GCxGC-(MS) methods

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Outline

- Principles of GCxGC
- Selection of detectors
- PCB, PBDE analysis
- Other examples

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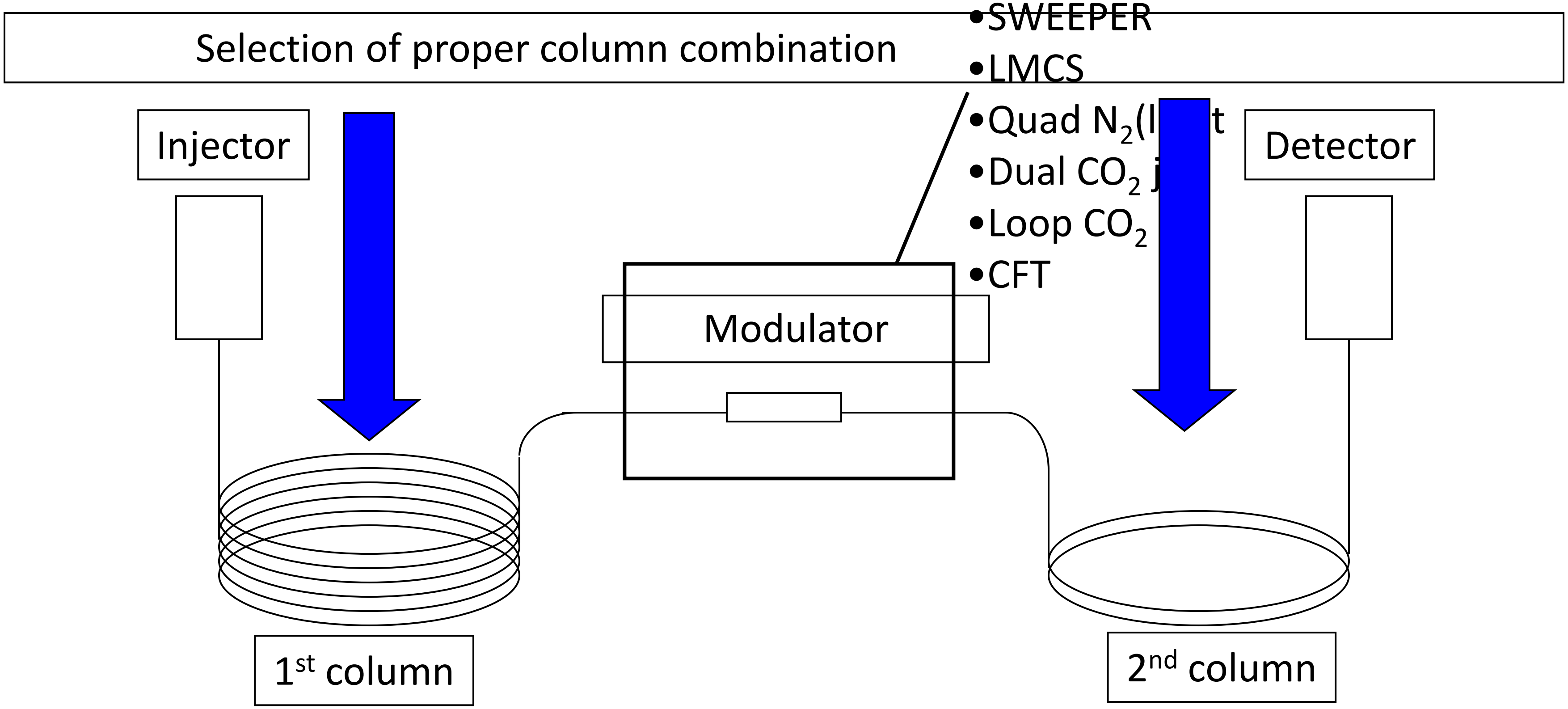
Principles of GCxGC

- Selection of modulator
- 6 different modulators:
  - SWEEPER
  - LMCS
  - Quad N_2(l t
  - Dual CO_2 j
  - Loop CO_2
  - CFT



Selection 1st and 2nd dimension GC columns

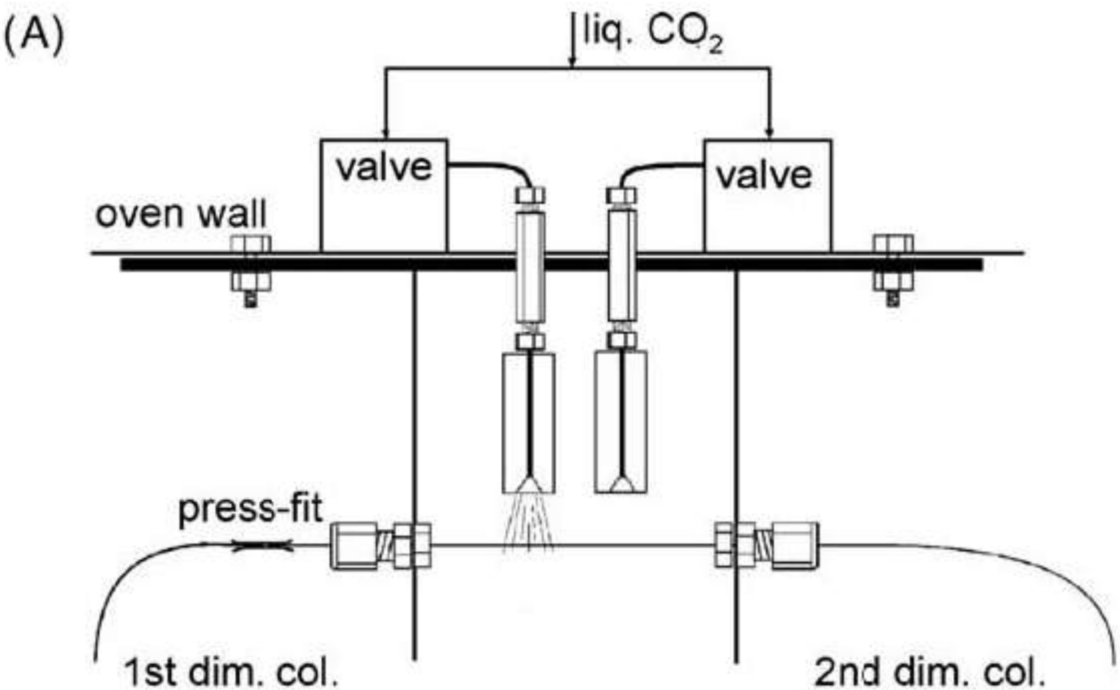
- 1st dimension
  - Apolar type phases:

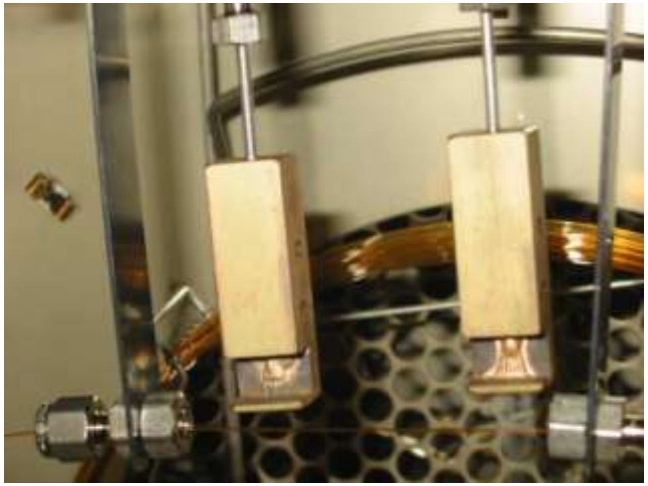
    DB-1, DB-5, CP-Sil 8 type of columns

2nd dimension

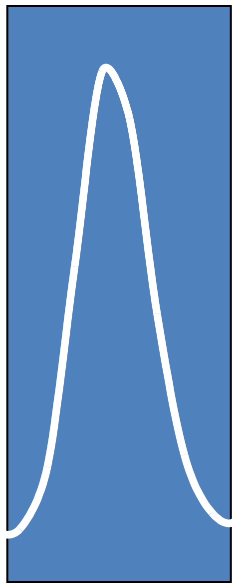
Second-dimension column		
Commercial code[a]	Stationary phase	Dimensions ($m \times mm \times \mu m$)
LC-50	50% liquid crystalline-methylpolysiloxane	0.8×0.1, 0.1
007-65HT	65% phenyl-methylpolysiloxane	1.0×0.1,0.1
VF-23ms	Proprietary (high cyano containing polymer; with absolute cyano content 70–90%)	1.5×0.1, 0.1
007-210	50% trifluoropropyl-methylpolysiloxane	2.0×0.1, 0.1
HT-8	8% phenyl-methylpolysiloxane (carborane)	1.0×0.1,0.1
SupelcoWax-10	Polyethylene glycol	1.0×0.1, 0.1

How does it work?
Cryogenic modulator

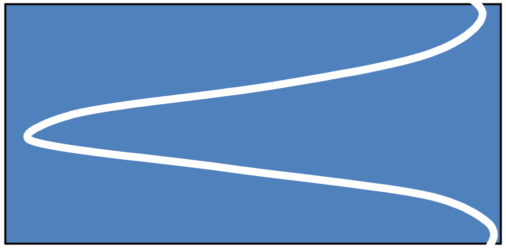




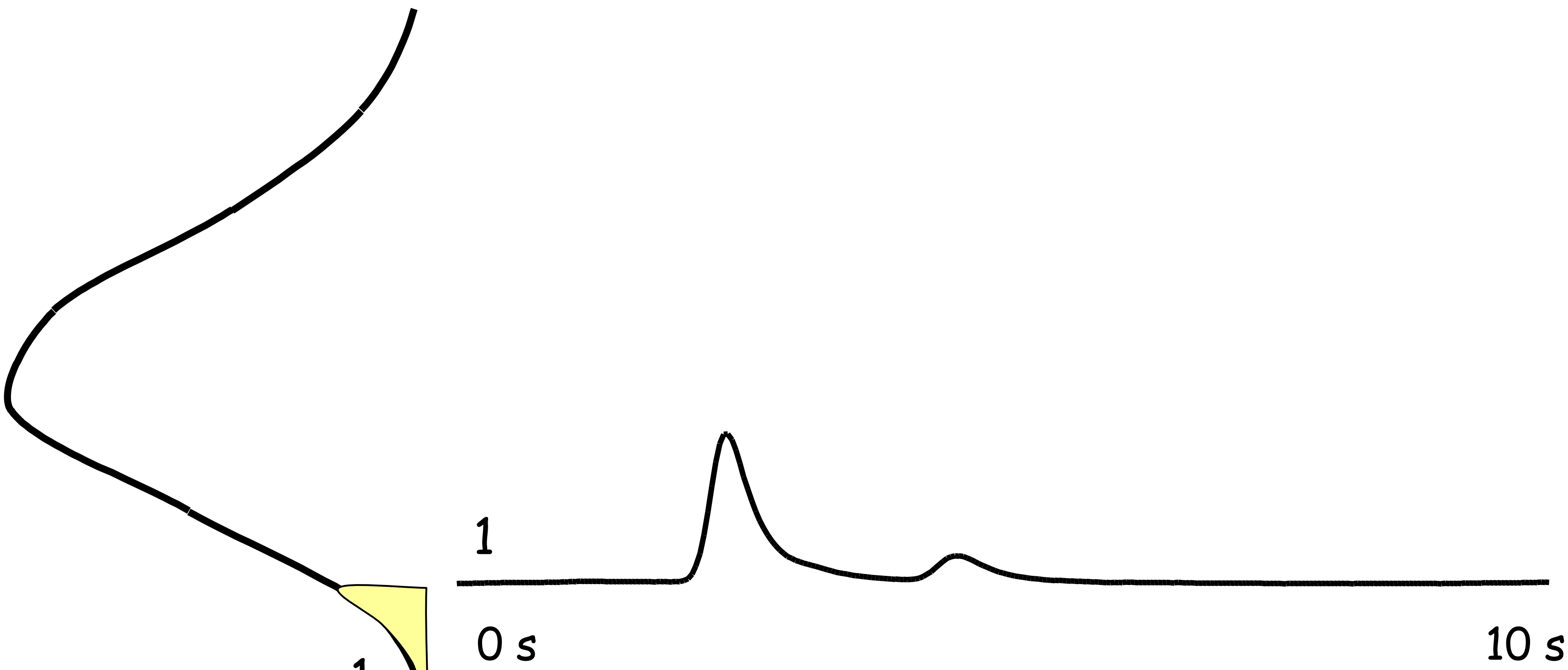
How does GCxGC work ?



How does GCxGC work ?

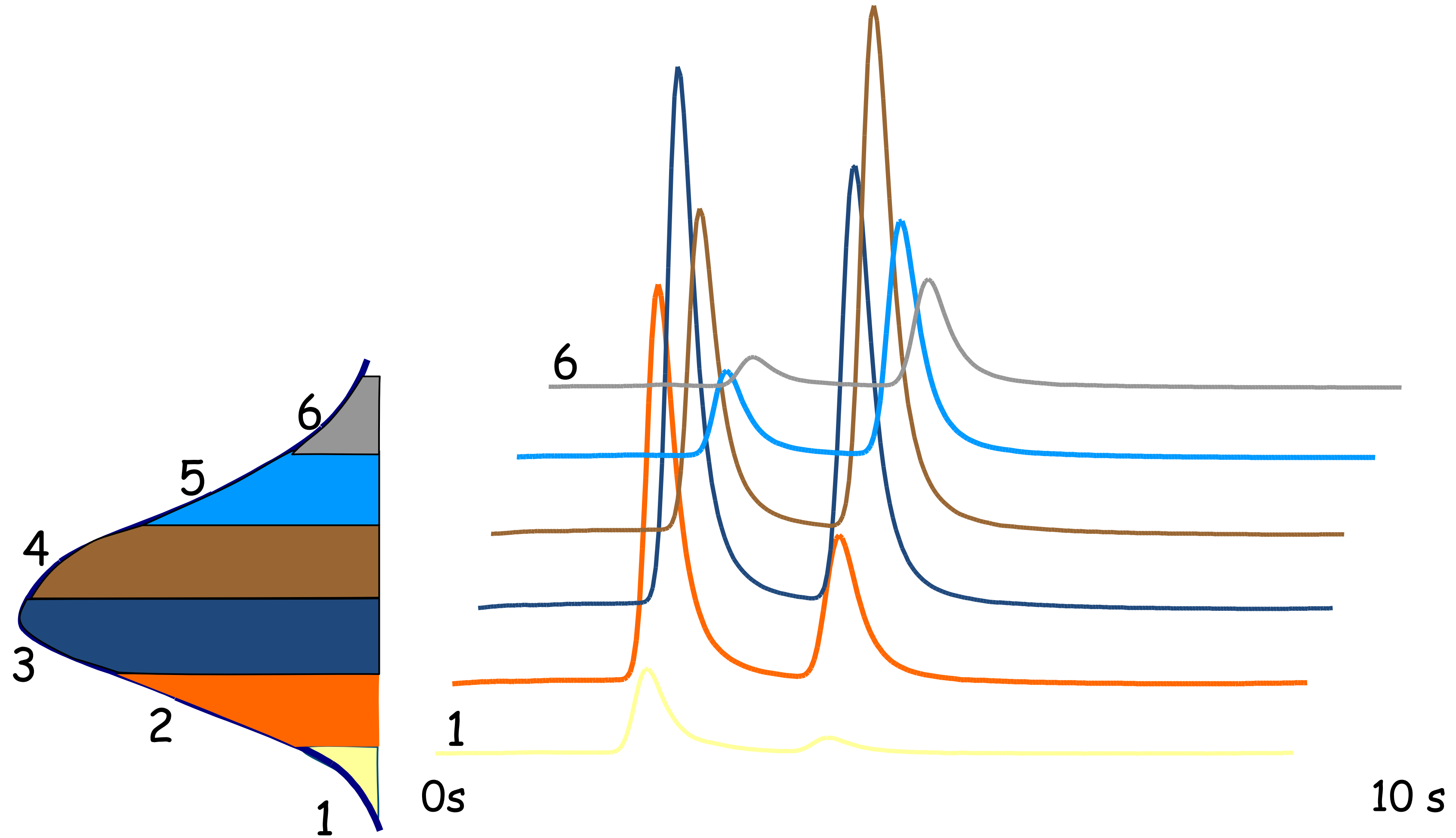


How does GCxGC work ?

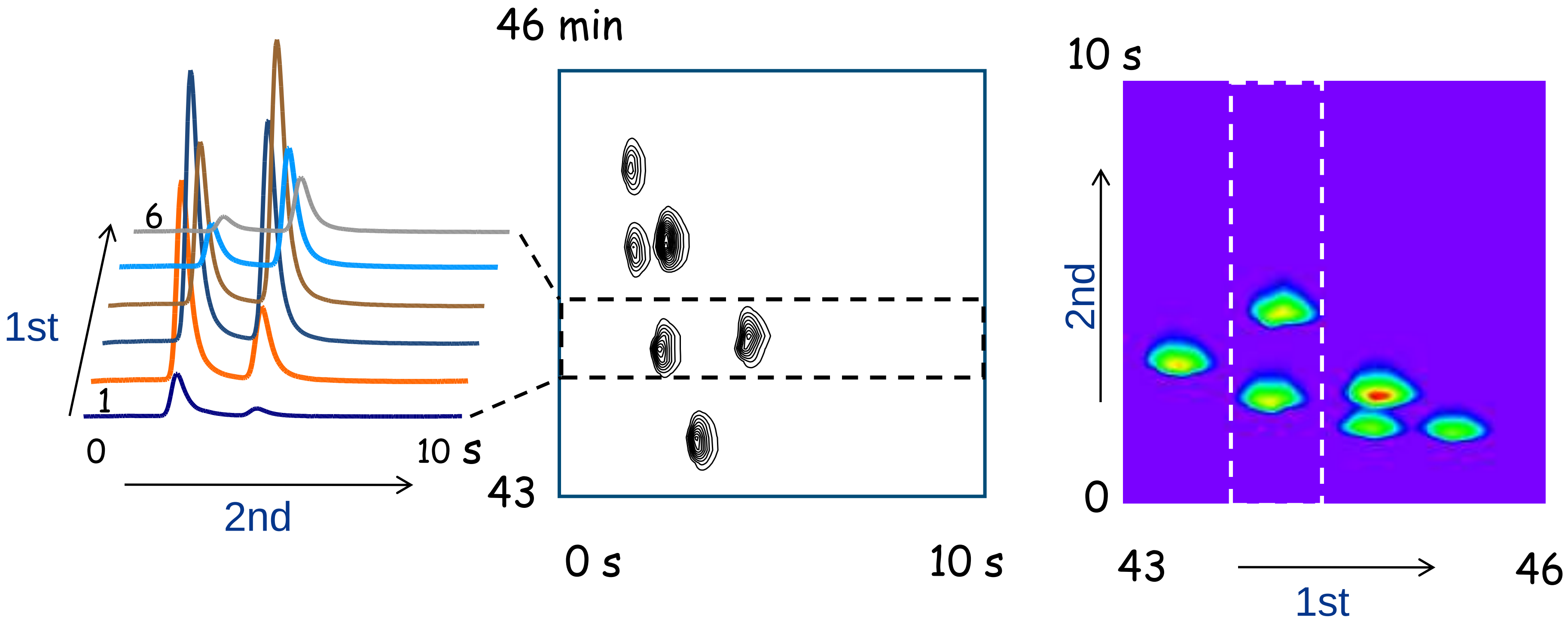


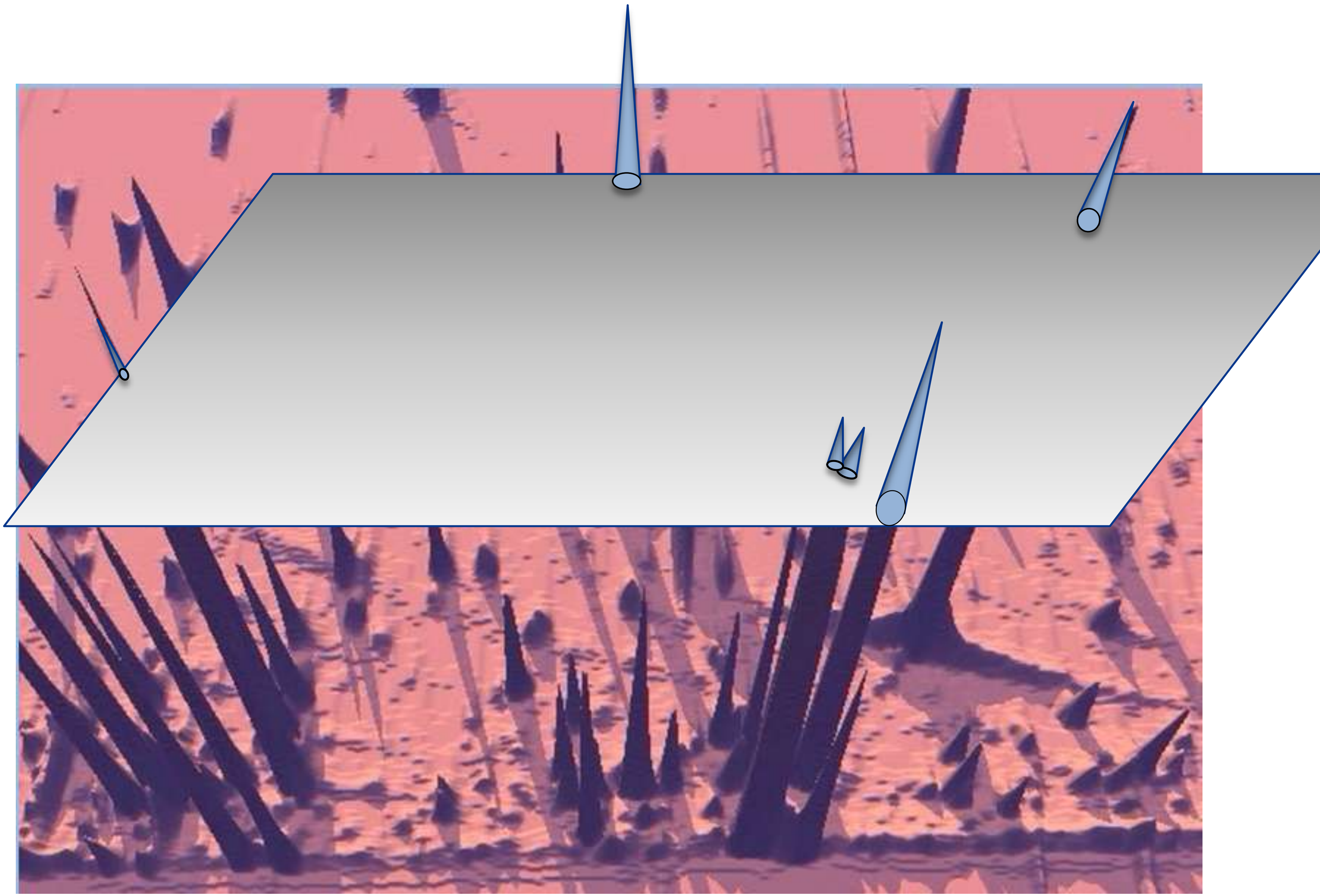
Separation on the 2nd dimension column

How does GCxGC work ?



Principle and contour plots



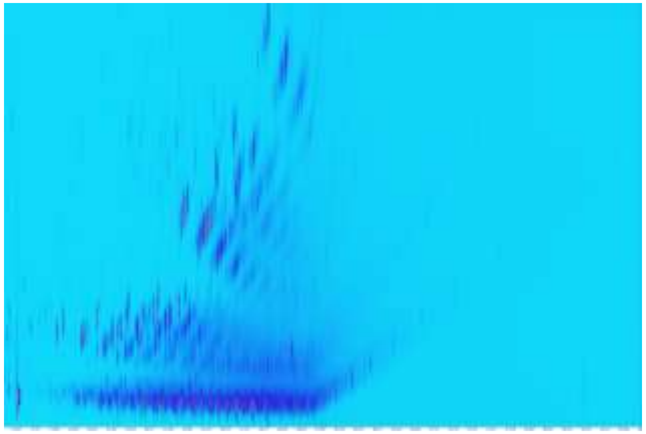


Contour plot

Detectors for GCxGC systems

- Fast scanning detectors
  - Acquisition rate >20 Hz
- Low dead volume detectors

Commercial equipment



- GCxGC-FID
- GCxGC-ECD
- GCxGC-qMS
- GCxGC-ToF-MS
- GCxGC-AED not commercial available

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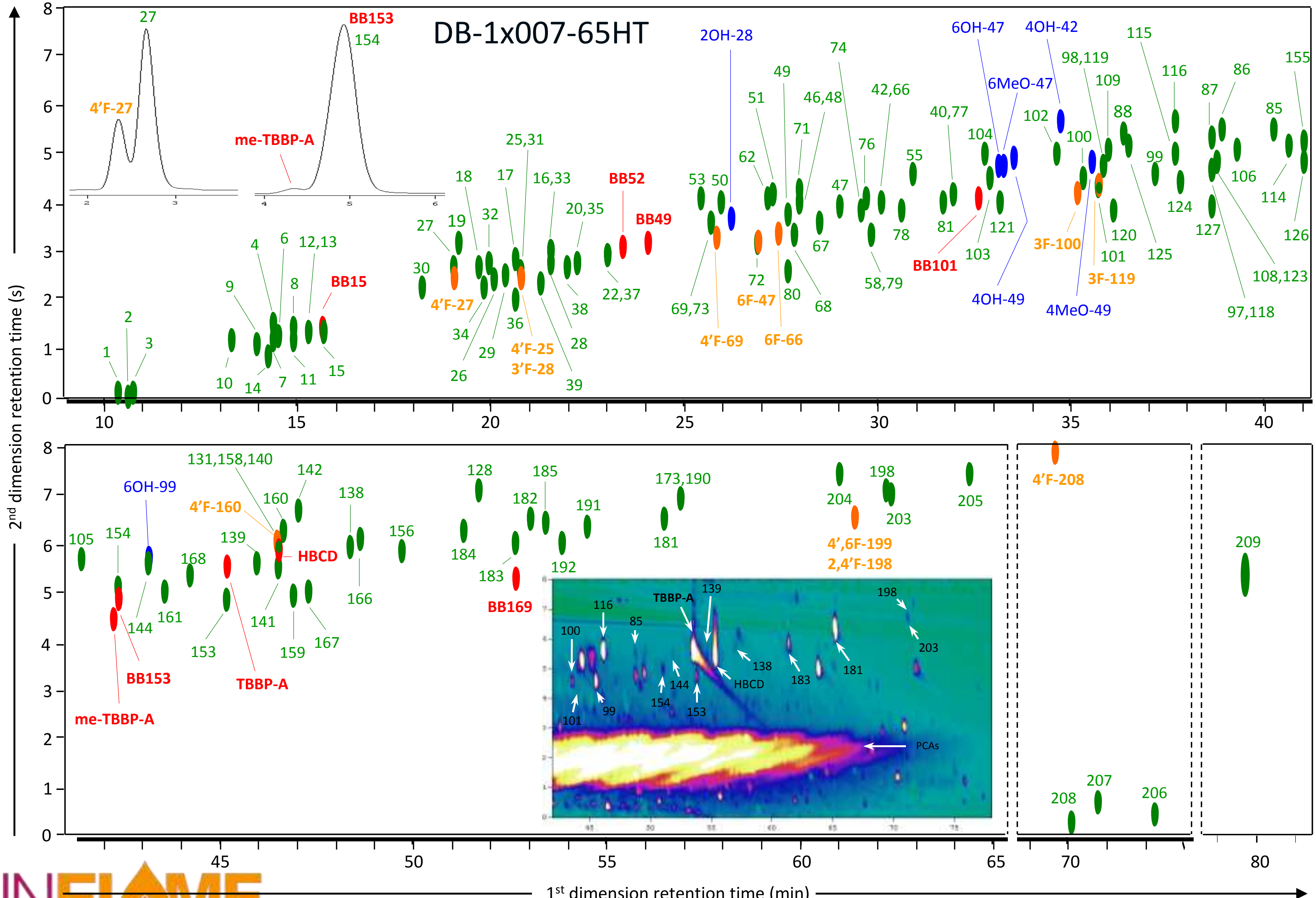
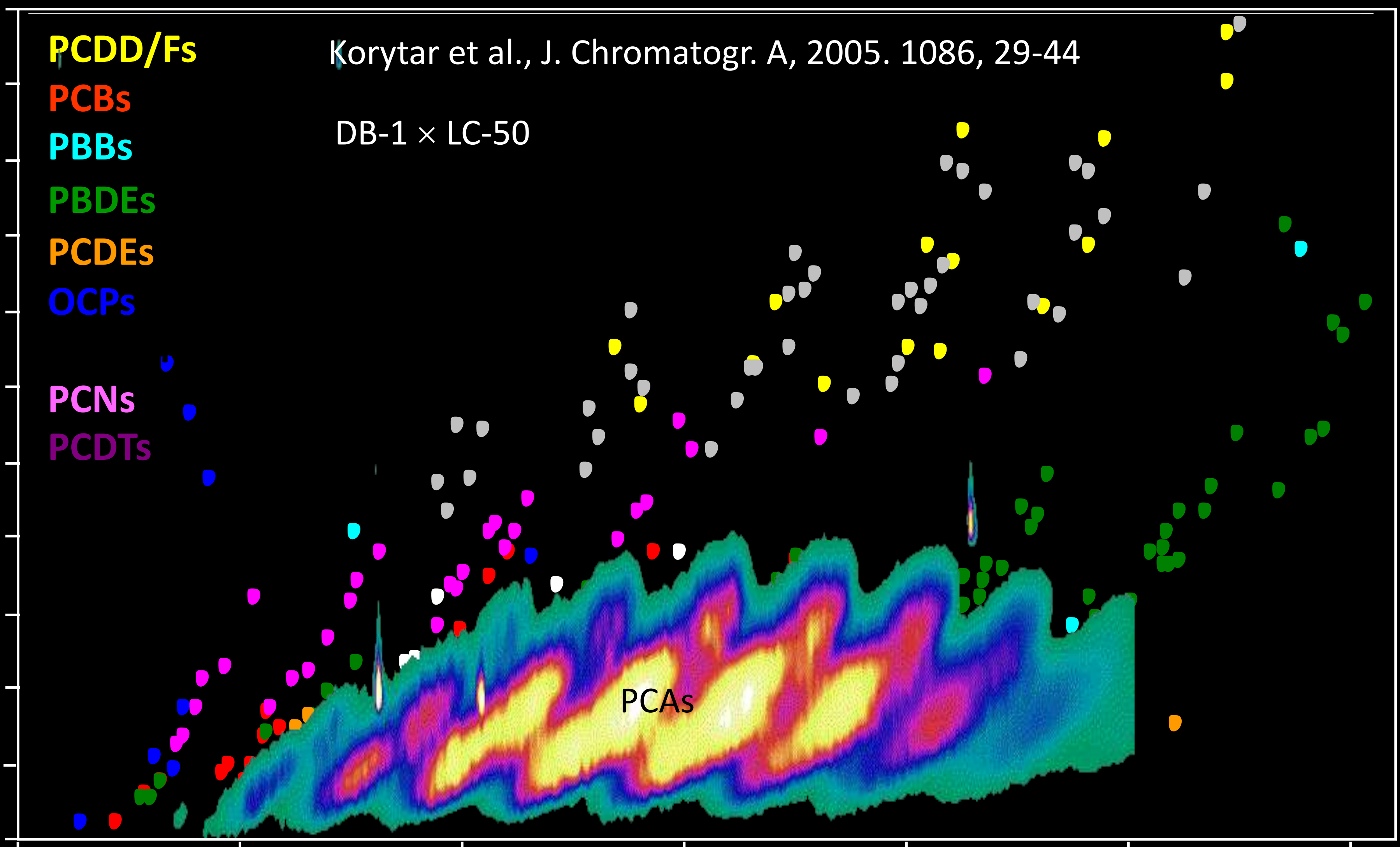
GCxGC-µECD

GCxGC-µECD 125 PBDE's

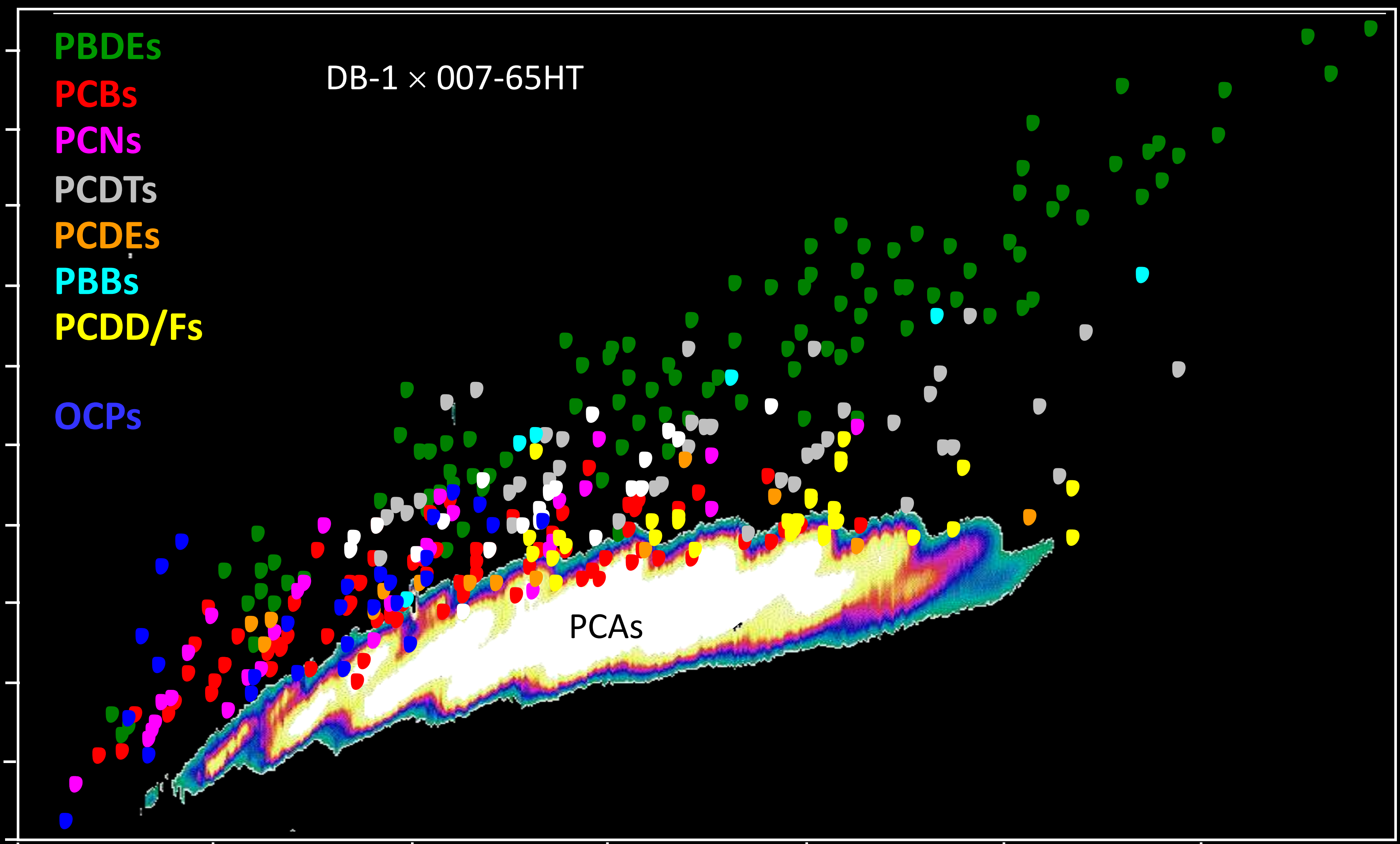


Korytar et al., J Chrom A, 1100 (2005) 200–207

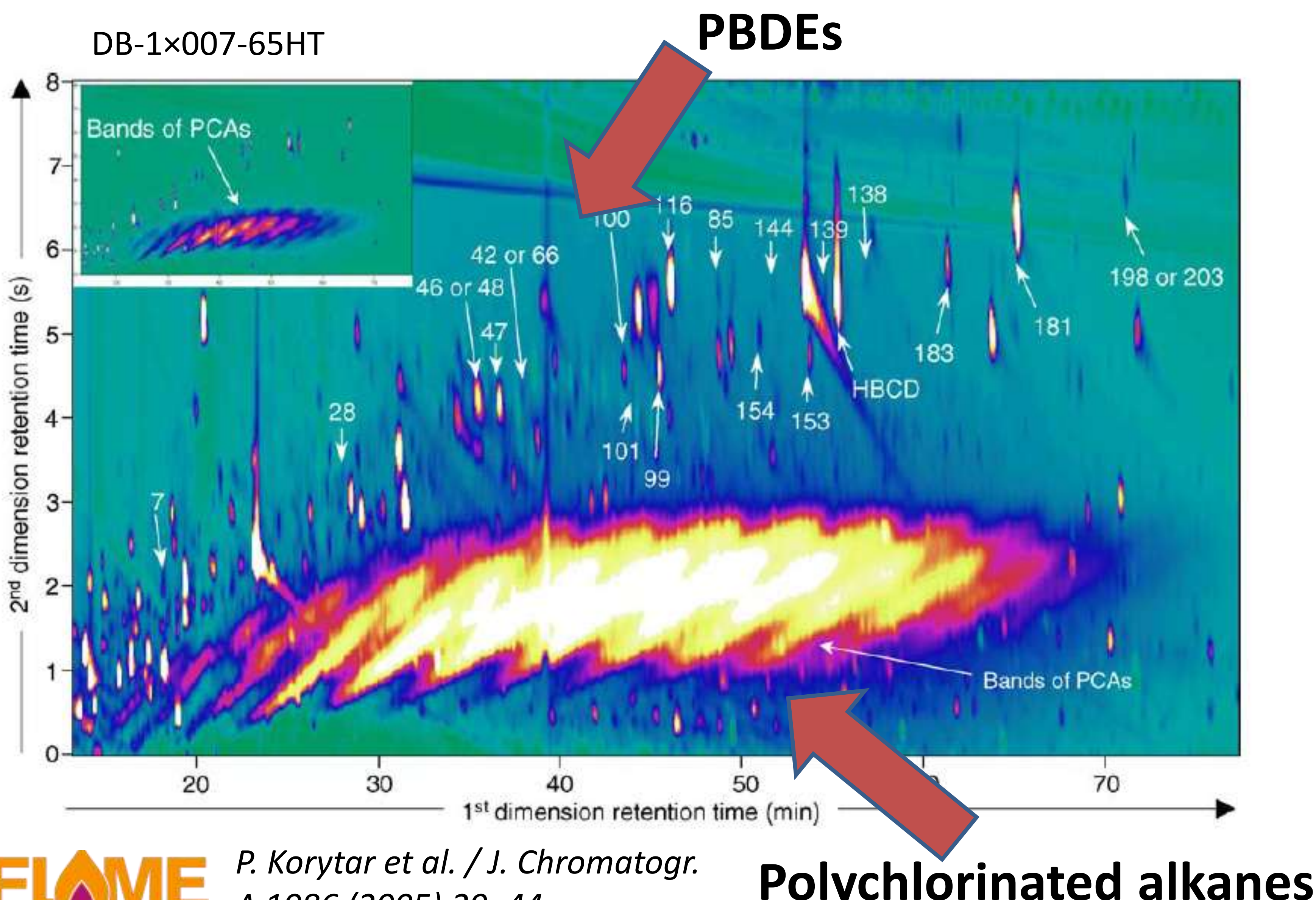
GCxGC-μECD various contaminants



GCxGC-µECD different column combination



GCxGC-μECD dust sample



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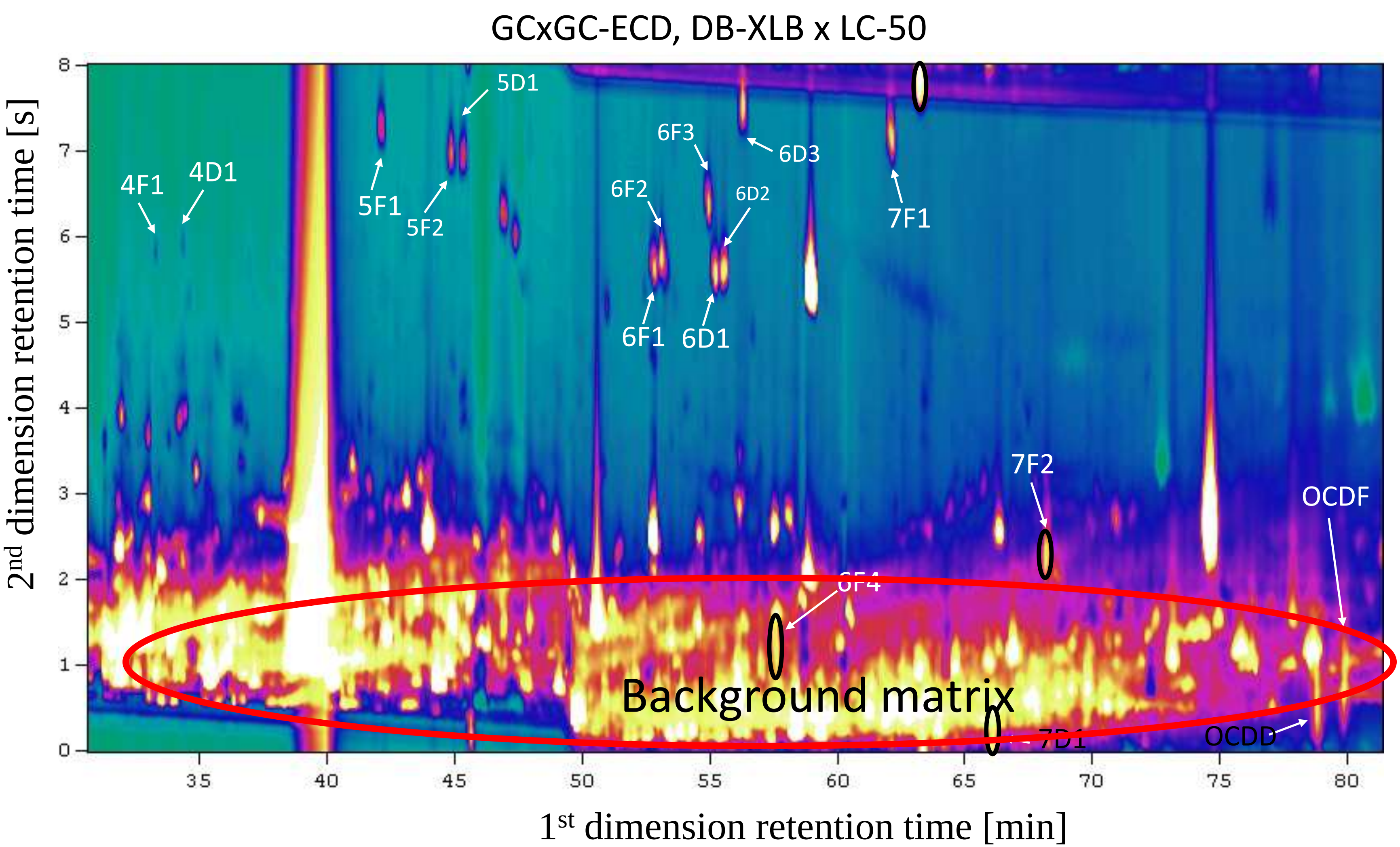
P. Korytar et al. / J. Chromatogr. A 1086 (2005) 29–44

Background matrix separation from dioxins



P. Korytar et al. / J. Chromatogr. A 1100 (2005) 200–207

GCxGC-MS

GCxGC with qMS

- Requirements

  fast acquisition

  spectral quality: no skewing

Set-up

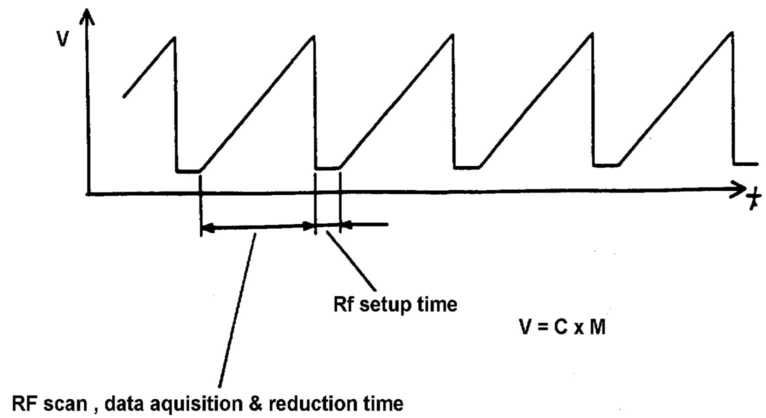
Modulator control

Dual-jet CO_2 modulator

GC

Single quadrupole MS

Quadrupole MS

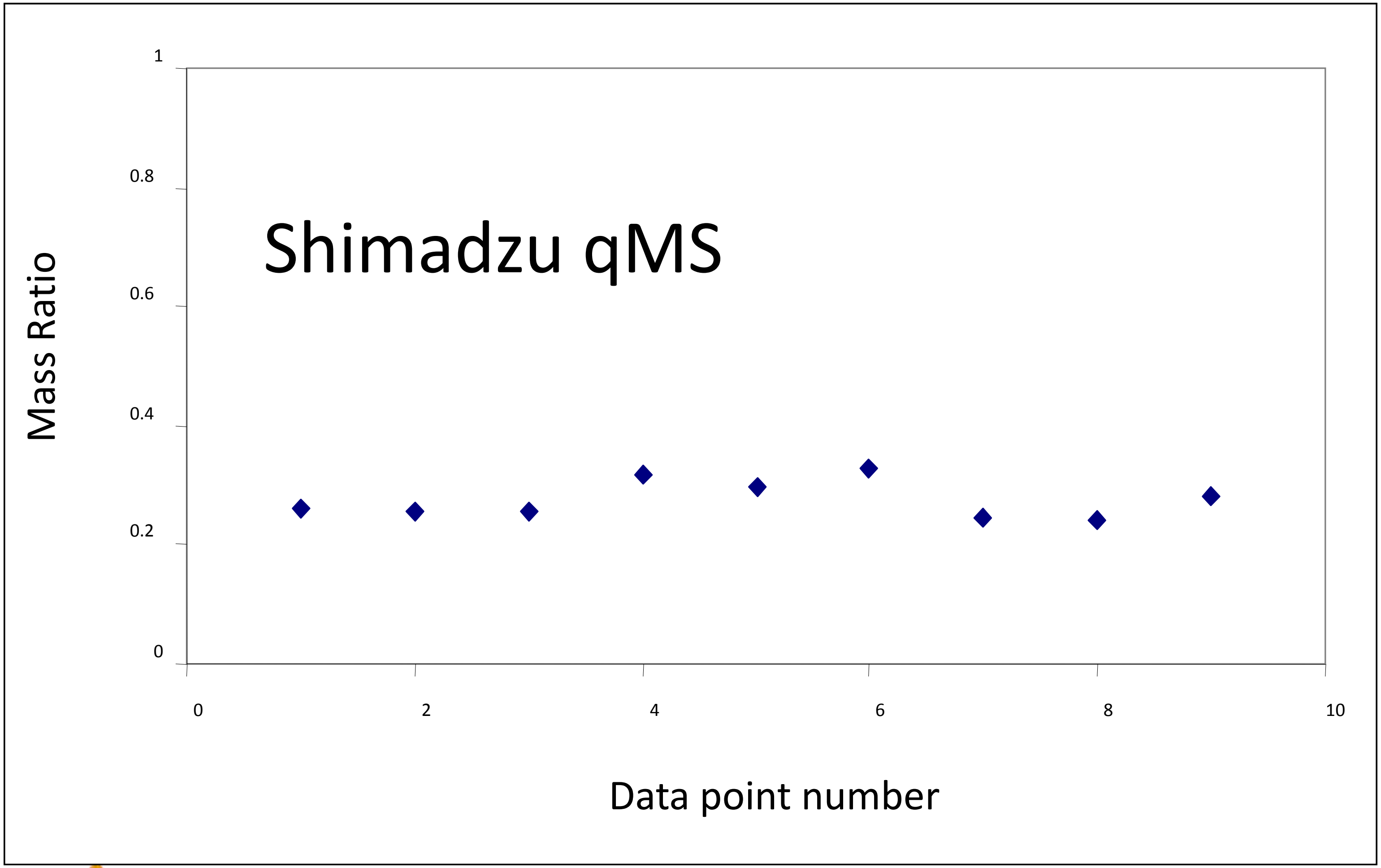


<u>High acquisition rates</u>

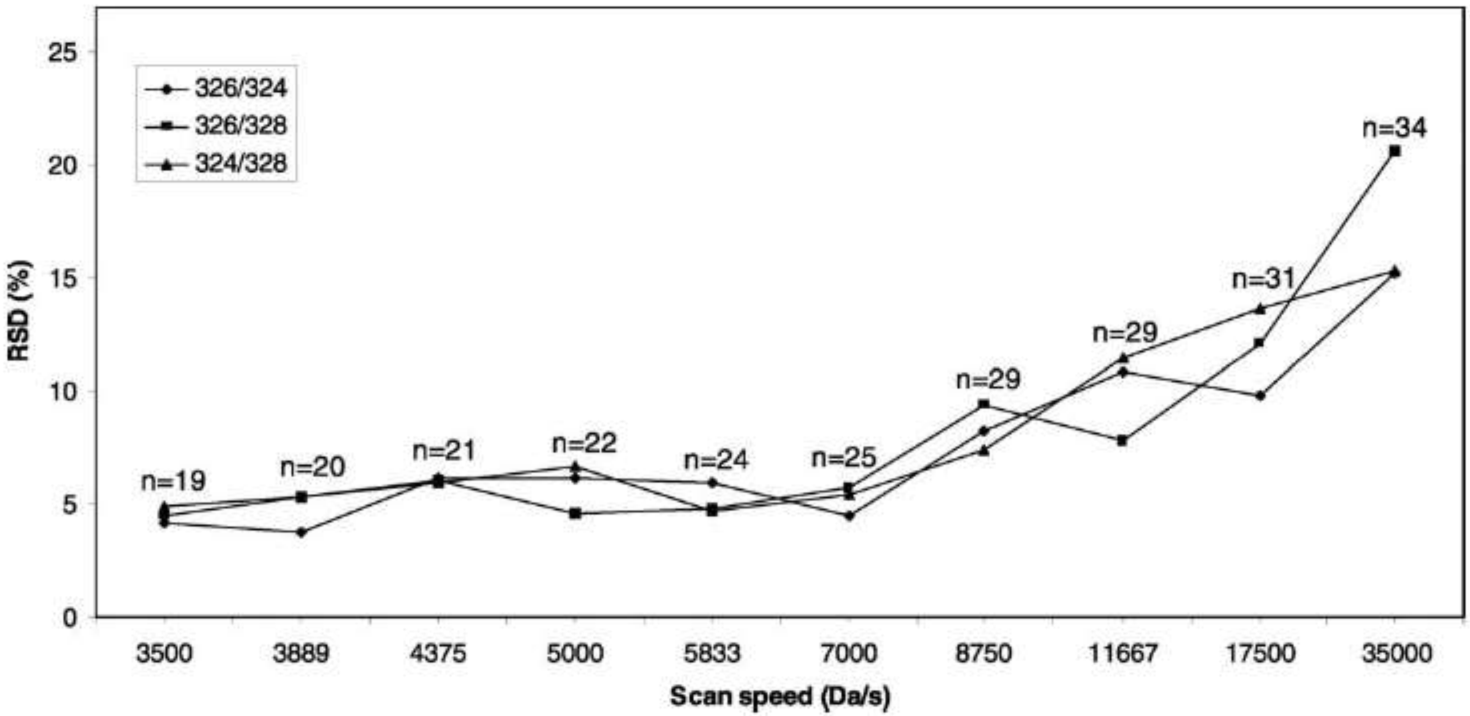
- short Rf setup time
- fast scanning

R_f setup time:	10.4 ms
Scan rate:	10000 amu/s
Scan width (amu):	@ 50Hz: 96
	@ 33 Hz: 195
	@ 25 Hz: 296

No skewing
mass ratio plot (m/z 330/326)



Quality of spectra



P. Korytar et al. / J. Chromatogr. A 1067 (2005) 255–264

Mass range scanned

Mass range scanned (Da)	Minimum inter-scan delay (s)	Maximum scan speed: 6700 Da/s		
		Scan time[a] (s)	Max. data acquisition rate[b] (Hz)	Min. detectable peak width[c] (ms)
400	0.014	0.060	14	510
300	0.011	0.045	18	380
200	0.010	0.030	25	280
100	0.005	0.015	50	140
50	0.001	0.007	125	56

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GCxGC-qMS

- Fast enough
- Selective enough
  - separation of coeluters
- Limited scanning range (300 Da)
- Not sensitive enough in EI
  - NCI required

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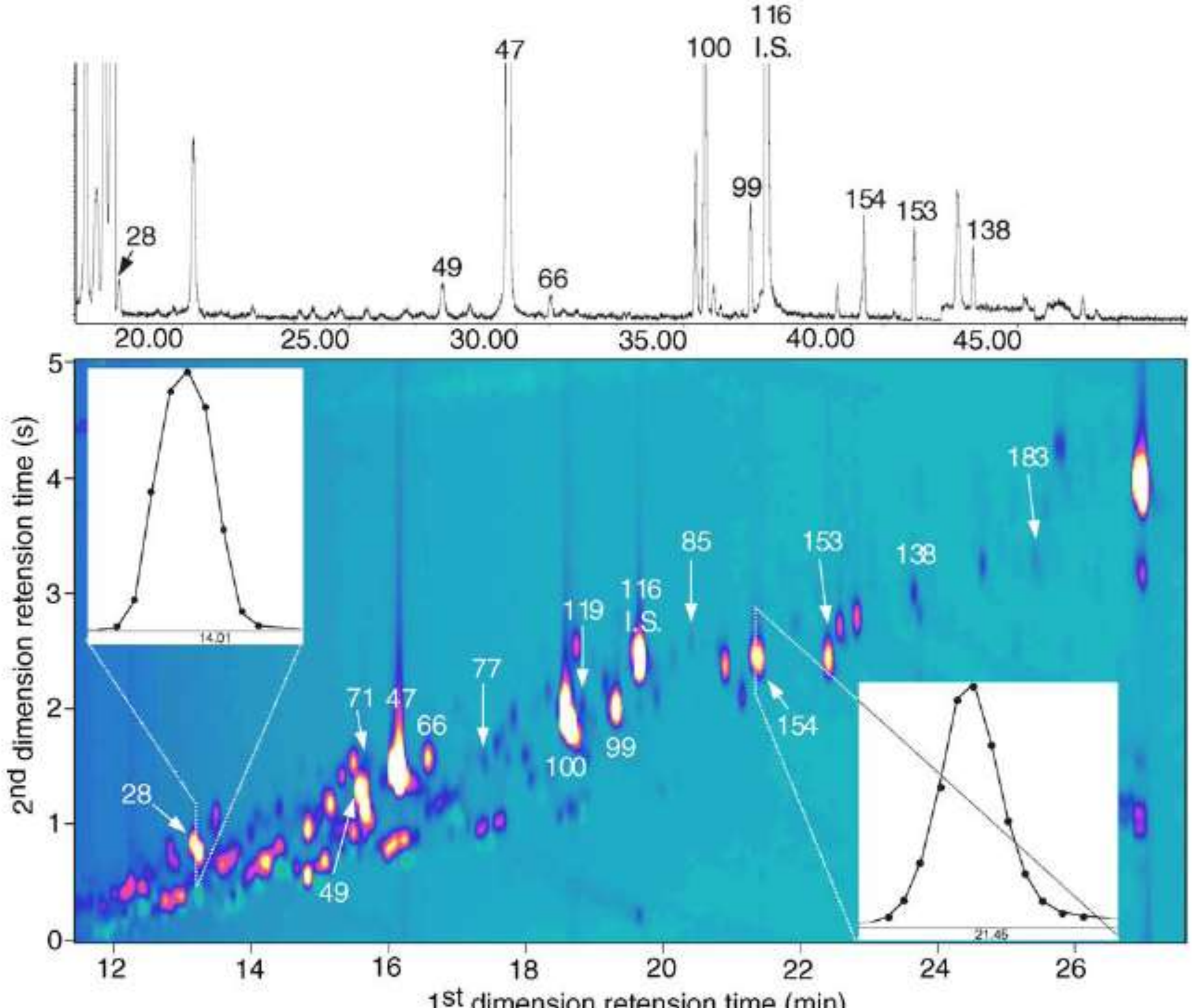
Eel extract GCxGC-qMS PBDE analysis



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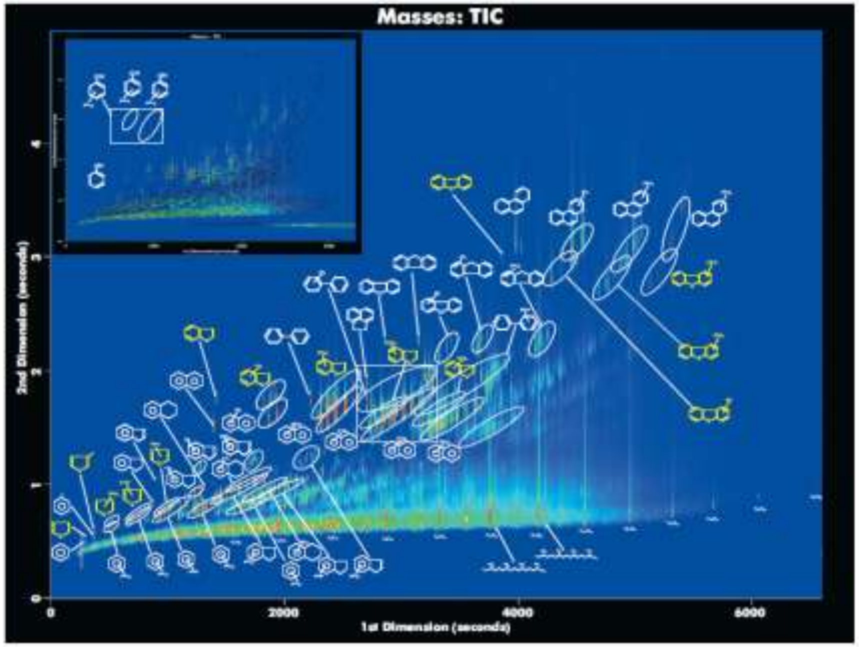
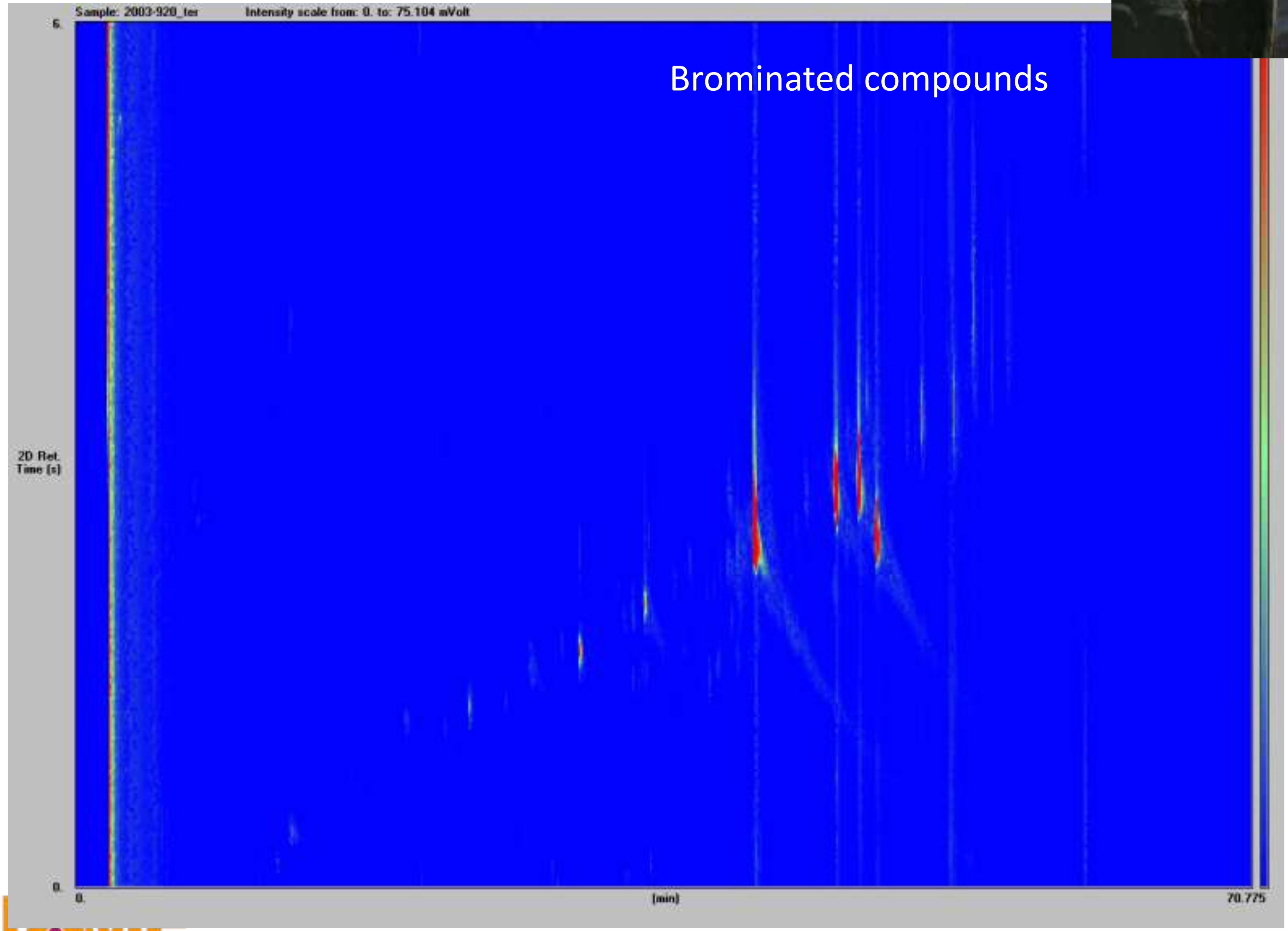
GCxGC ToFMS

- Fast scan speed: 100-500 Hz
- No mass skewing
- Automated search

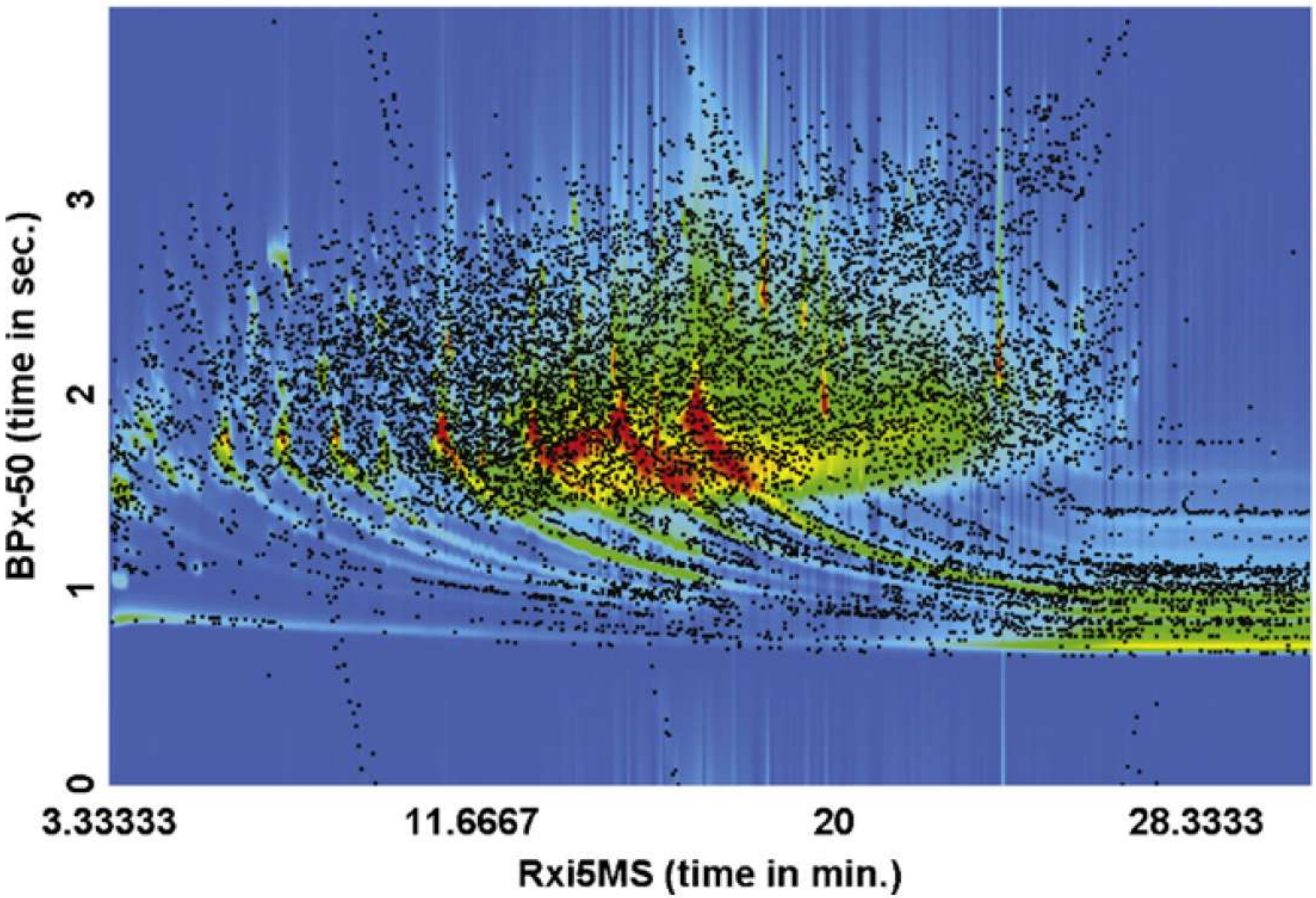


GCxGC-ToF-MS, Tern egg Western Scheldt



Screening chemicals in household dust

GCxGC-ToFMS of an hexane extract of dust

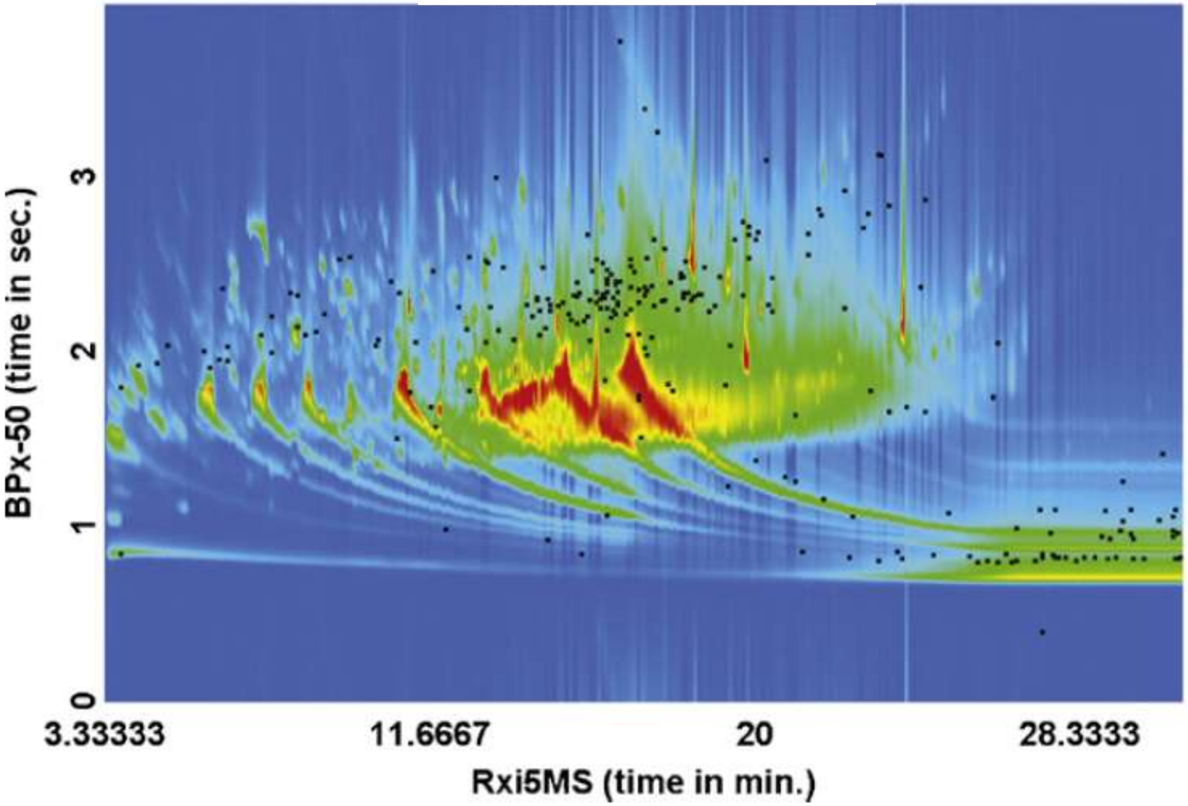


Hilton et al., 2010. J. Chrom A, 1217 (2010) 6851–6856

Chlorinated and brominated compounds in house dust

- >10,000 peaks detected
- 145 compounds contain chlorine or bromine

Cl and Br compounds



Hilton et al., 2010. J. Chrom A, 1217 (2010) 6851–6856

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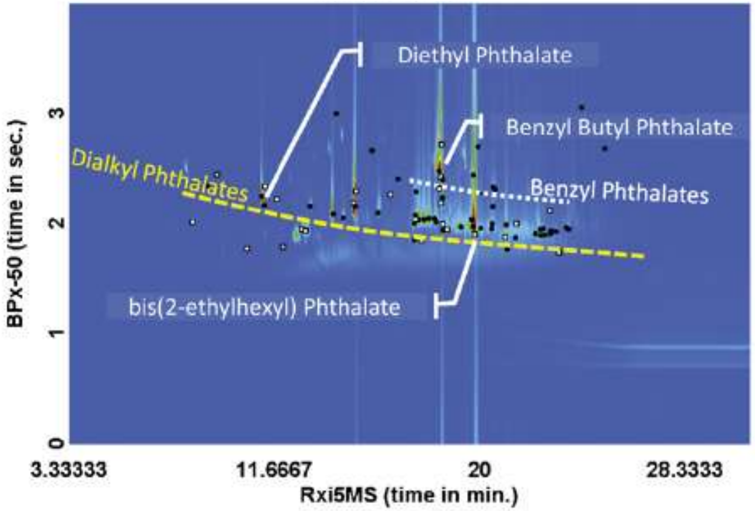
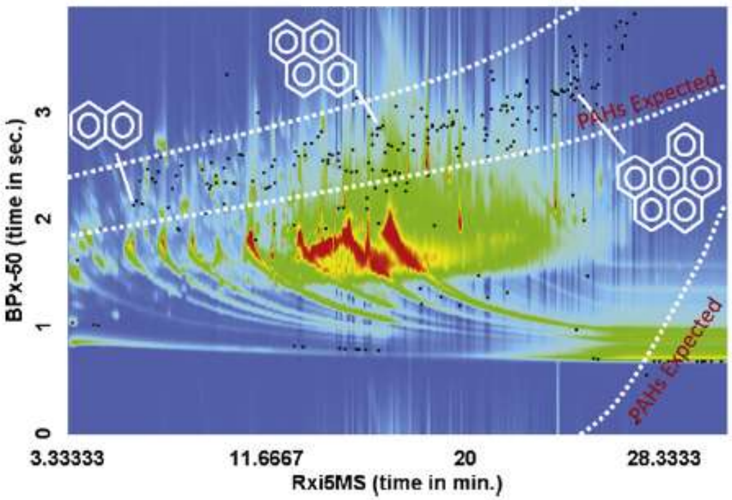
Other compounds identified in household dust

Compound class	Number found by filter	Plausible on review
Chlorine/bromine-containing	165	145 (93%)
Phthalates	52	33 (57%)
PAHs	145	94 (65%)
Nitro compounds	8	1 (13%)

Phthalates



PAHs



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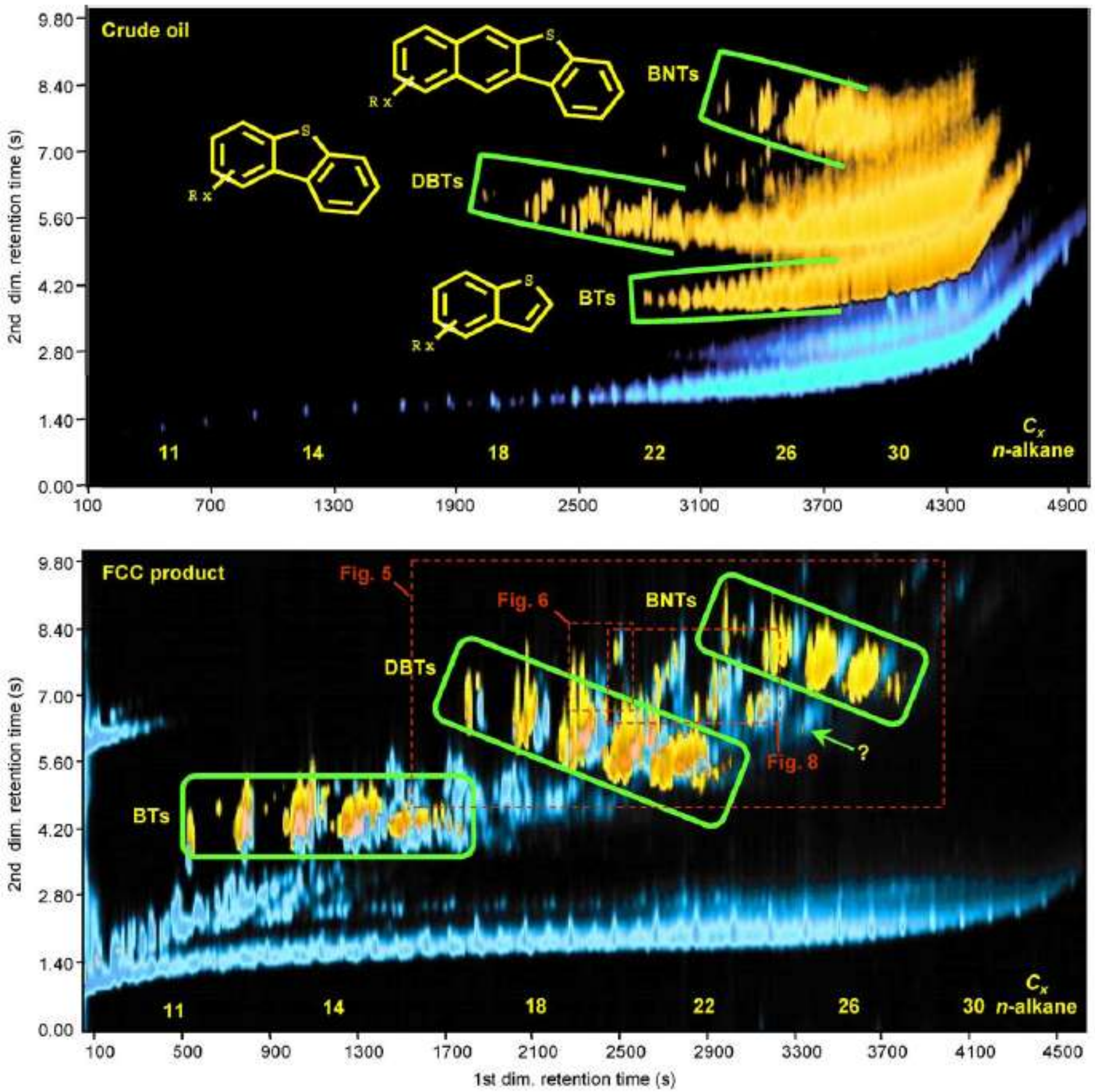
Hilton et al., 2010. J. Chrom A, 1217 (2010) 6851–6856

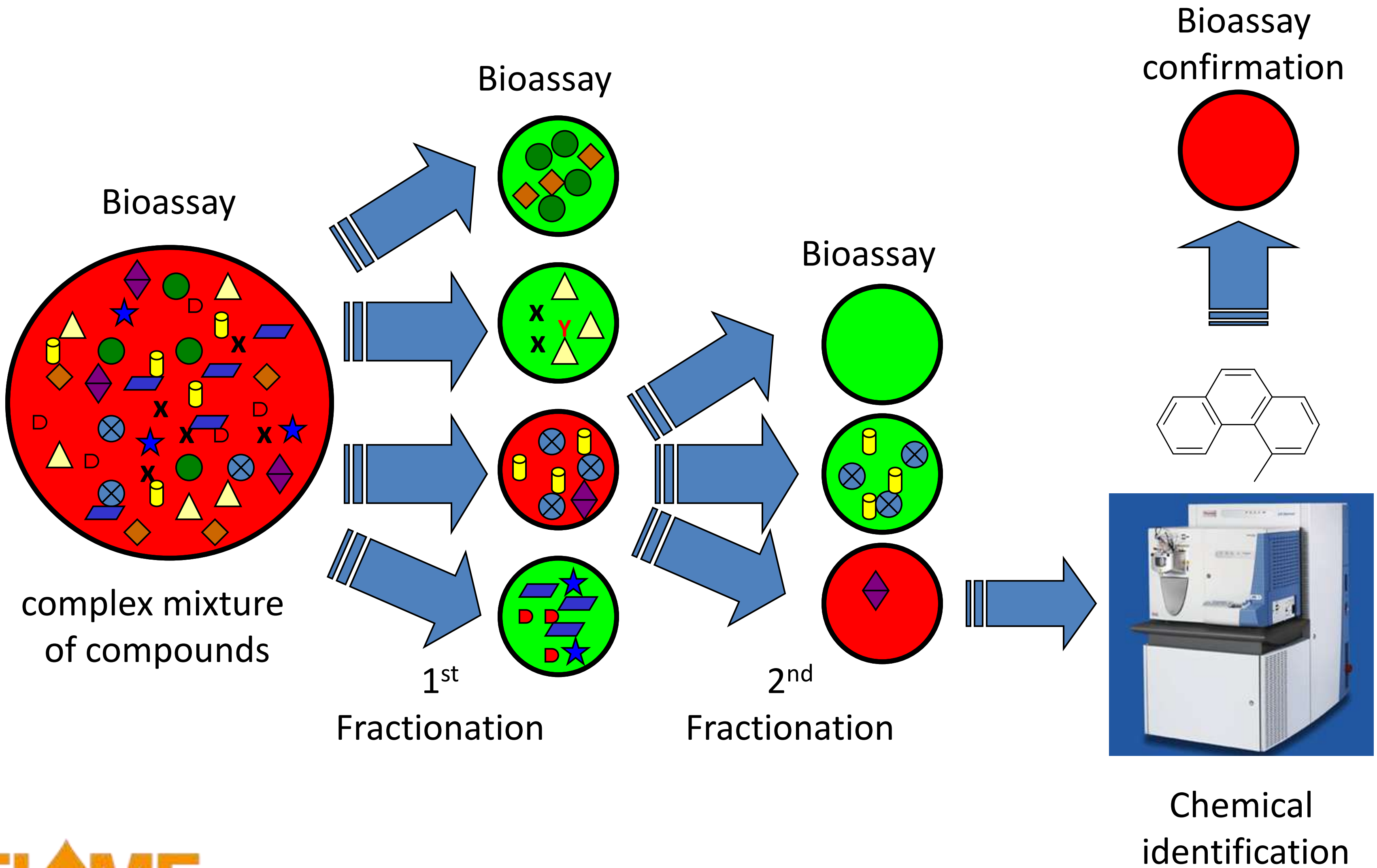
GCxGC-AED oil



Sulphur
Carbon

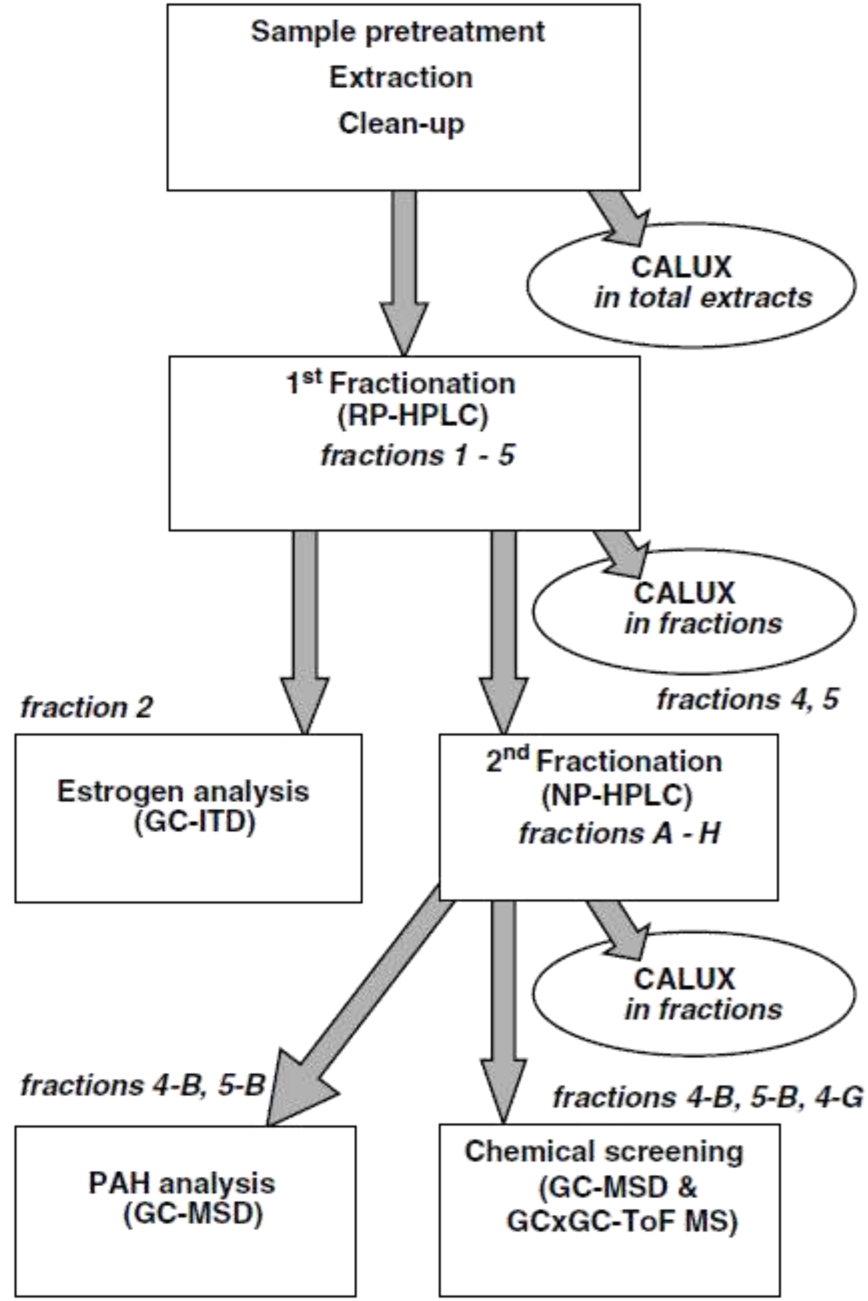
van Stee et al. / J. Chromatogr. A 1019 (2003) 89–99

Effect-directed analysis (EDA)



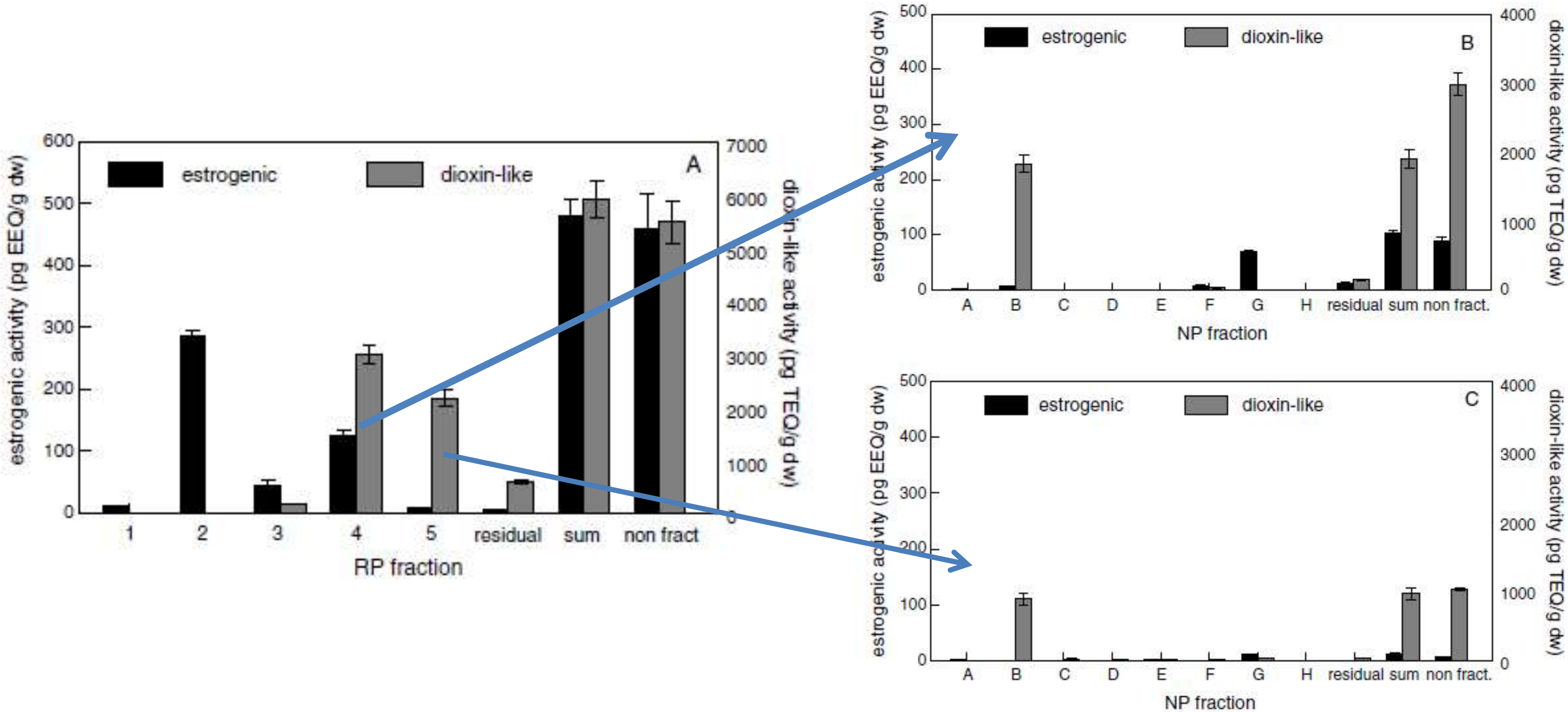
Combined sample treatment scheme chemical and bioassay analysis

Houtman et al. 2006
- Sediment sample from a harbour
- Bioassays
    - Dioxin like compounds (DR-CALUX)
    - Estrogenic compounds (ER-CALUX)
- Chemical identification
    - GC-MS
    - GCxGC-ToFMS



Houtman et al., 2006, Chemosphere 65, 2244–2252

Bioassay activity of the sediment



Houtman et al., 2006, Chemosphere 65, 2244–2252

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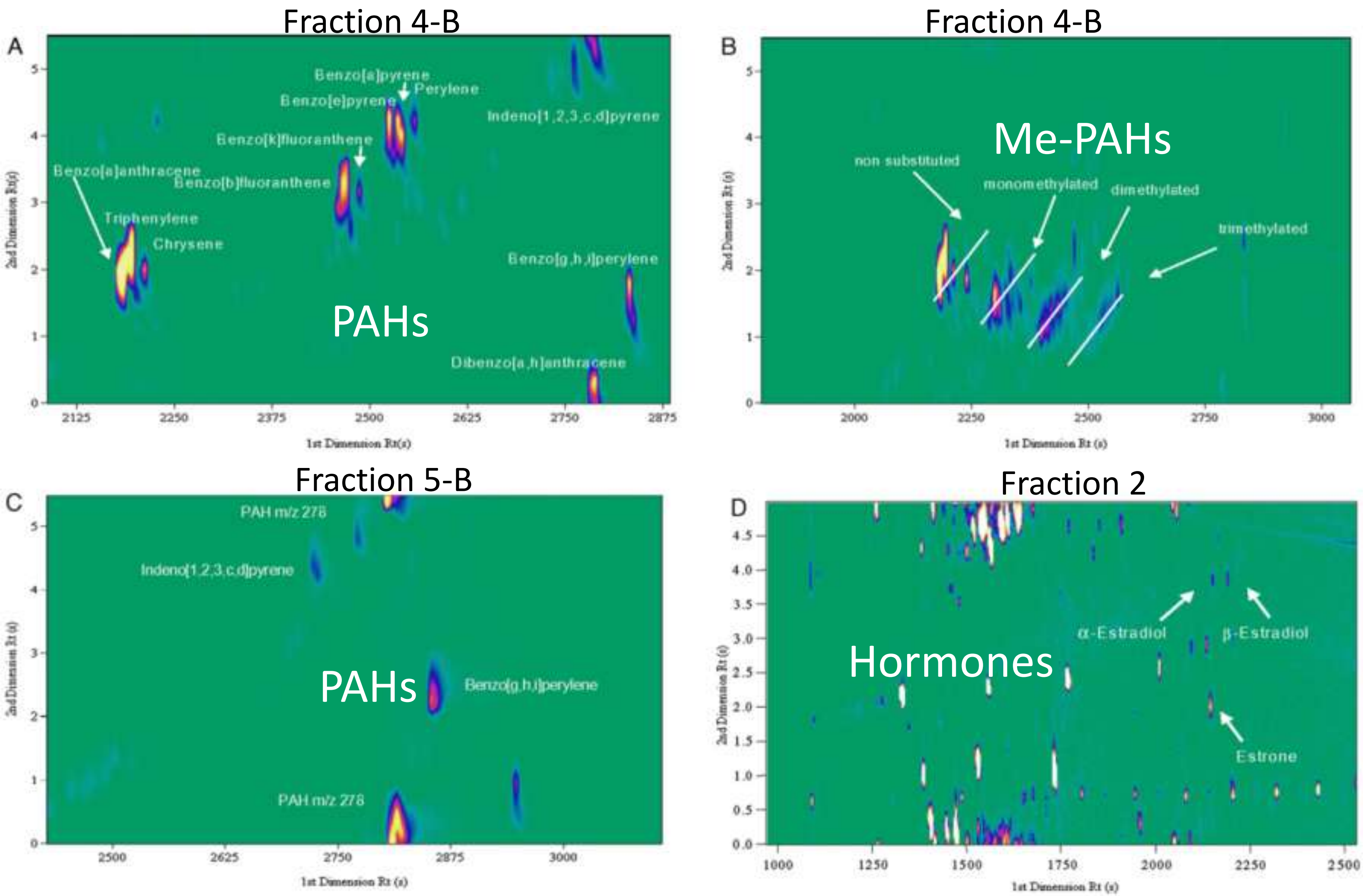
Active fraction GCxGC-ToFMS



Houtman et al., 2006, Chemosphere 65, 2244–2252

Identified compounds and explained bioassay activity

- 76% of the estrogenic activity was explained by 17α-, 17β-estradiol and estrone
- 38% of dioxin-like activity explained by PAHs

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Summary

- GCxGC is a powerful separation technique
- Separation of interfering compounds and matrix
- GCxGC is especially suitable for the separation of complex mixtures
- GCxGC combined with mass spectrometry can be used for the identification of “new” flame retardants

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