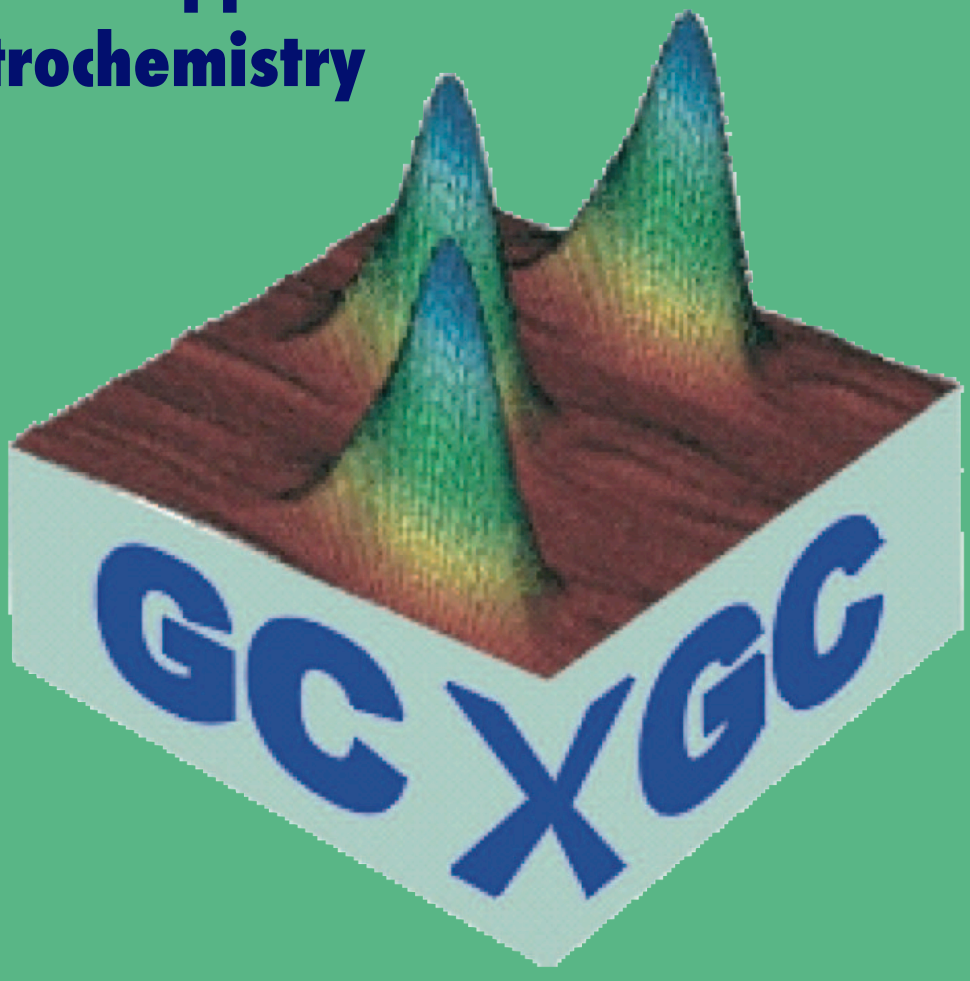
COMPREHENSIVE TWO-DIMENSIONAL GASCHROMATOGRAPHY

The state-of-separation-arts

Part II: Applications: Petrochemistry



JAN BEENS

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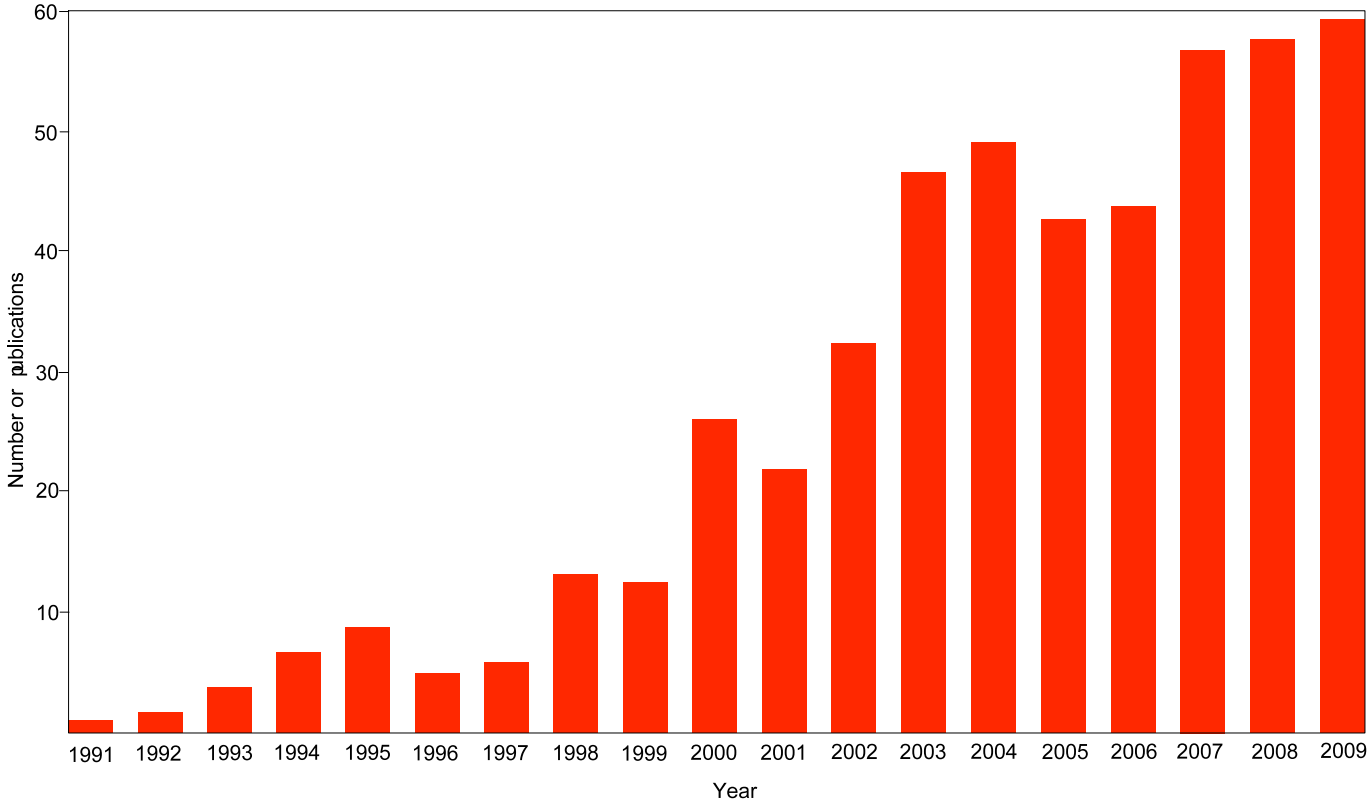
PART II

—APPLICATIONS—



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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1. Petrochemicals

Gasoline

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: two independent EPC regulators: 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 → 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 valve modulator allows the modulation and the thick film primary column the separation of the low boiling part of the sample, *viz*. butane at ^1t_R = 4 mins, the pentenes at ^1t_R = 4-6 mins, pentane at ^1t_R = 7 mins. and the hexenes at ^1t_R = 7-10 mins.
Comparable with separations performed with other modulators, the sample is further separated in clusters according to the chemical structures of the members, *viz*. aliphatics, mono-aromatics and di-aromatics.
The separation of this sample (leaded gasoline) was used to compare with the separation of aromatics in urban air (see there)

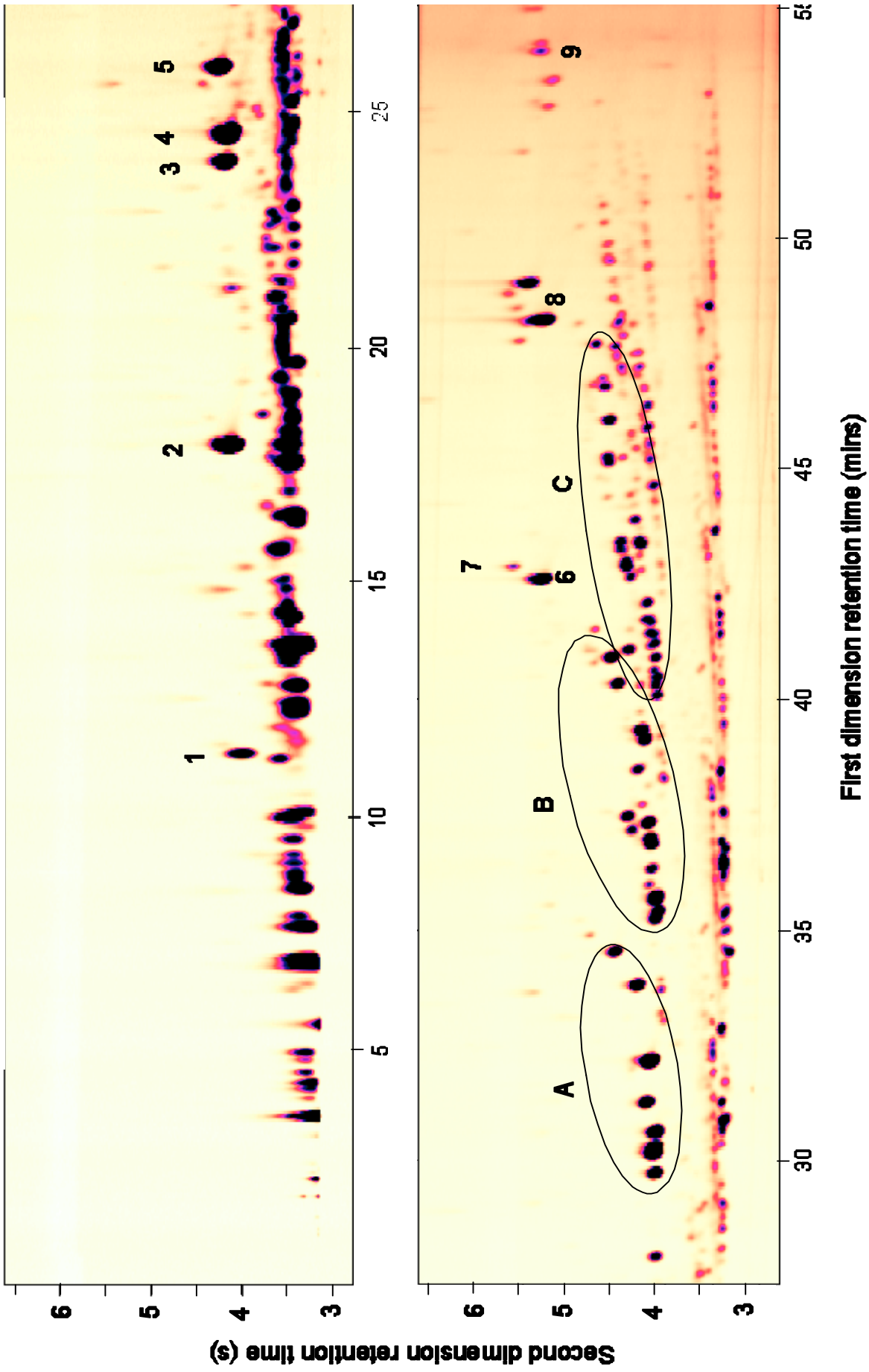


Figure 12.2 Valve modulated GC×GC of leaded gasoline. 1. benzene, 2. toluene, 3. ethyl-benzene, 4. para + meta xylene, 5. ortho xylene, 6. naphthalene,7. benzothiophene, 8. methyl-naphthalenes + methyl-benzothiophenes, 9. C2-naphthalenes. A. C_3-benzenes, B. C_4-benzenes, C. C_5-benzenes.

Naphtha

J. Blomberg, PhD thesis, *Multidimensional GC-based separations for the oil and petrochemical industry*, Vrije Universiteit, Amsterdam, the Netherlands, (2005)

Instrumental conditions:

***Columns*:**
First: 10m, 0.25 mm ID, 0.25 µm µm DB1
Second: 2.0m, 0.10 mm ID, 0.1 µm BPX50
Modulation cap.:

Carrier gas: helium @ 250 kPa

***Temperatures*:**
Main oven: 40°C (5 min), 2.5 °C/min → 300°C (20 min)
Second oven: 90°C (5 min), 2.5 °C/min → 350°C (20 min)

Injector: PTV, split, split ratio 1:100
Temperature: →350 °C
Injection volume: 0.1 µL

Modulator: loop modulator

Modulation time: 7.5 s

Detector: FID
Temperature: 375
Make up gas flow: nitrogen, 25 mL/min

Data acquisition: 100 Hz Digital

Sample description and separation:

With the use of liquid nitrogen as a coolant in the modulator, it is possible to modulate very volatile compounds as propane and butanes. In a low boiling fraction as naphtha, most of the compounds are separated and because of the structures obtained in the colour plot, it is rather easy to identify all the compounds provisionally.

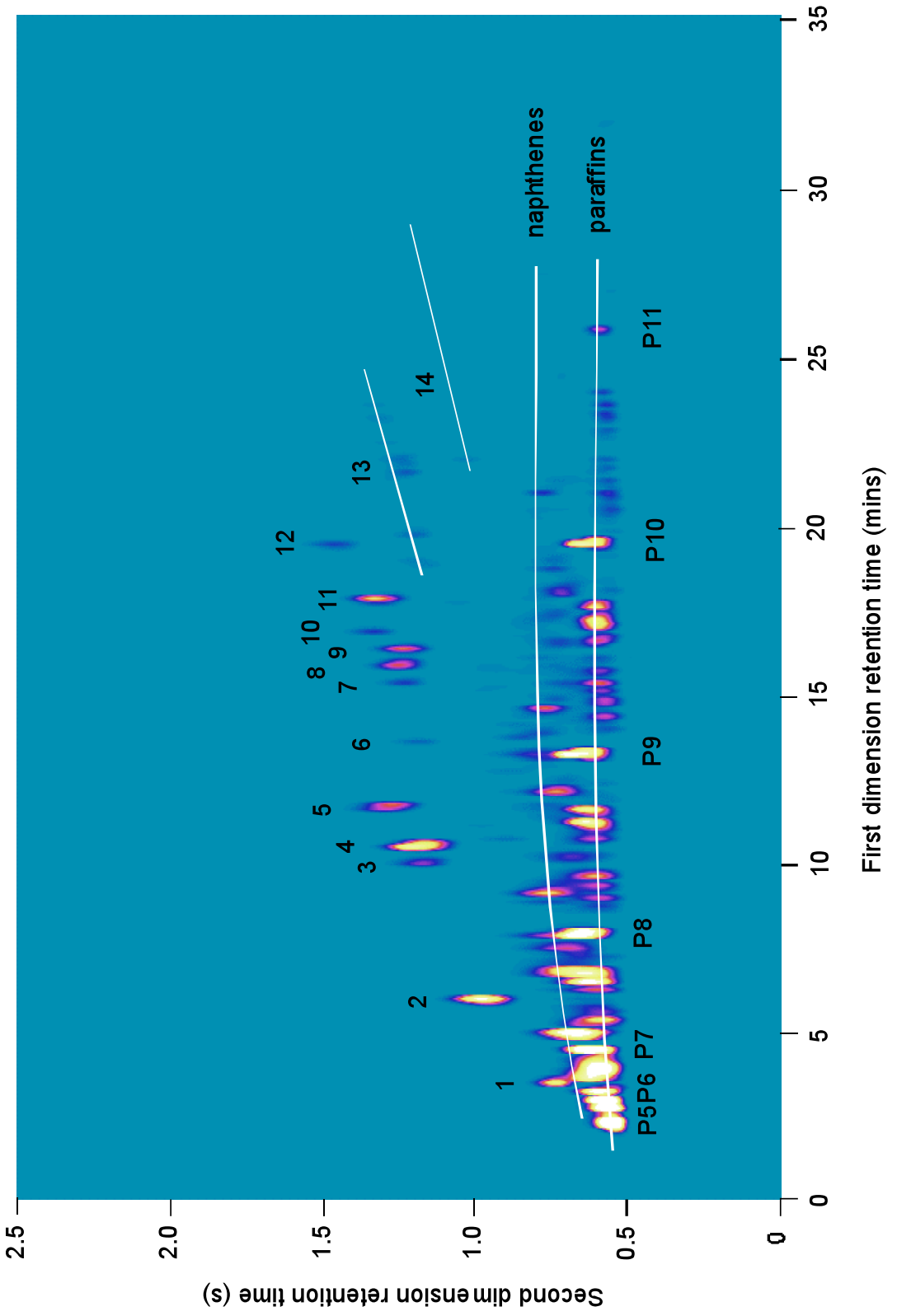


Figure 12.3 Colour plot of the GC×GC separation of a naphtha.
Identification: 1. benzene, 2. toluene, 3. ethylbenzene, 4. para + meta xylene, 5. ortho xylene, 6. isopropylbenzene, 7. n-propylbenzene,
8. 1-methyl-3- + 1-methyl-4-ethylbenzene, 9. 1,3,5-trimethylbenzene, 10. 1-methyl-2-ethylbenzene, 11. 1,2,4-trimethylbenzene, 12. 1,2,3-trimethylbenzene, 13 C_{10}-aromatics, 14. C_{11}-aromatics, P5 through P11. n-pentane through n-undecane.

Kerosene

J.B. Phillips, J. Xu, *Comprehensive multi-dimensional gas chromatography,* J. Chromatogr. A, 703 (1995) 327-334

Instrumental conditions:

***Columns*:**
First:
Second:
Modulation cap.:

Carrier gas: helium

***Temperatures*:**
Main oven:
Second oven:

Injector:
Temperature:
Injection volume:

Modulator: dual stage heated capillary

Modulation time:

Detector: FID
Temperature:
Make up gas flow:

Data acquisition:

Sample description and separation:

One of the very first comprehensive two-dimensional gas chromatograms of the separation of a kerosene. With this separation Phillips and Xu demonstrated for the first time the tremendous separation power of GC×GC.

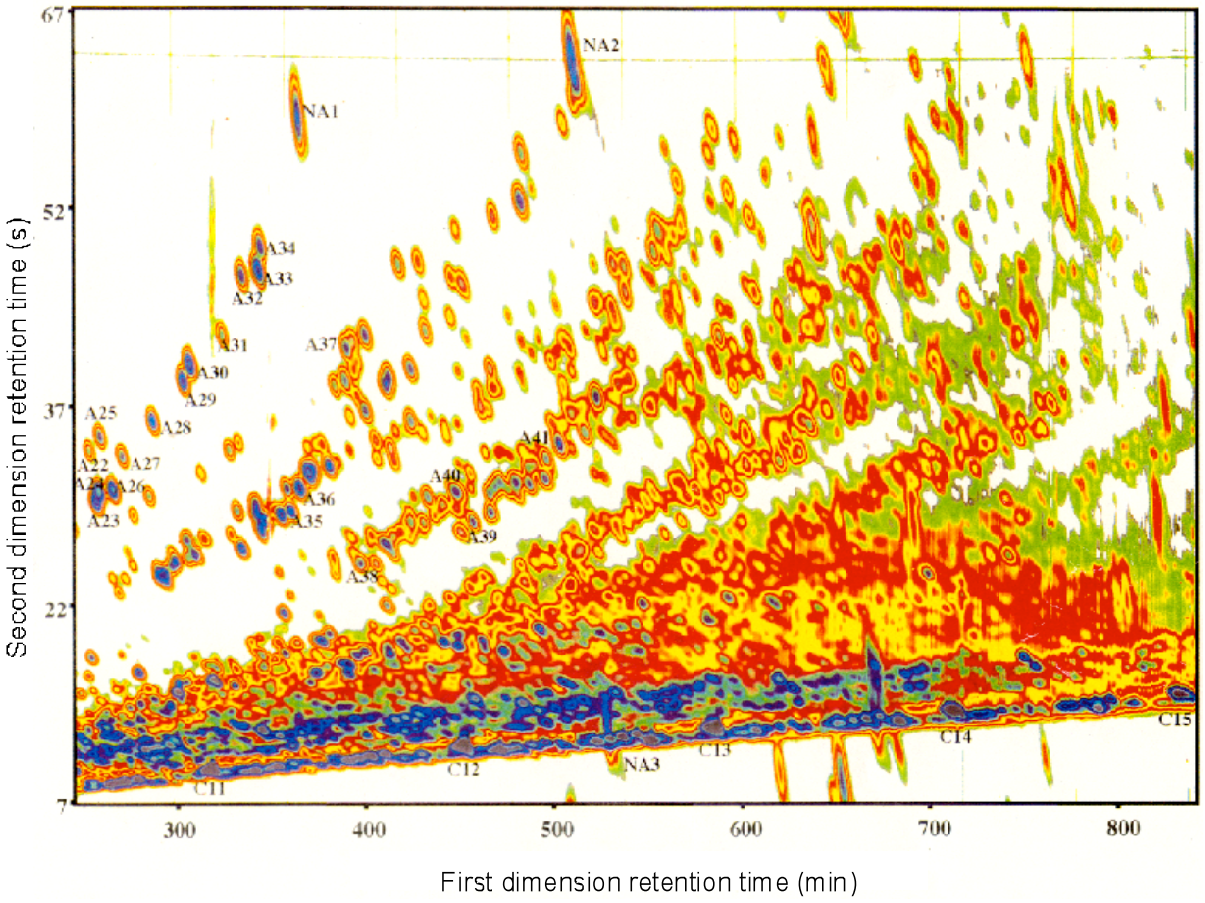


Figure 12.4. Colour plot of a comprehensive two-dimensional gas chromatograms of the separation of a kerosene. Assignment: A22, A24, A25=C9 aromatics; A23, A26-A34=C10 aromatics; A35-A37=C11 aromatics; A38, A40=C12 Aromatics; C39, C41=C13 aromatics; NA1=naphthalene; NA2=2-methyl-naphthalene; NA3=1-methyl-naphthalene

Cycle oil and non-aromatic hydrocarbon solvent

J. Beens, H. Boelens, R. Tijssen, J. Blomberg, *Quantitatve aspects of comprehensive two dimensional gas chromatography (GC×GC),* J. High Resolut. Chromatogr. 21 (1998) 47-54

Instrumental conditions:

***Columns*:**

First:	Top: 25 m × 0.25 mm × 0.25 μm DB-1
	Bottom : 10 m × 0.25 mm × 0.25 μm CP Sil-2 CB
Second:	Top:1.5 m × 0.1 mm × 0.1 μm OV-1701
	Bottom: 2.5 m × 0.1 mm × 0.1 μm BPX-50
Modulation cap.:	

Carrier gas: helium

***Temperatures*:**
Main oven:
Second oven:

Injector:	PTV
Temperature:	250ºC
Injection volume:	

Modulator: Sweeper

Modulation time: 7.5 and 4 s

Detector:	FID
Temperature:	
Make up gas flow:	

Data acquisition: 100 Hz

Sample description and separation:

The bottom sample, a non-aromatic hydrocarbon solvent. In this case, special care was taken to optimize the 2D separation, and exploit a very large part of the available separation space. Again, there is much structure and many sub-classes can be recognized. The roof-tiles (marked by ellipses) observed for the alkanes and mono- and dinaphthenes, each only contain compounds with the same number of carbon atoms. Highly branched alkanes were separated in the second dimension from their less branched isomers, with branching within one roof-tile increasing from the right-hand (top) to the left-hand (bottom) side. This enables the determination of the degree of branching, which is valuable information to predict octane and cetane numbers. Further, alkylcyclopentanes and alkylcyclohexanes were found to be separated from each other. One example of this much appreciated result (*n*-C_7 cyC_6 *vs.* *n*-C_8 cyC_5) is indicated in the figure.

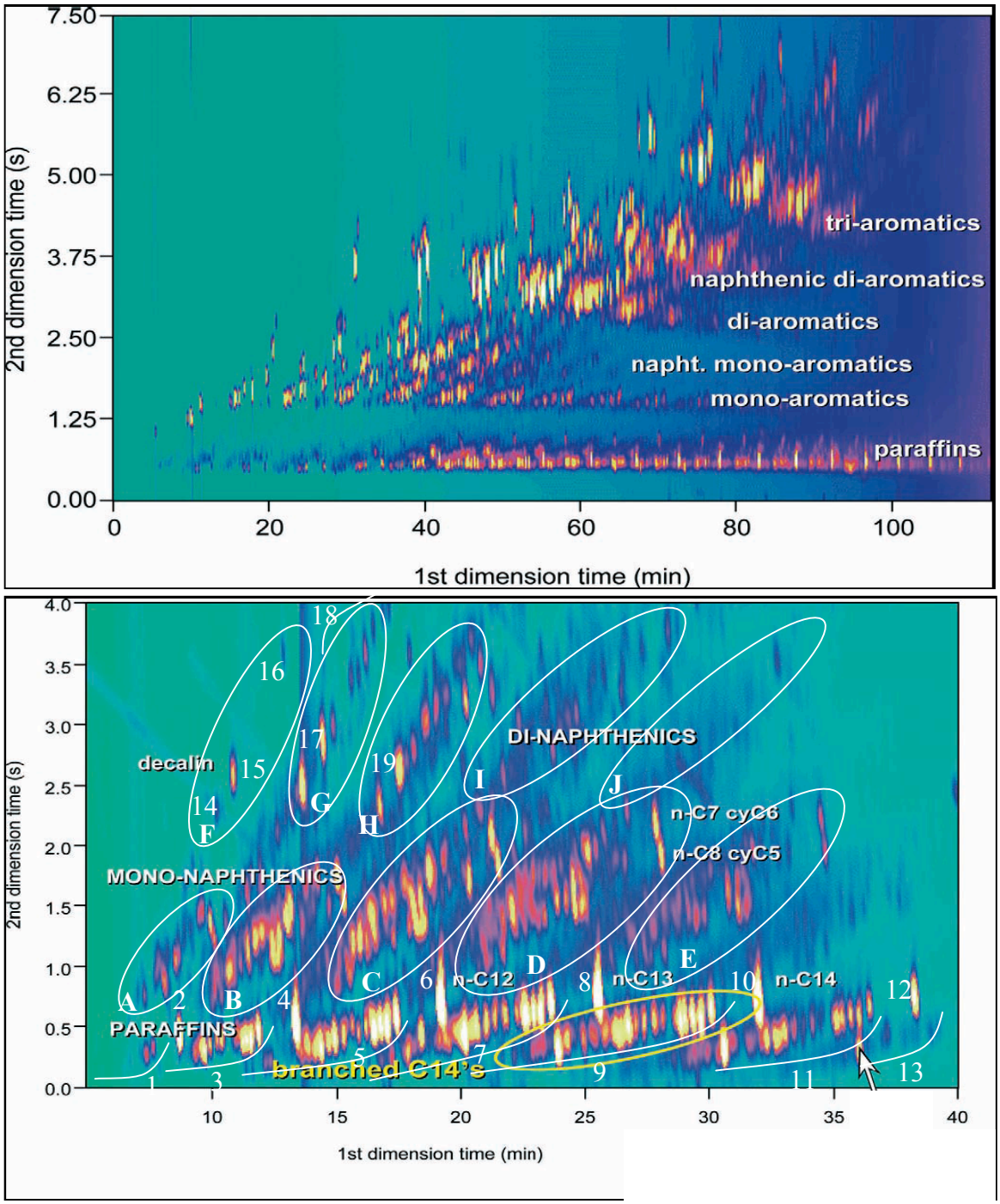


Figure 12.5. GC×GC–FID of

Top: a light cycle oil

Bottom: a non-aromatic hydrocarbon solvent

Identification: 1 through 13: alkanes; 1: branched C_{10}'s; 2: n-C_{10}, 3: branched C_{11}'s; 4: n-C11, 5: branched C_{12}'s; 6: n-C_{12}; 7: branched C_{13}'s; 8: n-C_{13}; 9: branched C_{14}'s; 10: n-C_{14}; 11: branched C_{15}'s; 12: n-C_{15}; 13: branched C_{16}'s; 14: unknown; 15: trans-decalin; 16: cis-decalin; 17: trans-methyl-decalins; 18: cis-methyl-decalins; A through E: mono-naphthenes C_{10} through C_{14}; F through J: di-naphthenes C_{10} through C_{13} .

Diesel (high resolution)

J. Blomberg, P.J. Schoenmakers, U.A.Th. Brinkman, *Gas chromatographic methods for oil analyses*, J. Chromatogr. A 972 (2002) 137-173

Instrumental conditions:

***Columns*:**
First: 10 m, 0.25 mm ID, 0.25 µm DB-1
Second: 2.0 m, 0.10 mm ID, 0.1 µm BPX50
Modulation cap.:

Carrier gas: helium @ 250 kPa

***Temperatures*:**
Main oven: 40°C (5 min), 0.5 °C/min → 275°C (10 min)
Second oven:

Injector: PTV, split, split ratio 1:100
Temperature: →300 °C
Injection volume: 0.2 µL

Modulator: loop modulator

Modulation time: 20 s

Detector: FID
Temperature: 375ºC
Make up gas flow: nitrogen, 25 mL/min

Data acquisition: 100 Hz

Sample description and separation:

When using these extreme long GC conditions, an incredible number of compounds could be separated. And although the analysis lasted over 6 hours (!), hundreds of thousands of compounds are separated and through the clustering and some chemical knowledge and logic, the majority of them could be classified.

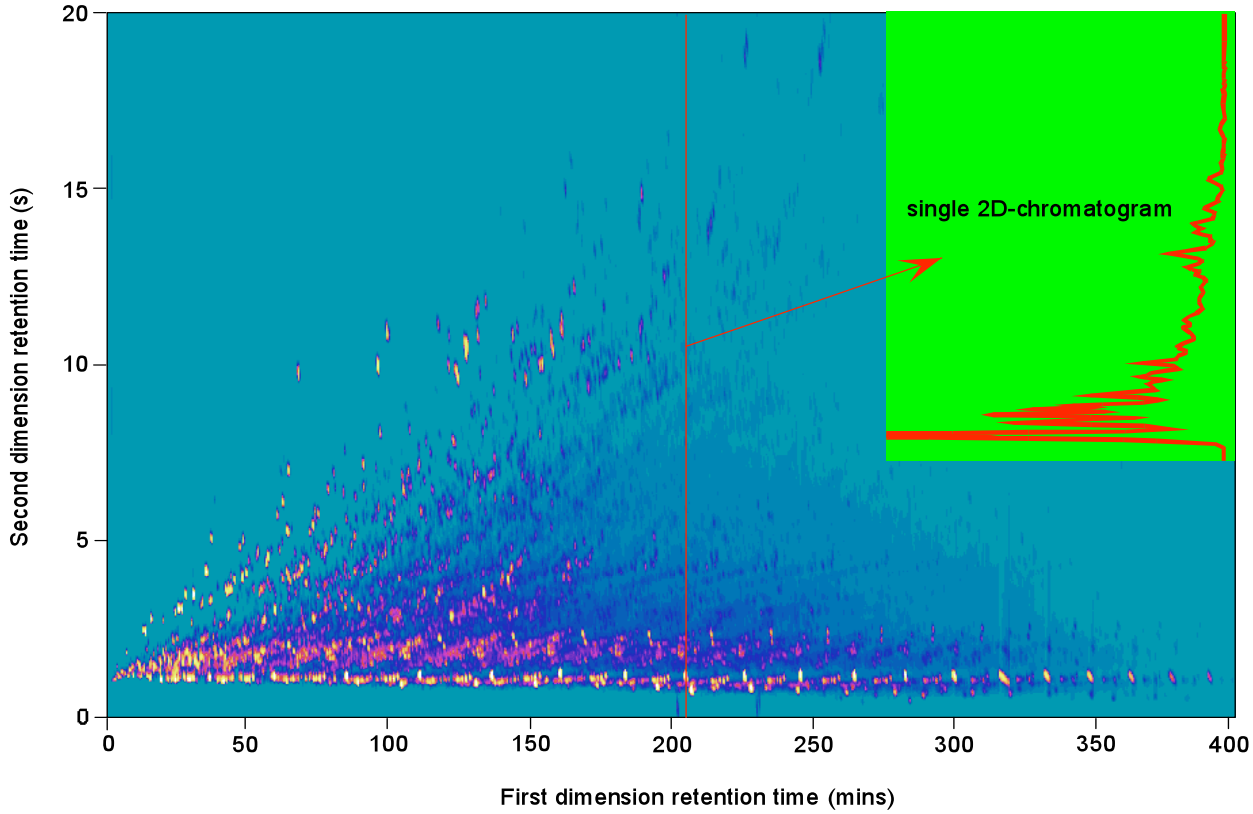


Figure 12.6. Colour plot of the GC×GC High Resolution separation of a diesel.
Because of the clustering, all the hydrocarbon classes can be identified, from n-C_7 through n-C_{28} and the branched alkanes in between, to toluene through C_{20}-monoaromatics. From naphthalenes (second dimension retention times 10 seconds) through the triaromatics in the top of the plot.
The inser depicts one single second dimension chromatogram, showing that in a single one-dimensional peak at least thirty compounds co-elute.

Diesel (reversed phase)

M. Adachour, J. Beens, R.J.J. Vreuls, A.M. Batenburg, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography of complex samples by using a "reversed-type" column combination: application to food analysis*, J. Chromatogr. A 1054 (2004) 47-64

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 µm DB-21 (Carbowax58)
Second: 1.35 m × 0.10 mm ID, 0.1 µm BPX35
Modulation capillary:

Carrier gas: helium

***Temperatures*:**
Main oven: 40°C (2 min), 2.5°C/min → 220°C
Second oven: 100°C (2 min), 2.6°C/min → 210°C, 0.5°C/min → 225°C

Injector: split, ratio 1:250
Temperature: 250°C
Injection volume: 0.5 µL

Modulator: dual jet cryogenic

Modulation time: 6 s

Detector: FID
Temperature: 250°C
Make up gas flow:

Data acquisition: 100 Hz

Sample description and separation:

In this so-called "reversed-phase"GC×GC separation the polar and non-polar stationary phases are interchanged. Consequently, the colour plot, still showing a nice clustering of chemical groups, also shows a reversed order. Now the most polarizable group, *viz*. the di-aromatics has the shortest second dimension retention time. The paraffins now have the longest second dimension retention times and can be found in the top of the GC×GC plot.

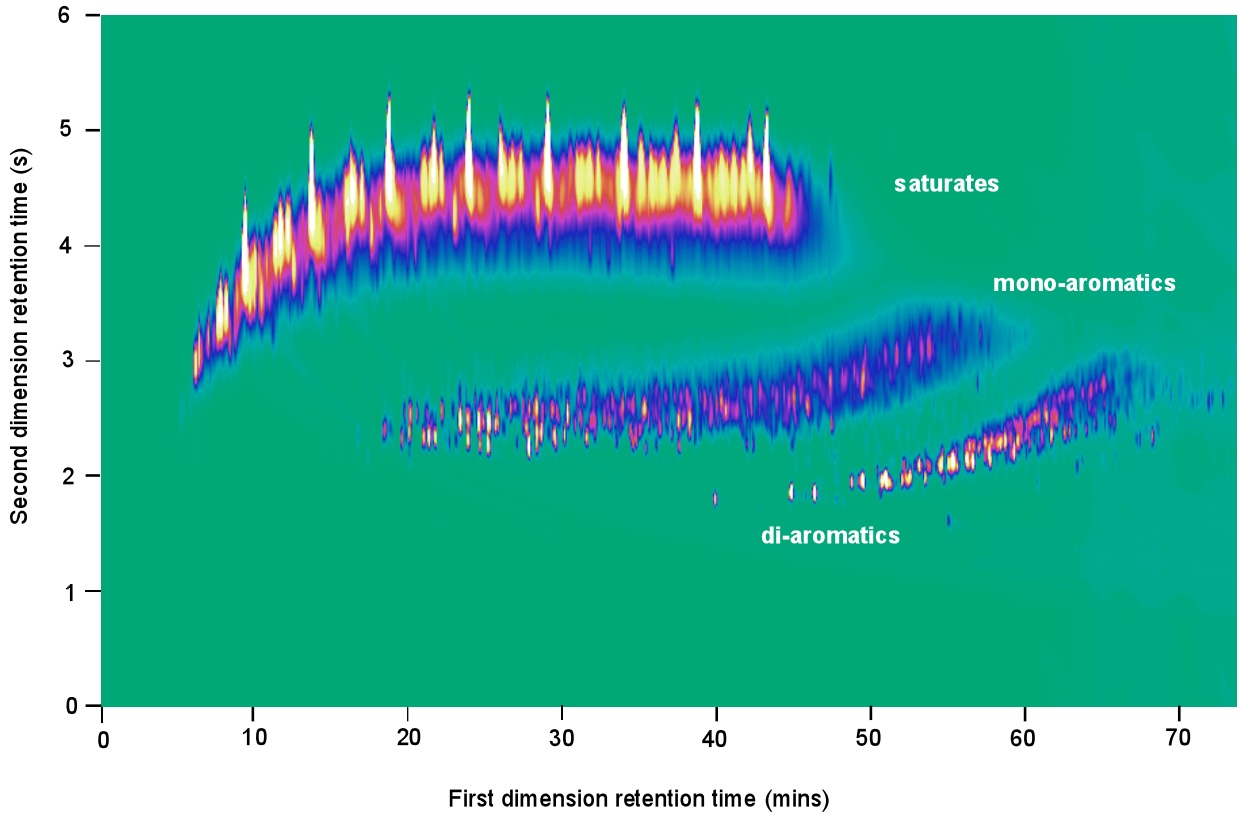


Figure 12.7. Colour plot of a "reversed-phase" GC×GC separation of a diesel oil. Although the column combination (first polar, second non-polar) is certainly non-orthogonal, the plot still exhibits the well-known clustering of related chemical groups. But now compounds of the least polar group, the paraffins have the longest second dimension retention times. The more polarizable groups, viz. the mono- and di-aromatics now have lower second-dimension retention times.

Fischer-Tropsch product

J. Blomberg, Shell Technology and Innovation Support, Shell Technology Centre Amsterdam, the Netherlands*, unpublished results*

Instrumental conditions:

***Columns*:**
First: 10m, 0.25 mm ID, 0.25 µm µm DB-1
Second: 2.0m, 0.10 mm ID, 0.1 µm BPX50
Modulation cap.:

Carrier gas: helium @ 250 kPa

***Temperatures*:**
Main oven: 40°C (5 min), 2.5 °C/min → 300°C (20 min)
Second oven: 50°C (5 min), 2.5 °C/min → 310°C (20 min)

Injector: PTV, split, split ratio 1:100
Temperature: →350 °C
Injection volume: 0.1 µL

Modulator: loop modulator

Modulation time: 7.5 s

Detector: FID
Temperature: 375
Make up gas flow: nitrogen @ 25 mL/min

Data acquisition: 100 Hz

Sample description and separation:

Since the sample originates from a Low-Temperature Fischer-Tropsch process (LTFT), it contains a regular series of mainly n-alkanes, n-alkenes and n-alcohols. In between these unbranched species, depending on the process conditions also a number of branched species can be found. GC×GC is the right technique to separate and identify all the compounds that are present in the product.

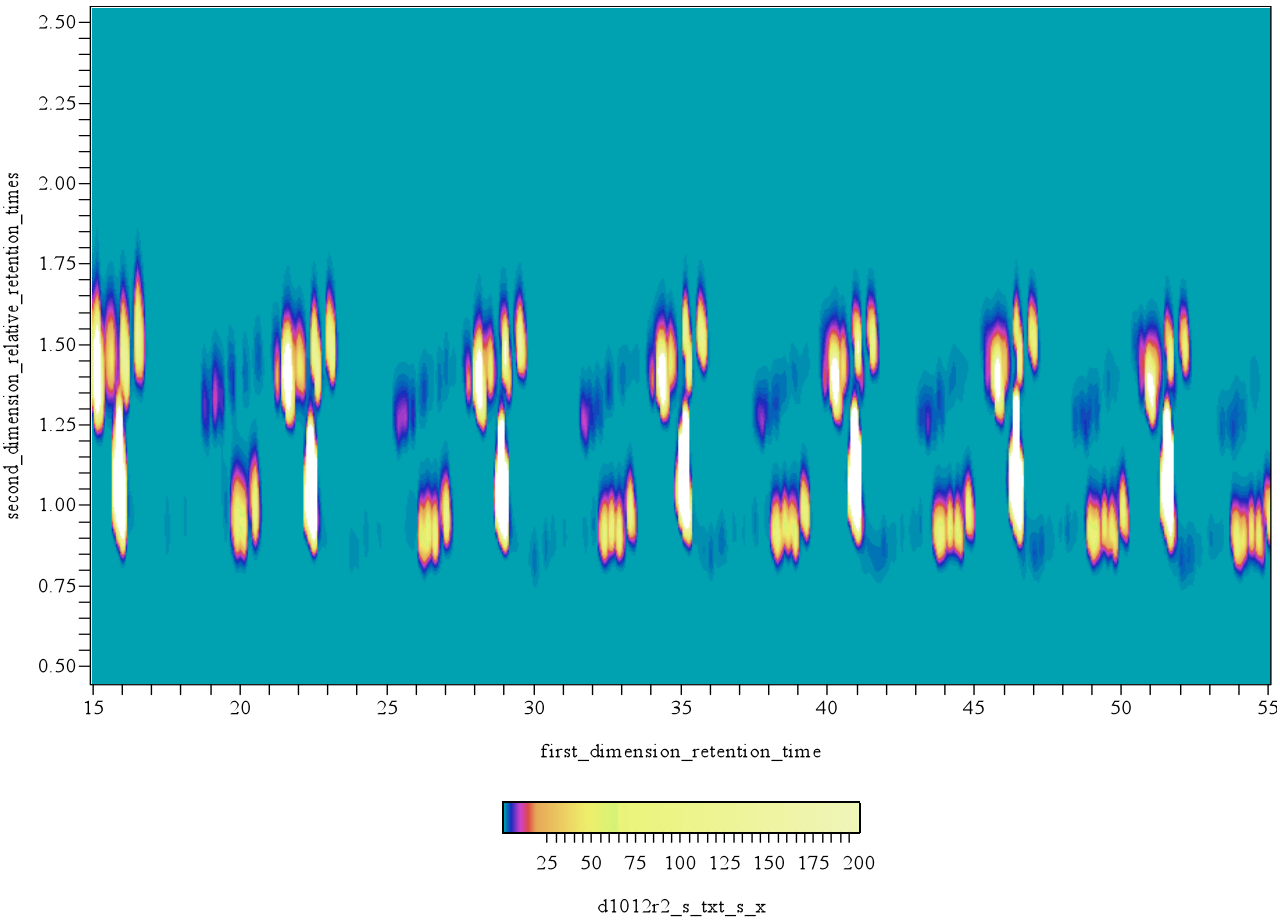


Figure 12.8. Detail of a GC×GC separation of a Fischer-Tropsch product.
The lower series of compounds are the alkanes, with the high-intensity (white spots) n-alkanes. The higher series depicts the alkenes, again with the high-intensity (white spots) n-alkenes. The part of the chromatogram depicting the alcohols (retention times 6 min) is not included.

Virtual fractionation of non-aromatic solvents from hydrogenated kerosene

H. Chaabani, masters thesis, University of Amsterdam, (2002)

Instrumental conditions:

***Columns*:**
First: 10 m, 0.25 mm ID, 0.25 µm DB1
Second: 0.8 m, 0.10 mm ID, 0.1 µm BPX50
Modulation cap.:

Carrier gas: helium @ 200 kPa

***Temperatures*:**
Main oven: 40°C (5 min), 2.5 °C/min → 275°C (10 min)
Second oven: 65°C (5 min), 2.5 °C/min → 300°C (10 min)

Injector: PTV, split, split ratio 1:100
Temperature: → 350°C
Injection volume: 0.2 µL

Modulator: Sweeper

Modulation time: 7.5 s

Detector: FID
Temperature: 375 °C
Make up gas flow: nitrogen @ 25 mL/min

Data acquisition: 50 Hz

Sample description and separation:

In order to judge whether different feedstocks of hydrogenated kerosenes could be used to produce non-aromatic solvents, and how much naphthenic species these products would contain, a number of kerosenes were analysed by GC×GC. These analyses were used to predict the composition of the distilled fractions.

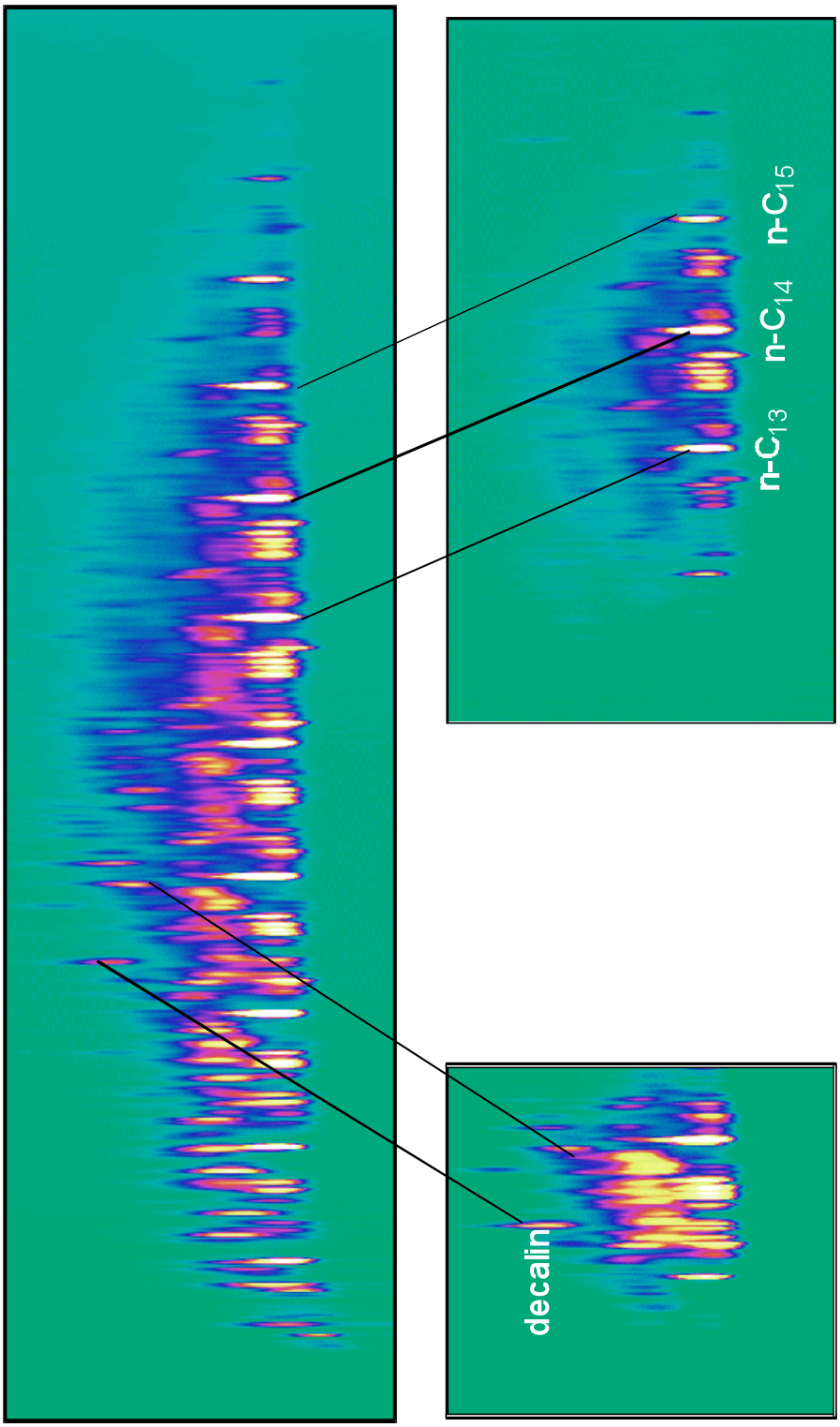


Figure 12.9. Colour plots of the GC×GC separation of a kerosene.
The upper plot is the original separation, the two lower plots depict the composition of two virtual fractions.

Fire debris material

G.S. Frysinger, R.B. Gaines, *Forensic analysis of ignitable liquids in fire debris by comprehensive two-dimensional gas chromatography*, J. Forensic Science 47 (3) (2002) 471-482

Instrumental conditions:

***Columns*:**
First: 4.75 m × 0.10 mm ID, 3.5 μm Phase 007-1
Second: 2.0 m × 0.10 mm ID, 0.10 μm Phase 007-1701
Modulation capillary: 8 cm × 0.10 mm ID, 3.5 μm dimethylpolysiloxane

Carrier gas: hydrogen, constant flow @ 0.4 mL/min, 65 cm/s @ –20ºC

***Temperatures*:**
First column: –20°C (10 min), 2°C/min → 240°C
Second column: 20°C (20 min), 2°C/min → 260°C
Modulator tube: –20°C (10 min), 2°C/min → 240°C

Injector: split, ratio 1:10
Temperature: 250°C
Injection volume: 1 μL in CS_2

Modulator: Sweeper, stainless steel version, 0.25 rev/s, $\Delta T = 100°C$

Modulation time: 4 s

Detector: FID
Temperature: 250°C
Make up gas flow:

Data acquisition: 100 Hz

Sample: Fire debris samples produced by charring carpet (nylon) over Bunsen burner. Volatiles were extracted with activated carbon strip, eluted with CS_2.

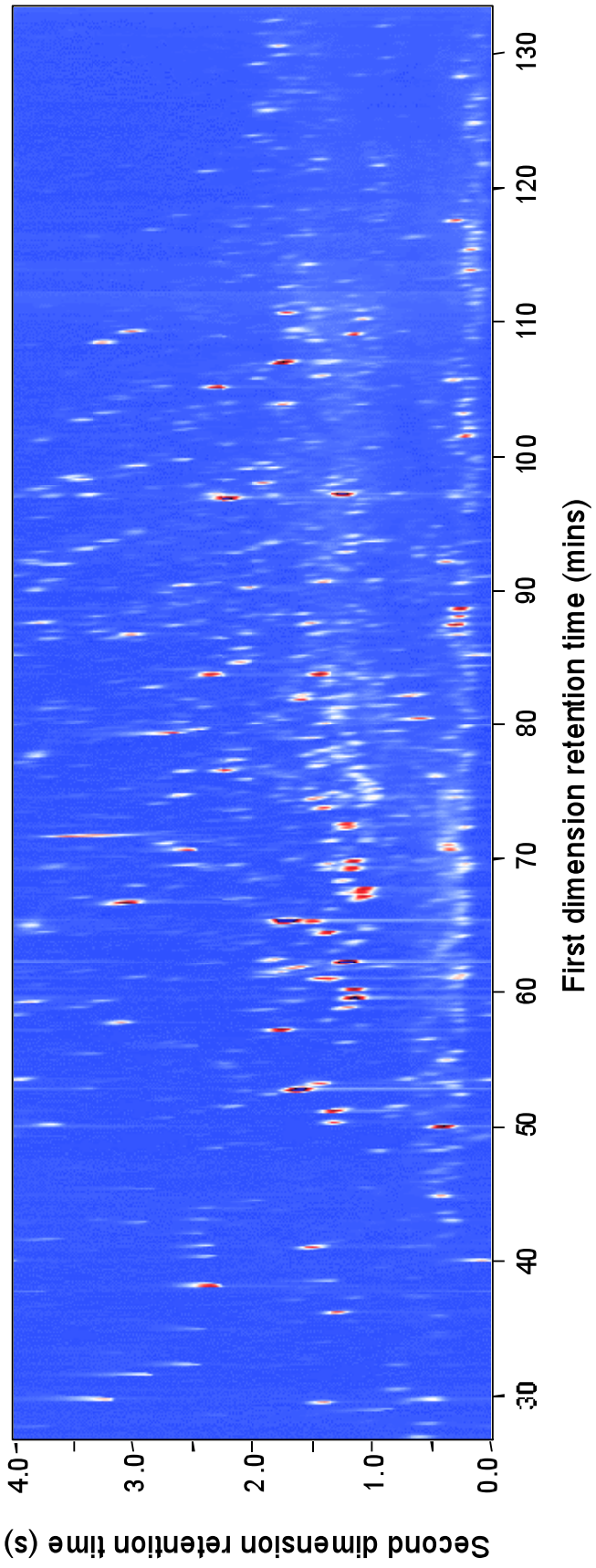


Figure 12.10. Colour plot of a GC×GC separation of a simulated fire debris material.

Ignitable fluids

G.S. Frysinger, R.B. Gaines, *Forensic analysis of ignitable liquids in fire debris by comprehensive two-dimensional gas chromatography*, J. Forensic Sci. 47 (3) (2002) 471-482

Instrumental conditions:

***Columns*:**
First: 4.75 m × 0.10 mm ID, 3.5 μm Phase 007-1
Second: 2.0 m × 0.10 mm ID, 0.10 μm Phase 007-1701
Modulation capillary: 8 cm × 0.10 mm ID, 3.5 μm dimethylpolysiloxane

Carrier gas: hydrogen, constant flow @ 0.4 mL/min, 65 cm/s @ –20ºC

***Temperatures*:**
First column: –20°C (10 min), 2°C/min → 240°C
Second column: 20°C (20 min), 2°C/min → 260°C
Modulator tube: –20°C (10 min), 2°C/min → 240°C

Injector: split, ratio 1:300
Temperature: 250°C
Injection volume: 0.1 μL

Modulator: Sweeper, stainless steel version, 0.25 rev/s, ΔT = 100°C

Modulation time: 4 s

Detector: FID
Temperature: 250°C
Make up gas flow:

Data acquisition: 100 Hz

Sample: Ignitable liquids were analyzed neat or after evaporative weathering.

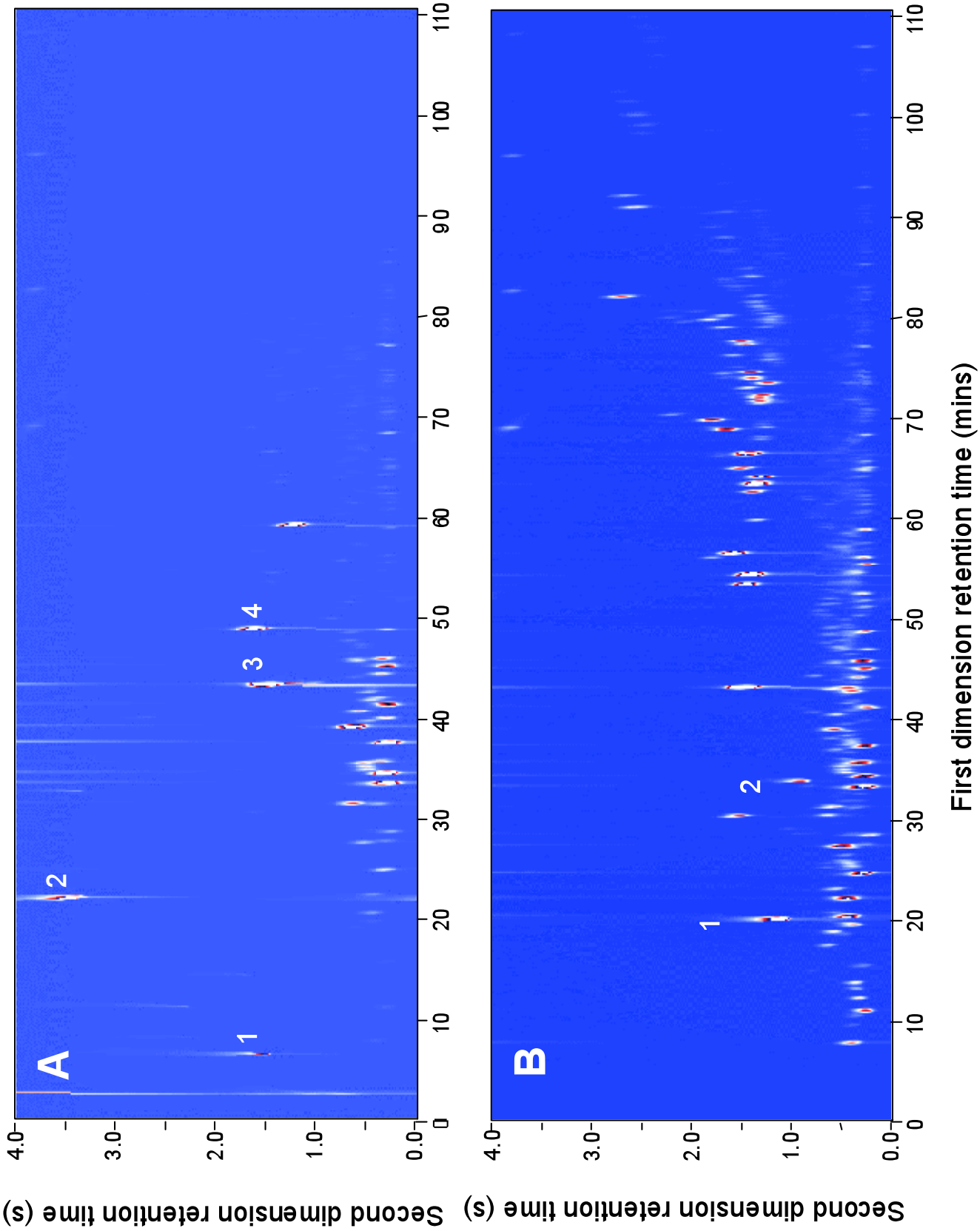


Figure 12.11. Colour plot of a GC×GC separation of ignitable fluids

A. Lacquer thinner, 1. ethanol, 2-butanone, 3. toluene, 4. butyl-acetate

B. *Super gasoline, 1. methyl tert. butyl ether (MTBE), 2. tert. amyl-methyl ether (TAME)*

C_{15}-C_{16} olefins

J. Beens, J. Blomberg and P.J. Schoenmakers, *Proper tuning of comprehensive two-dimensional gas chromatography (GC×GC) to optimize the separation of complex hydrocarbon mixtures*, J. High Resol. Chromatogr., 23 (2000) 182-188

Instrumental conditions:

***Columns*:**
First: 60 m, 0.25 mm ID, 0.25 µm DB1
Second: 3 m, 0.10 mm ID, 0.1 µm BPX50
Modulation cap.: 7.8 cm, 0.10 mm ID, 3.0 µm SE-54

Carrier gas: helium @ 350 kPa

***Temperatures*:**
Main oven: 30 °C (5 min), 0.5 °C/min → 225 °C (10 min)
Second oven:

Injector: PTV, split, split ratio 1:400
Temperature: → 350°C
Injection volume: 0.1 µL

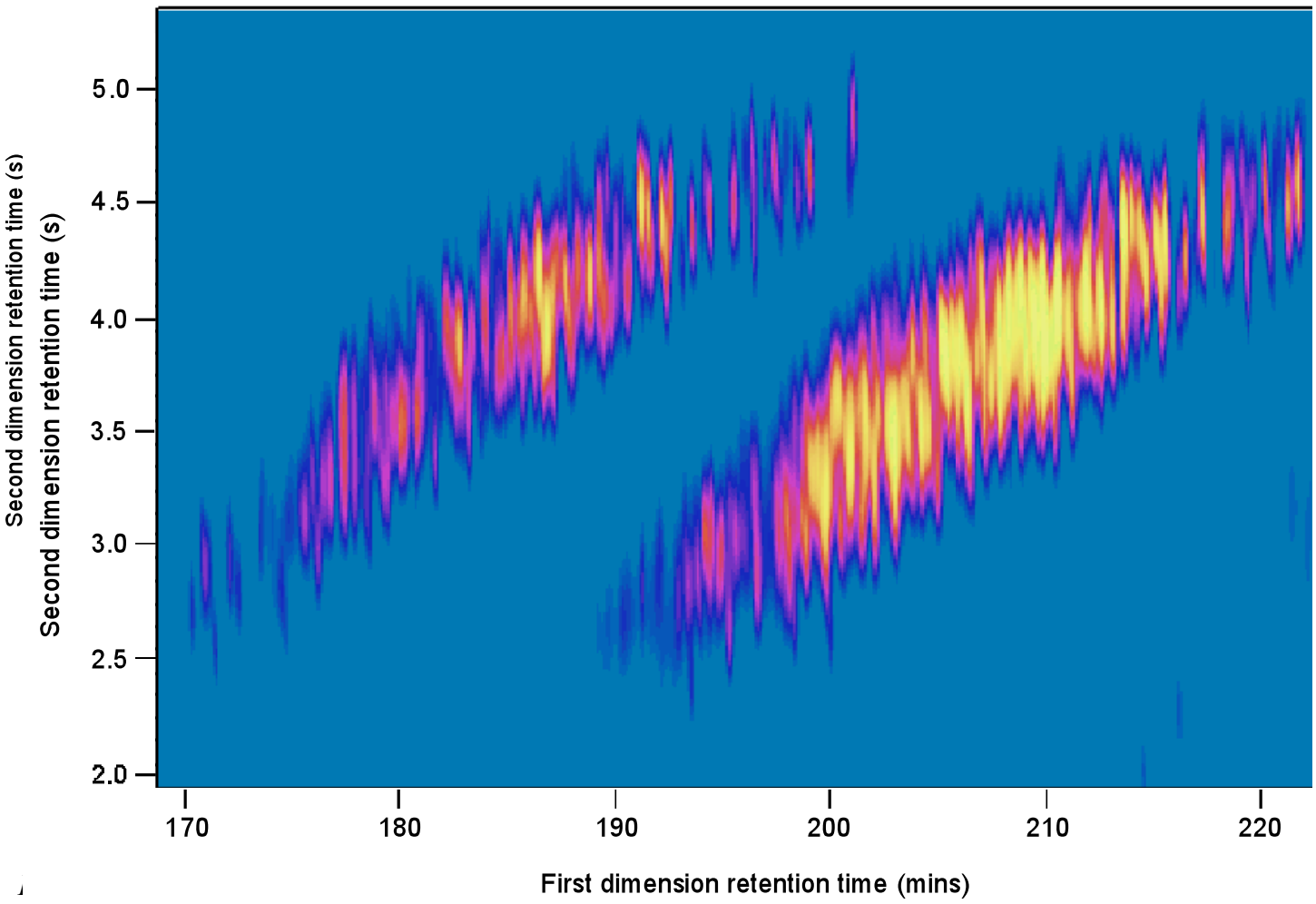
Modulator: Sweeper

Modulation time: 7.5 s

Detector: FID
Temperature: 300 °C
Make up gas flow: nitrogen @ 25 mL/min

Data acquisition: 50 Hz

Sample description and separation:
This was a high-resolution GC×GC run performed as a late friday-afternoon experiment in august 1999 during the PhD studies of Jan Blomberg and Jan Beens. Within each of the rooftiles of the branched olefins some one hundred isomers could be discerned. After publication in J. High Resol. Chromatogr., the creative people responsible for the design and the lay-out of the new Journal of Separation Sciences thought this chromatogram together with the reconstructed 1-D trace would make a great cover. From 2001 on this particular chromatogram can be found on the front cover of JSS.



Biomarkers in crude oil

G.S. Frysinger, R.B. Gaines, *Separation and identification of petroleum biomarkers by comprehensive two-dimensional gas chromatography*, J. Sep. Sci. 24 (2001) 87-96

see also: R.K. Nelson, B.M. Kile, D.L. Plata, S.P. Sylva, L. Xu, C.M. Reddy, R.B. Gaines, G.S. Frysinger, S.E. Reichenbach, *Tracking the weathering of an oil spill with comprehensive two-dimensional gas chromatography*, Environmental Forensics, 7 (2006) 33–44

Instrumental conditions:

***Columns*:**
First: 10 m × 0.10 mm ID, 0.5 µm dimethylpolysiloxane
Second: 0.50 m × 0.10 mm ID, 0.10 µm BPX50
Modulation capillary: 8 cm × 0.10 mm ID, 0.5 µm dimethylpolysiloxane

Carrier gas: hydrogen, constant flow @ 0.4 mL/min

***Temperatures*:**
Main oven: 50°C, 2°C/min → 320°C, (40 min)
Second oven: 80°C, 2°C/min → 360°C, (35 min)

Injector: split, ratio 1:20
Temperature: 300°C
Injection volume: 2.0 µL

Modulator: Sweeper, velocity 0.25 rev/s, ΔT 100 °C
Modulation time: 5.0 s
Detector:
Temperature: 375°C
Make up gas flow:
Data acquisition:

Sample description and separation:

Modified, thin film, double-ended modulation capillary used to extend rotating modulator analysis to nonvolatiles > C_{40}.

The biomarkers examined include aromatics (naphthalene, biphenyl, fluorene, phenanthrene, chrysene), sulfur-containing aromatics (dibenzothiophenes, benzonaphthothiophenes), steranes, hopanes, and triaromatic steranes. These biomarkers, which are frequently used in forensic oil spill analysis and petroleum exploration, were separated into easily recognizable bands in the GC×GC colour plot. Methods used to identify the bands included peak matching with chemical standards, comparison with GC–MS extracted ion chromatograms, and the application of chemical logic based on the known volatility and polarity properties of the biomarkers.

First separation and identification of sterane and hopane biomarkers with GCxGC methods. Peaks correlated with GC/MS EICs for tentative peak identification.

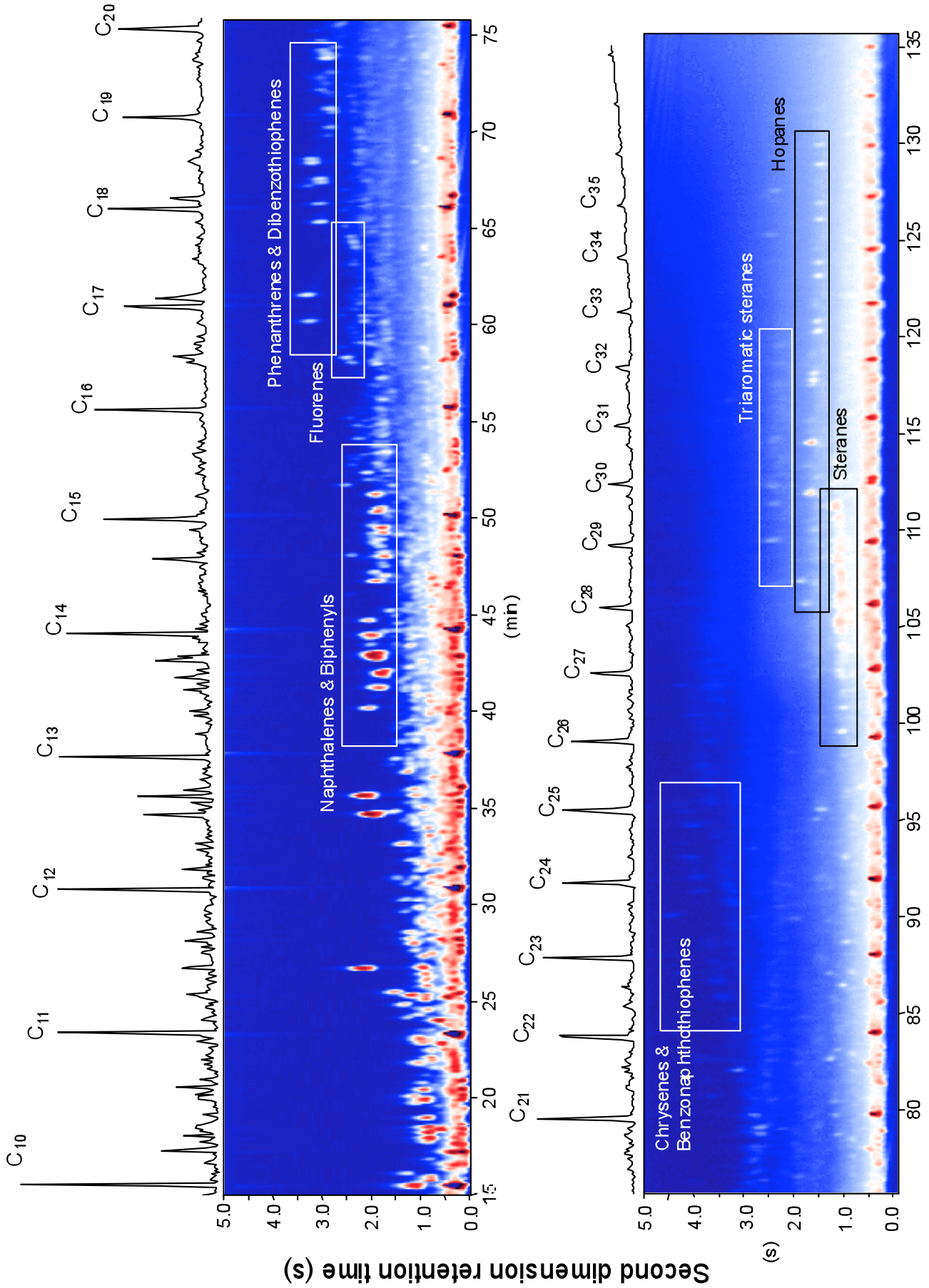


Figure 12.13. GC×GC chromatogram of Exxon Valdez crude oil. The ^{10}logFID response is displayed to compress the large dynamic range. Groups of significant biomarker compounds are identified in boxes. The corresponding one-dimensional volatility-based gas chromatogram is overlaid for comparison.

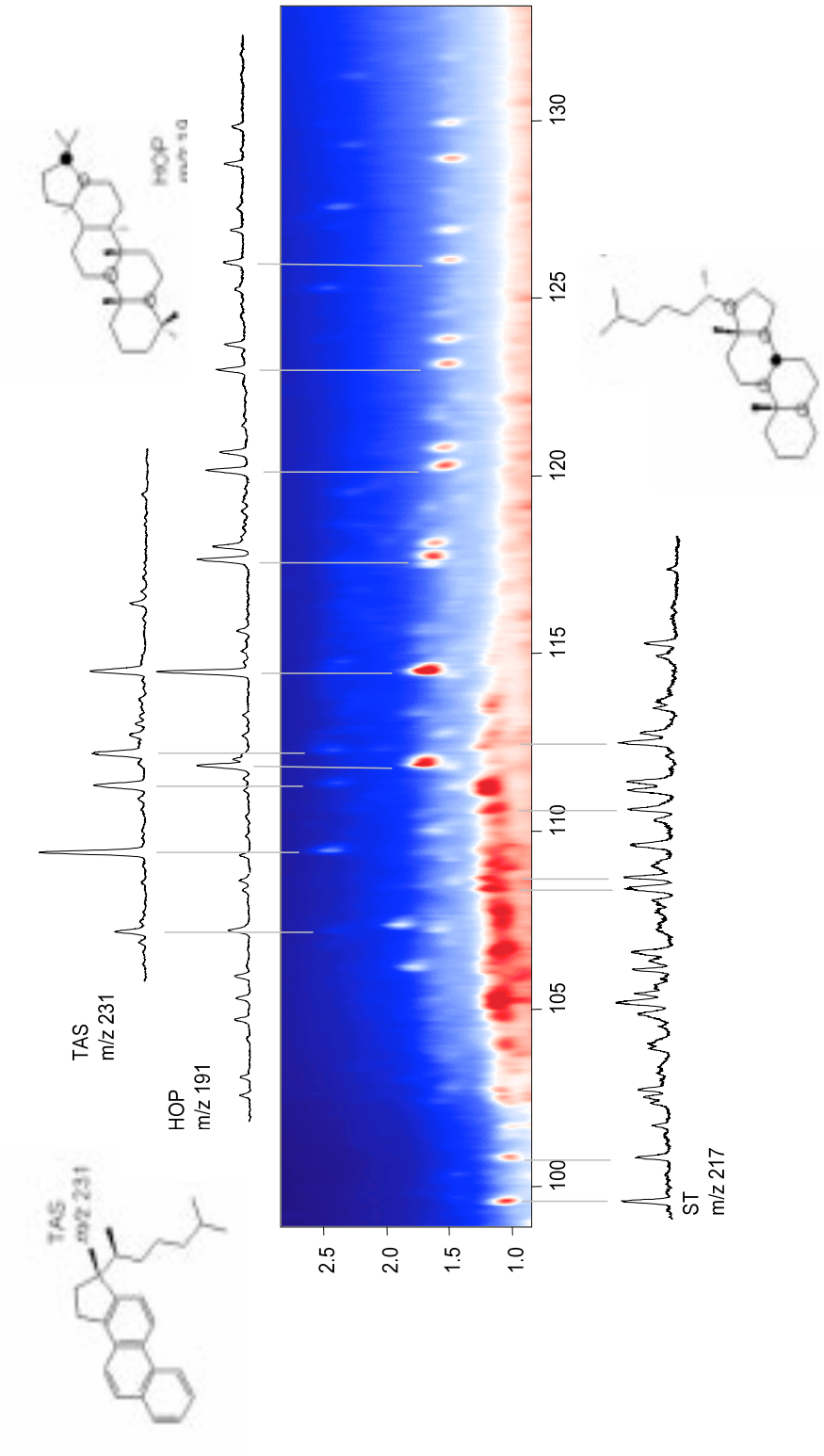


Figure 12.14. Extracted region of GC×GC–FID chromatogram of crude oil. GC–MS extracted ion chromatograms of triaromatic steranes (TAS), hopanes (HOP) and steranes (ST) overlaid for identification and comparison.

For chromatographic conditions, see previous example.

G.S. Frysinger, R.B. Gaines, *Separation and identification of petroleum biomarkers by comprehensive two-dimensional gas chromatography,* J. Sep. Sci. 24 (2001) 87-96.

Drilling fluids in Crude Oil

C.M. Reddy, R.K. Nelson, S.P. Sylva, L. Xu, E.A. Peacock, B. Raghuraman, O.C. Mullins, *Comprehensive two-dimensional gas chromatography with flame ionization detection to identify and quantify alkene-based drilling fluids in crude oils*, J. Chromatogr. 1148 (2007) 100-107

Instrumental conditions:

***Columns*:**
First: 7.5 m, 0.10 mm ID, 0.1 µm µm Rtx-1
Second: 2.0 m, 0.10 mm ID, 0.1 µm BPX50
Modulation cap.: 1.5 m, 0.10 mm ID

Carrier gas: hydrogen @ 0.7 mL/min

***Temperatures*:**
Main oven: 33°C (5 min), 1.5 °C/min → 285°C
Second oven: 46°C (5 min), 1.5 °C/min → 298°C

Injector: split/splitless, purge open @ 0.5 min
Temperature: 295 °C
Injection volume:

Modulator: loop modulator with liq. Ar chilled N_2

Modulation time: 10 s

Detector: FID
Temperature: 375
Make up gas flow:

Data acquisition: 100 Hz

Sample description and separation:

Although this is a rather peculiar column combination (second column only 10 times faster than the first one!), as a result of the low hydrogen flow and the slow temperature program, a quite acceptable separation is acquired.

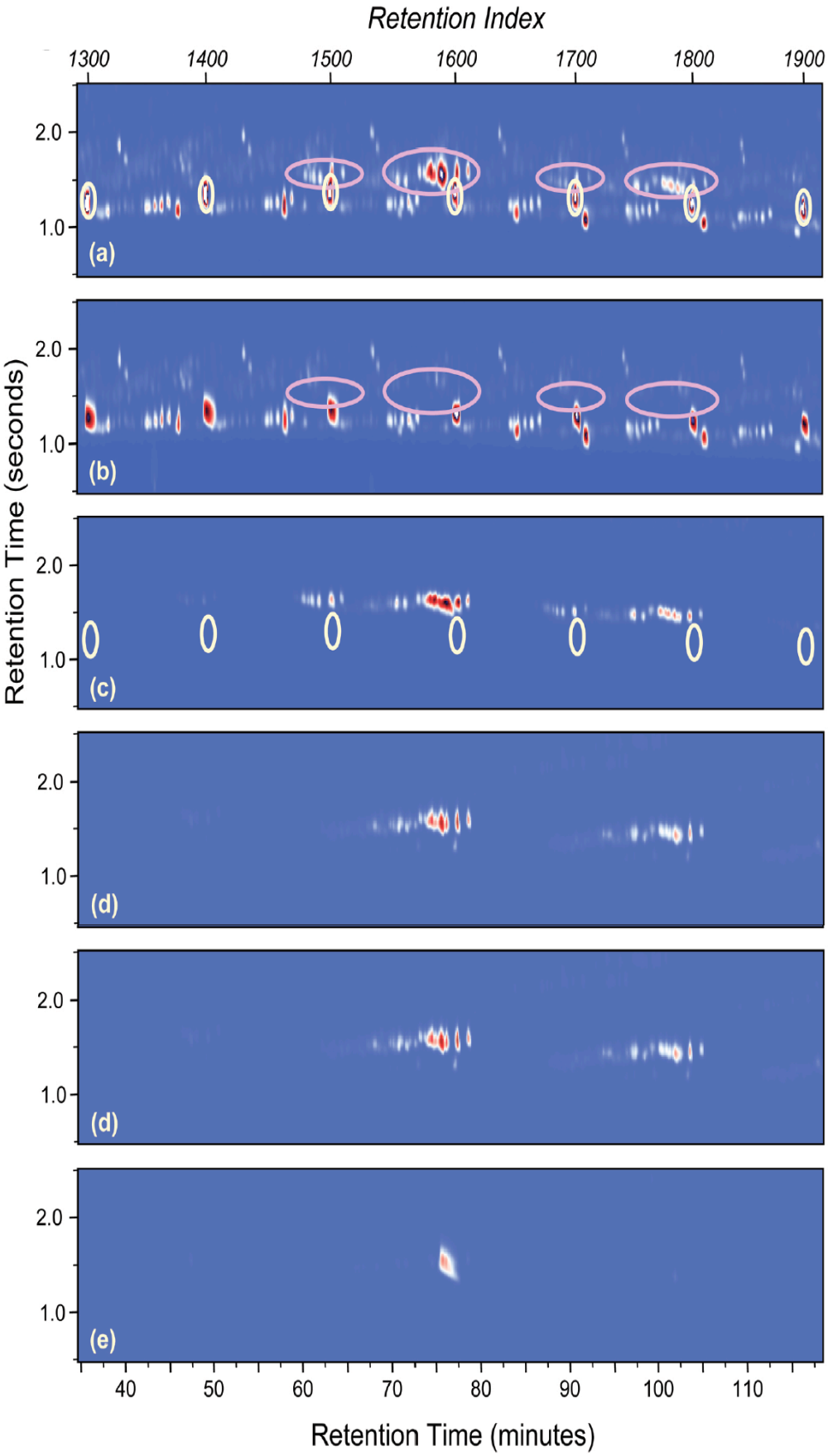


Figure 12.15. GC×GC-FID colour flot for (a) total extract, (b) non aromatics fraction of the extract, (c) olefin fraction of the extract, (d) iso-olefins (synthetic), and (e) alpha olefins. In Figures a and c, the ovals indicate retention of the alkenes and circles denote the location of n-alkane.

Oxygenates in gasoline

G.S. Frysinger, R.B. Gaines, *Determination of oxygenates in gasoline by GC×GC*, JHRC-J. High Res. Chrom. 23 (3) (2000) 197-201

see also: A. Venter P.R. Makgwane, E.R. Rohwer, *Group-type analysis of oxygenated compounds with a silica gel porous layer open tubular column and comprehensive two-dimensional supercritical fluid and gas chromatography*, Anal. Chem. 78 (2006) 2051-2054

Instrumental conditions:

***Columns*:**

First:	3.25 m × 0.10 mm ID, 5.0 µm dimethylpolysiloxane (Phase 007-1)
Second:	1.00 m × 0.10 mm ID, 0.10 µm, β-DEX 120
Modulation capillary:	10 cm × 0.10 mm ID, 5.0 µm dimethylpolysiloxane (Phase 007-1

Carrier gas: hydrogen, constant pressure @ 106 kPa, 75 cm/s @ – 40ºC

***Temperatures*:**

First column:	– 40°C (6 min), 4°C/min → 180 °C
Second column	40°C (6 min), 2°C/min → 75°C, 4°C/min → 220°C

Injector:	split, ratio 1:300
Temperature:	250°C
Injection volume:	0.1 µL

Modulator: Sweeper, velocity 0.25 rev/s, rotation angle 155 degrees, ΔT 75°C

Modulation time: 4.0 s

Detector:

Temperature:	250°C
Make up gas flow:	

Data acquisition: 100 Hz

Sample description and separation:

Sample: Reformulated gasoline with oxygenate standards (alcohols and ethers) added.

Thick film modulation capillary and cryogenic first oven and modulator tube temperatures required to modulate low boiling gasoline components (butane). Mixed phase second-dimension (Wax/β-cyclodextrin) used to improve separation of ether containing oxygenates. Quantitative application with results directly comparable to those obtained with standard ASTM methods

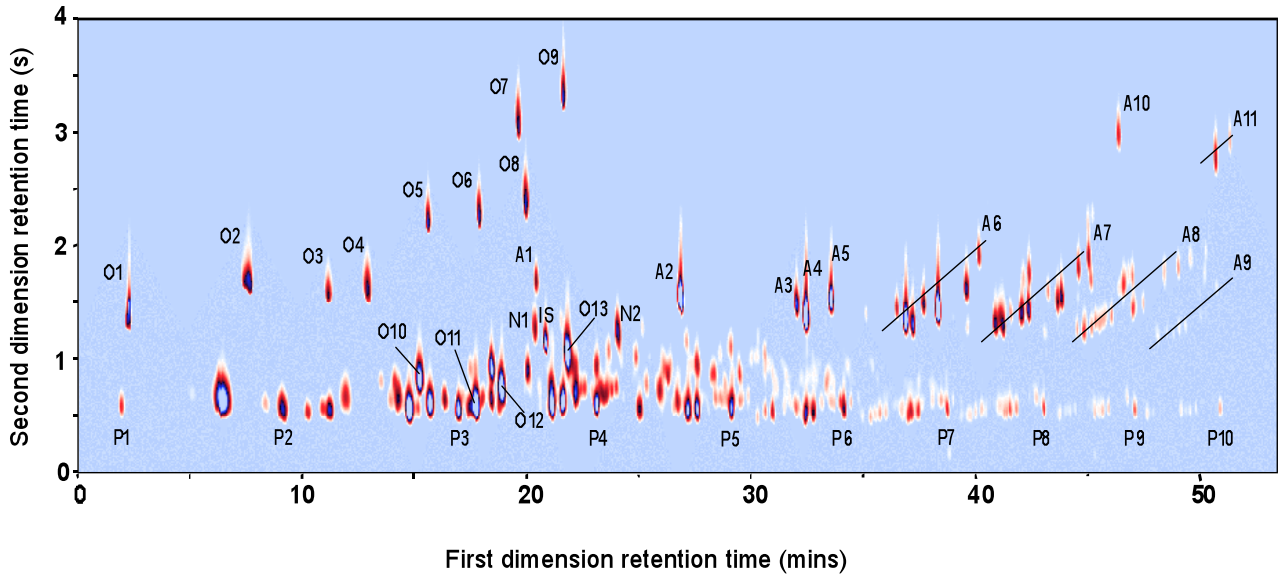


Figure 12.16. Colour plot of a GC×GC separation of reformulated gasoline.

O1. methanol , O2. ethanol , O3. isoproyl alcohol , O4. tert-butanol, O5. n-propanol , O6. sec-butanol, O7. iso butanol, O8. tert-pentanol,

O9. n-butanol, O10. methyl tert-butyl ether, O11. diisopropyl ether, O12. ethyl tert-butyl ether, O13. tert-amyl methyl ether,

N1. cyclo hexane, N2. methylcyclo hexane, IS. 1,2-dimethoxy ethane as internal standard:

P1. n-C_4, P2. n-C_5, P3. n-C_6, P4. n-C_7, P5. n-C_8, P6. n-C_9, P7. n-C_{10}, P8. n-C_{11}, P9. n-C_{12}, P10. n-C_{13}

A1. benzene, A2. toluene, A3. ethyl benzene, A4. para + meta xylene, A5. ortho xylene, A6. C_9 mono-aromatics, A7. C_{10} mono-aromatics,

A8. C_{11} mono-aromatics, A9. C_{12} mono-aromatics, A10. naphthalene, A11. Methylnaphthalene

Kerosene with GC×GC–ToF MS

M. van Deursen, J. Bseens, J. Reijenga, P. Lipman, C. Cramers, J. Blomberg, *Group-type identification of oil samples using comprehensive two-dimensional gas chromatography coupled to a time-of-flight mass spectrometer,* JHRC-J. High Res. Chrom. 23 (2000) 507-510

Instrumental conditions:

***Columns*:**
First: 10 m, 0.25 mm ID, 0.25 µm DB1
Second: 0.6 m, 0.10 mm ID, 0.1 µm BPX50
Modulation capillary: 7 cm, 0.10 mm ID, 3 µm SE30

Carrier gas: helium @ 75 kPa
***Temperatures*:**
Main oven: 40°C + 5 minutes, 3°C/min → 250°C + 5 minutes
Second oven: 55°C + 5 minutes, 3°C/min → 265°C + 5 minutes

Injector: PTV, split ratio 1:50
Temperature: → 350°C
Injection volume: 1 µL

Modulator: Sweeper, 0.25 revs/s, 1 s delay at the end of modulation capillary

Modulation time: 7.5 s

Detector: ToF-MS
Temperature: ion source: 180°C, transfer line: 275°C
Make up gas flow:

Data acquisition: 50 spectra/s

Sample description and separation:

The kerosene was separated according to the upper colour plot in the Fig. As can be seen, the structures in the plot using the TIC, enable the identification of the different groups. To enhance the selectivity, selective ions were extracted from the MS-data file:

- for the alkanes: the sum of the ions *m/z* 71, 85, 99 and 113;
- for the mono-naphthenes (not shown here): the sum of the ions m/z 69, 83, 97, 98, 111, 112, 153;
- for the di-naphthenes (not shown here): the sum of the ions m/z 67, 81, 95, 109;
- for the mono-aromatics, shown in the lower colour plot: 77, 91, 105;
- benzothiophenes (not shown here): 148, 162, 176.

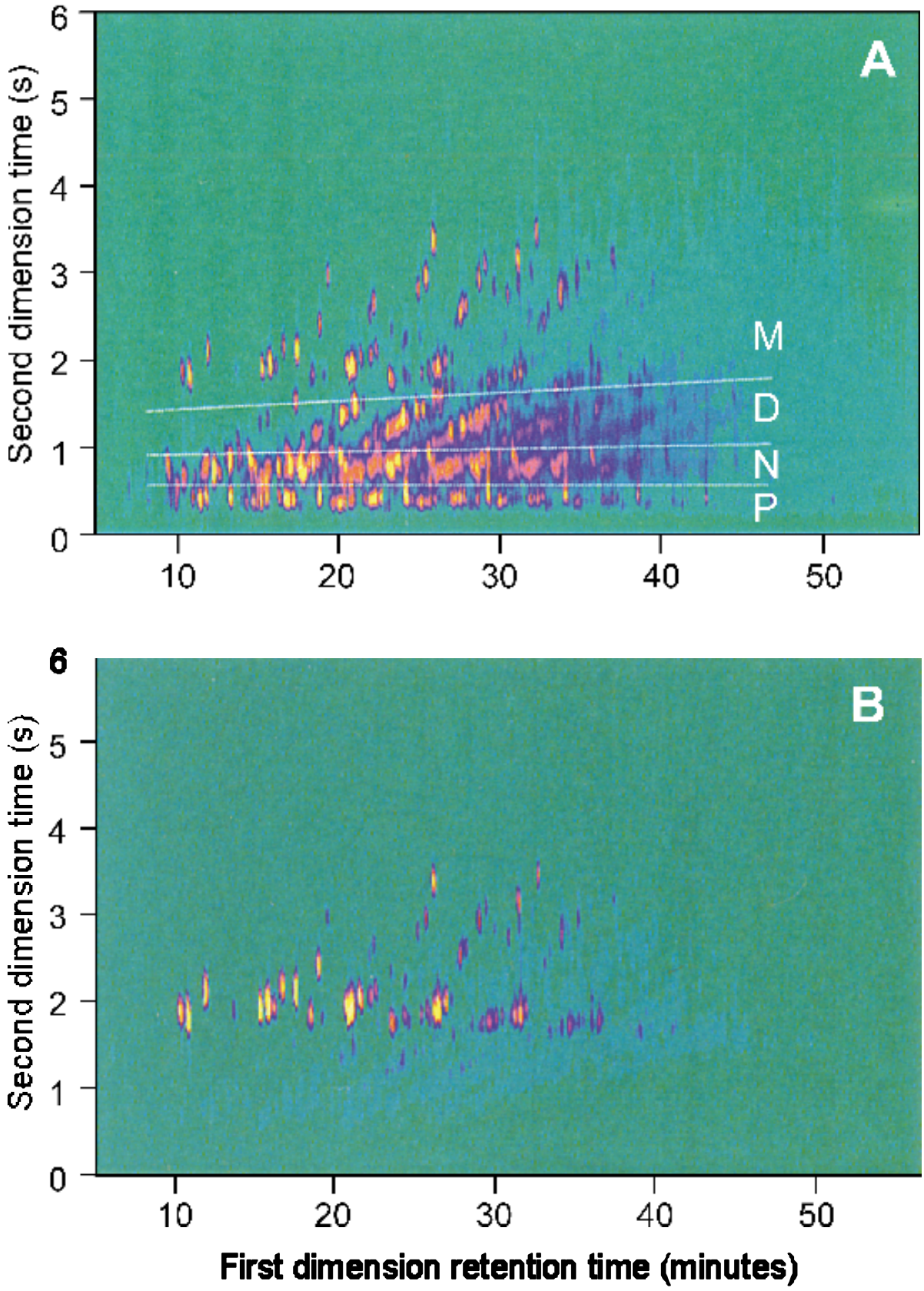


Figure 12.17. Colour plots of: A. TIC plot of the GC×GC separation of a kerosene. P = paraffins, N = mono-naphthenes, D = di-naphthenes, M = mono-aromatics. B. Selected ion plot of the mono-aromatics.

Sulphur compounds in LCCCO with ToF MS

J. Dallüge, J. Beens, U.A.Th. Brinkman, *Comprehensive two-dimensional gas chromatography: a powerful and versatile analytical tool*, J. Chromatogr. A 1000 (2003) 69-108.

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:	40°C + 5 minutes, 3°C/min → 250°C + 5 minutes
Second oven:	
Injector:	split/splitless
Temperature:	
Injection volume:	1 μL
Modulator:	dual stage cryogenic
Modulation time:	7 s
Detector:	ToF-MS
Temperature:	ion source: 2500°C, transfer line: 280°C
Make up gas flow:	
Data acquisition:	100 spectra/s

Sample description and separation:

Due to coelution it is not possible to distinguish the benzothiophenes from the hydrocarbon compounds. This required the use of properlyed extracted-ion chromatograms. In Fig. 12.18B the molecular ions of the C - to C -substituted benzothiophenes were used to generate the chromatogram. They clearly show the presence of several compounds belonging to each of the benzothiophene subclasses, as well as the typical roof-tile structure.

The detection of (if possible individual) alkyl-substituted benzothiophenes and benzonaphthothiophenes is highly important when low-sulphur fuels have to be produced, since these compounds are much more difficult to remove by hydrotreating.

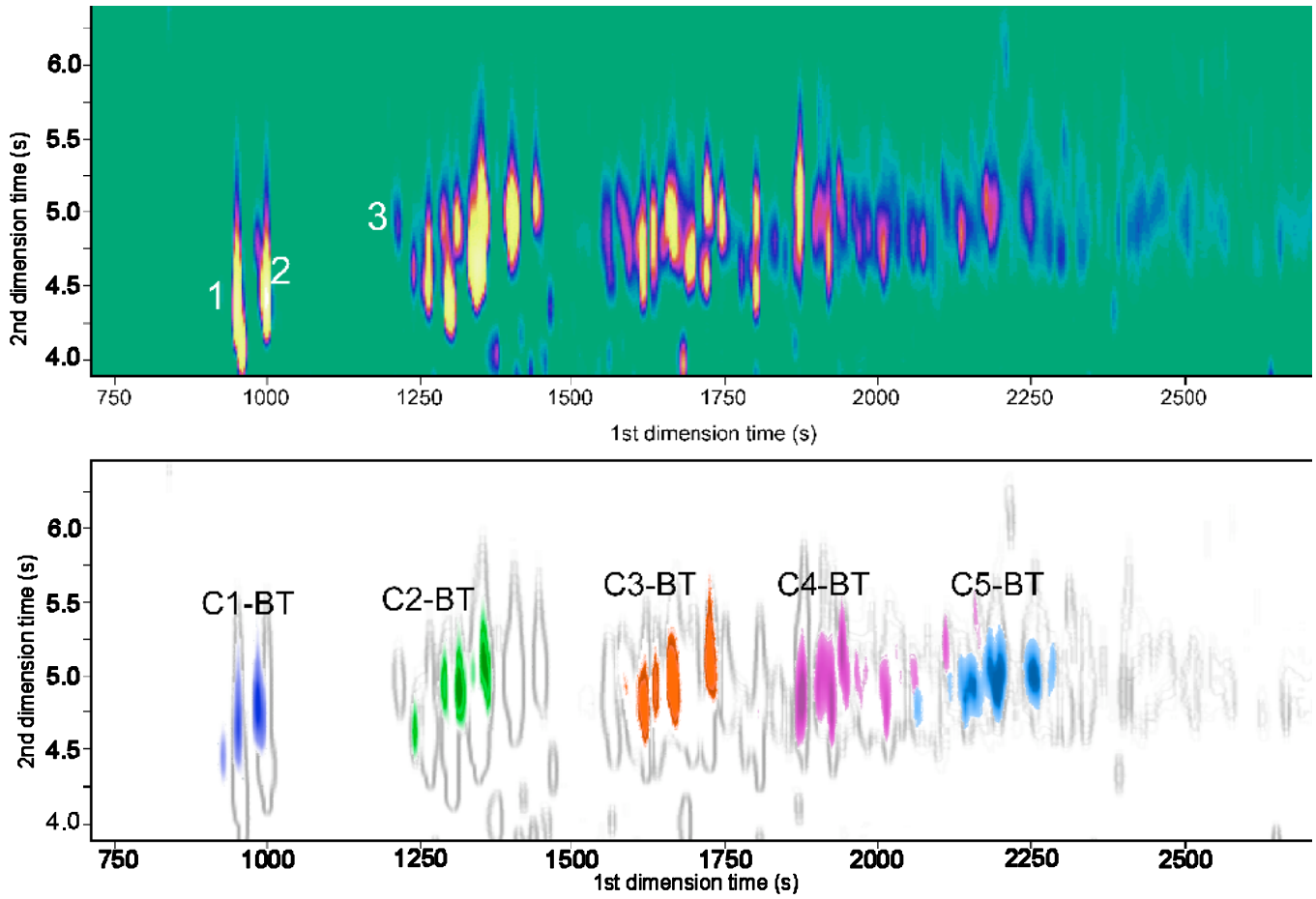


Figure 12.18. Di-aromatics section of a GC×GC separation of an LCCCO.
Upper colour plot: TIC, 1. 2-methyl-naphthalene, 2. 1-methyl-naphthalene, 3. ethyl- and dimethyl-naphthalenes + methyl-benzothiophenes.
Lower colour plot: selected ions colour plot. The benzothiophenes (BT) are indicated in colour, the original TIC contour plot is shadowed behind the selected compounds in grey.

Sulphur in Fluid Cat. Cracked Cycle Oil (FCCCO) with FPD

D. Cavagnino, Thermo Electron, Milan, Italy, *unpublished results*

Instrumental conditions:

***Columns*:**
First: 30 m, 0.32 mm ID, 0.25 μm Rtx-5
Second: 1 m, 0.10 mm ID, 0.1 μm BPX50
Modulation capillary:

Carrier gas: helium

***Temperatures*:**
Main oven: 50°C (1 min), 3°C/min → 300°C
Second oven:

Injector: split/splitless, split ratio 1:200
Temperature:
Injection volume: 0.4 μL

Modulator: dual cryojet

Modulation time: 4 s

Detector: FPD
Temperature:
Make up gas flow:

Data acquisition: 200 Hz

Sample description and separation:

A light catalytically cracked cycle oil (LCCCO, boiling range 100 - 500ºC) was injected without dilution and separated.

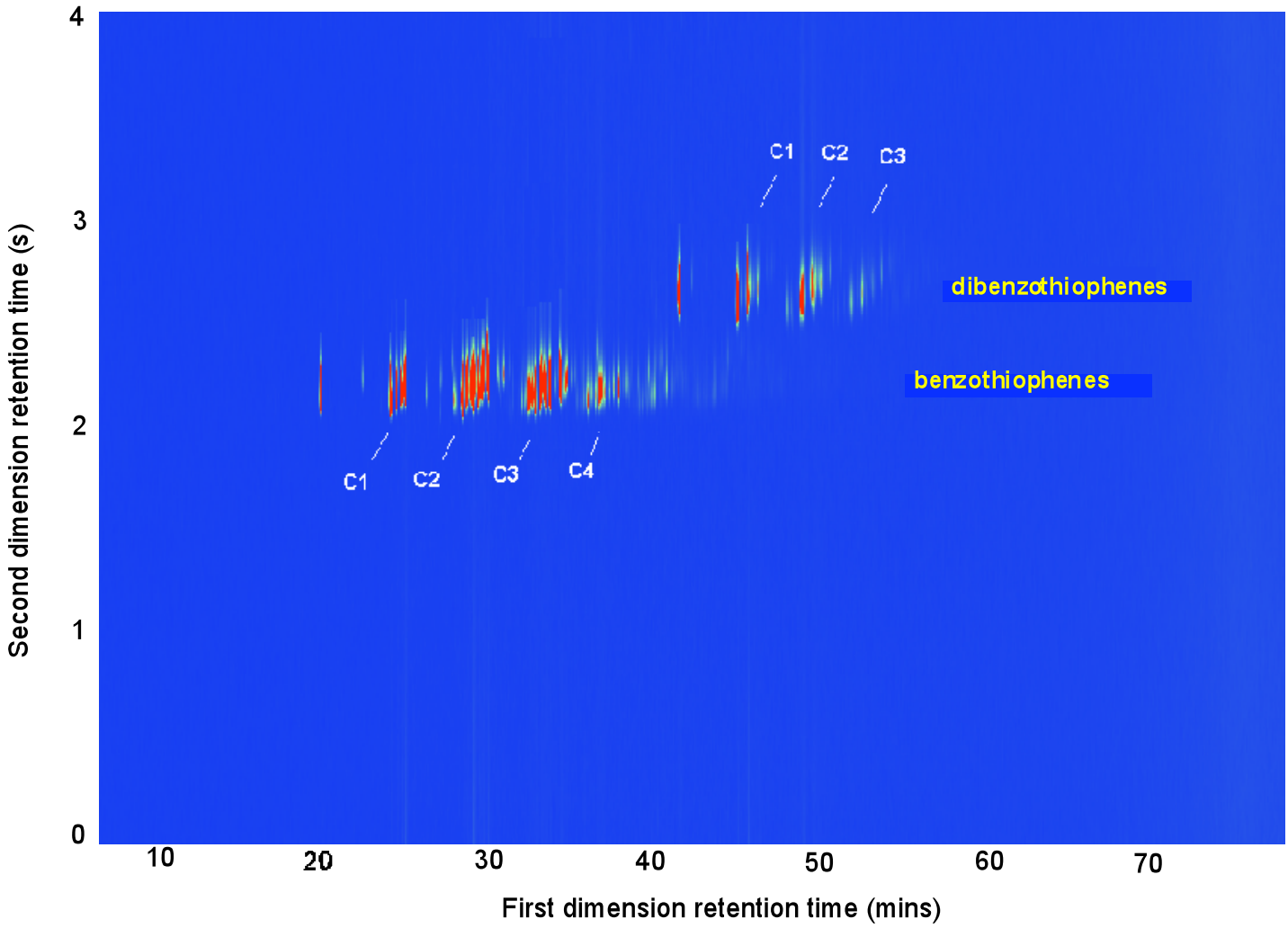


Figure 12.19. GC×GC–FPD separation of sulphur compounds in a Light Catalytically Cracked Cycle Oil (LCCCO).

The two groups, viz. benzothiophenes and dibenzothiophenes are clearly ordered and separated. C1 through C4: alkyl substitution onto the rings.

Nitrogen in Diesel

F.C-Y. Wang, W.K. Robinson, F.P. DiSanzo. F.C. McElroy, *The applications of comprehensive two-dimensional gas chromatography in the petroleum industry,* J. Chromatogr. Sci. 41 (2003) 519-525
see also: F. Adam, F. Bertocini, N. Brodusch, E. Durand, D. Thiébaut, D. Espinat, M-C. Hennion, *New benchmark for basic and neutral nitrogen compounds speciation in middle distillates using comprehensive two-dimensional gas chromatography*. J. Chromatogr. A. 1148 (2007) 55-64

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 1.0 μm, SBP-5
Second: 3 m × 0.25 mm ID, 0.25 μm, BPX50

Carrier gas: helium, constant flow @ 6.2 mL/min

***Temperatures*:**
Main oven: 60°C, 3°C/min → 300°C
Second oven:

Injector: split, ratio 1:750
Temperature: 300°C
Injection volume: 1 μL

Modulator: dual cryogenic, dual heated jet modulator

Modulation time: 10 s

Detector: NCD
Temperature:
Make up gas flow:

Data acquisition: 100 Hz

Sample description and separation:

Typical untreated diesel sample. Contains approx. 40 ppm nitrogen.

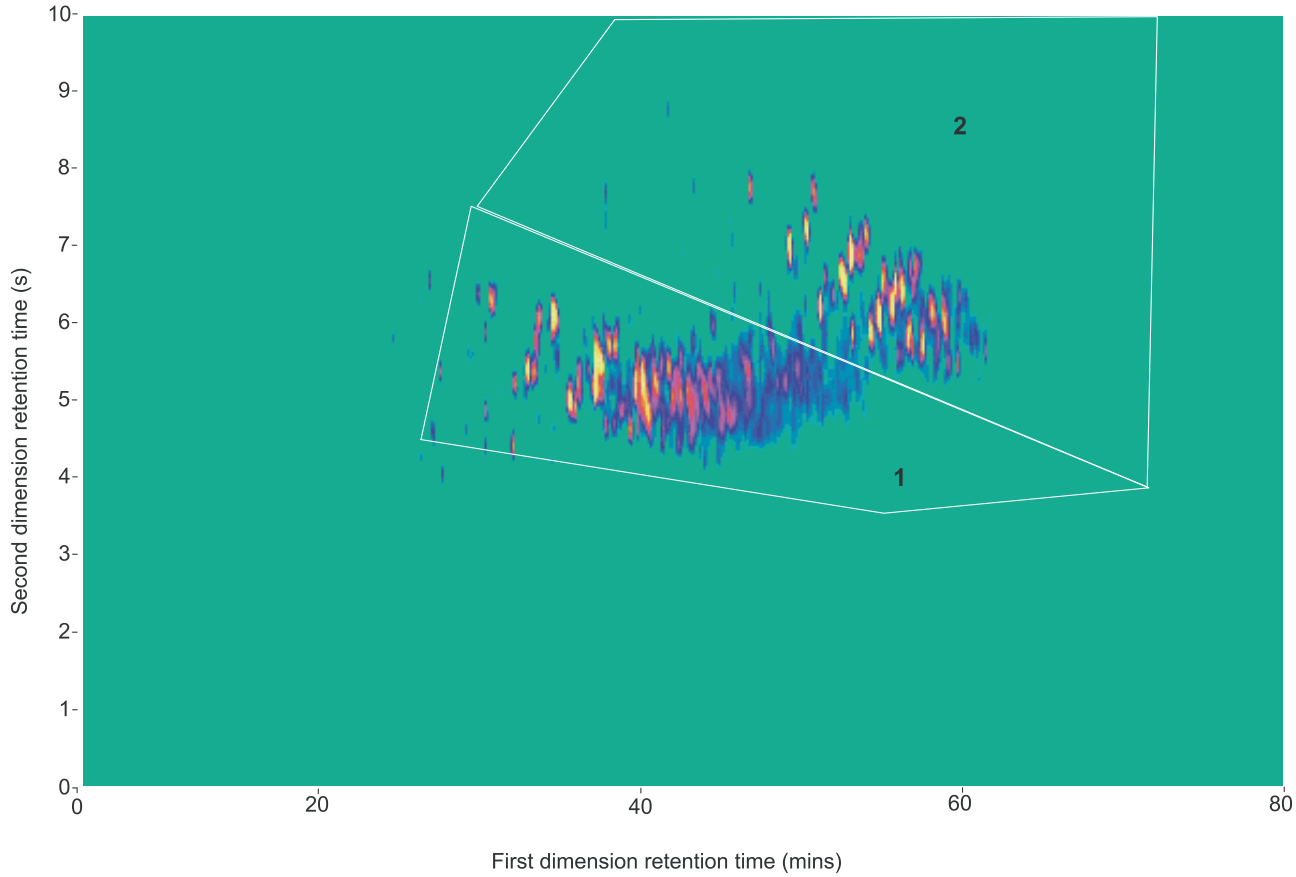


Figure 12.20. Colour plot of a GC×GC separation of the nitrogen compounds of a diesel. The two different groups are nicely separated.
1. carbazoles, 2. benzocarbazoles

Biodiesel blends in diesel

F. Adam, F. Bertoncini, V. Coupard, N. Charon, D. Thiébaut, D. Espinat, M.-C. Hennion, *Using comprehensive two-dimensional gas chromatography for the analysis of oxygenates in middle distillates I. Determination of the nature of biodiesels blend in diesel fuel,* J. of Chromatogr. A, 1186 (2008) 236–244

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.25 µm Solgel Wax
Second: 1.1 m × 0.1 mm ID, 0.1 µm DB1
Modulation capillary:

Carrier gas: helium, constant flow @ 0.9 mL/min

***Temperatures*:**
Main oven: 50°C, 2 °C/min → 300°C
Second oven:

Injector: split/splitless, 1:100
Temperature:
Injection volume: 0.5 µL

Modulator: quad-jet cryogenic

Modulation time: 10 s

Detector: ToF MS
Temperature:
Make up gas flow:

Data acquisition: 100 spectra/s 35-500 *m/z*

Sample description and separation:

Blending of fatty acid alkyl esters from vegetable oils (biodiesel) with conventional diesel fuel is one of the solutions technologically available; Blends with up to 5% w/w esters in fossil fuel are marketed over Europe.

Several first and the second dimension columns have been investigated to achieve (i) a group type separation of hydrocarbons and (ii) individual identification and quantitation of fatty acid ester blends. It is demonstrates that GC×GC enables fast and reliable individual quantitation of fatty acid esters in one single run. Results show that simultaneous quantification of hydrocarbons and fatty acid esters can be achieved in one single run

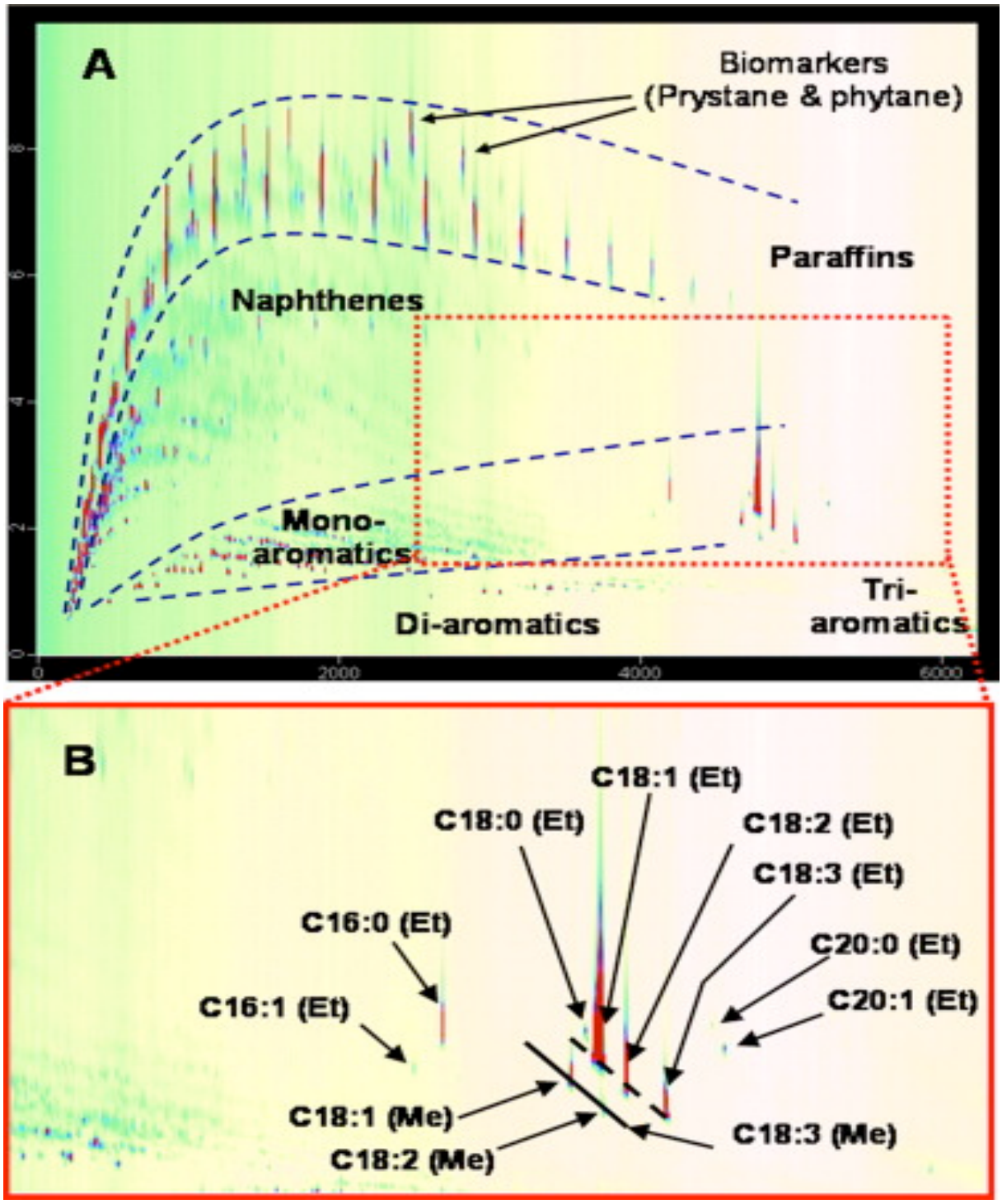


Figure 12.21. Illustration of a polar×non-polar approach for the separation of fatty acid esters occurring in esterified rapeseed oil and hydrocarbons in synthetic B5 diesel samples.

Pyrolisis of petroleum source rock

F. C.-Y. Wang, C.C. Walters, *Pyrolysis comprehensive two-dimensional gas chromatography study of petroleum source rock,* Anal. Chem. 2007, 79, 5642-5650

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 1 µm BPX-5
Second: 3 m × 0.25 mm ID, 0.25 µm BPX-50
Modulation capillary:

Carrier gas: helium, constant flow @ 6.2 mL/min

***Temperatures*:**
Main oven: 60°C, 3°C/min → 390°C
Second oven:

Injector: split 1:50
Temperature: 300°C
Injection volume: pyrolisis product

Modulator: quad-jet cryogenic

Modulation time: 0 s

Detector: FID, SCD
Temperature: ion source 250°C
Make up gas flow:

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

Sample description and separation:

A micro-oven type of pyrolyzer (Frontier Lab. model 2020iD), was used. A small piece of rock (approximately 2 mg) sample was deposited into a sample cup, which was then mounted on the pyrolyzer connected to the injection port. Pyrolysis occurred by dropping the sample cup through the micro-oven held at a calibrated temperature of 650 °C.

In the hydrocarbon analysis by FID, paraffins, naphthenes, and aromatics form distinct two-dimensional separated groups. In the analysis with SCD, sulfur-containing compounds
can be distinguished as different classes, such as mercaptans, sulfides, thiophenes, benzothiophenes, and dibenzothiophenes.

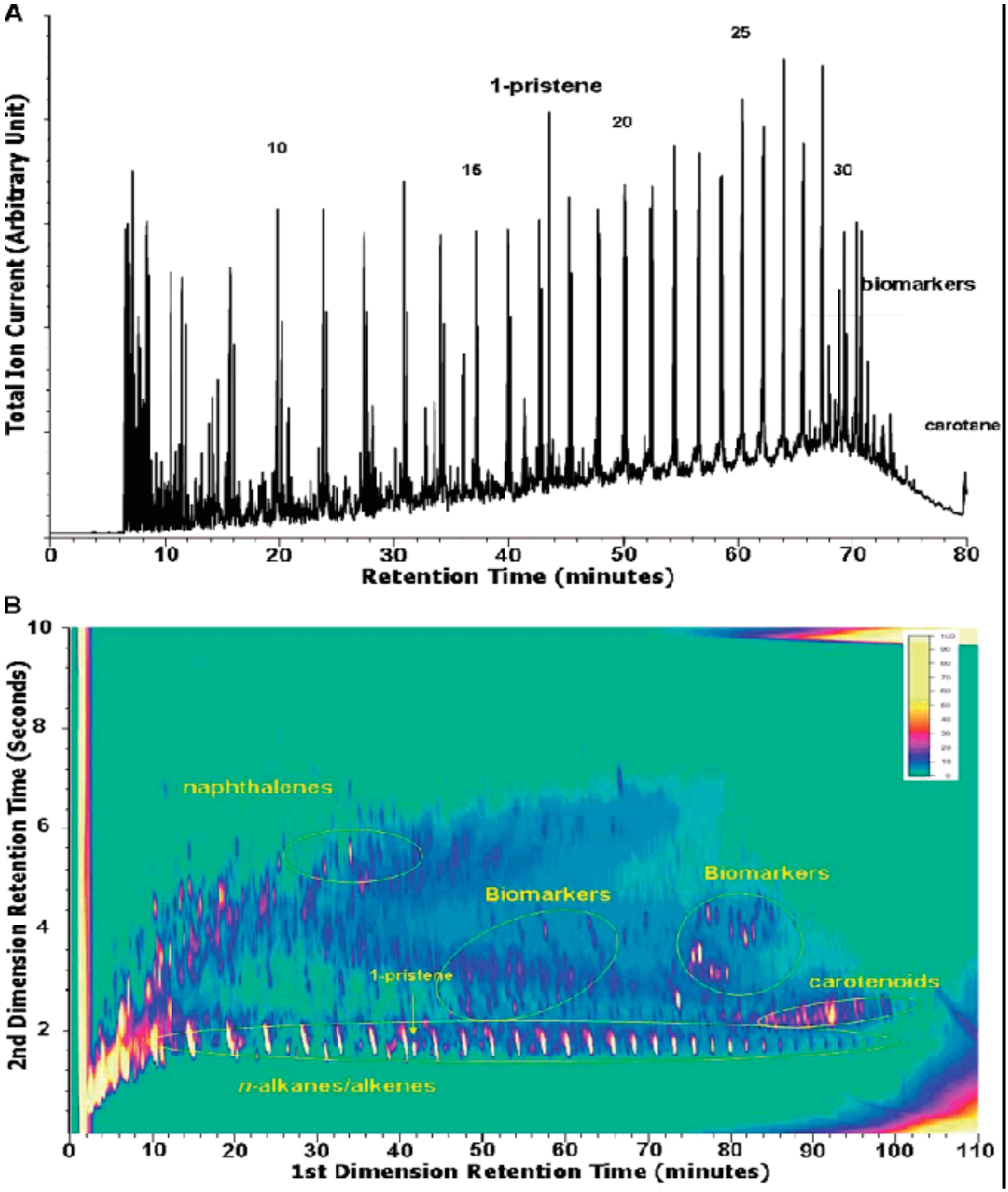


Figure 12.22. Top: Conventional py–GC–MS TIC of Green River shale. The numbers in the figures are numbers of carbons in the molecules.

Bottom: Py–GC×GC–FID chromatogram of Green River shale.

Biodegradation of a petroleum spill

G.F. Slater, R.K. Nelson, B.M. Kile, C.M. Reddy, *Intrinsic bacterial biodegradation of petroleum contamination demonstrated in situ using natural abundance, molecular-level ^{14}C analysis*, Organic Geochemistry 37 (2006) 981–989,
see also S. Penet, C. Vendeuvre, F. Bertoncini, R. Marchal, F. Monot, *Characterisation of biodegradation capacities of environmental microflorae for diesel oil by comprehensive two-dimensional gas chromatography*, Biodegradation 17 (2006) 577–585

Instrumental conditions:

***Columns*:**
First: 7 m × 0.1 mm ID, 0.4 µm, Rtx-1
Second: 0.82 m × 0.1 mm ID, 0.1µm, BPX50

Carrier gas: not specified

***Temperatures*:**
Main oven: 40°C (1 min), 20°C/min → 130°C, 4°C/min → 160°C, 8°C/min → 300°C

Second oven:

Injector: split/splitless
Temperature:
Injection volume:

Modulator: loop jet modulator

Modulation time:

Detector: FID
Temperature:
Make up gas flow:

Data acquisition: 100 Hz

Sample description and separation:

Natural abundance, molecular-level ^{14}C analysis was combined with GC×GC to investigate, *in situ*, the role of intrinsic biodegradation in the loss of petroleum hydrocarbons from the rocky, inter-tidal zone impacted by the Bouchard 120 oil spill. The analysis indicated accelerated losses of n-alkane components of the residual hydrocarbons between day 40 and day 50 after the spill. ^{14}C analysis of bacterial phospholipid fatty acids from the impacted zone on day 44 showed that the polyunsaturated fatty acids attributed to the photoautotrophic component of the microbial community had the same $D^{14}C$ as the local dissolved inorganic carbon (DIC), indicating that this DIC was their carbon source.

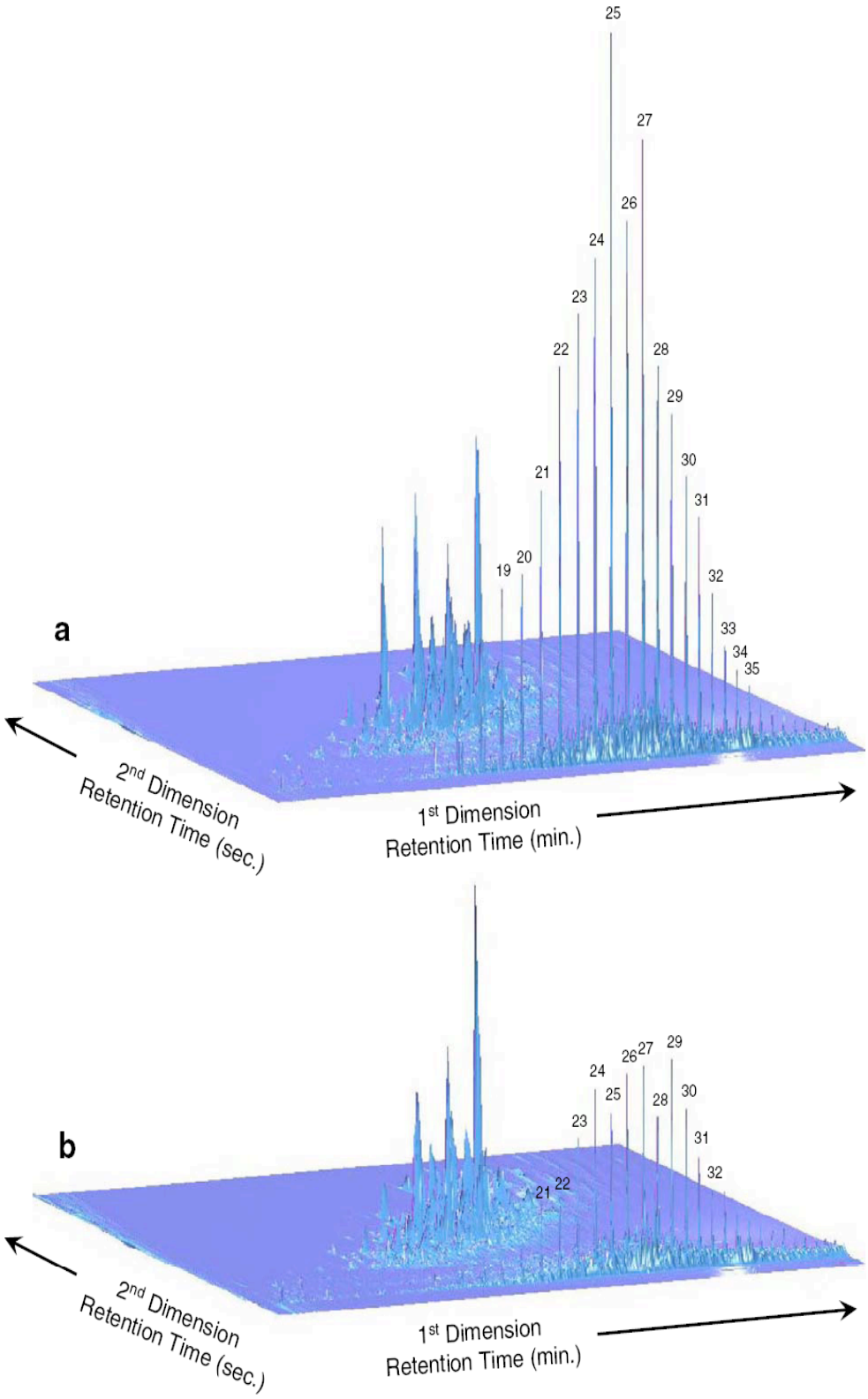


Figure 12.23. GC×GC 3D-colour plots of the petroleum hydrocarbons at the site on day 40 (a) and day 50 (b) after the spill illustrating the extent of loss of the n-alkane envelope (n-alkanes are denoted by carbon number at the top of the peaks) relative to the aromatic components of the petroleum hydrocarbons that appear behind the alkanes (i.e. at higher second dimension retention times).

Wash oil

K. Sun, W. Winniford, J. Griffith, K. Colura, S. Green, M Pursch, J. Luong, *Comprehensive two-dimensional gas chromatography for fast screening of wash oils* J. Chromatogr. Sci. 41 (2003) 506-518

Instrumental conditions:

***Columns*:**
First: 15 m × 0.25 mm ID, 0.25 µm, DB-5
Second: 1 m × 0.1 mm ID, 0.1µm, DB-Wax

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

***Temperatures*:**
Main oven: 80°C (1 min), 2°C/min → 250°C
Second oven:

Injector: split @ 50 mL/min
Temperature: 250°C
Injection volume:

Modulator: quad-jet cryo modulator

Modulation time: 16 s

Detector: FID
Temperature: 350°C
Make up gas flow:

Data acquisition: 100 Hz

Sample description and separation:

Wash oils are used in ethylene production plants to minimize compressor fouling. The composition of wash oils determines its effectiveness in solubilising heavy hydrocarbons. In particular, the relative amount of one- and two-ring aromatics is important. The presence of oxygenates is undesirable because of adverse effects to the process.

Species in wash oils are separated and grouped into three bands: a nonpolar aliphatics band, one- and two-ring aromatics band, and polyaromatics band.

Consistent quantitative results are obtained using integration programs for well-separated GC×GC peaks with relative differences for individual peak ranging from 0.04% to 1.6%. Peak responses are integrated by the GC×GC software, and the relative amounts of aromatics content and aliphatics content are estimated by peak response percent with relative standard deviations ranging from 0.15% to 2.8% (n=3).

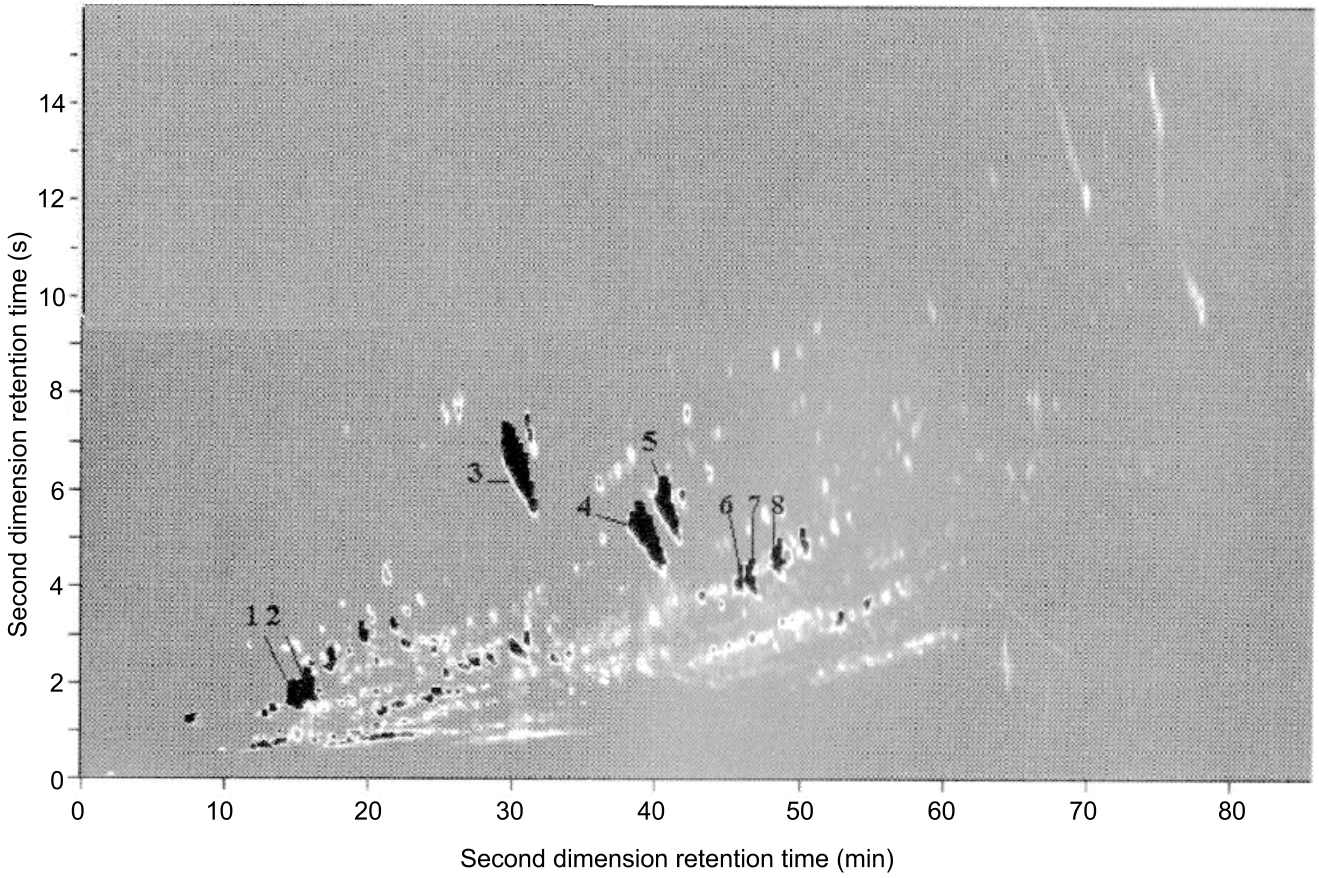


Figure 12.24. Two-dimensional plot of the separation of a wash oil.
Identification: 1. isomer of triethyl-benzene, 2. isomer of triethyl-benzene, 3. diphenylethane, 4. 1,1' ethylidene bis(4-methylbenzene),
5. isomer of 4, 6. 1,1-bis-(p- ethylphenyl)ethane, 7. isomer of 6, 8. isomer of 6.

Flash pyrolysis and hydrodeoxygenated oils

J.H. Marsmana, J. Wildschut, P. Evers, S. de Koning, H.J. Heeres, *Identification and classification of components in flash pyrolysis oil and hydrodeoxygenated oils by two-dimensional gas chromatography and time-of-flight mass spectrometry,* J. of Chromatography (2008)

Instrumental conditions:

***Columns*:**
First: 30 m × 0.25 mm ID, 0.5 µm VF-5 MS
Second: 2 m × 0.1 mm ID, 0.2 µm VF-17 MS
Modulation capillary:

Carrier gas: helium, constant flow @ 1 mL/min

***Temperatures*:**
Main oven: 40°C (5 min), 3°C/min → 330°C
Second oven: 50°C (5 min), 3°C/min → 340°C

Injector: split, 1:10
Temperature: 275°C
Injection volume: 0.1 µL

Modulator: quad-jet cryogenic

Modulation time: 10 s

Detector: ToF MS
Temperature: ion source 200°C
Make up gas flow:

Data acquisition: 100 spectra/s, 50-500 *m/z*

Sample description and separation:

Fractionation of the hydrodeoxygenated oils by hexane extraction was applied to show the distribution of analytes over the phases. Some 1000 and 2000 components in the pyrolysis and HDO oil, respectively could be identified and classified. By group-type classification of the main components (>0.3% relative area), it was possible to characterize the oils by 250 and 350 analytes, respectively pyrolysis oil and HDO oil, describing 75% of the chromatographable fraction. The method showed to be a useful and fast technique to determine the composition of (upgraded) pyrolysis oil and is potentially a very useful tool for exploratory catalyst research and kinetic studies.

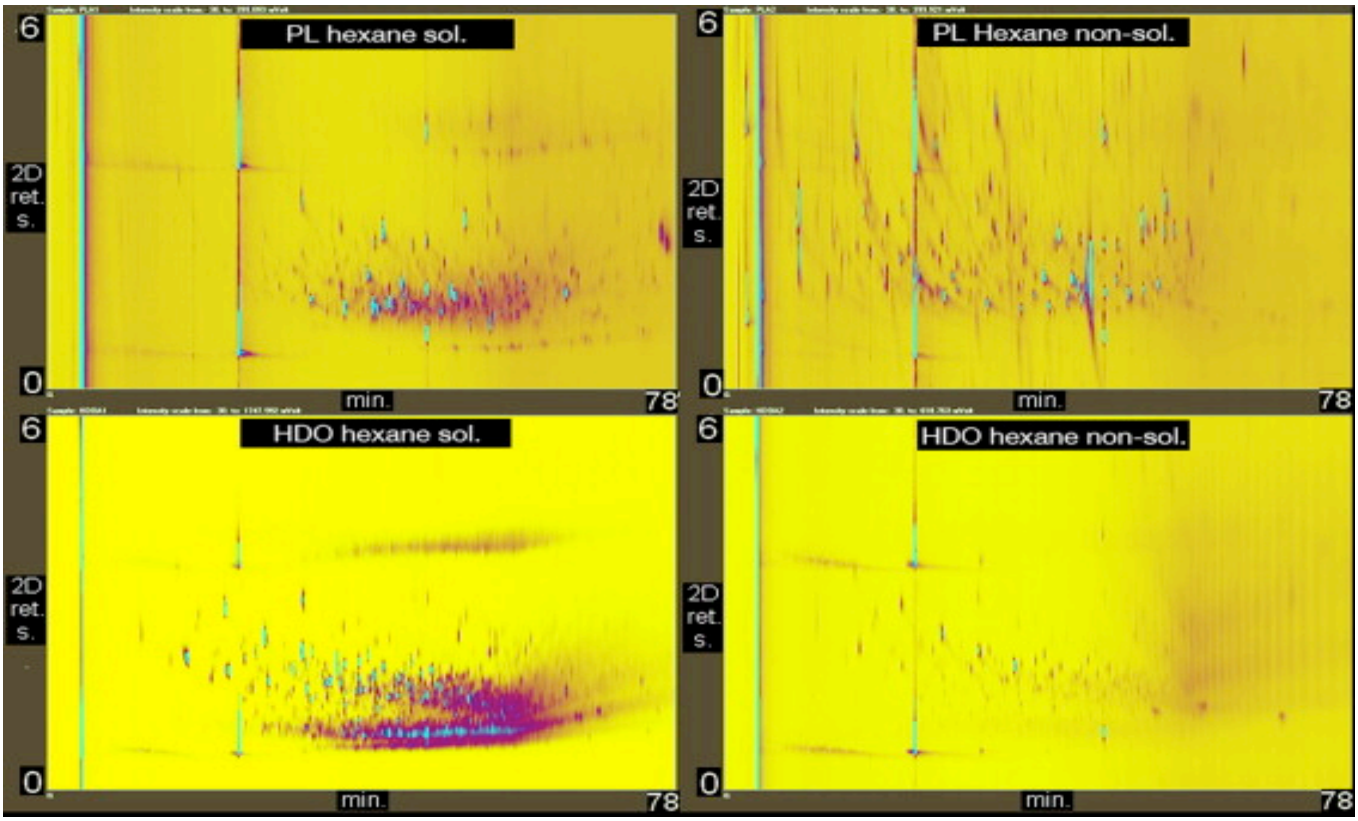


Figure 12.25. Contour plots of the hexane solubles and hexane non-solubles after hexane extraction of pyrolysis oil and its converted HDO oil.

Group-type characterisation of oil polutions

D. Mao, H. Van De Weghe, L. Diels, N. De Brucker, R. Lookman, G. Vanermen,
High-performance liquid chromatography fractionation using a silver-modified column followed by two-dimensional comprehensive gas chromatography for detailed group-type characterization of oils and oil pollutions, J of Chromatography 1179 (2008) 33-40

Instrumental conditions:

***Columns*:**
First: 30 m × 0.32 mm ID, 0.25 µm Rtx-1
Second: 2.5 m × 0.1 mm ID, 0.1 µm BPX-50
Modulation capillary:

Carrier gas: helium, constant flow @ 1 mL/min

***Temperatures*:**
Main oven: 40°C (5 min), 3°C/min → 330°C
Second oven: 50°C (5 min), 3°C/min → 340°C

Injector: PTV, splitless time 3 min
Temperature: 50°C(0.1 min), 14.5°C/s → 330°C
Injection volume: 4 µL

Modulator: dual-jet cryogenic

Modulation time: 10 s

Detector: FID
Temperature: 300°C
Make up gas flow:

Data acquisition: *2*00 Hz

Sample description and separation:

With a silver-modified column in HPLC, the petroleum hydrocarbons were baseline separated into a saturated fraction (including alkanes and cycloalkanes) and an unsaturated fraction (including alkenes, aromatic hydrocarbons and heterocyclic components). Each fraction eluted in a narrow time window limiting the dilution caused by HPLC. The two fractions were collected and quantitatively analysed with GC×GC–FID. Cold splitless injection of 4 µL was adopted to compensate the dilution caused by the prefractionation step. With oil-spiked soil samples, a good reproducibility was obtained (RSD = 3.5%; *n* = 7) and the recovery was satisfactory (87.7%).

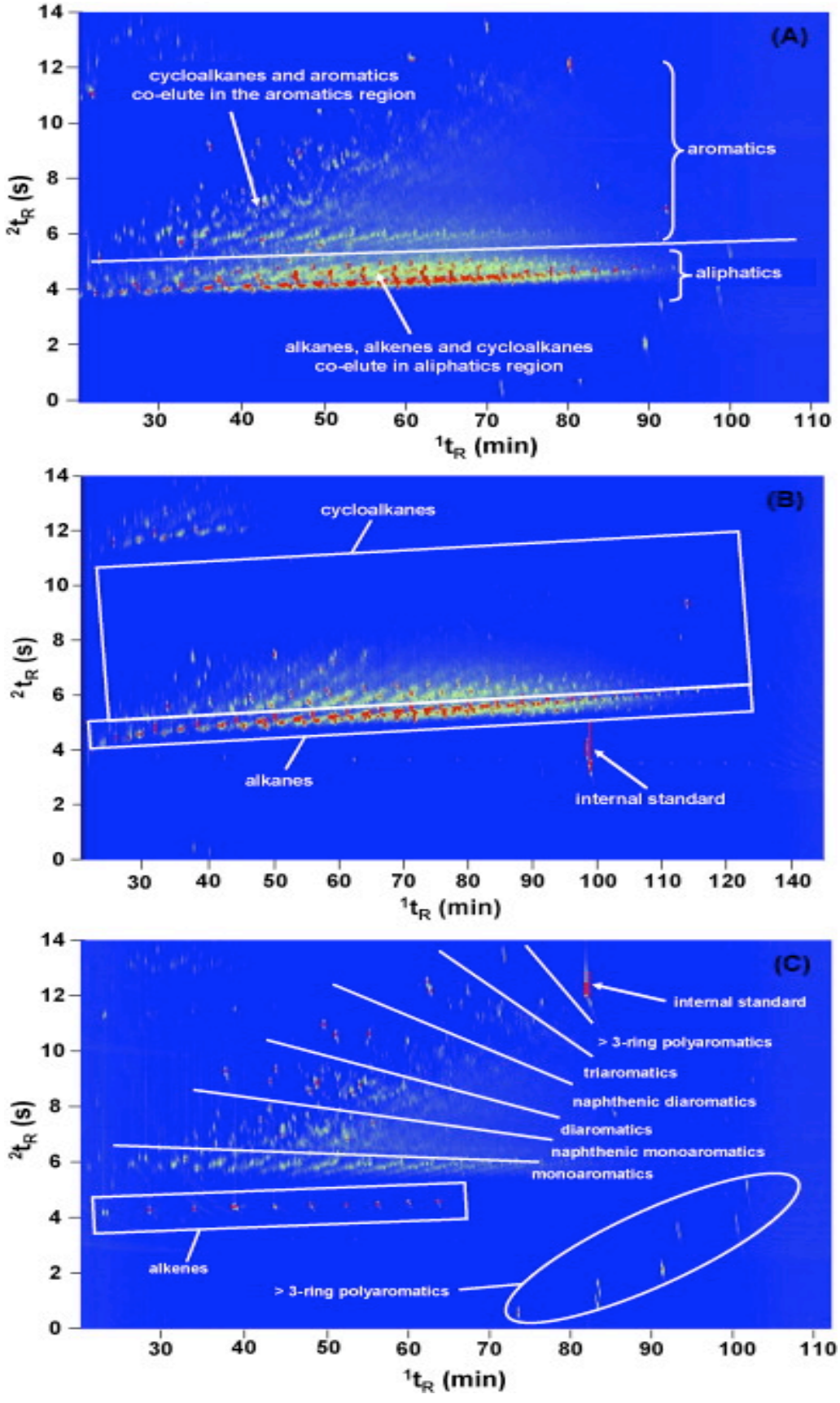


Figure 12.26. Colour plots of the spiked soil sample. (A) GC×GC–FID (without HPLC fractionation), (B) HPLC–GC×GC–FID saturated fraction, (C) HPLC–GC×GC–FID unsaturated fraction. Tentative identification was based on retention time matching and GC×GC–ToF MS data.

Coal liquefaction products

J.F. Hamilton, A.C. Lewis, M. Millan, K.D. Bartle, A.A. Herod, R. Kandiyoti, *Comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry of coal liquids produced during a coal liquefaction process,* Energy & Fuels 2007, 21, 286-294

Instrumental conditions:

***Columns*:**
First: 10 m × 0.18 mm ID, 0.18 µm HP-5
Second: 1.9 m × 0.1 mm ID, 0.1 µm DB17
Modulation capillary:

Carrier gas: helium, constant flow @ 1 mL/min

***Temperatures*:**
Main oven: 70°C (5 min), 5°C/min → 250°C (10 min)
Second oven: 85°C (5 min), 5°C/min → 265°C (10 min)

Injector: split/splitless
Temperature:
Injection volume: 1µL

Modulator: quad-jet cryogenic

Modulation time: 8 s

Detector: ToF MS
Temperature:
Make up gas flow:

Data acquisition: not mentioned

Sample description and separation:
The feed to the hydrocracker of the coal liquefaction plant and the resulting products were analyzed. The method allows for the resolution of the numerous structural isomers of tetralin and methyl indan, one pair of hydrogen-donor (necessary for the dissolution of coal) and isomeric nondonor (that reduce the hydrogen donors) components of the recycle solvent. In addition, the *n*-alkanes that concentrate in the recycle solvent are easily observed in comparison with the results from one-dimensional GC-MS.

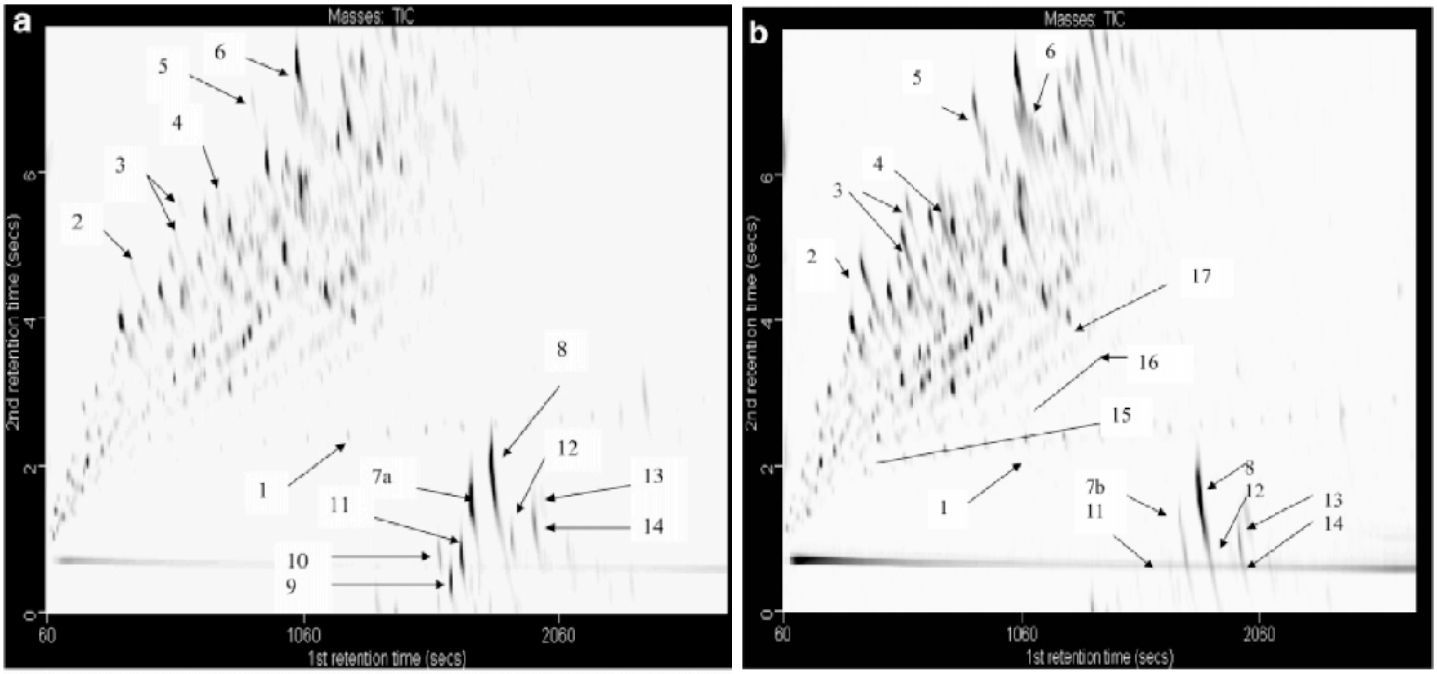


Figure 12.27. a: Total ion chromatogram as a 2D plot of the product from the hydrocracker. Components are 1, n-alkanes; 2, naphthalene; 3, methyl naphthalenes; 4, C_2 alkyl naphthalenes; 5, acenaphthene; 6, C_2 alkyl diphenyls; 7a, dihydropyrene; 8, pyrene; 9, 6H-fluoranthene; 10, 4H-fluoranthene; 11, 6H-fluoranthene; 12, isomer of pyrene and benzonaphthofuran; 13, benzofluorene isomer; and 14, benzofluoreneisomer.

b: Total ion chromatogram as a 2D plot of the feed to the hydrocracker. Components are 1, n-alkanes; 2, naphthalene; 3, methylnaphthalenes; 4, C_2 alkyl naphthalenes; 5, acenaphthene; 6, C_2 alkyl diphenyls; 7b, fluoranthene; 8, pyrene; 9, 6H-fluoranthene; 10, 4H-fluoranthene; 11, 6H-fluoranthene; 12, isomer of pyrene and benzonaphthofuran; 13, benzofluorene isomer; 14, benzofluorene isomer; 15, alkyl cyclohexanes; 16, bicyclic alkanes; and 17, tricyclic alkane 18H-fluoranthene isomer.