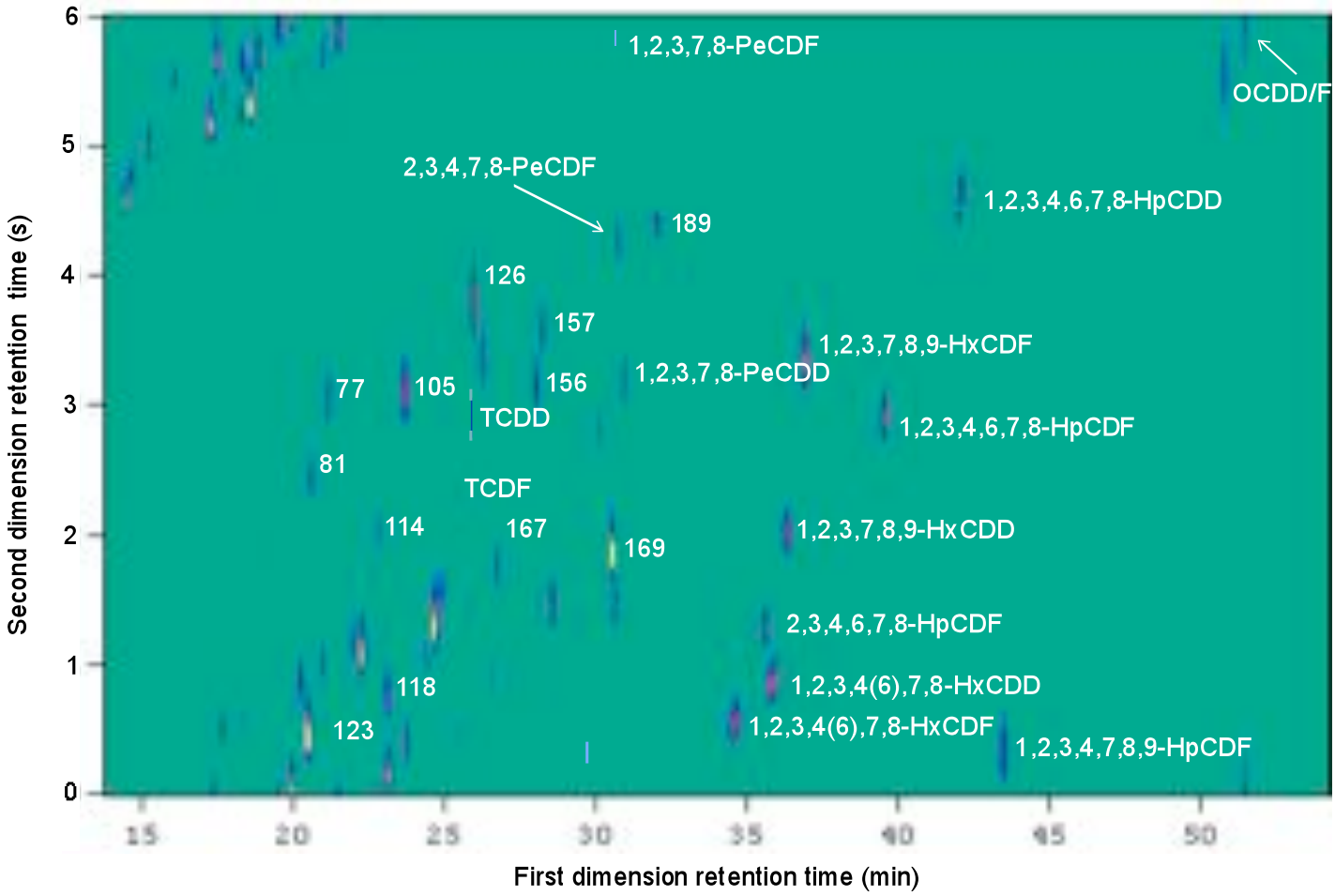

Figure 12.29. GC×GC colour plot of the separation of Clophen A50 fortified with PCBs and PCDD/Fs. The numbers refer to IUPAC numbering.

PCB enantiomers

M. Harju, P. Haglund, *Comprehensive two-dimensional gas chromatography (GC×GC) of atropisomeric PCBs, combining a narrow bore beta-cyclodextrin column and a liquid crystal column,* J. Microcol. Sep. 13 (2001) 300-305

Instrumental conditions:

***Columns*:**
Precolumn: 3 m × 0.25 mm ID
First: 10 m × 0.10 mm ID, 0.1µm Chirasil-Dex
Second: 1.4 m × 0.15 mm ID, 0.1µm LC-50
Modulation cap.:

Carrier gas: hydrogen @ 290 kPa

***Temperatures*:**
Main oven: 80°C (2 min) 30°C/min → 110°C, 0.5°C/min → 155ºC, 10ºC/min → 250ºC (5 min)
Second oven: main oven, Δt = +70ºC

Injector: splitless
Temperature: 250°C
Injection volume: 1 µL

Modulator: LMCS

Modulation time: 5 s

Detector: µECD
Temperature: 300ºC
Make up gas flow: 150 mL/min

Data acquisition: 50 Hz

Sample description and separation:

Nine atropisomeric PCBs were studied, all of which have an enantioselectivity on Chirasil-Dex and are the most frequently found congeners in biological samples. A standard with 144 CBs > 0.05% w/w in Aroclors with added CBs 126 and 169 and a non Aroclor internal standard CB 142 was used for evaluating possible analytical bias from coeluting CBs. The atropisomers of CBs 84, 91, 135, 136, 149, 174 and 176 atropisomers was successfully resolved in 2D while the atropisomers of CB 95 was still coeluting with CB 93 on Chirasil-Dex – LC-50 but resolved on column combination Chirasil-Dex – VF23MS. The second eluting enantiomer of CB 132 is only partially resolved (Rs = 0.7) from CB 141 in the second dimension.

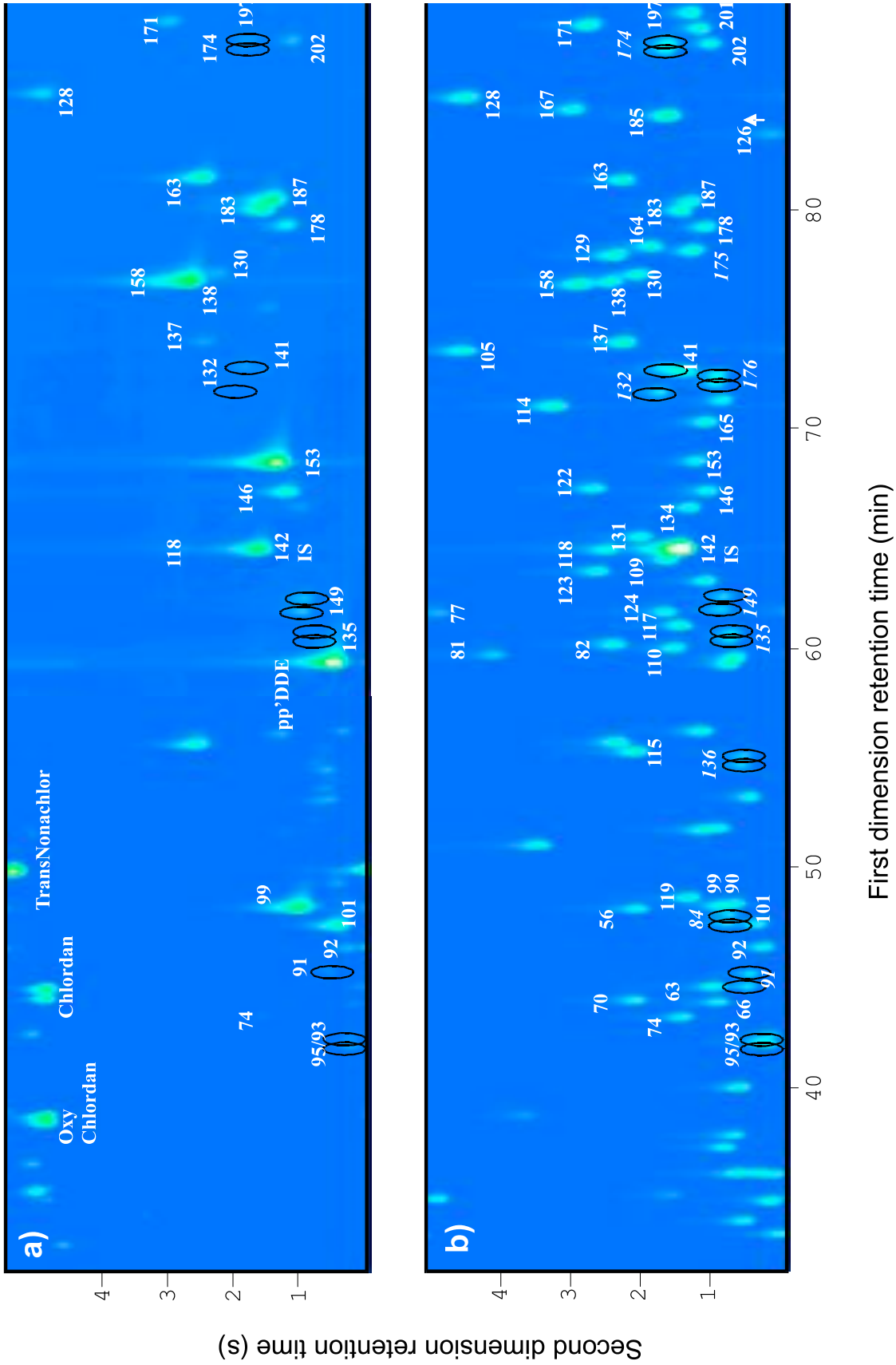

Figure 12.30. Part of theGC×GC contour plot of a) Grey seal blubber and b) Standard of the 144 Aroclor PCBs. The PCBs and a few nonachlorinated bornanes and a oxychlordane were tentatively identified by GC retention times and GC×GC–ToF MS spectra

Herring oil: mono-ortho PCB fraction

M. Harju, C. Danielson, P.J. Haglund, *Trace analysis of PCDD/Fs and WHO-PCBs in food and feed using comprehensive two-dimensional gas chromatography (GC×GC)*, Organo Halogen compounds 60 (2003) 395-398

see also: P. Korytár, P. Haglund, J. de Boer, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography for the analysis of organohalogenated micro-contaminants*, Trends in Analytical Chemistry, Vol. 25, No. 4, 2006, 373-396

Instrumental conditions:

***Columns*:**

First:	30 m × 0.25 mm ID, 0.25 µm DB-XLB
Second:	1.4m × 0.15 mm ID, 0.10 µm LC-50
Modulation cap.:	0.15m × 0.10 mm ID, 0.10 µm Quadrex 007-1

Carrier gas: helium @ 1.0 mL/min

***Temperatures*:**

Main oven:	80°C (2 min), 10°/min →180°C, 1.5°C/min → 240°C (2 min), 30°/min → 270°C.
Second oven:	

Injector:	PTV, splitless
Temperature:	280°C
Injection volume:	2 µL

Modulator: cryojets

Modulation time: 6 s

Detector:	µECD
Temperature:	300°C
Make up gas flow:	150 mL/min

Data acquisition: 50 Hz

Sample description and separation.

The herring was caught in May 2000 West of the Shetland Islands. In the final step of the sample preparation an activated carbon column was utilized to fractionate (according to planarity) the target compounds into three fractions, *i.e*. 'bulk PCBs', 'mono-*ortho* PCBs' and non-*ortho* PCBs and PCDD/Fs, respectively.

In the mono-*ortho* PCB fraction of the fish oil, 6 of the 8 mono-*ortho* PCBs were identified and quantified with GC×GC–µECD.

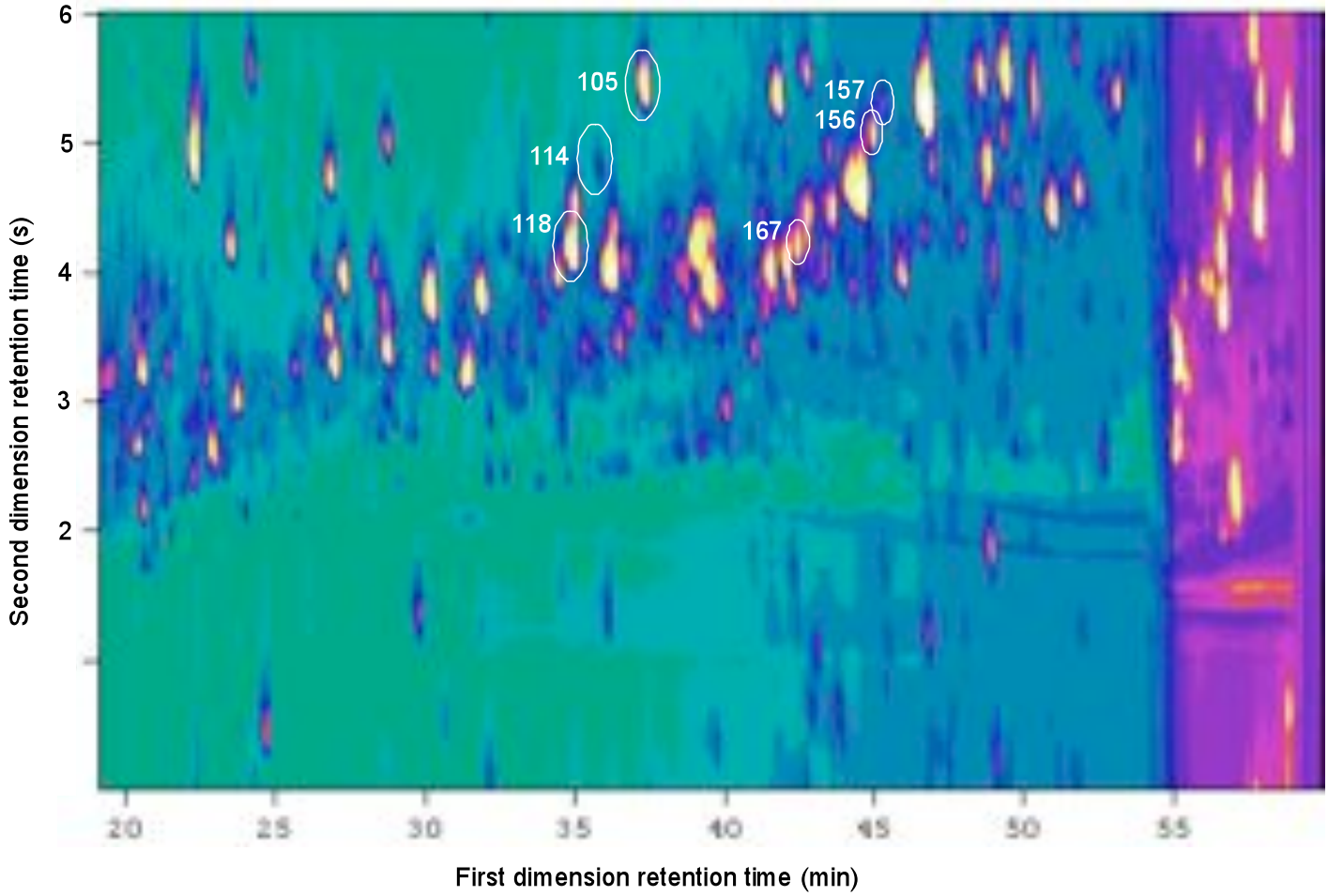

Figure 12.31. GC×GC contour plot of the mono-ortho PCB fraction of herring oil. The numbers refer to the identified mono-ortho PCBs.

Mixture of 90 PCBs

P. Korytár, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, *High-resolution separation of polychlorinated biphenyls by comprehensive two-dimensional gas chromatography*, J. Chromatogr. A, 958 (2002) 203–218

see also: P. Korytár, P. Haglund, J. de Boer, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography for the analysis of organohalogenated micro-contaminants*, Trends in Analytical Chemistry, Vol. 25, No. 4, (2006) 373-396

Instrumental conditions:

***Columns*:**

First:	30 m × 0.25 mm ID, 0.25 μm HP-1
Second:	1 m × 0.1 mm ID, 0.1 μm SupelcoWax-10
Modulation capillary:	7 cm × 0.1 mm ID, 3.5 μm 007-1

Carrier gas: helium @ 50 psi

***Temperatures*:**

Main oven:	90°C (2 min), 5°C/min →110°C, 1°C/min →230°C (25 min)
Second oven:	140°C (2 min), 5°C/min →160°C, 1°C/min →280°C (25 min)

Injector:	splitless, purge time 2 min
Temperature:	300°C
Injection volume:	1.0 μL
Modulator:	Sweeper, stroke velocity 0.15 revs/s, pause before return 0.4 s
Modulation time:	6.5 s
Detector:	μECD
Temperature:	300 °C
Make up gas flow:	60 mL/min
Data acquisition:	50 Hz

Sample description and separation:

PCB analyses have been mainly focused on the predominant marker congeners in recent years, attention has been devoted to the non- and mono-ortho CBs.

WHO has recommended an acceptable daily intake for dioxins, furans and PCBs, which includes non-ortho (77, 81, 126 and 169) and mono-ortho (105, 114, 118, 123, 156, 157, 167 and 189) CBs.

- 84 CBs elute as resolved peaks; only 3 pairs remain not resolved
- all 12 priority CBs are baseline separated
- bleeding of stationary phase.

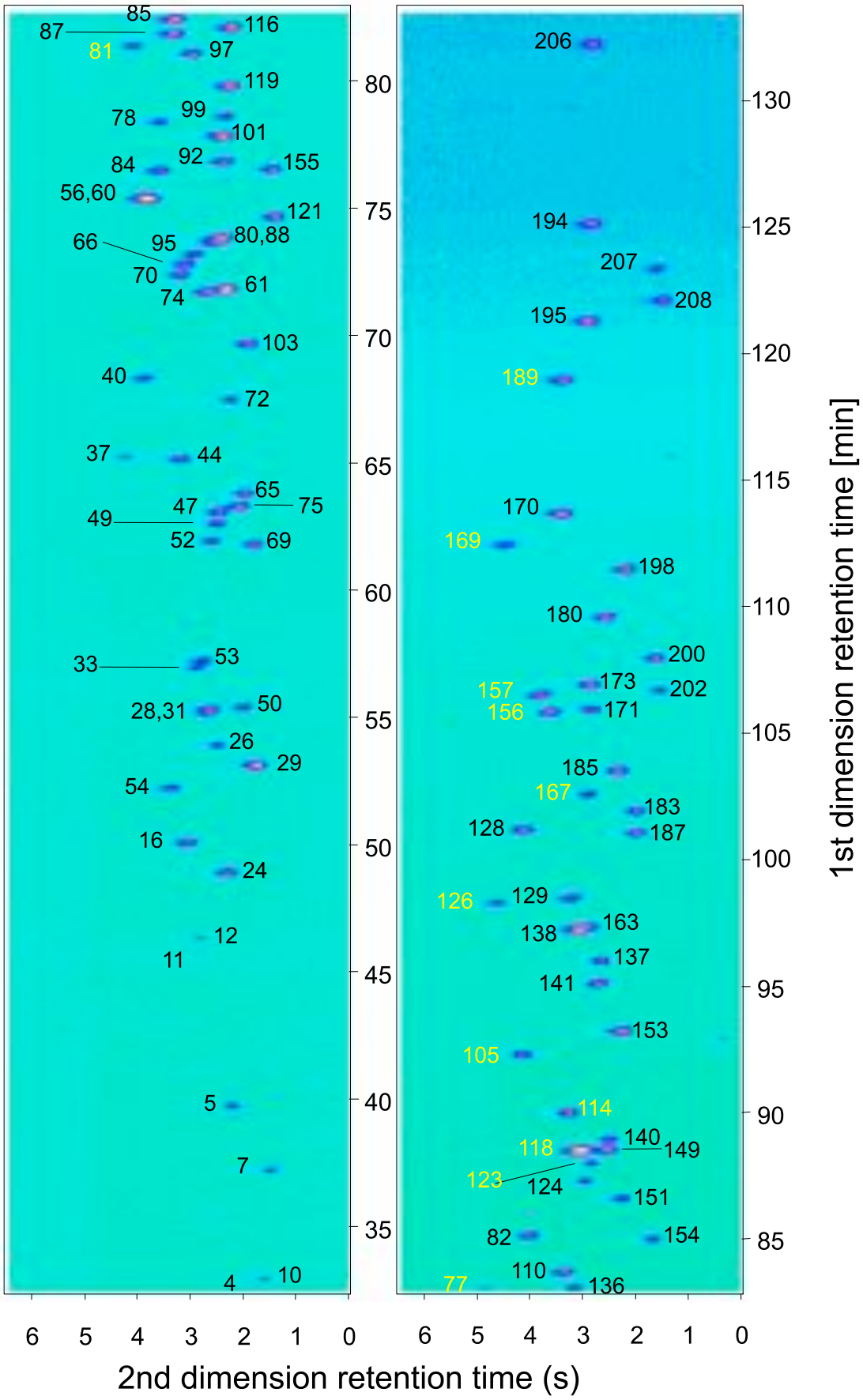

Figure 12.32. GC×GC separation of PCBs on HP-1/Supelcowax

The numbers refer to IUPAC numbering. The spots indicated with a yellow number are non-ortho and mono-ortho sustituted PCBs.

PCB standards

P. Korytár, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, *High-resolution separation of polychlorinated biphenyls by comprehensive two-dimensional gas chromatography*, J. Chromatogr. A, 958 (2002) 203–218

see also: P. Korytár, P. Haglund, J. de Boer, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography for the analysis of organohalogenated micro-contaminants*, Trends in Analytical Chemistry, Vol. 25, No. 4 (2006) 373-396

Instrumental conditions:

***Columns*:**		
First:	30 m × 0.25mm ID, 0.25 μm HP-1,	
Second:	1 m × 0.1mm ID, 0.1 μm HT-8	
Modulation capillary:	7 cm × 0.1mm ID, 3.5 μm 007-1	
Carrier gas:	helium @ 50 psi	
***Temperatures*:**		
Main oven:	90°C (2 min), 5°C/min →130°C, 1°C/min →240°C (40 min)	
Second oven:	110°C (2 min), 5°C/min →150°C, 1°C/min →260°C (40 min)	
Injector:	*s*plitless, purge time 2 min	
Temperature:	300°C	
Injection volume:	1.0 μL	
Modulator:	Sweeper, stroke velocity 0.15 revs/s, pause before return 0.4 s	
Modulation time:	6.5 s	
Detector:	μECD	ToF-MS
Temperature:	300°C	Ion source: 200°C, transfer line: 300°C
Make up gas flow:	60 mL/min	
Data acquisition:	50 Hz	10 spectra/s

Sample description and separation:

This column combination not only separates the planar PCB from the non-planar ones, but also provides a structure in which compounds with the same number of chlorine atoms are clustered in bands.

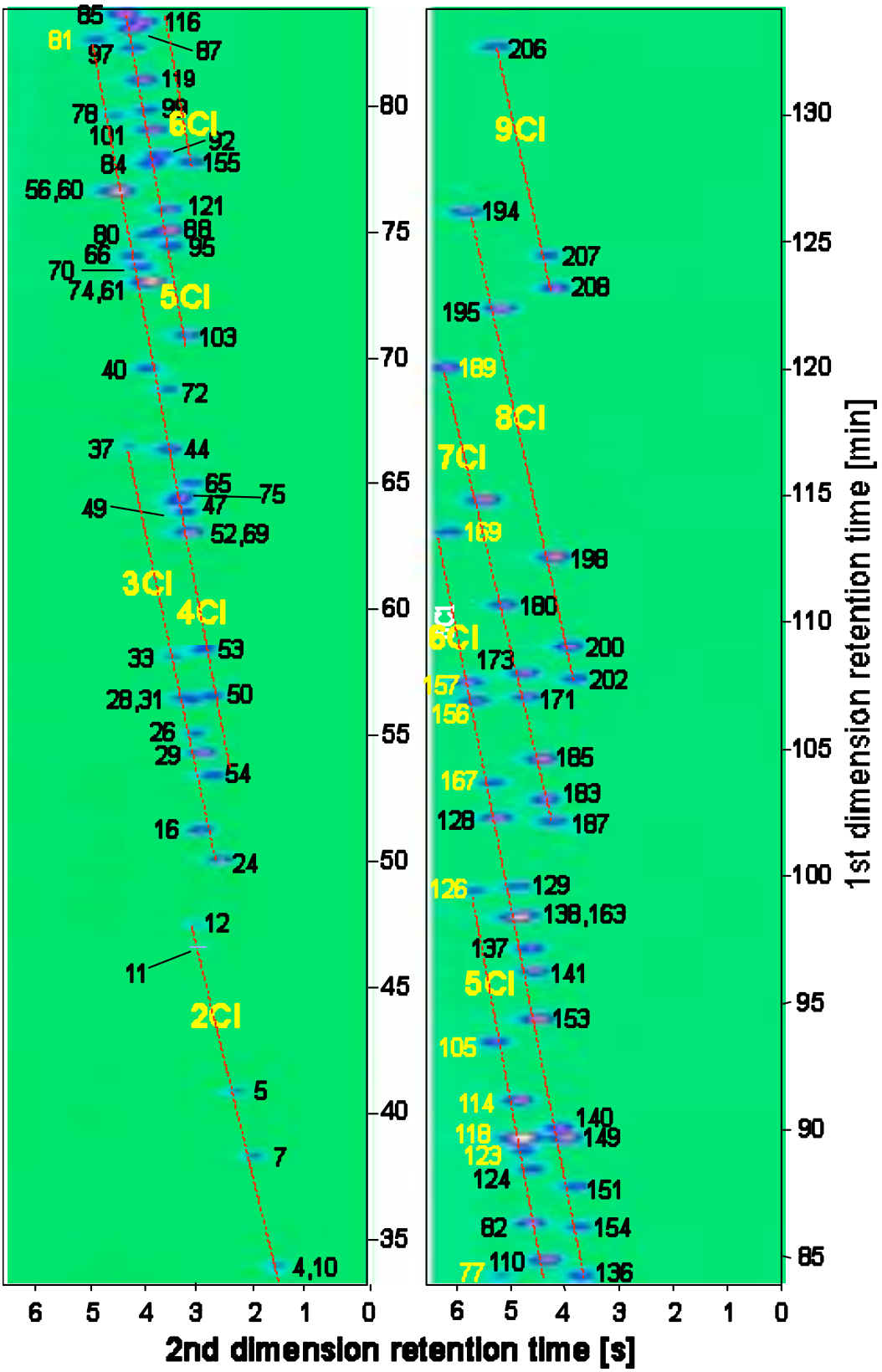

Figure 12.33. GC×GC separation of PCB standards. The red dotted lines indicate the different clusters with the same number of chlorine atoms. The numbers refer to IUPAC numbering. The spots indicated with a yellow number are non-ortho and mono-ortho sustituted PCBs.

PCDDs, PCDFs and PCBs

P. Korytár, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, *High-resolution separation of polychlorinated biphenyls by comprehensive two-dimensional gas chromatography*, J. Chromatogr. A, 958 (2002) 203–218

see also: P. Korytár, P. Haglund, J. de Boer, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography for the analysis of organohalogenated micro-contaminants, Trends in Analytical Chemistry,* Vol. 25, No. 4 (2006) 373-396

Instrumental conditions:

***Columns*:**

First:	30 m × 0.25mm ID, 0.25 μm HP-1,
Second:	1 m × 0.1mm ID, 0.1 μm HT-8
Modulation capillary:	7 cm × 0.1mm ID, 3.5 μm 007-1

Carrier gas: helium @ 50 psi

***Temperatures*:**

Main oven:	90°C (2 min), 5°C/min →130°C, 1°C/min →240°C (40 min)
Second oven:	110°C (2 min), 5°C/min →150°C, 1°C/min →260°C (40 min)

Injector:	*s*plitless, purge time 2 min
Temperature:	300°C
Injection volume:	1.0 μL

Modulator: Sweeper, stroke velocity 0.15 revs/s, pause before return 0.4 s

Modulation time: 6.5 s

Detector:	μECD:
Temperature:	300°C
Make up gas flow:	60 mL/min

Data acquisition: 50 Hz

Sample description and separation:

16 CDD and CDF congeners were separated from each other and also from all PCBs; only one penta-CDD or -CDF co-eluted with CB 169. Some co-elutions can be seen for the Hx-CDD and Hx-CDF, however, on an enlarged picture the valley between the peaks could be observed.

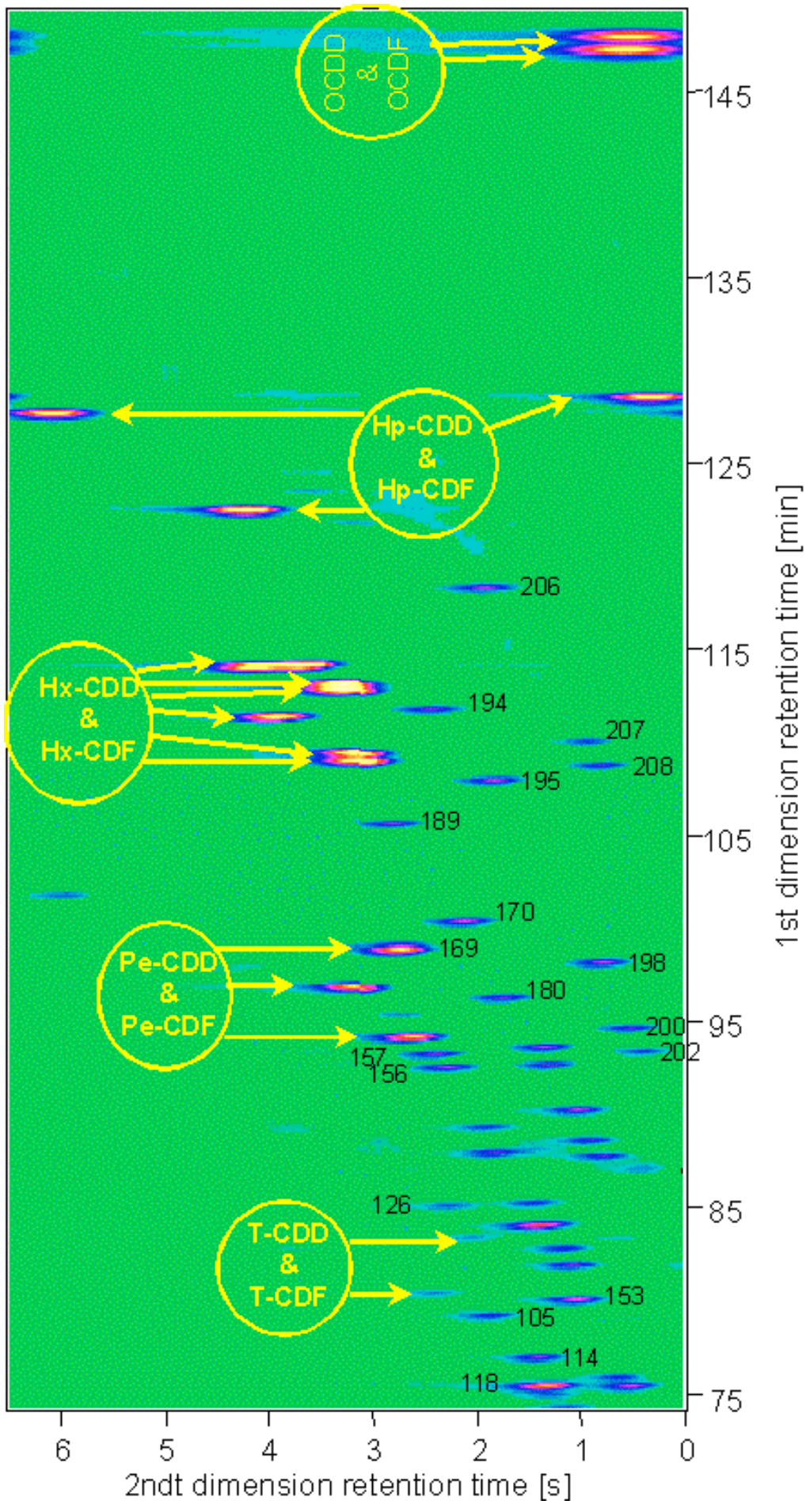

Figure 12.34. GC×GC separation on HP-1 + HT-8. The numbers refer to IUPAC numbering of PCBs

Toxaphene mixture

P. Korytár, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, *High-resolution separation of polychlorinated biphenyls by comprehensive two-dimensional gas chromatography*, J. Chromatogr. A, 958 (2002) 203–218

see also: P. Korytár, P. Haglund, J. de Boer, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography for the analysis of organohalogenated micro-contaminants*, Trends in Analytical Chemistry, Vol. 25, No. 4 (2006) 373-396

Instrumental conditions:

***Columns*:**

First:	30 m × 0.25mm ID, 0.25 μm HP-1,
Second:	1 m × 0.1mm ID, 0.1 μm HT-8
Modulation capillary:	7 cm × 0.1mm ID, 3.5 μm 007-1

Carrier gas: helium @ 50 psi

***Temperatures*:**

Main oven:	90°C (2 min), 5°C/min →130°C, 1°C/min →240°C (40 min)
Second oven:	110°C (2 min), 5°C/min →150°C, 1°C/min →260°C (40 min)

Injector:	*s*plitless, purge time 2 min
Temperature:	300°C
Injection volume:	1.0 μL

Modulator: Sweeper, stroke velocity 0.15 revs/s, pause before return 0.4 s

Modulation time: 6.5 s

Detector:	μECD:
Temperature:	300°C
Make up gas flow:	60 mL/min

Data acquisition: 50 Hz

Sample description and separation:

From a reference mixture, the system resolved 19 of the 23 compounds present and only the congener pairs P40/41 and P42a/42b were not separated. Significantly improved separation compared to 1D-GC was achieved for the congener pairs P32/31, P51/50 and P41/42a/b and, also relevant, between toxaphene congeners such as P58, P59, P62 and P63 and impurities present in the standard mixture. The ordered structure of the reference mixture fully confirms that each group of peaks comprises congeners with the same number of chlorine substituents. As regards compound classes, the mixture of standards contains five chlorinated camphenes (*cf.* Wester codes) next to the chlorinated bornanes. .

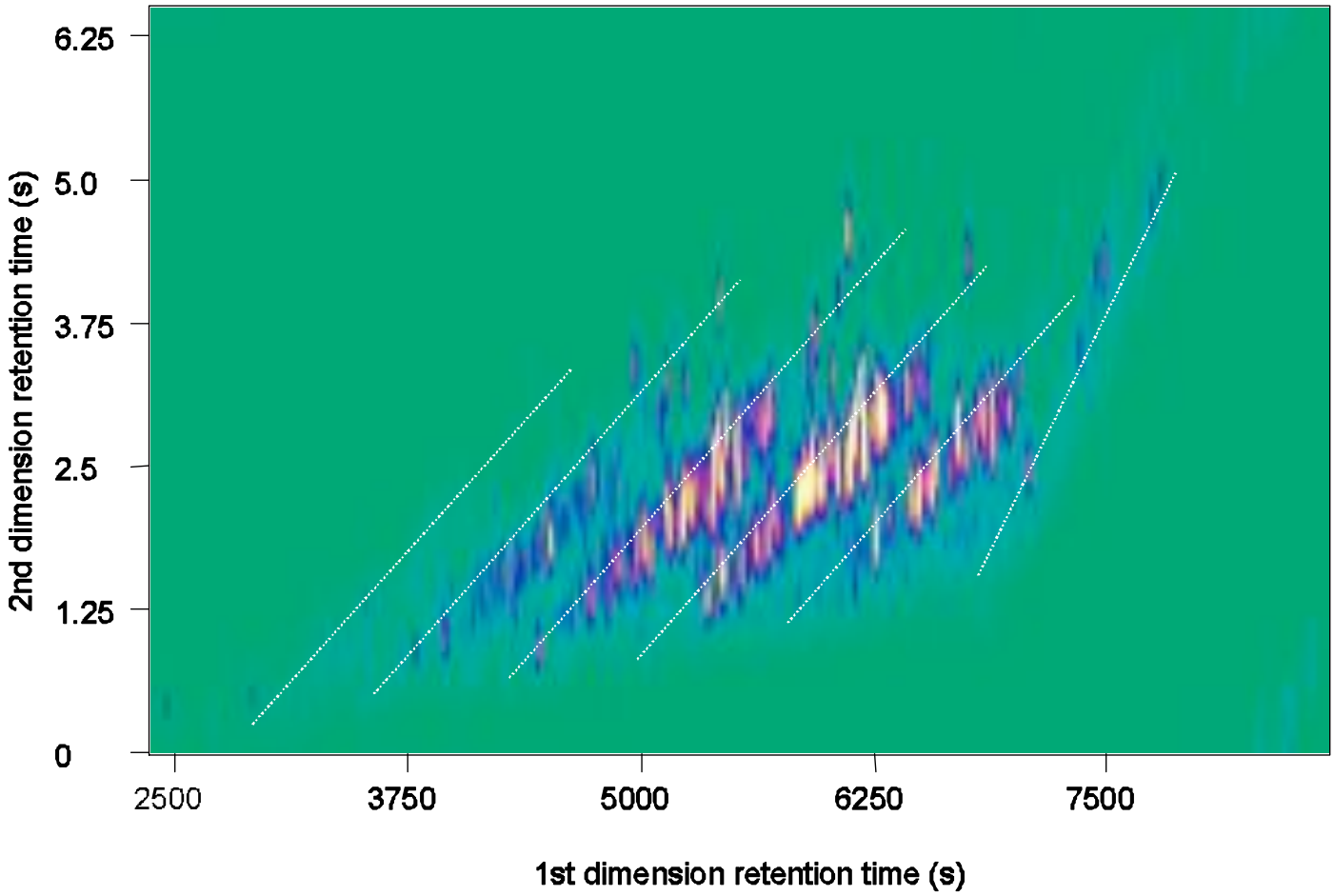

Figure 12.35. GC×GC separation of toxaphene mixture. The white dotted lines indicate the clusters with the same number of chlorine atoms.

Toxaphene enantiomers

L.R. Bordajandi, L. Ramos, M. J. González, *Determination of toxaphene enantiomers by comprehensive two-dimensional gas chromatography with electron-capture detection*, J. Chromatogr. A, 1125 (2006) 220-228

Instrumental conditions:

***Columns*:**	
First:	30 m × 0.25 mm ID, 0.25 μm BGB-176SE
Second:	A: 2 m×0.10 mm I.D, 0.10 HT8 B: 2 m×0.10 mm I.D, 0.10 μm BPX50 C: 1 m×0.10 mm I.D, 0.10 μm Supelcowax-10
Carrier gas:	helium, constant flow @ initial 45 psi
***Temperatures*:**	90ºC (1 min), 15ºC/min→190ºC (5 min), 2ºC/min→210ºC (40 min), 10ºC/min→220ºC.
Injector:	*s*plitless
Temperature:	240°C
Injection volume:	1.0 μL
Modulator:	loop modulator
Modulation time:	6 s
Detector:	μECD:
Temperature:	250°C
Make up gas flow:	30 mL/min
Data acquisition:	50 Hz

Sample description and separation:

The system has been evaluated for the enantioseparation of five chiral toxaphenes typically found in real-life samples (Parlar 26, 32, 40, 44 and 50).

A satisfactory repeatability and reproducibility of the retention times in both the first and the second dimension were observed for all target compounds (RSDs below 0.8%, $n = 4$). Linear responses in the tested range of 10–200 pg/μL and limits of detection in the range of 2–6 pg/μL were obtained. The repeatability and reproducibility at a concentration of 100 pg/μL, (as the RSDs) calculated for the enantiomeric fraction (EF), was better than 11% (n=4) in all instances.

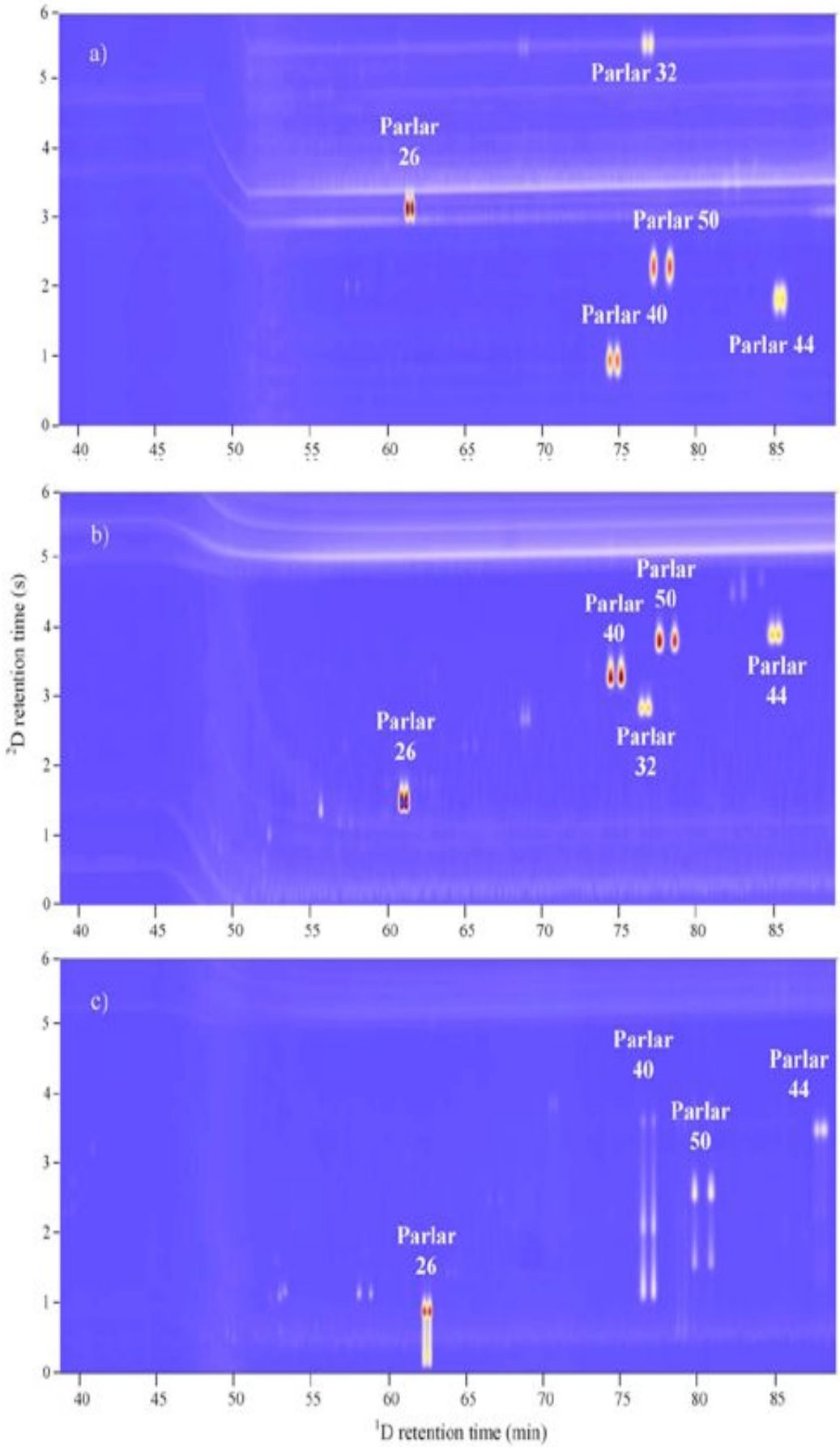

Figure 12.36. GC×GC–μECD colour plot of the five selected toxaphene congeners

Three different organohaloganed group type samples

P. Korytár, P.E.G. Leonards, J. de Boer, U.A.Th. Brinkman, *Group separation of organohaloganed compounds by means of comprehensive two-dimensional gas chromatography*, J. Chromatogr. A, 1086 (2005) 92-115

see also: P. Korytár, P. Haglund, J. de Boer, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography for the analysis of organohalogenated micro-contaminants*, Trends in Analytical Chemistry, Vol. 25, No. 4 (2006) 373-396

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25mm ID, 0.25 μm DB1,
Second: 1 m × 0.1mm ID, 0.1 μm 007-65HT
Modulation capillary:

Carrier gas: helium, constant flow @ 1.2 mL/min

***Temperatures*:**
Main oven: 90°C (2 min), 20°C/min →170°C, 2°C/min →335°C (10 min)
Second oven:

Injector: *s*plitless, purge time 2 min
Temperature: *2*80°C
Injection volume: 1.0 μL

Modulator: loop modulator

Modulation time: 8 s

Detector: μECD:
Temperature: 280°C
Make up gas flow: 150 mL/min

Data acquisition: 50 Hz

Sample description and separation:

The chromatograms exhibit the overall separation of three different classes of haloganeted compounds, viz. polychlorinated n-alkanes (PCA-60), polychlorinated terphenyls (PCTs) and a technical toxaphene mixture. According to the excellent group type separation of this column combination, the three groups are nicely separated from each other. Apart from that, there is also a 'within group type' separation.

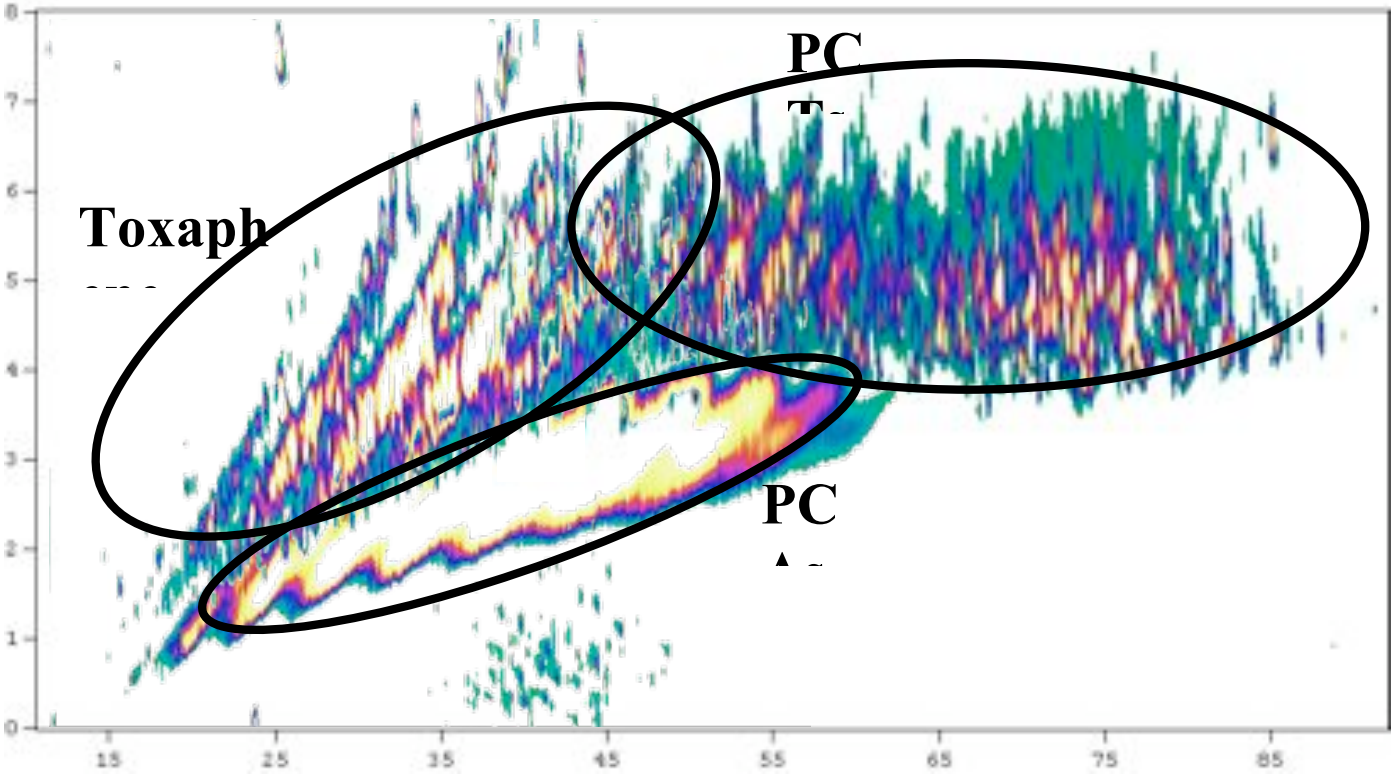

Figure 12.37. Overlaid chromatograms of PCAs, PCTs and toxaphene.

Surface water contaminants

J. Beens, J. Dallüge, M. Adahchour, R.J.J. Vreuls, U.A.Th. Brinkman, *Moving cryogenic modulator for the comprehensive two-dimensional gas chromatography (GC x GC) of surface water contaminants*, J Microcolumn Sep. 13 (2001) 134-140

Instrumental conditions:

***Columns*:**
First: 10 m × 0.25 mm ID, 0.25 μm DB1
Second: 1.5 m × 0.10 mm ID, 0.1 μm BPX50
Modulation capillary:

Carrier gas: helium

***Temperatures*:**
Main oven: 30°C (2 min), 2°C/min → 300°C
Second oven:

Injector: PTV, split ratio 1:100
Temperature: → 360°C
Injection volume: 1 μL

Modulator: Sweeper

Modulation time: 9 s

Detector: FID
Temperature: 320°C
Make up gas flow:

Data acquisition: 200 Hz

Sample description and separation:

The separation of 80 microcontaminants found to be present in surface water in the Netherlands, was complete. The mixture contained poly aromatics, chlorinated alkanes, chlorinated aromatics, aldehydes, nitriles, pyridines, anilines, alcohols, quinolines, phthalates, and a number of pesticides and herbicides. In order to facilitate the identification, which, in the end, was confirmed by means of single-column GC–MS, a series of alkanes was added to the sample. In the Figure these alkanes can be found in the contour plots at the lowest second dimension retention and serve as internal references.

Even though this synthetic mixture contains many different chemical families, the number of members of those families is rather low. Consequently, it is very hard to recognize structures in the colour plot. As can be seen from the groups inside the polygons, these structures nevertheless exist.

Table I in the paper summarizes the names of all compounds and the peak numbers.

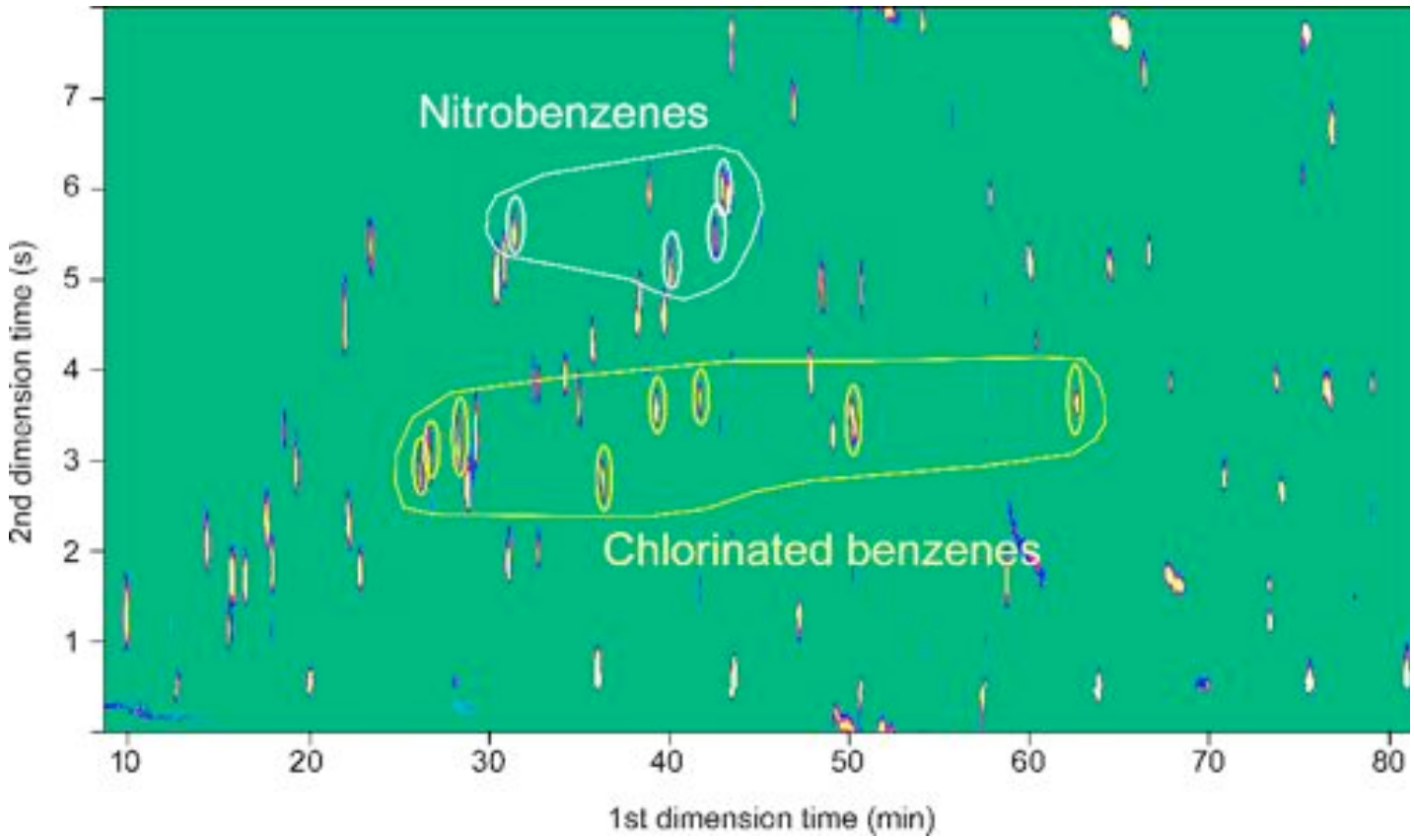

Figure 12.38. GC×GC separation of 80 surface water contaminants. The ellipses indicate the positions of: (white) nitrobenzenes and (yellow) chlorinated benzenes. For further identification, see the referenced paper.

Pesticides in food extracts (leek)

J. Dallüge, R.J.J. Vreuls, J. Beens, U.A.Th. Brinkman, *Optimization and characterization of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection (GC×GC–ToF MS),* J. Sep. Sci. 25 (2002) 201-214

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 0.25 μm CP-Sil 5CB
Second: 0.8 m × 0.10 mm ID, 0.05 μm BPX50
Modulation capillary:

Carrier gas: helium, constant flow @ 1.3 mL/min

***Temperatures*:**
Main oven: 50°C (4 min), 5°C/min → 280°C
Second oven:

Injector: PTV, split ratio 1:125
Temperature: → 350°C
Injection volume: 0.1 μL

Modulator: LMCS (modified)

Modulation time: 6 s

Detector: ToF-MS
Temperature:
Make up gas flow:

Data acquisition: 50 spectra/s

Sample description and separation:

This paper is focused on the complex data processing procedures needed in GC×GC–ToF MS analyses. It extensively explains the influence of various parameters for separation, sensitivity and LODs in GC×GC–ToF MS. It also explains, with various examples, the data processing procedures as visualisation, conversion, deconvolution and peak recognition.

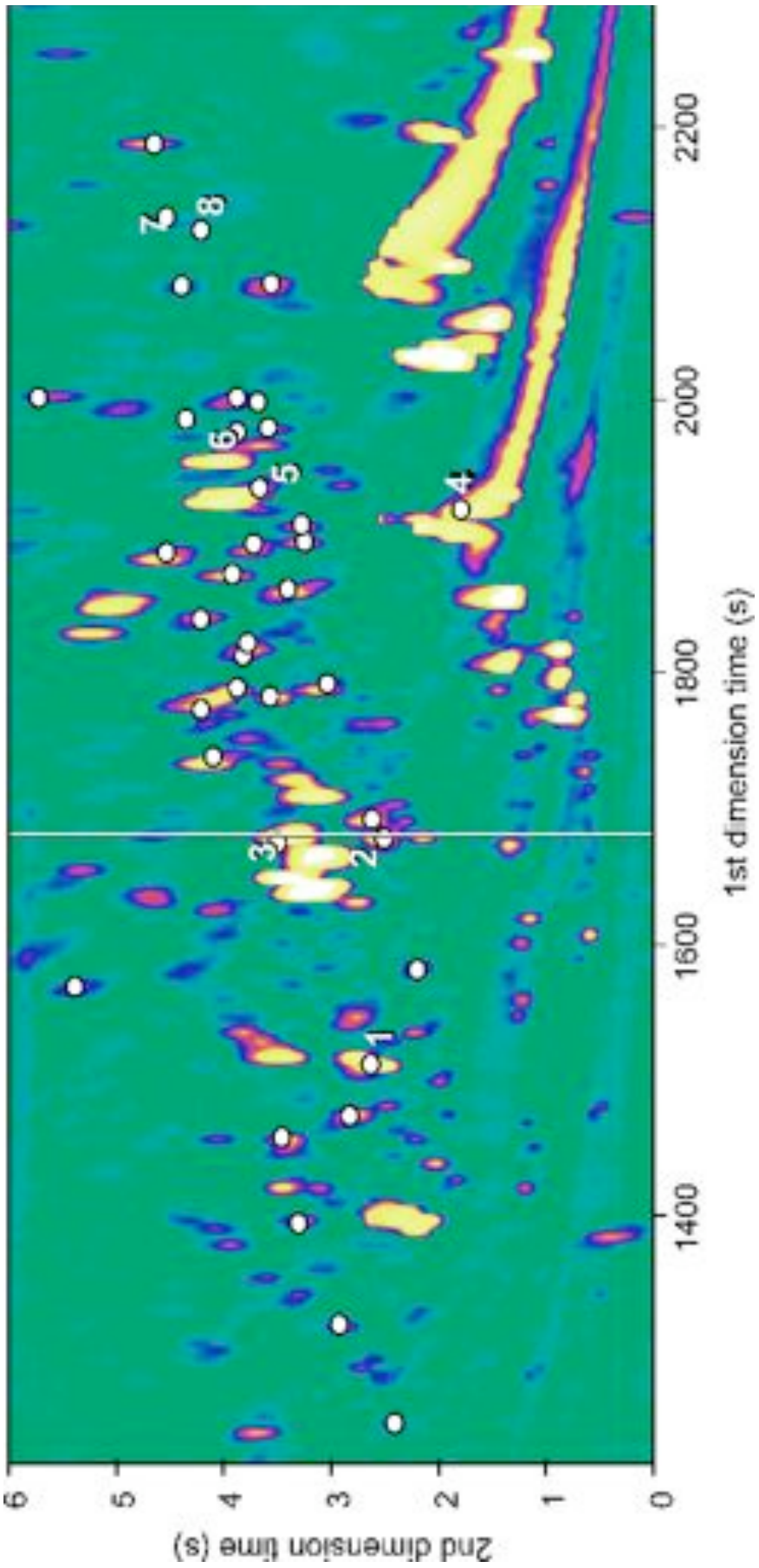

Figure 12.39. Colour plot of the separation of pesticides in a leek extract. The white dots denote the apices of pesticide peaks. 1. Chlorpropham, 2. propyzamide, 3. pyrimethanil, 4. fenpropimorph, 5. bromophosmethyl, 6. chlorfenvinphos, 7. bupirimate, 8. flusilazole.

Pesticides in food extracts (celeriac)

J. Dallüge, M. van Rijn, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the determination of pesticides in food extracts*, J. Chromatogr. A 965 (2002) 207-217

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 0.25 μm CP-Sil 5CB
Second: 0.8 m × 0.10 mm ID, 0.05 μm BPX50
Modulation capillary:

Carrier gas: helium, constant flow @ 1.3 mL/min

***Temperatures*:**
Main oven: 50°C (4 min), 5°C/min → 280°C
Second oven:

Injector: PTV, split ratio 1:125
Temperature: → 350°C
Injection volume: 0.1 μL

Modulator: moving cryogenic

Modulation time: 6 s

Detector: ToF-MS
Temperature:
Make up gas flow:

Data acquisition: 50 spectra/s

Sample description and separation:

As the identification indicates, dimethoate, provinphos and bupirimate could not be detected with 1D-GC–TOF MS either, since they co-eluted with the most matrix compounds or other analytes, while no problems were encountered once GC×GC–TOF MS was used as an alternative. With triadimenol (1) and pyridaphenthion, rather poor GC–MS results were found to be considerably improved using the GC×GC set-up.

The identification of non-target compounds such as bergaptan, psoralen and hexadecanoic acid in the Fig requires high-quality mass spectra. Here, the much better resolution of GC×GC compared with 1D-GC analysis, which causes co-elution to be less severe, has a beneficial influence.

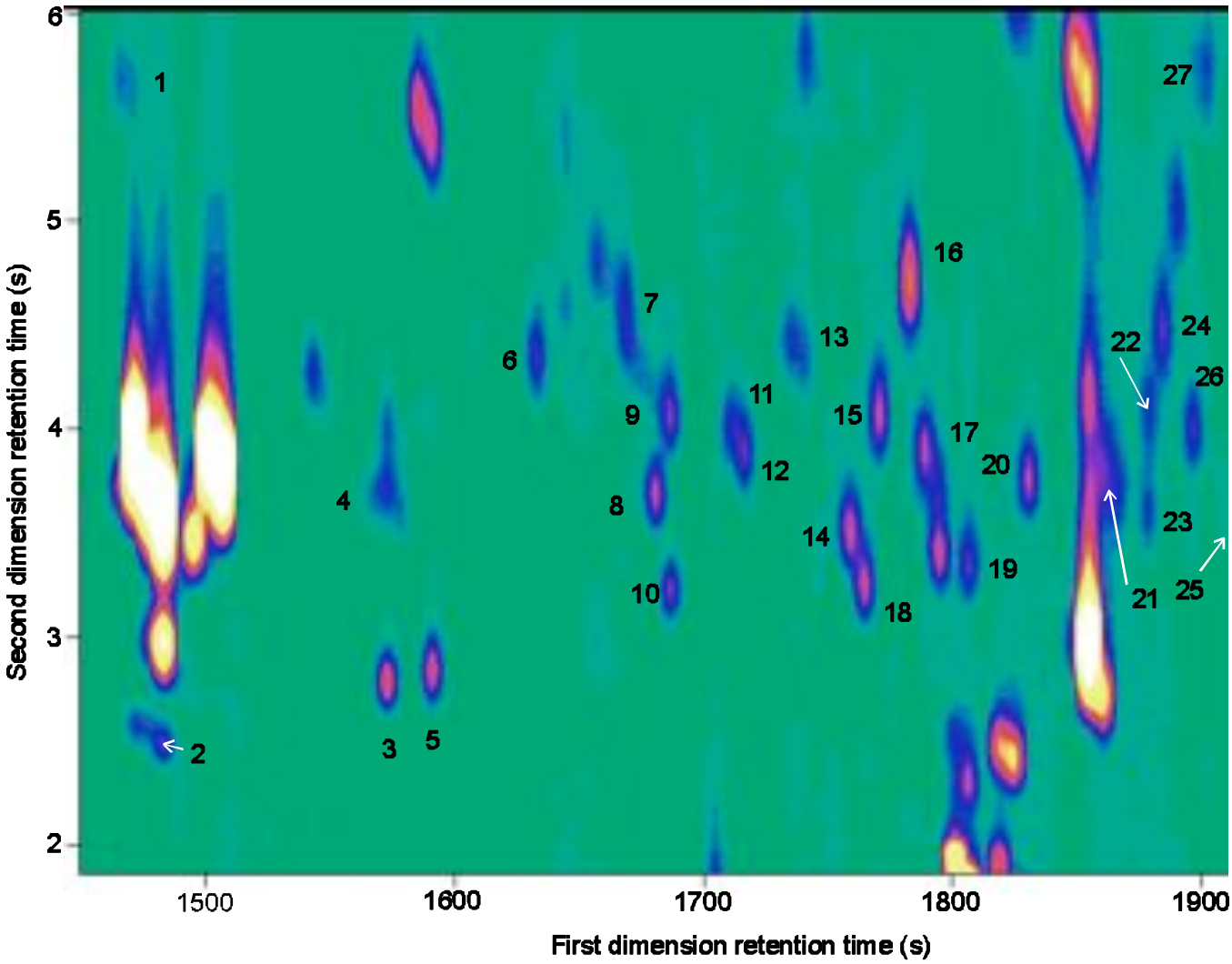

Figure 12.40. Colour plot of the separation of pesticides in a celeriac extract. 1. Dimethoate, 2. Hexachlorobenzene, 3. Propyzamide, 4. Pyrimethanil, 5. Diazinon, 6. Pirimicarb, 7. Parathion-methyl, 8. Chlorpyriphos-methyl, 9. Tolclofos-methyl, 10. Vinclozolin, 11. Metalaxyl, 12. Prometryn, 13. Fenitrothion, 14. Pirimiphos-methyl, 15. Malathion, 16. Fenthion, 17. Parathion-ethyl, 18. Chlorpyriphos-ethyl, 19. Triadimefon, 20. Fenpropimorph, 21. Bromophos-methyl, 22. Chlorfenvinphos, 23. Chlozolinate, 24. Chlorfenvinphos, 25. Quinalphos, 26. Triadimenol, 27. Procymidone.

Pesticides in food extracts (apple)

J. Dallüge , M. van Rijn, J. Beens, R.J.J. Vreuls, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the determination of pesticides in food extracts*, J. Chromatogr. A 965 (2002) 207-217

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 0.25 μm CP-Sil 5CB
Second: 0.8 m × 0.10 mm ID, 0.05 μm BPX50
Modulation capillary:

Carrier gas: helium, constant flow @ 1.3 mL/min

***Temperatures*:**
Main oven: 50°C (4 min), 5°C/min → 280°C
Second oven:

Injector: PTV, split ratio 1:125
Temperature: → 350°C
Injection volume: 0.1 μL

Modulator: moving cryogenic

Modulation time: 6 s

Detector: ToF-MS
Temperature:
Make up gas flow:

Data acquisition: 50 spectra/s

Sample description and separation:

As the identification indicates, dimethoate, provinphos and bupirimate could not be detected with 1D-GC–TOF MS either, since they co-eluted with the most matrix compounds or other analytes, while no problems were encountered once GC×GC–TOF MS was used as an alternative. With triadimenol (1) and pyridaphenthion, rather poor GC–MS results were found to be considerably improved using the GC×GC set-up.

The identification of non-target compounds such as bergaptan, psoralen and hexadecanoic acid in the Fig requires high-quality mass spectra. Here, the much better resolution of GC×GC compared with 1D-GC analysis, which causes co-elution to be less severe, has a beneficial influence.

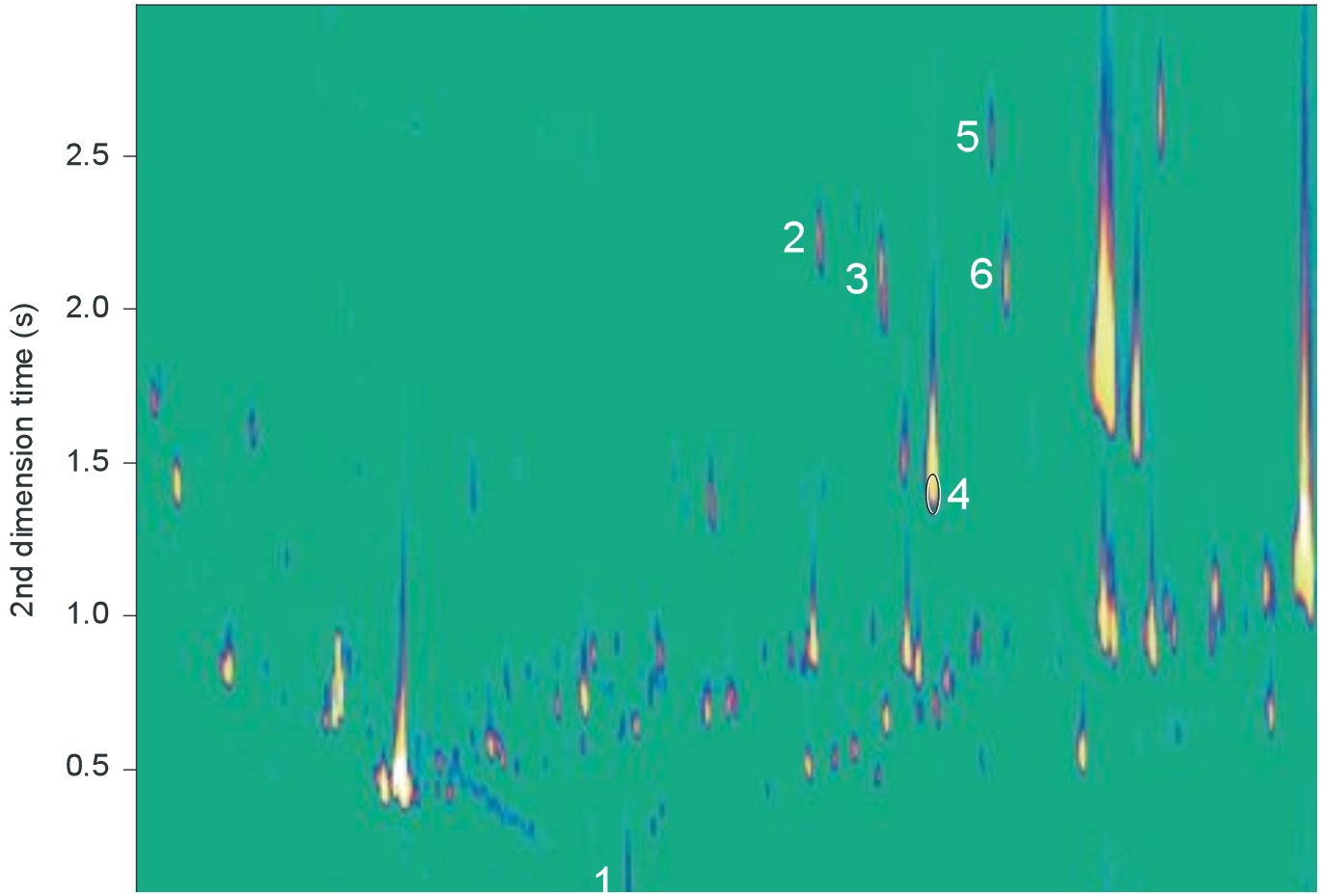

Figure 12.41. Colour plot of the GC×GC–ToF MS separation of an apple extract.
1. Dimethoate, 2. Methyl parathion, 3. Fenitrothion, 4. Chlorpyriphos (coeluting with hexanoic acid), 5. Captan, 6. Tolylfluanide, 7. Azinphos-methyl.

Pesticides in grapes

L. Mondello, A.. Casilli, P.Q. Tranchida, M. Lo Presti, P. Dugo. G. Dugo, *Comprehensive gas chromatography coupled to mass spectrometry for the separation of pesticides in a very complex matrix*, Anal Bioanal Chem (2007) 389:1755–1763

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 µm SLB-5 MS
Second: 1 m × 0.1 mm ID, 0.1 µm Omegawax
Modulation capillary:

Carrier gas: helium, constant pressure @ 242.7 kPa

***Temperatures*:**
Main oven: 70°C, 2°C/min → 300°C
Second oven: 100°C, 2°C/min → 330°C

Injector: split/splitless
Temperature: 300°C
Injection volume: 1µL

Modulator: loop, hot period 375 ms

Modulation time: 6 s

Detector: qMS
Temperature:
Make up gas flow:

Data acquisition: 10,000 amu/s, 50-495 *m/z*

Sample description and separation:

The development of a GC×GC–qMS (rapid scanning) system for the analysis of trace-amount pesticides in a complex real-world sample. Reliable peak assignment was carried out by dedicated pesticide MS library (for GC×GC), characterized by a twin-filter search procedure, the first based on a minimum degree of spectral similarity and the second on the interactive use of linear retention indices (LRI).
The certainty of peak assignment was attained by exploiting both the enhanced separation power of dual-oven GC×GC and the highly effective search procedure.

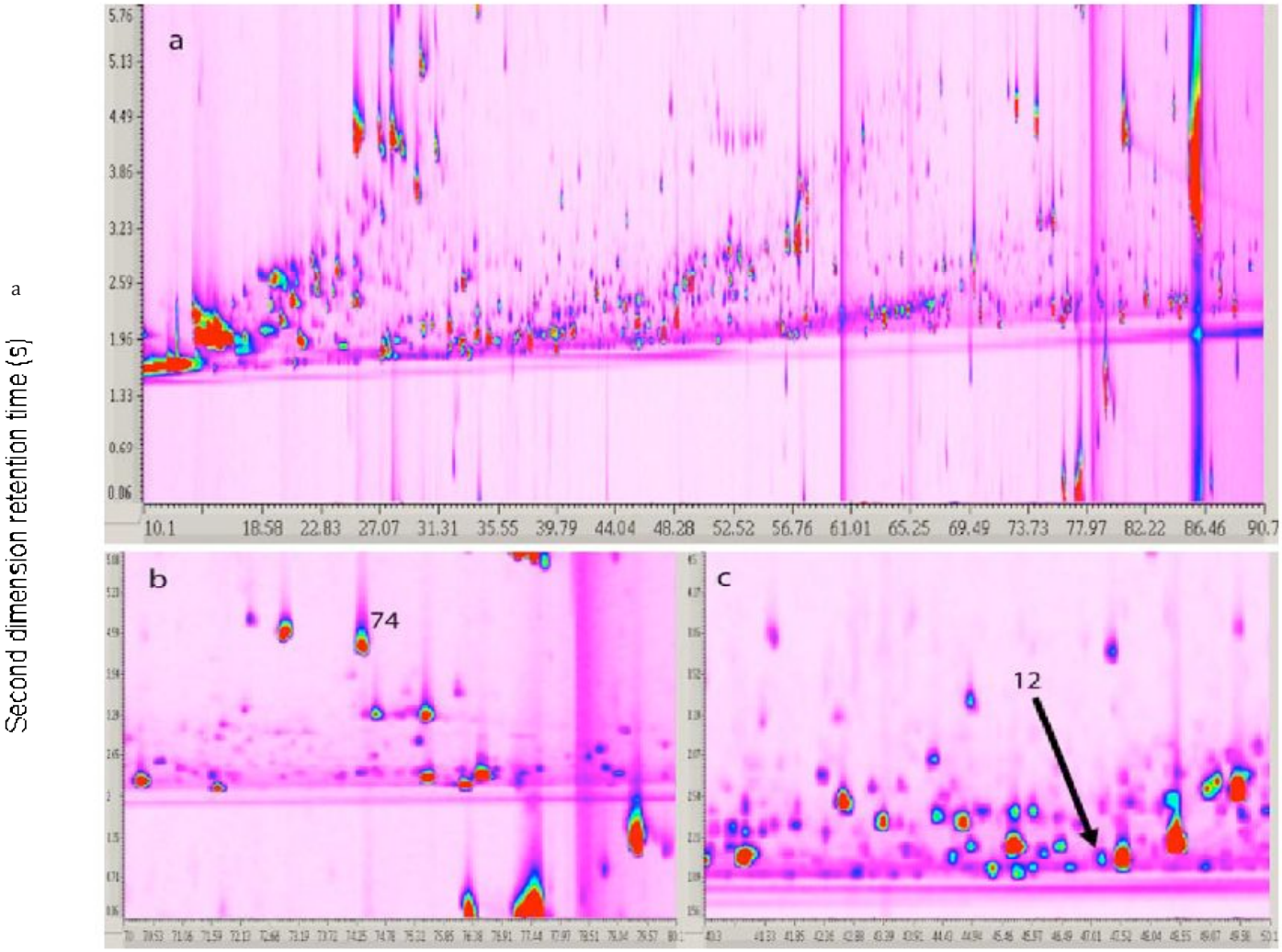

Figure 12.42. GC×GC–qMS analysis of a contaminated red grapefruit extract, (a) TIC 2D chromatogram location of imizalil, (b) TIC 2D chromatogram location of demeton-S-methyl.

Pesticides in animal feed

M.K. van der Lee, G. van der Weg, W.A. Traag, H.G.J. Mol, *Qualitative screening and quantitative determination of pesticides and contaminants in animal feed using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry,* J. of Chromatogr. A, 1186 (2008) 325–339

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 µm Rtx-CL
Second: 2 m × 0.1 mm ID, 0.1 µm BPX-50
Modulation capillary:

Carrier gas: helium, constant pressure @ 324 kPa

***Temperatures*:**
Main oven: 60°C (2 min), 10°C/min → 200°C, 7°C/min → 270°C, 10°C/min → 300°C (15 min)
Second oven: 70°C (3 min), 10°C/min → 360°C (15 min)

Injector: PTV, splitless time 3 min
Temperature: 20°C (0.5 min), 0.5°C/s → 50°C, 6C/s → 280°C (20 min)
Injection volume: 10 µL

Modulator: quad-jet cryogenic

Modulation time: 5 s

Detector: ToF MS
Temperature: ion source 250°C
Make up gas flow:

Data acquisition: 200 spectra/s 50-600 *m/z*

Sample description and separation:

Target analysis of over 100 pesticides and contaminants in a complex feed matrix. It is based on extraction by gel permeation chromatography and dispersive solid-phase extraction with primary secondary amine phase (PSA) before GC×GC analysis. Parameters studied included a dispersive SPE cleanup step after GPC, large volume injection and the GC×GC separation. Qualitative and quantitative performance of the GC×GC system was evaluated by analyzing spiked extracts in the range equivalent to 1–100 _g/kg in feed. At levels of 50 _g/kg and higher, all compounds targeted for could be identified fully automatically by the software based on their mass spectra.

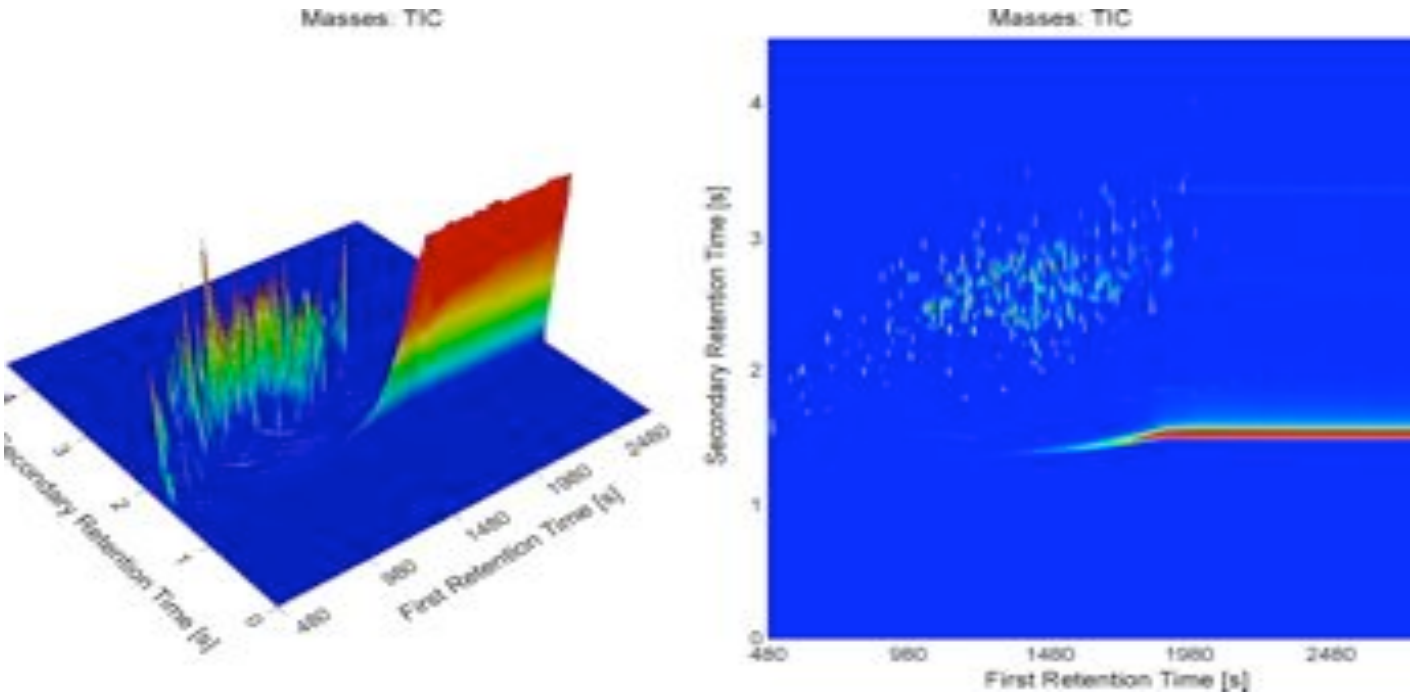

Figure 12.43. Three-dimensional GC×GC–ToF MS image and contour plot obtained after 10µL injection of a standard solution containing 360 pesticides (1 ng on-column for each compound). The high intensity band starting at 1500 (first dimension) and 1.5 s in second dimension is column bleed. Color legend: responses increase from dark blue, light blue, green, yellow, orange, red (red color starts at 1 million counts).

Polyclic aromatics in vegetable oils

G. Purcaro, P.Morrison, S. Moret, L.S. Conte, P.J. Marriott, *Determination of polycyclic aromatic hydrocarbons in vegetable oils using solid-phase microextraction–comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry*, J. of Chromatography 1161 (2007) 284-291

Instrumental conditions:

***Columns*:**
Guard column: 5 m × 0.32 mm ID
First: 30 m × 0.25 mm ID, 0.25 μm BPX-5
Second: 1 m × 0.1 mm ID, 0.1 μm BPX-50
Modulation capillary:

Carrier gas: He

***Temperatures*:**
Main oven: 40°C (2 min), 30°C/min → 210°C, 5°C/min → 360°C (15 min)
Second oven:

Injector: splitless
Temperature: 340°C
Injection volume: SPME fiber (10 min)

Modulator: LMCS

Modulation time: 3 s

Detector: ToF MS (EI mode)
Temperature: ion source 250°C
Make up gas flow:

Data acquisition: 100 spectra/s

Sample description and separation:
Simple solid phase extraction sampling conditions (solvent used, extraction time, extraction temperature and fiber rinsing time) were optimized by using a sample of oil fortified with a standard solution of polycyclic aromatic hydrocarbons. The method was validated by calculating linear range, correlation coefficient, accuracy, repeatability, detection limit and quantification limit. The method was applied to several oils collected from the market and directly from an olive pomace extraction plant.

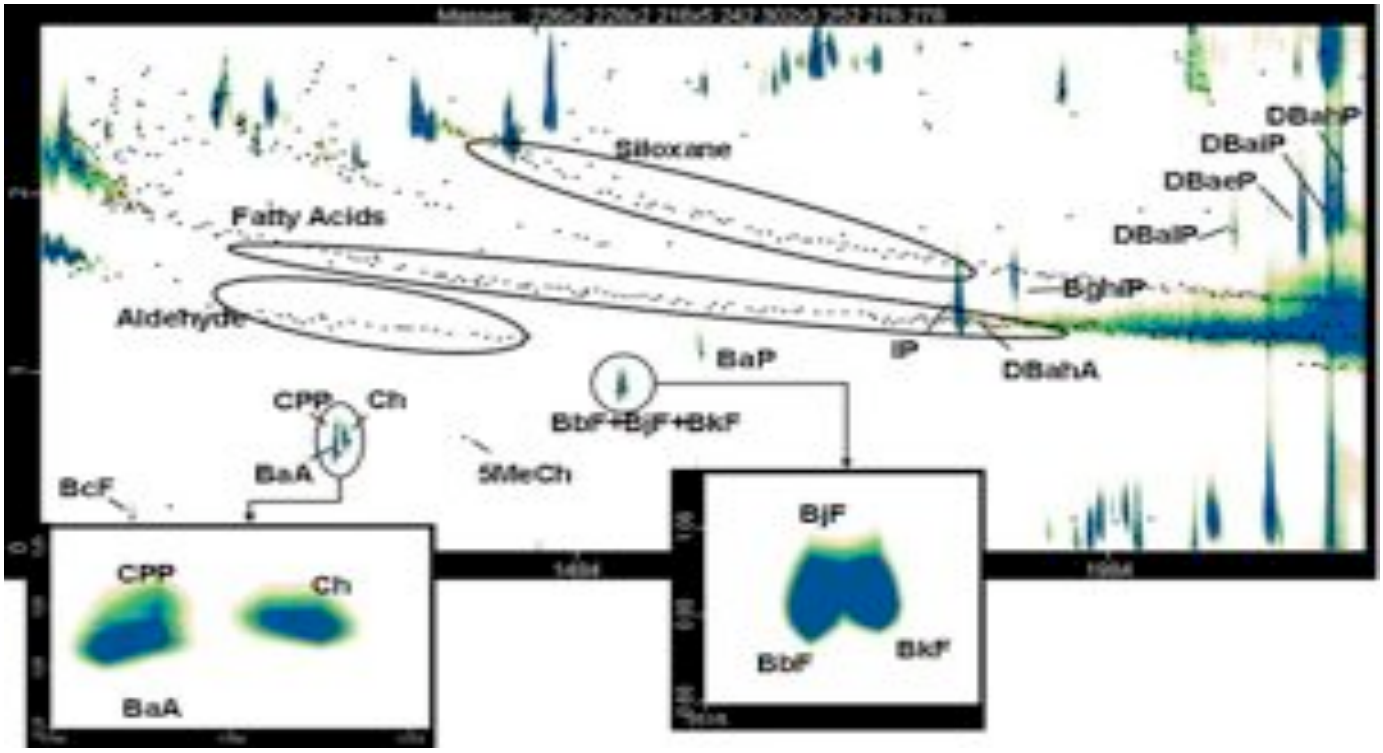

Figure 12.44. Contour plot example of an oil fortified with PAHs. Others class of compounds are present in the chromatogram as identified (aldehydes, fatty acids and siloxanes).

PAHs in soil extract

R. Ong, S. Lundstedt, P. Haglund, P. Marriott, *Pressurised liquid extraction–comprehensive two-dimensional gas chromatography for fast-screening of polycyclic aromatic hydrocarbons in soil*, J. Chromatogr. A, 1019 (2003) 221–232

see also: P.J. Marriott, P. Haglund, R.C.Y. Ong, *A review of environmental toxicant analysis by using multidimensional gas chromatography and comprehensive GC*, Clinica Chimica Acta 328 (2003) 1 –19

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 μm, BPX5
Second: 1.2 m × 0.10 mm ID, 0.10 μm BPX50

Carrier gas: helium, constant pressure @ 16 psi

***Temperatures*:**
Main oven: 80°C (2 min), 8°C/min → 330°C
Second oven:

Injector: splitless (2 min)
Temperature:
Injection volume:

Modulator: LMCS

Modulation time: 5 s

Detector: FID
Temperature: 330°C
Make up gas flow:

Data acquisition: *50* Hz

Sample description and separation:

Pressurised liquid extraction was applied to the extraction of polycyclic aromatic hydrocarbons from contaminated soils from Husarviken in Stockholm, Sweden. The extraction step was followed by GC×GC. PLE provides a reliable extraction technique with all PAHs extracted in one extraction step; no carry over was observed. Since PLE–GC×GC is proposed as a broad screening tool, the demand for precise quantification may be relaxed in the present situation. GC×GC has the added advantage of providing chemical structural information within the two-dimensional contour presentation. Reproducibilities for GC×GC results (peak area) and 2*t*R were acceptable with relative standard deviations of 8 and 1%, respectively (at the mg/kg level), and good repeatability within samples was achieved.

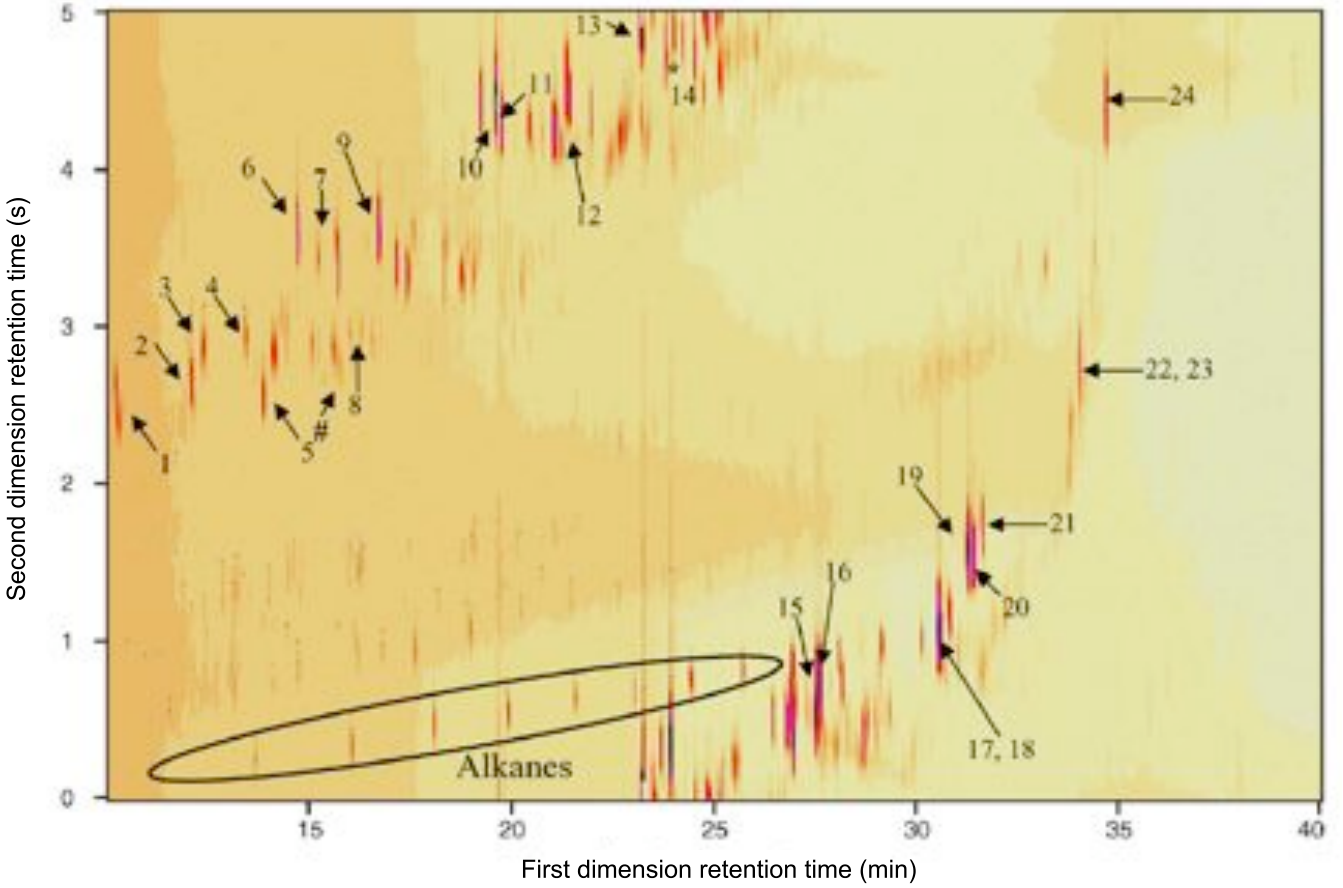

Figure 12.45. Colour plot of GC × GC results for the analysis of the soil sample extracted. For identification of the numbered peaks, see paper.

PAHs in contaminated soil

H. Van De Weghe, G. Vanermen, J. Gemoets, R. Lookman, D. Bertels, *Application of comprehensive two-dimensional gas chromatography for the assessment of oil contaminated soils*, J. Chromatogr. A, 1130 (2006) 122-129

Instrumental conditions:

***Columns*:**
First: 30 m × 0.32 mm ID, 0.25 µm Rtx-1
Second: 0.8 m × 0.10 mm ID, 0.05 µm BPX50
Modulation capillary:

Carrier gas: hydrogen, constant flow @ 1.2 mL/min

***Temperatures*:**
Main oven: 40°C (2.5 min), 25°C/min → 75°C (5 min), 1.7°C/min → 330°C (30 min)
Second oven:

Injector: PTV
Temperature: → 300°C (splitless time 3 min)
Injection volume:

Modulator: cryogenic dual-stage CO_2 jet modulator

Modulation time: 8 s

Detector: FID
Temperature:
Make up gas flow:

Data acquisition: 200 Hz

Sample description and separation:

Sample preparation was limited to pressurized liquid extraction (PLE). Compared to the TPH method (Total Petroleum Hydrocarbon Workin Group), the group-types in the GC×GC analysis are chemically better defined and more specific information is obtained especially for the (toxicologically important) aromatic hydrocarbon fraction. Preliminary results indicate that higher recoveries and lower RSDs are obtained with GC×GC. Furthermore a data processing method was developed to generate TPH results from GC×GC data; the volatility distribution profiles compared very well with conventional TPH data.

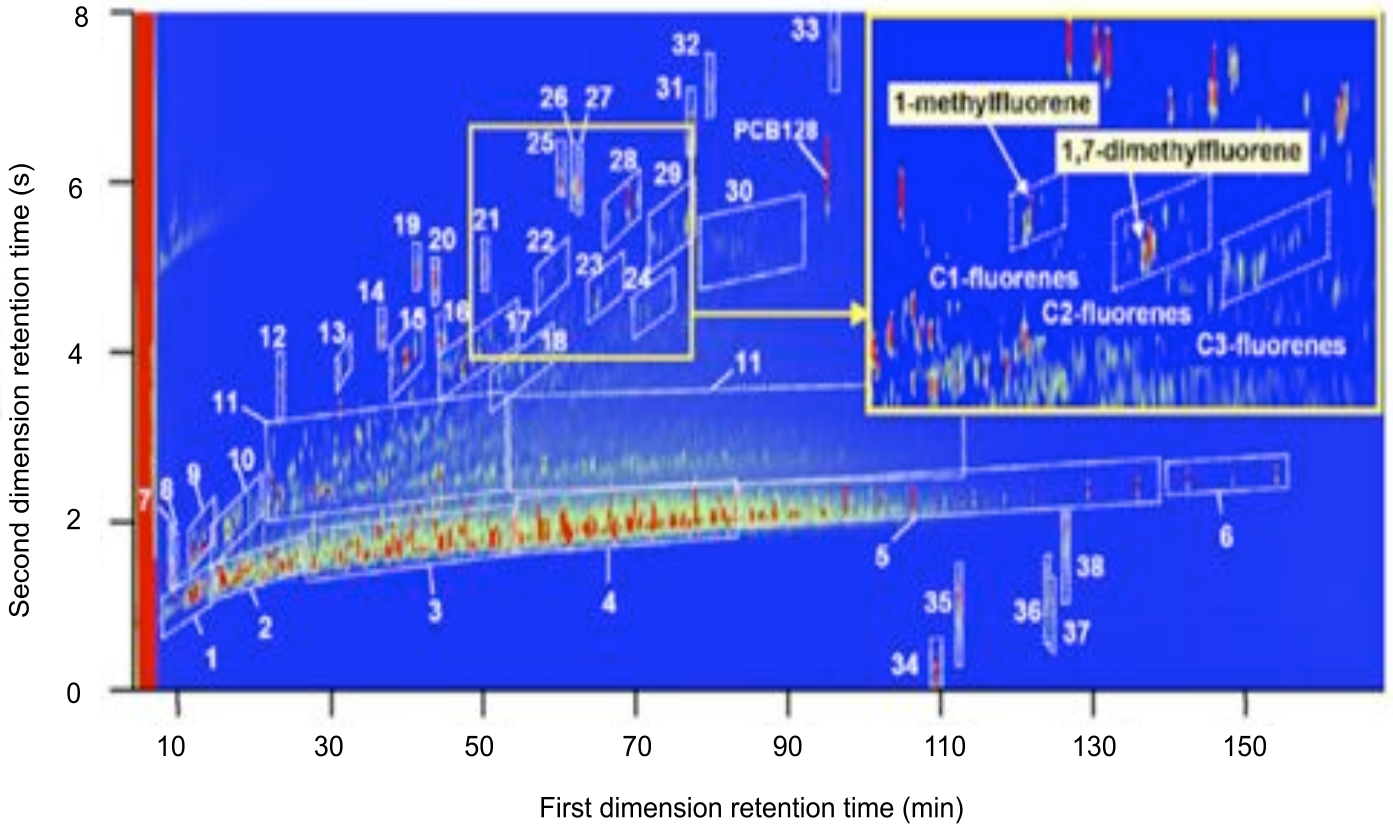

Figure 12.46. Colour plot of an extract of contaminated soil. For identification of the numbered species, see referenced paper.

Extract of fly ash

J. Dallüge, R.J.J. Vreuls, J. Beens, U.A.Th. Brinkman, *Optimization and characterization of comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection (GC×GC–ToF MS),* J. Sep. Sci. 25 (2002) 201-214

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 0.25 μm DB-1
Second: 0.8 m × 0.10 mm ID, 0.1 μm BPX50
Modulation capillary:

Carrier gas: helium, constant flow @ 1.3 mL/min

***Temperatures*:**
Main oven: 70°C (4 min), 5°C/min → 300°C (3 min)
Second oven:

Injector: PTV, solvent vent mode
Temperature: → 360°C
Injection volume: 10 μL

Modulator: LMCS

Modulation time: 6 s

Detector: ToF-MS
Temperature:
Make up gas flow:

Data acquisition: 50 spectra/s

Sample description and separation:

A fly ash sample from a household waste incineration plant was extracted with pentane using pressurized liquid extraction (LPE) at 100ºC at 2000 psi.
Surprisingly, the sample was found to contain a rather high concentration of saturated hydrocarbons (C_{14}–C_{30}), which appear as a horizontal band in the lower part of the colour plot (indicated by P). The clearly visible "band" of siloxanes (S) have even shorter 2D retention times and originate from the sample preparation. It is obvious that both these types of compounds will dramatically interfere in 1D-GC with the compounds of interest, such as chlorinated benzenes and phtalate esters. This will result in poor-quality mass spectra and missed (*i.e*. non-identified) compounds.

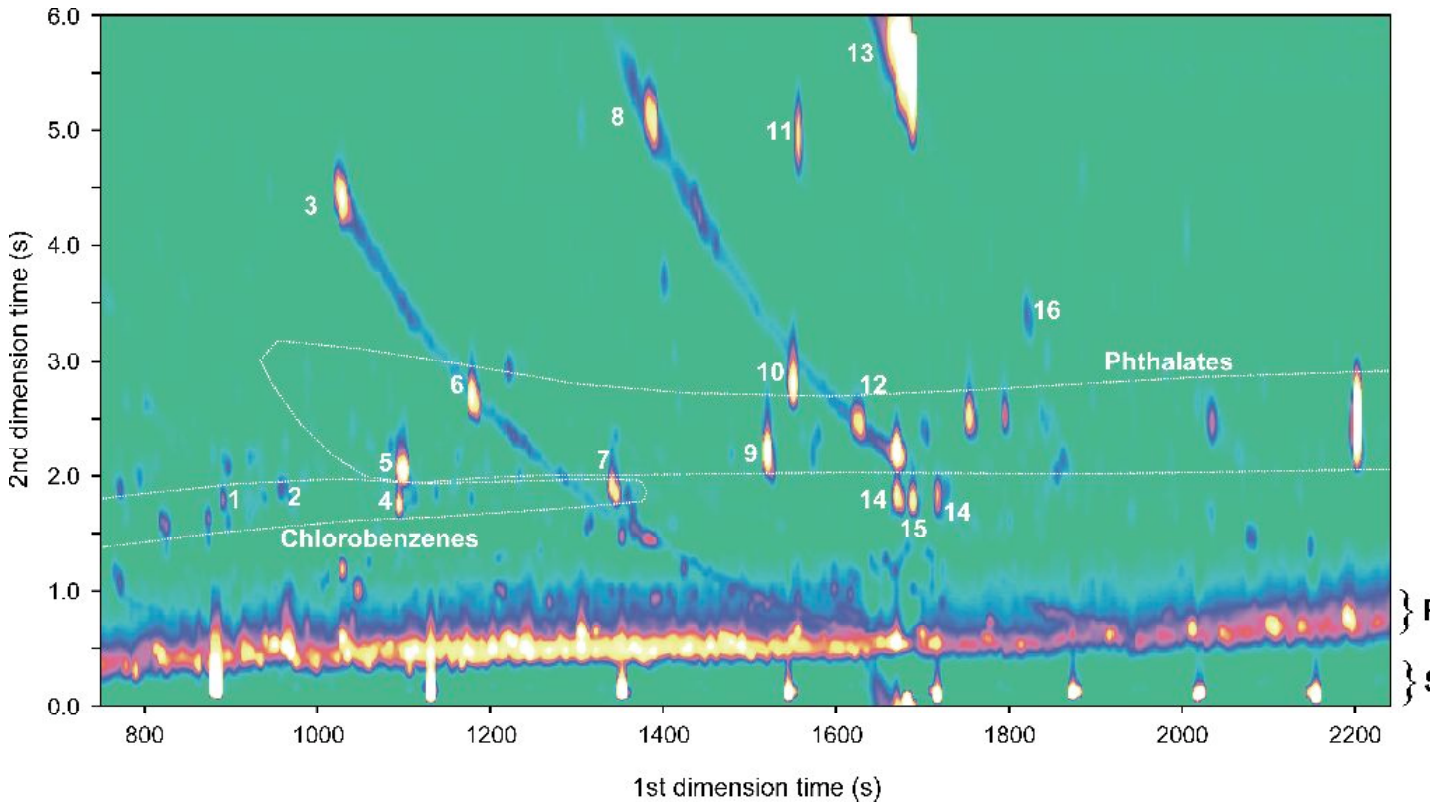

Figure 12.47. GC×GC separation of a fly ash extract of a waste incineration plant, obtained by PLE. 1. Tetrachlorobenzene, 2. 1-bromo-2,4,6-trichlorobenzene, 3. cyclo S_6, 4. pentachlorobenzene, 5. 4-ethoxy ethyl ester of benzoic acid, 6. diethyl-phtalate, 7. hexachlorobenzene, 8. cyclo S_7, 9. and 12. dibutylphtalates, 10. 0rtho terphenyl, 11. diphenyl-sulfone, 13. cyclo S_8, 14. dicyclohexylbenzenes (2 isomers), 15. 4-phenyl-bicyclohexyl, 16. para terphenyl, S. siloxanes, P. saturated hydrocarbons.

Titan tholin pyrolysis products

M. McGuigan, J.H. Waite, H. Imanaka, R.D. Sacks, *Analysis of Titan tholin pyrolysis products by comprehensive two-dimensional gas chromatography–time-of-flight mass spectrometry*, J. Chromatogr. A 1132 (2006) 280-288

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 1.0 μm, DB1
Second: 2 m × 0.10 mm ID, 0.1 μm, Rtx-wax
Modulation capillary:

Carrier gas: hydrogen @ 1.5 mL/min

***Temperatures*:**
Main oven: 40°C (5 min),3°C/min → 190°C (45 min)
Second oven: 45°C (5 min),3°C/min → 195°C (45 min)

Injector: interfaced pyrolyzer, filament 25 mm, 2.5-mm OD, 1.9 mm ID quartz
Temperature: flashed heated → 1000°C < 1 s
Injection volume: split 3:1

Modulator: quad-jet cryo modulator

Modulation time: 11 s

Detector: ToF-MS, 35-350 Da
Temperature:
Make up gas flow:

Data acquisition: 50 spectra/s

Sample description and separation:

The reddish brown haze that surrounds Titan, Saturn's largest moon, is thought to consist of tholin-like organic aerosols. Tholins are complex materials of largely unknown structure. GC×GC with time-of-flight MS detection and a flash pyrolysis inlet is used to characterize tholin pyrolysis products. Identified pyrolysis products include low-molecular-weight
nitriles, alkyl substituted pyrroles, linear and branched hydrocarbons, alkyl-substituted benzenes and PAH compounds. The pyrolysis of standards found in tholin pyrolysate showed that little alteration occurred and thus these structures are likely present in the tholin material.

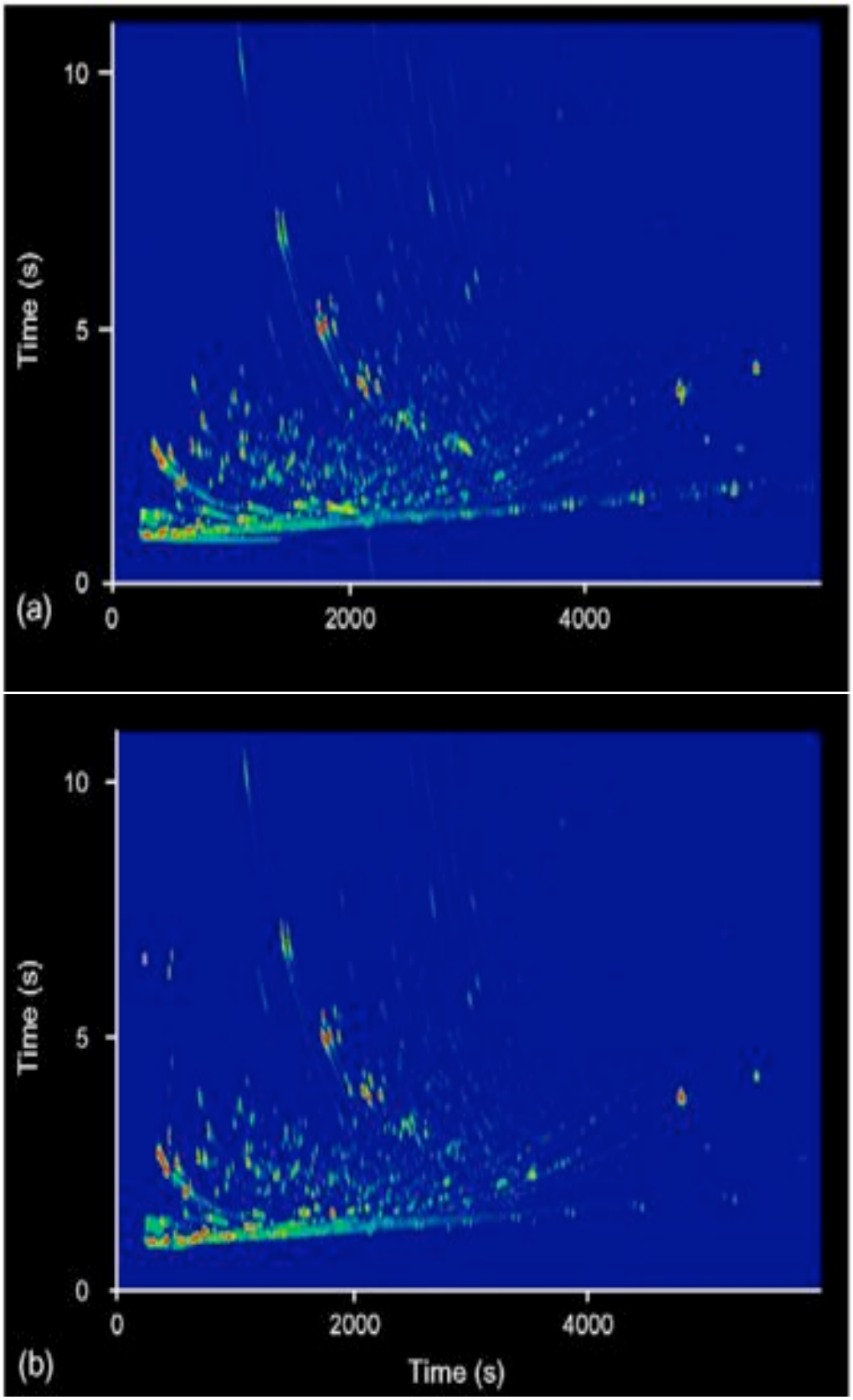

Figure 12.48. GC×GC chromatograms showing the total ion current for the pyrolysis of tholin in H_2 at 600°C using (a) a fresh sample and (b) a sample that was previously pyrolyzed at 250°C and 400°C.

VOCs in urban air

A.C. Lewis and J.M Hamilton, University of Leeds, *unpublished results*

Instrumental conditions:

***Columns*:**
First: 50 m × 0.32 mm ID, 3 μm BP1
Second: 2.3 m × 0.10 mm ID, 0.1 μm BPX50
Modulation capillary:

Carrier gas: helium, two EPC injectors: column 1, 4 mL/min, column 2, 1 mL /min

***Temperatures*:**
Main oven: 35°C (4 min), 8 °C/min → 220 °C (5 min)
Second oven:

Injector: on-line Tenax trap collecting 5 L air at –20°C. Thermally desorbed at 16°C/s → 240°C using 10 mL/min helium for 30 min
Temperature: –20°C to 240°C
Injection volume: 40 mg adsorbent

Modulator: Valco fast switching valve with 100 μm ID, 10μL heated sample loop

Modulation time: 5.3 s

Detector: ToF-MS
Temperature: 240°C ion source, 220°C transfer line
Make up gas flow:

Data acquisition: 50 spectra/s 35-350 amu

Sample description and separation:
A series of oxygenated species, generllay hidden in the hydrocarbon species, can be easily identified.

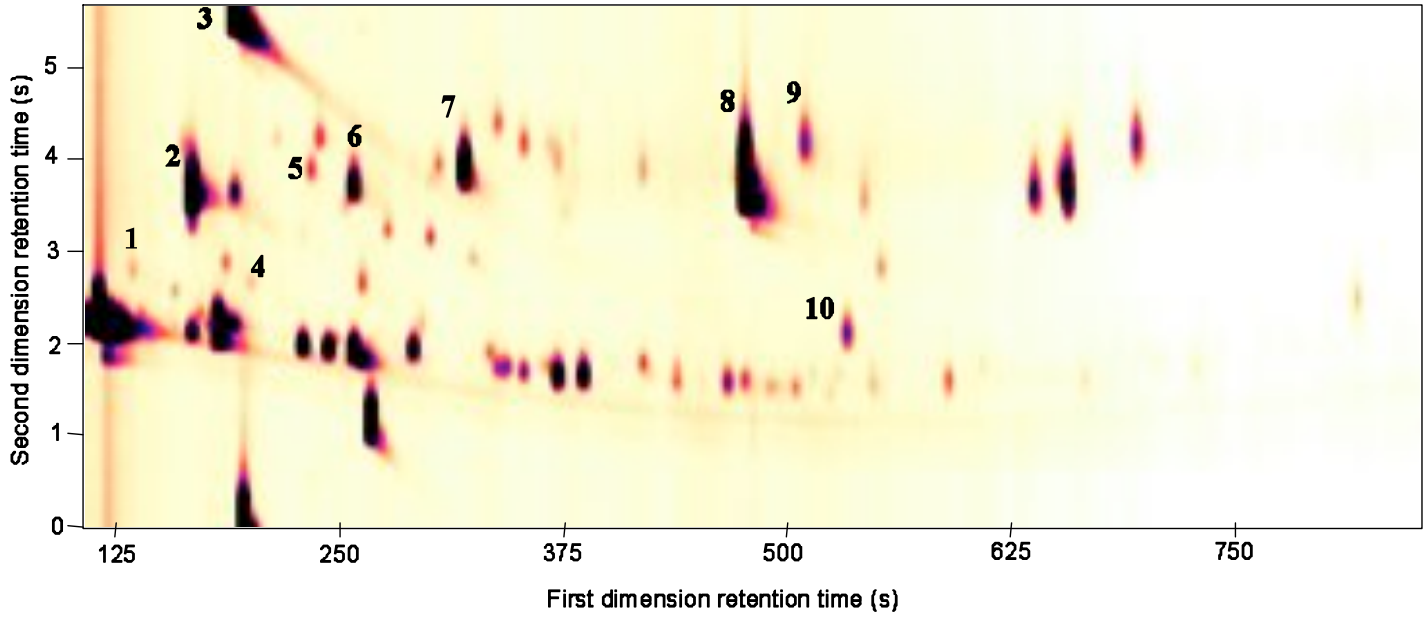

Figure 12.49. Section of a GC×GC separation of VOCs in urban air. 1. acetaldehyde, 2. acetone, 3. DCM, 4. CS_2, 5. butanal, 6. ethylacetate, 7. benzene, 8. toluene, 9. hexanal, 10. tetrame-THF.

Aromatics in urban air

J.F. Hamilton, A.C. Lewis, *Monoaromatic complexity in urban air and gasoline assessed using comprehensive GC and fast GC–ToF MS*, Atmos. Environ. 37 (2003) 589-602

Instrumental conditions:

***Columns*:**	
First:	50 m × 0.32 mm ID, 3 μm BP1
Second:	2.3 m × 0.10 mm ID, 0.1 μm BPX50
Modulation capillary:	
Carrier gas:	helium, two EPC injectors: column 1, 4 mL/min, column 2, 1 mL /min
***Temperatures*:**	
Main oven:	35°C (4 min), 8 °C/min → 220°C (5 min)
Second oven:	
Injector:	on-line Tenax trap collecting 5 L air at –20°C. Thermally desorbed at 16°C/s → 240°C using 10 mL/min helium for 30 min
Temperature:	–20°C to 240°C
Injection volume:	40 mg adsorbent
Modulator:	Valco fast switching valve with 100 μm ID, 10 μL heated sample loop
Modulation time:	5.3 s
Detector:	ToF-MS
Temperature:	240°C ion source, 220°C transfer line
Make up gas flow:	
Data acquisition:	50 spectra/s 35-350 amu

Sample description and separation:

The enhanced resolution achieved using the multidimensional technique is very clear, and in the higher boiling regions that are successively expanded at higher gain in the Fig., there are many hundreds of components individually isolated in the C_5-aromatic to C_8-aromatic range. The peak amplitude enhancement combined with the separation power of the GC×GC system allows observation of very low concentration of species which are normally either below the detection limit or masked by the signal of other components.

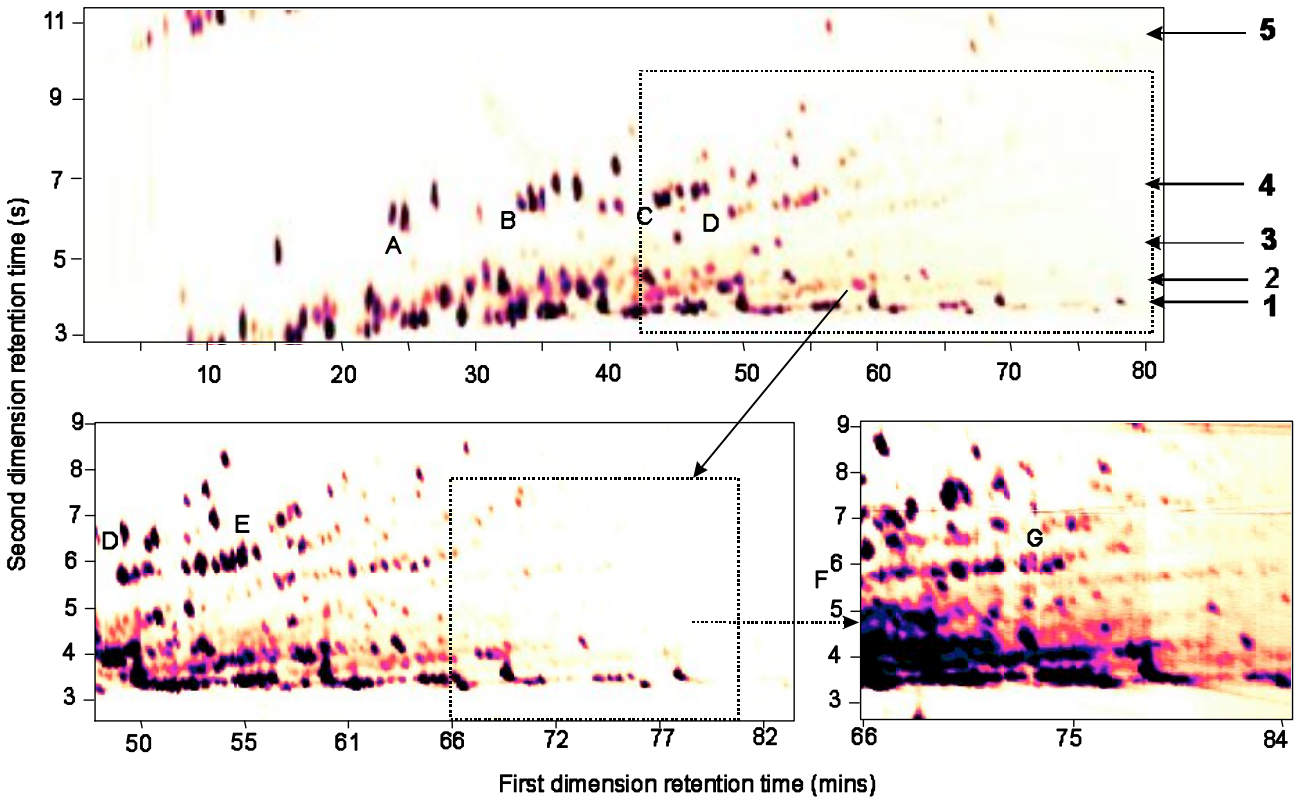

Figure 12.50. GC×GC separations of a Leeds urban air sample. Areas of the full chromatogram are successively extracted at higher gain to illustrate increasing isomeric complexity at higher boiling points. GC×GC chromatograms are annotated with start of individual Cx isomer band (running right to left) where A = C_2 ,B = C_3 ,C = C_4 ,D = C_5 , E = C_6 ,F = C_7 ,G = C_8 . H = naphthalene.
Chemical banding assignments, 1. aliphatic, 2. olefins, 3. oxygenates, 4. mono-aromatics, 5. polyaromatics.

Indoor Air

J.V. Seeley, F.J. Kramp, K.S. Sharpe, and S.K. Seeley, *Characterization of gaseous mixtures of organic compounds with dual-secondary column comprehensive two-dimensional gas chromatography,* J. Sep. Sci., 25, 53-59, 2002

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 1.4 µm DB-624
Second: secondary A: 5 m × 0.25 mm ID, 0.25 µm DB-Wax
secondary B: 5 m × 0.25 mm ID, 0.50 µm DB-210

Carrier gas: first 0.75 mL/min
second 20 mL/min (evenly split between two secondary columns)

***Temperatures*:**
Main oven: 40°C (0.5 min), 33°C/min → 95°C, 23.7°C/min → 140°C, 16.5°C/min → 200°C, 200°C (1 min)

Injector: thermal desorption of multi-layer sorbent tube, 1:3 inlet split
Temperature: 300ºC
Injection volume: up to 3.0 L of air passed through tubes prior to desorption

Modulator: 6-port diaphragm valve operated with differential flow conditions.

Modulation time: 1 s

Detector: FID
Temperature: 200°C
Make up gas flow:

Data acquisition: 200 Hz

Sample description and separation:

Gaseous samples were collected on multi-layer sorbent tubes containing 200 mg of Carbotrap C, 200 mg of Carbotrap, and 100 mg Carbosieve adsorbents. Similar sampling tubes have been shown to effectively trap VOCs within the volatility range of C_3 - C_{15} alkanes. Gaseous VOCs were collected by drawing air through sorbent tubes at 100 mL/min. Sorbent tubes were heated to 45 ºC during sampling to reduce water accumulation. Air samples were drawn directly through the tubes for 30 min. VOCs collected on the sorbent tubes were injected into the GC×2GC system with a Perkin-Elmer ATD 400 thermal desorption unit. The chromatogram is typical of those obtained for laboratory air.

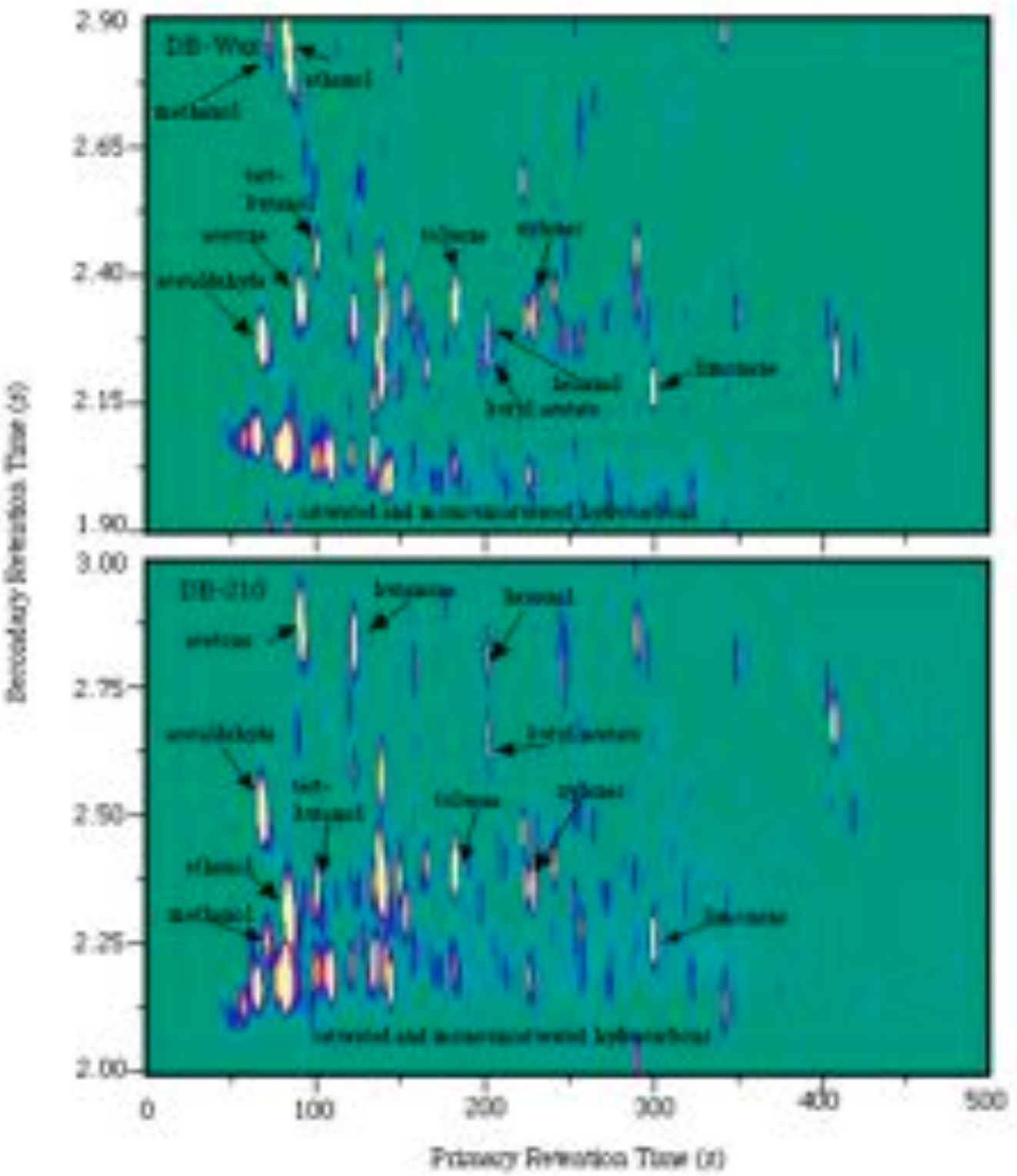

Figure 12.51. GC×2GC colour plot of indoor air.
The upper plot is the result of the secondary DB-Wax-separation, which gives the structures of the saturates and aromatics; the lower plot of the DB-210-separation, which adds the separation of the more polar compounds.

Outdoor Air

(J.V. Seeley, F.J. Kramp, K.S. Sharpe, and S.K. Seeley, *Characterization of gaseous mixtures of organic compounds with dual-secondary column comprehensive two-dimensional gas chromatography*, J. Sep. Sci., 25, 53-59, 2002

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 1.4 µm DB-624
Second: secondary A: 5 m × 0.25 mm ID, 0.25 µm DB-Wax
secondary B: 5 m × 0.25 mm ID, 0.50 µm DB-210

Carrier gas: first 0.75 mL/min
second 20 mL/min (evenly split between two secondary columns)

***Temperatures*:**
Main oven: 40°C (0.5 min), 33°C/min → 95°C, 23.7°C/min → 140°C,
16.5°C/min → 200°C, 200°C (1 min)

Injector: thermal desorption of multi-layer sorbent tube, 1:3 inlet split
Temperature: 300ºC
Injection volume: up to 3.0 L of air passed through tubes prior to desorption

Modulator: 6-port diaphragm valve operated with differential flow conditions.

Modulation time: 1 s

Detector: FID
Temperature: 200°C
Make up gas flow:

Data acquisition: 200 Hz

Sample description and separation:

Gaseous samples were collected on multi-layer sorbent tubes containing 200 mg of Carbotrap C, 200 mg of Carbotrap, and 100 mg Carbosieve adsorbents. Similar sampling tubes have been shown to effectively trap VOCs within the volatility range of C_3 - C_{15} alkanes. Gaseous VOCs were collected by drawing air through sorbent tubes at 100 mL/min. Sorbent tubes were heated to 45ºC during sampling to reduce water accumulation. Air samples were drawn directly through the tubes for 30 mins. VOCs collected on the sorbent tubes were injected into the GC×2GC system with a Perkin-Elmer ATD 400 thermal desorption unit. The chromatogram is typical of those obtained for outdoor air in suburban and rural locations.

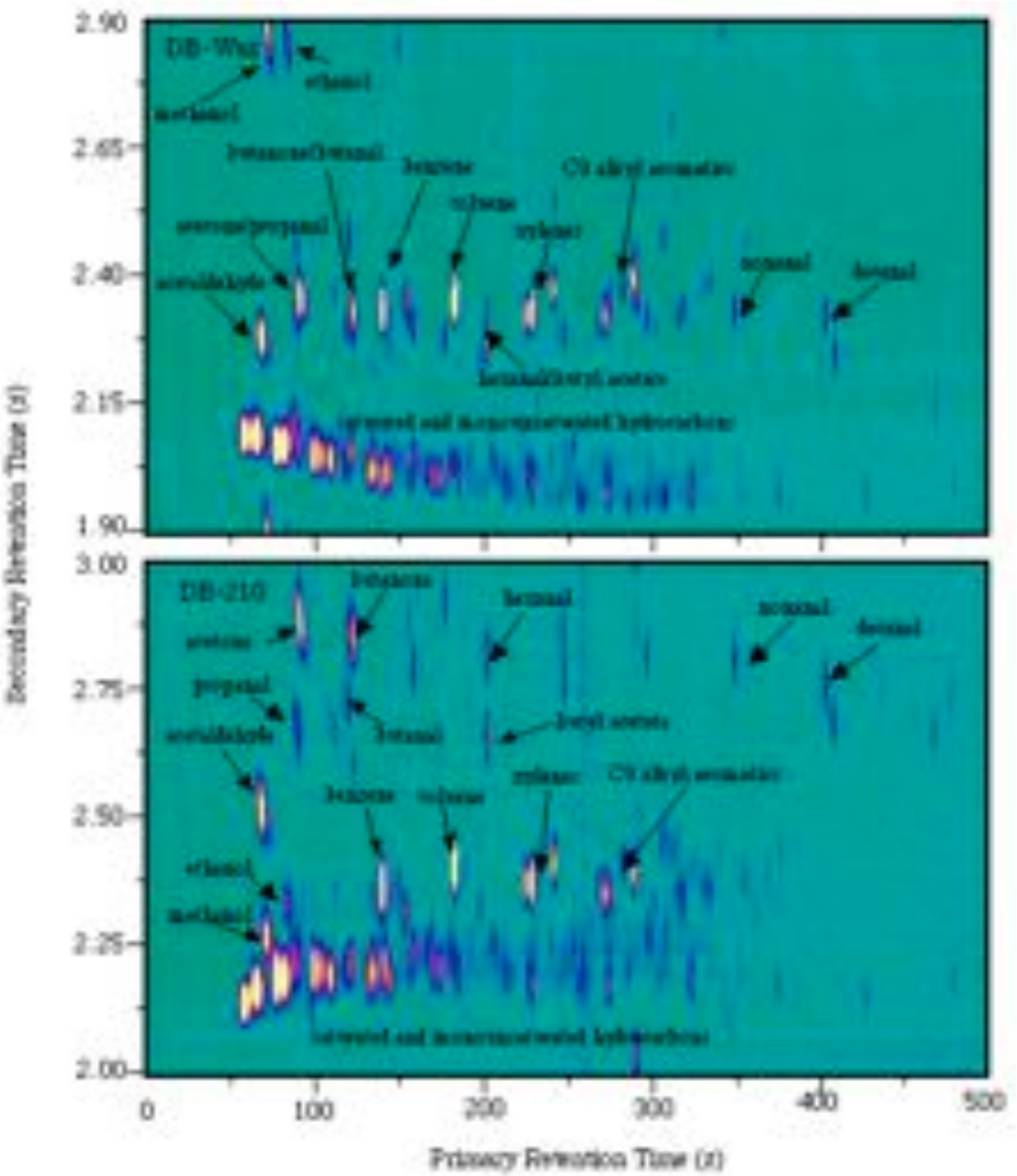

Figure 12.52. GC×2GC colour plot of outdoor air.
The upper plot is the result of the secondary DB-Wax-separation, which gives the structures of the saturates and aromatics; the lower plot of the DB-210-separation, which adds the separation of the more polar compounds.

Organic compounds in atmospheric aerosols from coniferous forest

T. Hyötyläinen, M. Kallio, K. Hartonen,M. Jussila, S. Palonen, M-L. Riekkola, *Modulator design for comprehensive two-dimensional gas chromatography: quantitative analysis of polyaromatic hydrocarbons and polychlorinated biphenyls,* Anal. Chem., 74 (2002) 4441-4446

Instrumental conditions:

***Columns*:**
First: 20 m, 0.25 mm ID, 0.25 µm HP 5MS
Second: 0.7 m, 0.1mm ID, 0.1 µm BGB1701
Modulation cap.:

Carrier gas: hydrogen @ constant flow, 170 kPa (60ºC)

***Temperatures*:**
Main oven: 60°C (5 min), 5°C/min → 300°C, (8 min)
Second oven:

Injector: splitless
Temperature: 300°C
Injection volume:

Modulator: dual-jet cryogenic

Modulation time: 5 s

Detector: ToF, EI-mode
Temperature: 300 °C, interface 300ºC, ionization source 150ºC
Make up gas flow: nitrogen, 150 mL/min

Data acquisition: 50 Hz

Sample description and separation:

GC×GC–TOF–MS was applied in the identification of organic compounds in atmospheric aerosols from coniferous forest. The samples were collected at Hyytiälä, Finland, as part of the QUEST campaign, in Spring 2003. Manual and automated search procedures were compared in the identification. An automated procedure
is preferable when a large number of data files need to be processed; but manual search was more accurate with the present samples, where the number of compounds was large and most of the compounds of interest were present at trace level. Altogether, about 50 compounds were identified on the basis of mass spectra and linear retention indices. The identified compounds included oxidised monoterpenes, acyclic alkanes, alkenes,
ketones and aldehydes, as well as a few alcohols, acids, and aromatic compounds.

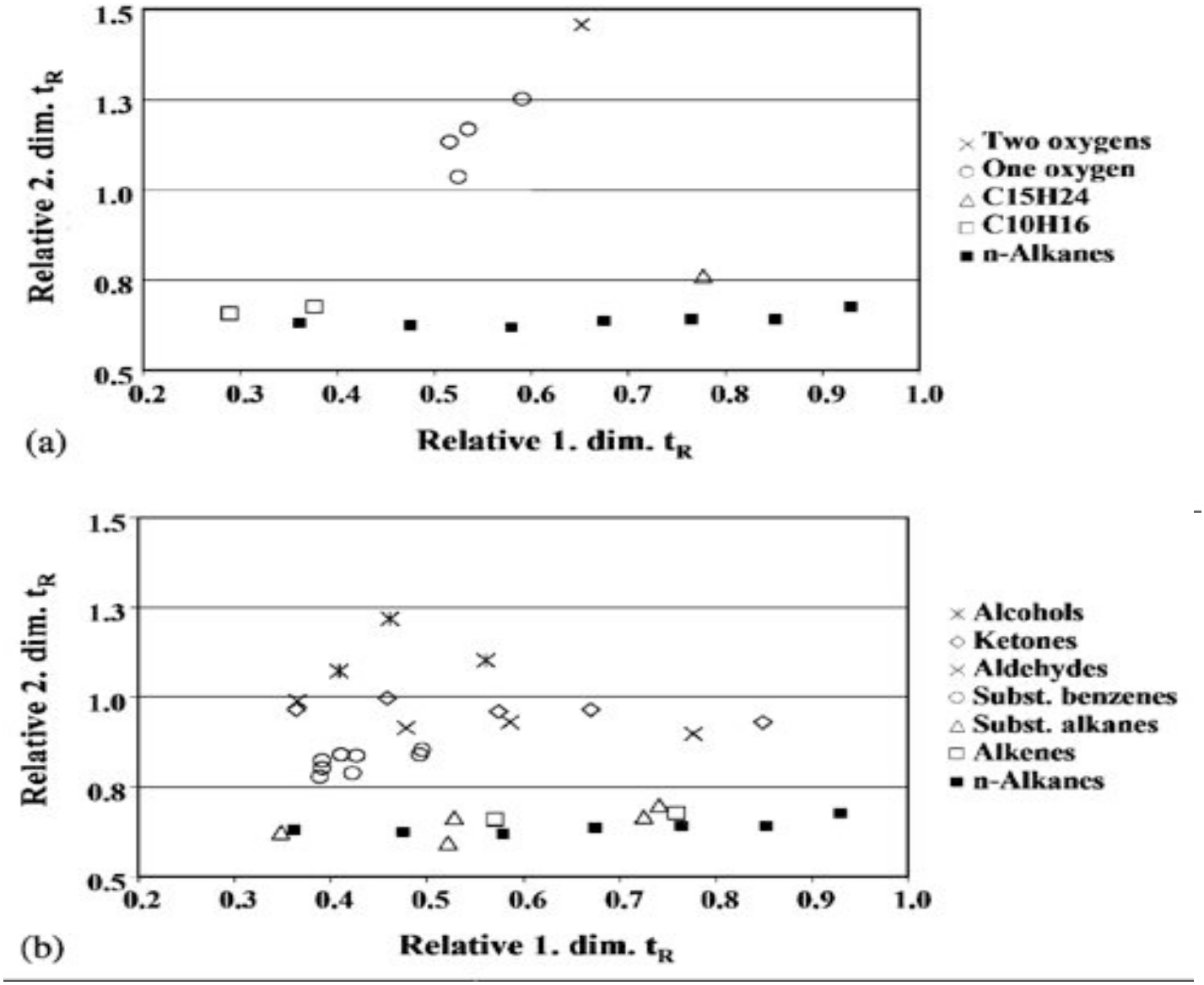

Figure 12.53. Apex plots of compound types identified in aerosol samples from Hyytiälä:
(a) cyclic and oxygenated hydrocarbons, (b) other compounds.
(b) Retention times are shown in relative scale and obtained by dividing the first and second dimension retention times by those of the internal standard.

Human breath samples

M. Libardoni, P.T. Stevens, J. Hunter Waite, R. Sacks, *Analysis of human breath samples with a multi-bed sorption trap and comprehensive two-dimensional gas chromatography (GC×GC)*, J. Chromatogr. B Analyt Technol Biomed Life Sci. 842 (2006) 13-21

Instrumental conditions:

***Columns*:**
First: 30 m, 0.25 mm ID, 0.25 µm Rtx-
Second: 1.5 m, 0.10 mm ID, 0.1 µm Rtx-wax
Modulation cap.:

Carrier gas: hydrogen, 2.2 mL/min

***Temperatures*:**
First column: at column heating 22°C (3 min), 3 °C/min → 175°C
Second column(oven) 30°C (3 min), 3 °C/min → 185°C

Injector: sorption trap
Temperature: → 300°C, pulsed
Injection volume:

Modulator: single stage thermal modulator

Modulation time: 5 s

Detector: FID

Data acquisition: 200 Hz

Sample description and separation:

The multoi-stage sorption trap uses four discreet beds, three containing different grades of graphitized carbon and one containing a carbon molecular sieve. The ordering of the beds in the trap tube is from the weakest to strongest adsorbent during sample collection. Breath samples are collected in gas sampling bags, and samples are passed through the trap at a flow rate of about 50 cm3/min. After sample collection, hydrogen carrier gas flow is initiated in the direction opposite to the sample collection flow, and the metal trap tube is resistively heated to inject a sample plug into the GC×GC. Performance data for the combined GC×GC−sorption-trap instrument is described, and human breath-sample chromatograms are presented

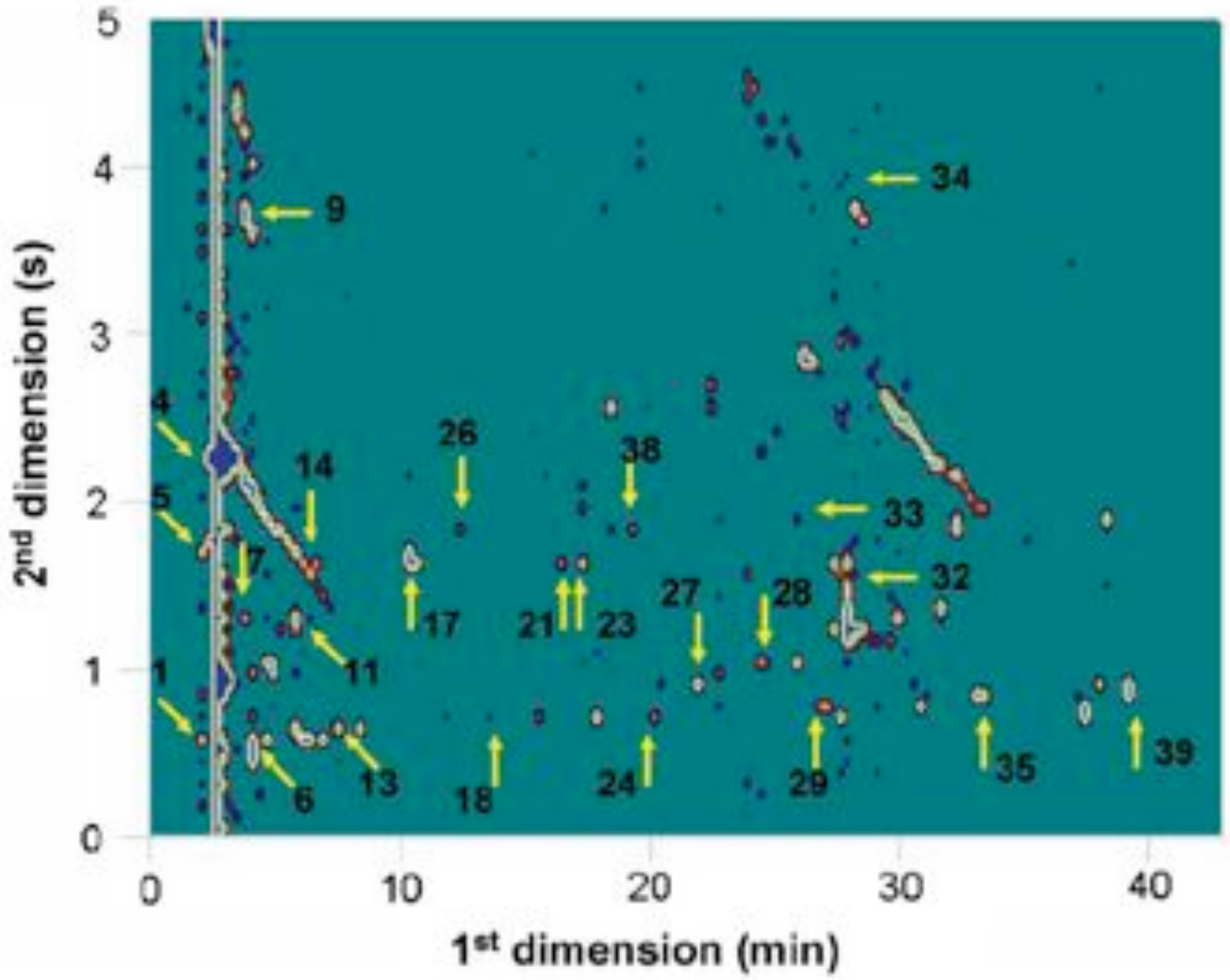

Figure 12.54. Two-dimensional (contour) chromatogram of human breath sample.

Volatiles in creosote-treated railway sleepers

E.P. Mateus, M.D.R. Gomes da Silva, A.B. Ribeiro, P.J. Marriott, *Qualitative mass spectrometric analysis of the volatile fraction of creosote-treated railway wood sleepers by using comprehensive two-dimensional gas chromatography*, J. Chromatogr. A 1187 (2008) 215-222

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 μm BPX-5
Second: 0.5 m × 0.15 mm ID, 0.25 μm BPX-50
Modulation capillary:

Carrier gas: hydrogen @ 1 mL/min

***Temperatures*:**
Main oven: 35°C (1 min), 20°C/min → 170°C, 2°C/min → 290°C (20 min)
Second oven: 70°C (3 min), 10°C/min → 360°C (15 min)

Injector: pulse splitless purge time 1 min, split 1:20 after 2 min
Temperature: 300°C
Injection volume: 1 μL

Modulator: LMCS

Modulation time: 6 s

Detector: ToF MS
Temperature: ion source 250°C
Make up gas flow:

Data acquisition: 100 spectra/s 45-600 *m/z*

Sample description and separation:

The volatile composition of 20-year-old out-of-service creosote-treated railway wood sleepers was studied. The emitted volatile fraction was collected by dynamic purge-and-trap concentration at ambient temperature, The analysis of mass spectrometry data and GC×GC retention time allowed the tentative identification of about 300 compounds based on spectrometric data and positioning of each compound in the GC×GC plot. Major important headspace components are polyaromatic hydrocarbons, phenols and benzene derivatives, hydrocarbons and heterocyclic compounds containing nitrogen, sulphur or oxygen atoms.

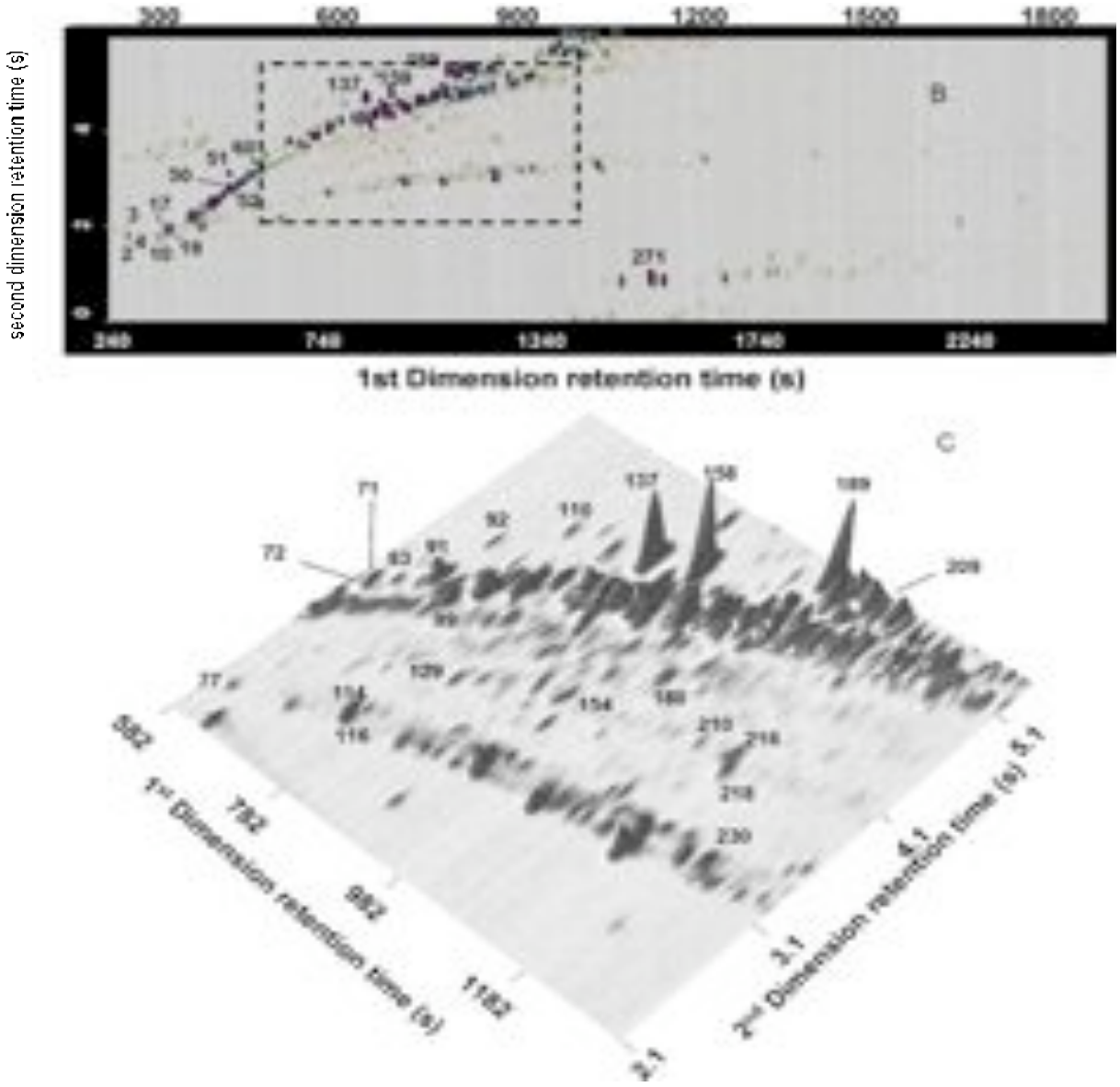

Figure 12.55. Contour plot after GC×GC–ToF MS analysis. It is indicated the enlarged zone in (C) which presents a 3D representation showing individual compounds separation. For peak assignments see referenced paper.

Nanoparticles roadside atmosphere

N. Ochiai, T. Ieda, K. Sasamoto, A. Fushimi, S. Hasegawa, K. Tanabe, S. Kobayashi, *Comprehensive two-dimensional gas chromatography coupled to high-resolution time-of-flight mass spectrometry and simultaneous nitrogen phosphorous and mass spectrometric detection for characterization of nanoparticles in roadside atmosphere*, J. Chromatogr. A, 1150 (2007) 13–20

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 μm BPX5
Second: 1 m × 0.1 mm ID, 0.1 μm BPX50
Modulation capillary:

Carrier gas: helium @ 2.5 mL/min (ToF MS) and 1.83 mL/min (NPD)

***Temperatures*:**
Main oven: 50°C (3 min), 5°C/min → 350°C (10 min)
Second oven:

Injector: PTV
Temperature:
Injection volume: 1μL

Modulator: loop, hot period 300 ms

Modulation time: 6 s

Detector: split to ToF MS and NPD
Temperature:
Make up gas flow:

Data acquisition: 26.316 spectra/s, 100 Hz (NPD)

Sample description and separation:
Size-resolved particles including the fraction with a diameter of 29–58 nm. Thermal desorption followed by GC×GC with novel detection capabilities, including HRToF MS and simultaneous NPD and a qMS. Quantitative analysis of selected was performed by TD–GC×GC–qMS with limited scan range. The method showed good linearity ($r^2 > 0.988$) and high sensitivity (limit of quantification: <10 pg) for most of the target PAHs.

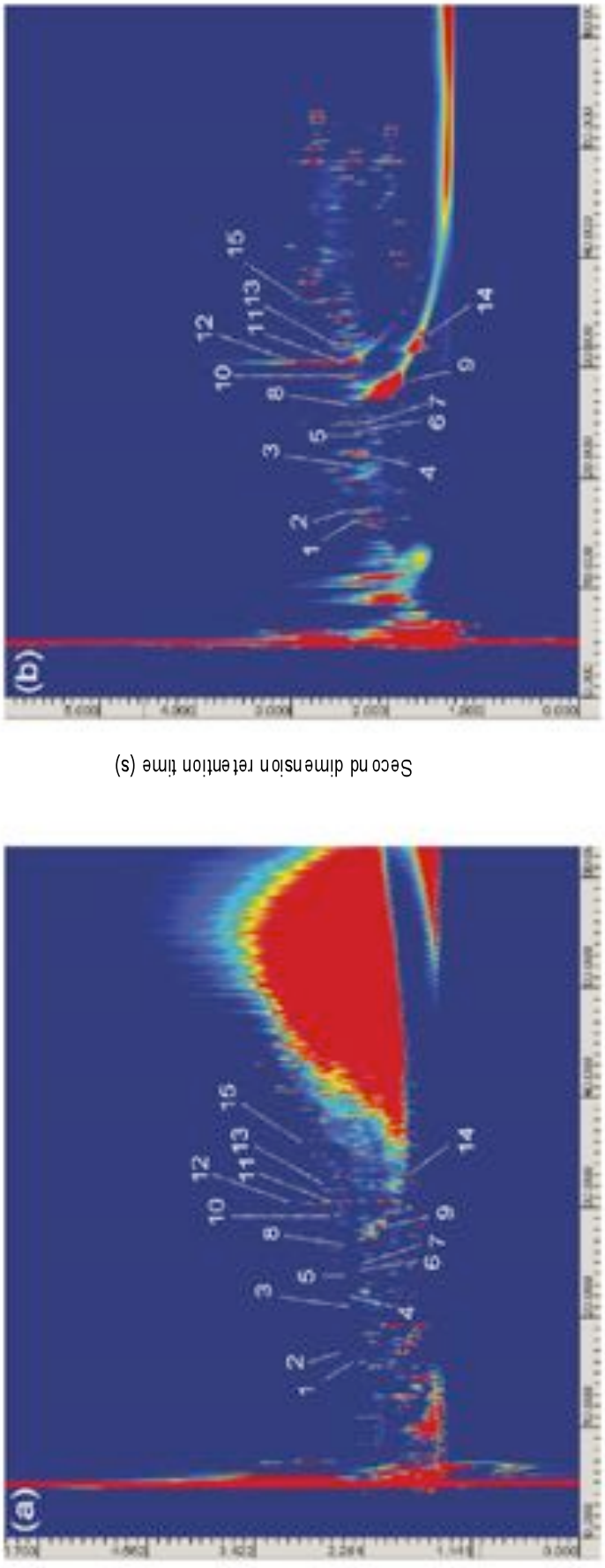

Figure 12.56. Comparison of the two-dimensional chromatograms obtained by TD–GC×GC–NPD/qMS of S2 (Dp 58–102 nm; 4.6_g-PM): (a, bottom) total ion chromatogram and (b, top) NPD chromatogram. The marked peaks represent tentatively identified nitrogen-containing compounds.

Incense smoke

T.C. Tran, P.J. Marriott, *Characterization of incense smoke by solid phase microextraction—comprehensive two-dimensional gas chromatography (GC×GC)*, Atmospheric Environment 41 (2007) 5756–5768

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 µm BPX5
Second: 1 m × 0.1 mm ID, 0.1 µm BP20
Modulation capillary:

Carrier gas: hydrogen @ 1.5 mL/min

***Temperatures*:**
Main oven: 40°C (2 min), 5°C/min → 260°C
Second oven:

Injector: splitless
Temperature: 250°C
Injection volume: fiber

Modulator: LMCS

Modulation time: 6 s

Detector: ToF MS
Temperature:
Make up gas flow:

Data acquisition: not specified

Sample description and separation:

One stick of each incense sample was powdered and transferred to a 4mL glass vial in order to sample the fragrance/essential oil H/S. A fiber was directly exposed to the smoke of burning incense.

A total of 324 compounds were tentatively identified, with more than 100 compounds in incense powders and more than 200 compounds in the incense smoke, by using GC coupled to quadrupole mass spectrometric detection. The smoke stream comprised compounds originating from the incense powder, and combustion products such as PAH, N-heterocyclics, and furans.

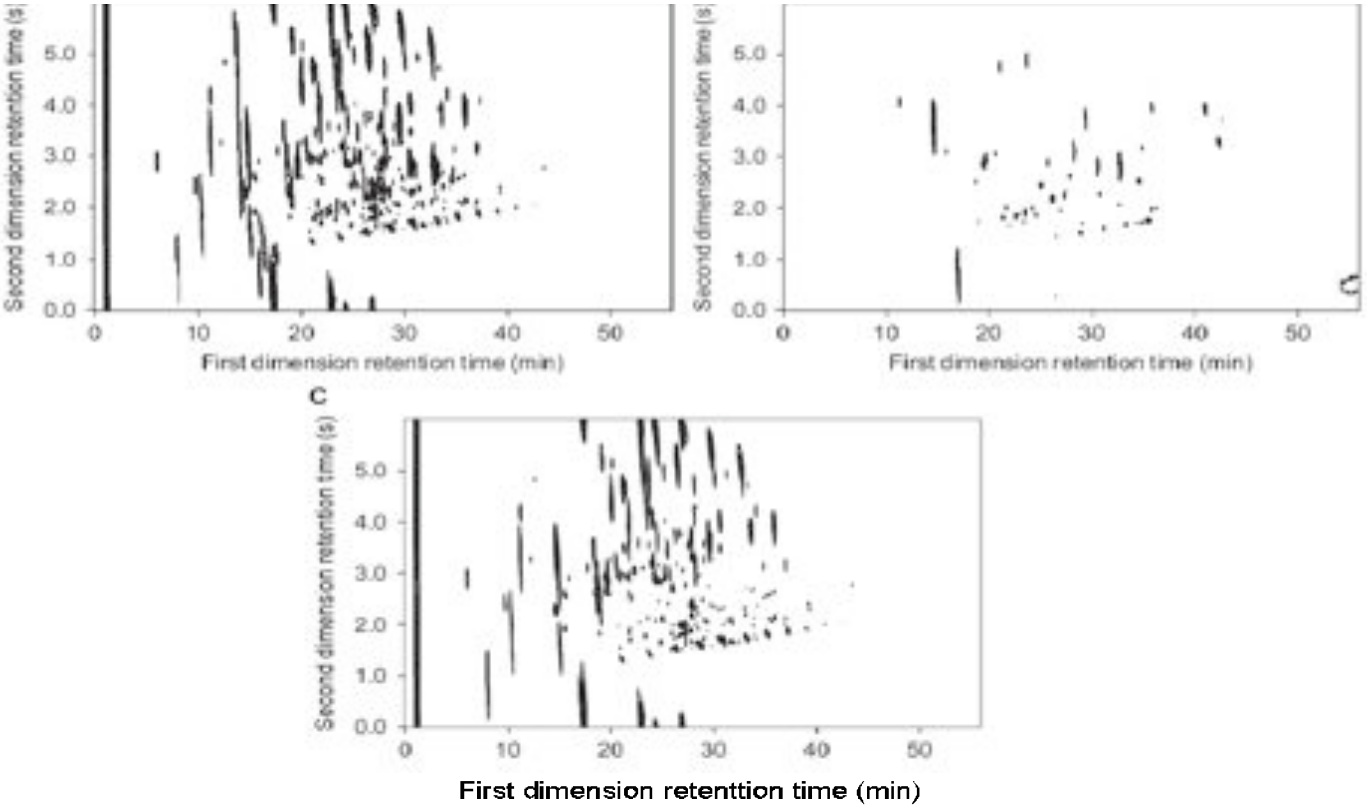

Figure 12.57. GC×GC–FID chromatograms of lotus-scented incense (a) smoke (b) powder and (c) subtracted chromatogram obtained by subtraction of powder H/S chromatogram from smoke chromatogram (a and b).

Contaminants in mussels

A.D. Booth, P. Sutton, C.A. Lewis, A.C. Lewis, A. Scarlett, W. Chau, J. Widdows, S.R. Rowland, *Unresolved complex mixtures of aromatic hydrocarbons: thousands of overlooked persistent, bioaccumulative, and toxic contaminants in mussels*, Environ. Sci. Technol. 2007, 41, 457-464

Instrumental conditions:

***Columns*:**
First: 10 m × 0.18 mm ID, 0.25 µm HP-5
Second: 1 m × 0.1 mm ID, 0.1 µm BP10
Modulation capillary:

Carrier gas: helium, constant flow @ 1.5 mL/min

***Temperatures*:**
Main oven: 40°C (0.2 min), 10°C/min → 160°C (1 min), 3°C/min → 270°C
Second oven: 50°C (0.2 min), 10°C/min → 170°C (1 min), 3°C/min → 280°C (12 min)

Injector: split/splitess
Temperature: 300°C
Injection volume:

Modulator: quad-jet cryogenic, hot pulse 1s

Modulation time: 2.5 s

Detector: ToF-MS
Temperature: ion source 250°C
Make up gas flow: 100 spectra/s

Data acquisition: not specified

Sample description and separation:

Mussels (*Mytilus edulis*) exhibiting a range of scope for growth values were collected from sites around the UK coast. Tissue extracts exhibiting impaired health contained large amounts of aromatic hydrocarbon UCMs compared to the extracts from healthy mussels. The UCMs (up to 125 μg/g dry tissue) contained thousands of previously unidentified branched alkyl homologues of known aromatic hydrocarbons such as branched alkylbenzenes (BABs), tetralins (BATs), and indanes and indenes (BINs).

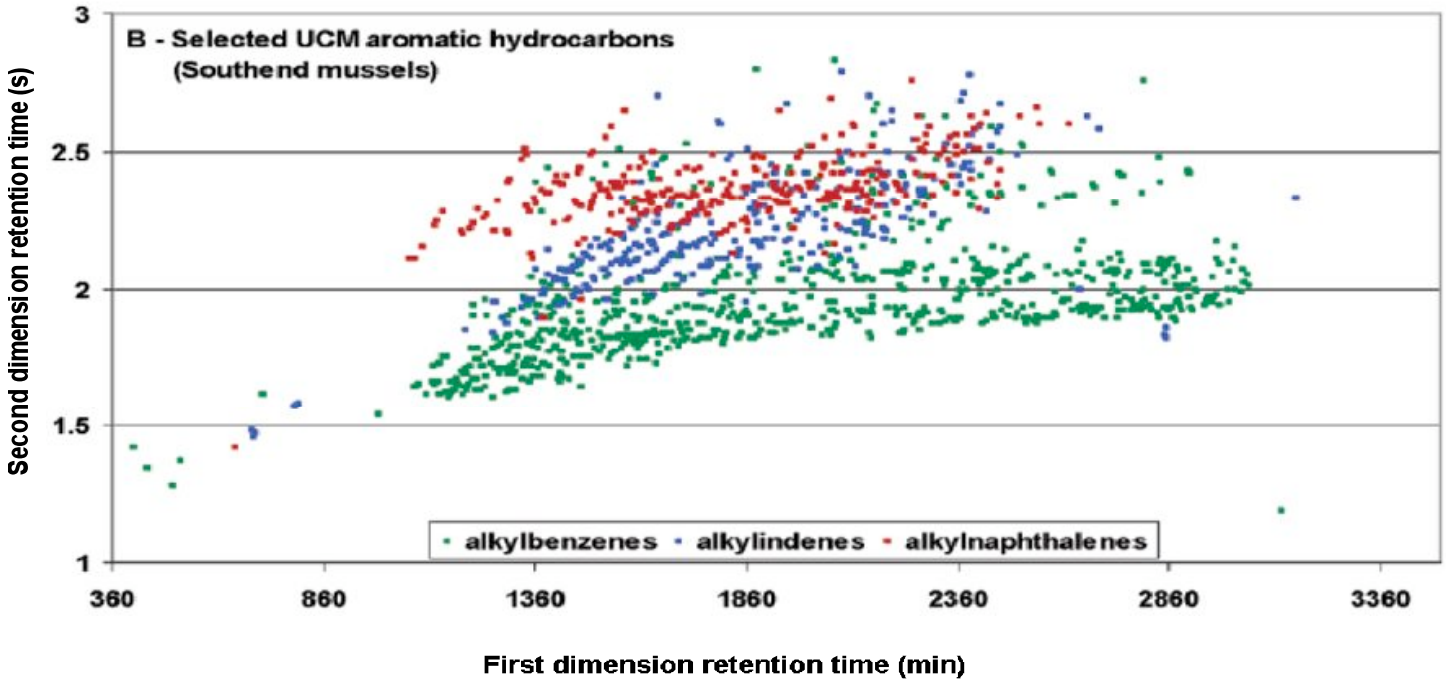

Figure 12.58. Apex plots of GC×GC–ToF MS analysis showing peak marker identifiers for each component in the mixture for which the mass spectrum contained base peak ions with mass:charge (m/z) ratios 91, 105 (■ alkylbenzenes), 129, 143 (■ alkylindenes), 141, 155 (■ alkylhaphthalenes).