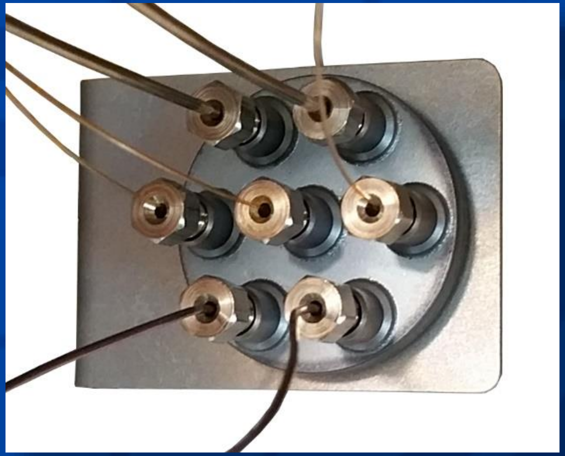
SepSolve Analytical

Comprehensive screening of environmental contaminants by flow-modulated GC×GC



Matthew Edwards, Separation Science Product Manager

NEMC, Fri 11th Aug 2017

GC×GC modulation

Over 20 years of innovation

1984
Giddings publishes theory of multidimensional separations

1991
Implementation of first GC ×GC separation (using a thermal desorption modulator) by Phillips & Liu

1996
Phillips & Ledford introduce rotating thermal modulator (or 'sweeper')

1997
Marriot develops the longitudinally modulated cryogenic system (LMCS)

2000
Seeley develops first differential flow modulator

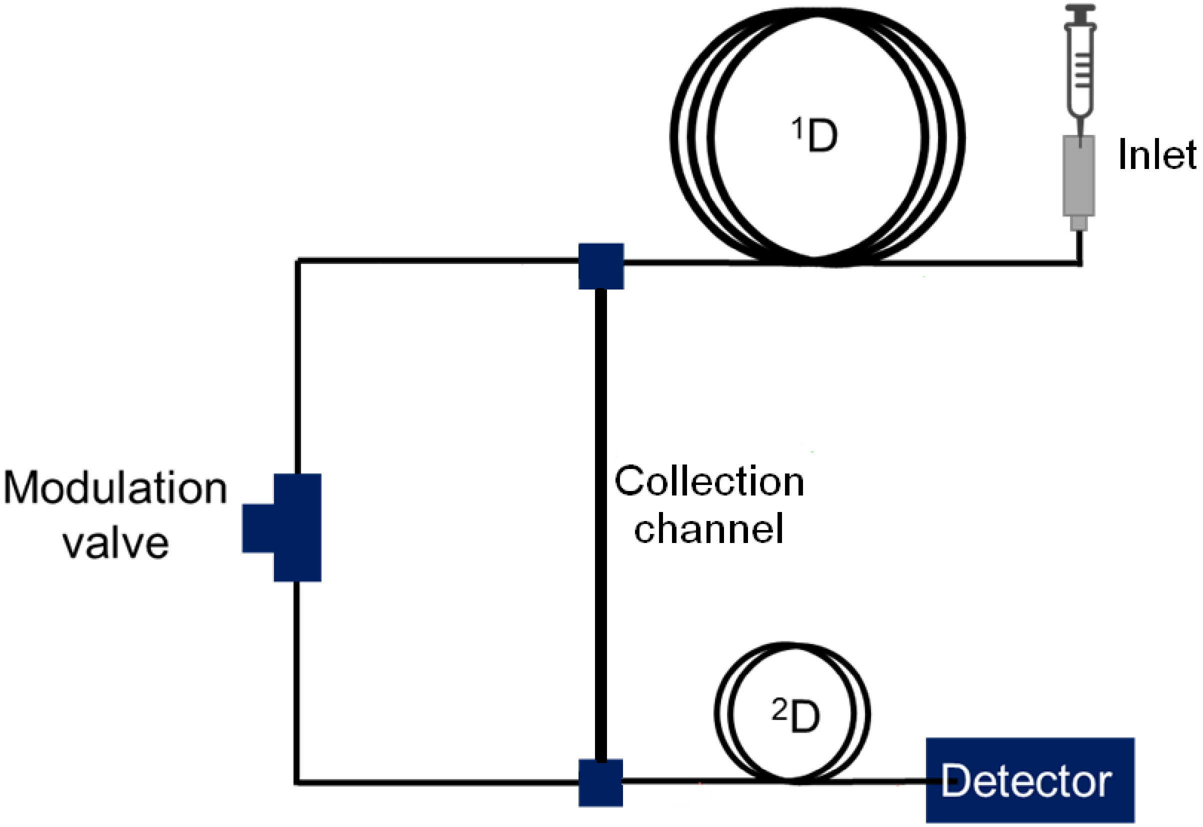
2003
Beens et al. develop liquid CO_2 single-stage modulator

2010
Miniaturisation of thermal modulation by Kim et al. for 2D micro-GC

2012
Griffith et al. publish on 'reverse fill/flush' flow modulation

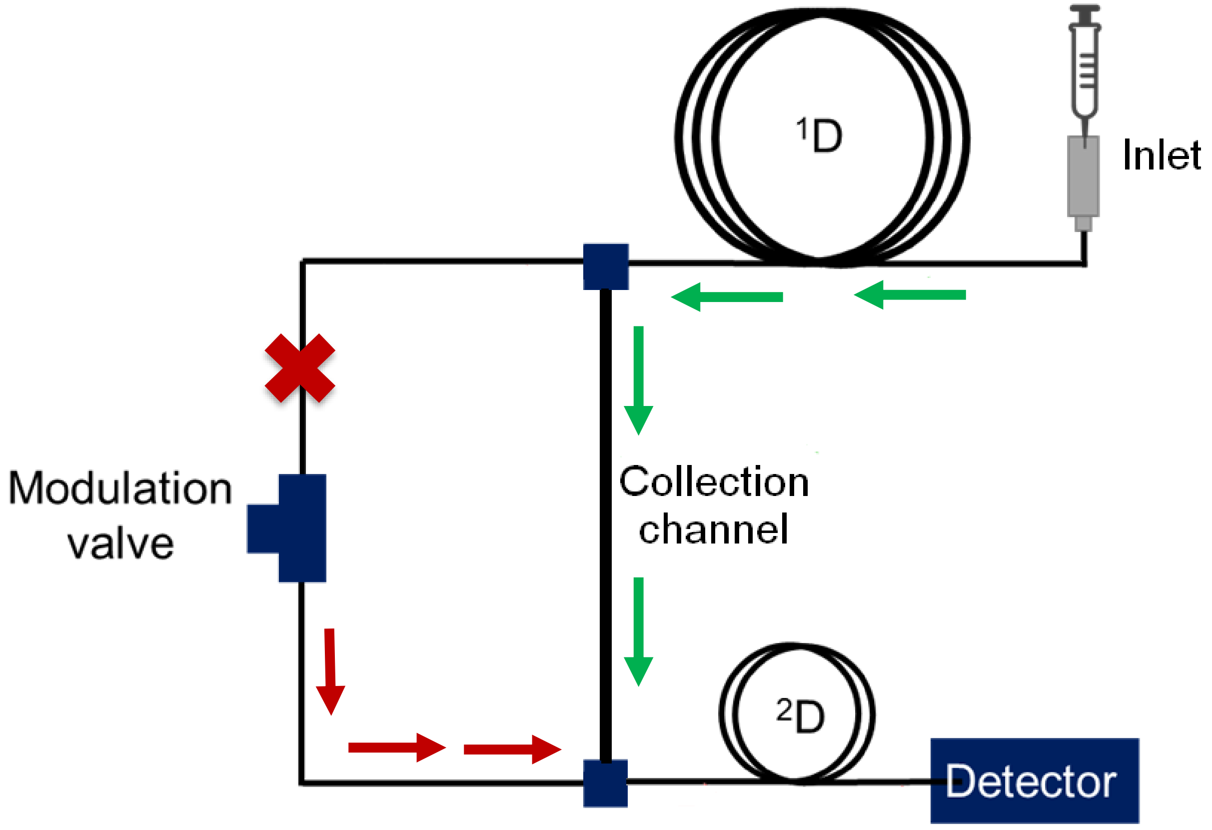
Forward fill/flush modulation

1st generation systems



Forward fill/flush modulation

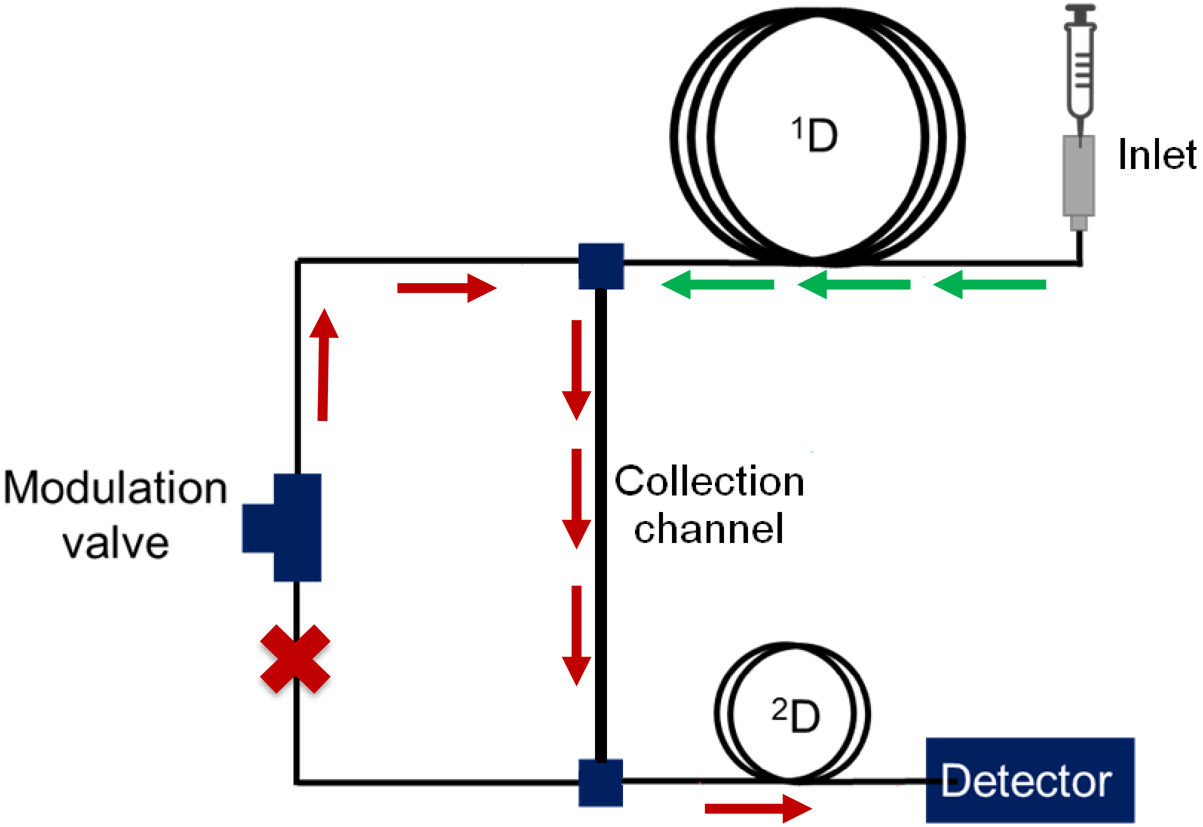
‘Fill’ mode



- Analytes fill the collection channel (or sample loop)

Forward fill/flush modulation

‘Flush’ mode

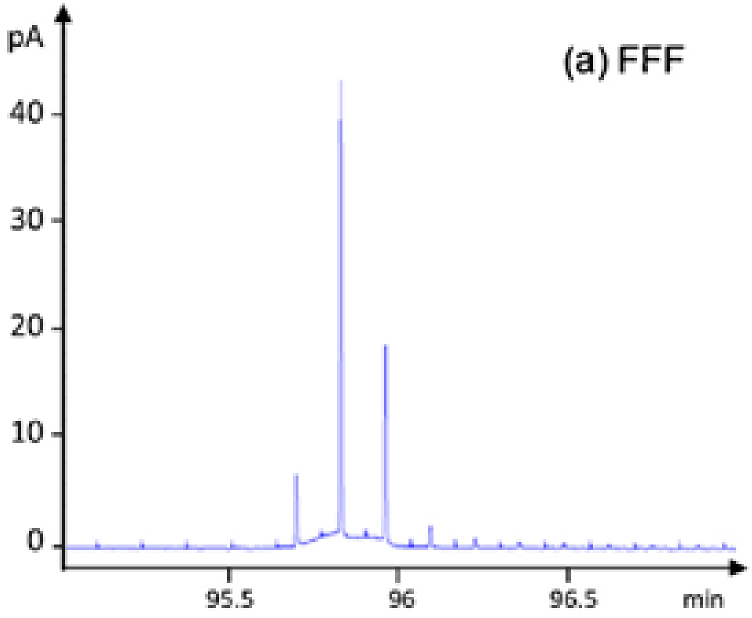


- Analytes injected in same direction they entered the channel (i.e. forward fill/flush)

Forward fill/flush modulation

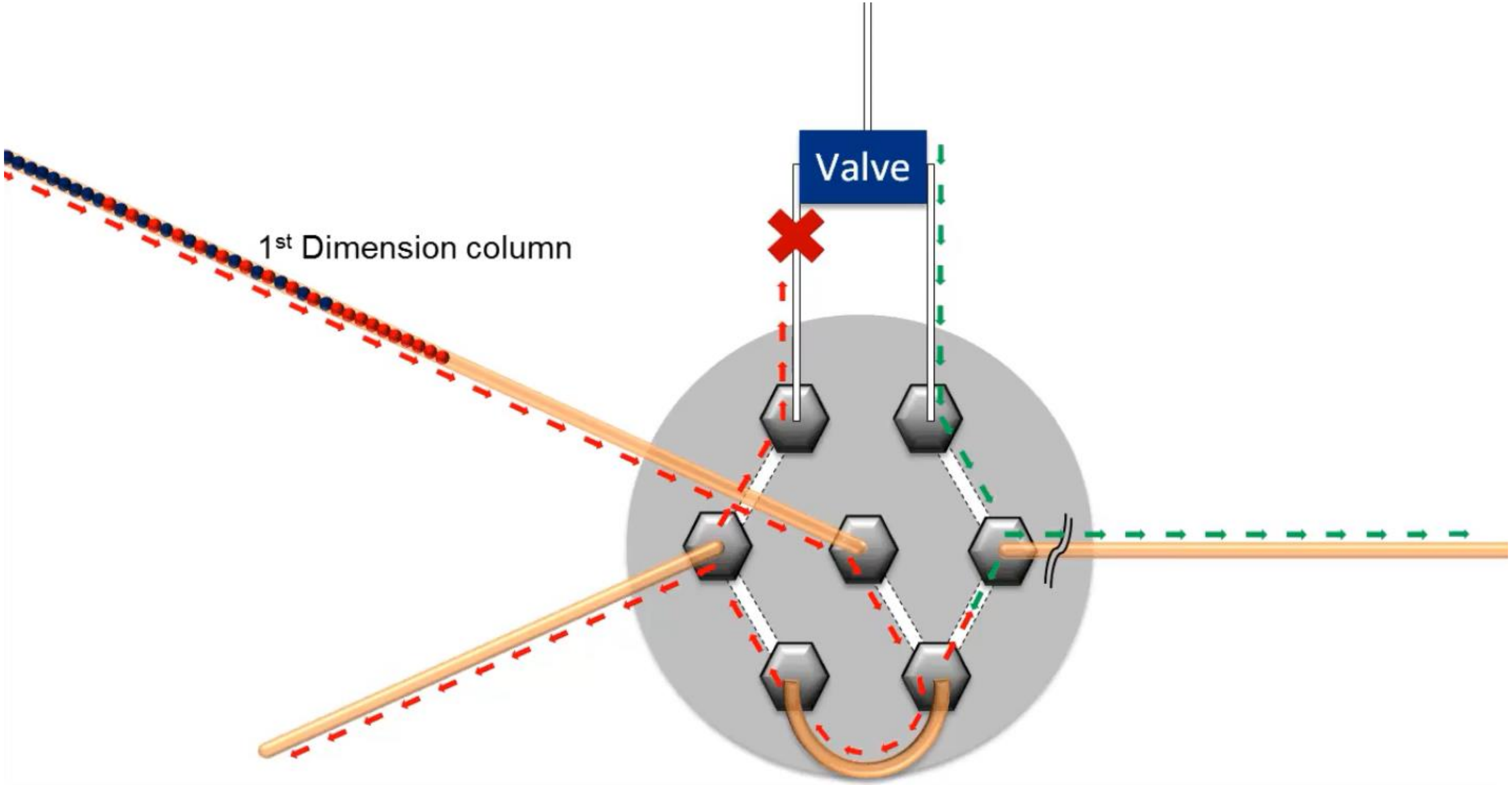
Performance summary

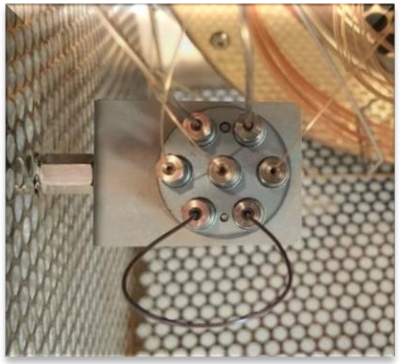
- Defined collection channel volume
  - Overfilling leads to breakthrough of effluent in to secondary column
- Must flush the channel before it reaches capacity
  - Very short P_M required (i.e. < 2 s)
  - Or very low ^{1}D column flow rates
- Many flow modulator applications often use skinny ^{1}D columns (0.100 mm i.d.)
  - Optimum linear velocity can be achieved at lower flow rates
  - Loading issues
  - Variability in column i.d.



Journal of Chromatography A, 1387 (2015) 95–103

Reverse fill/flush dynamics



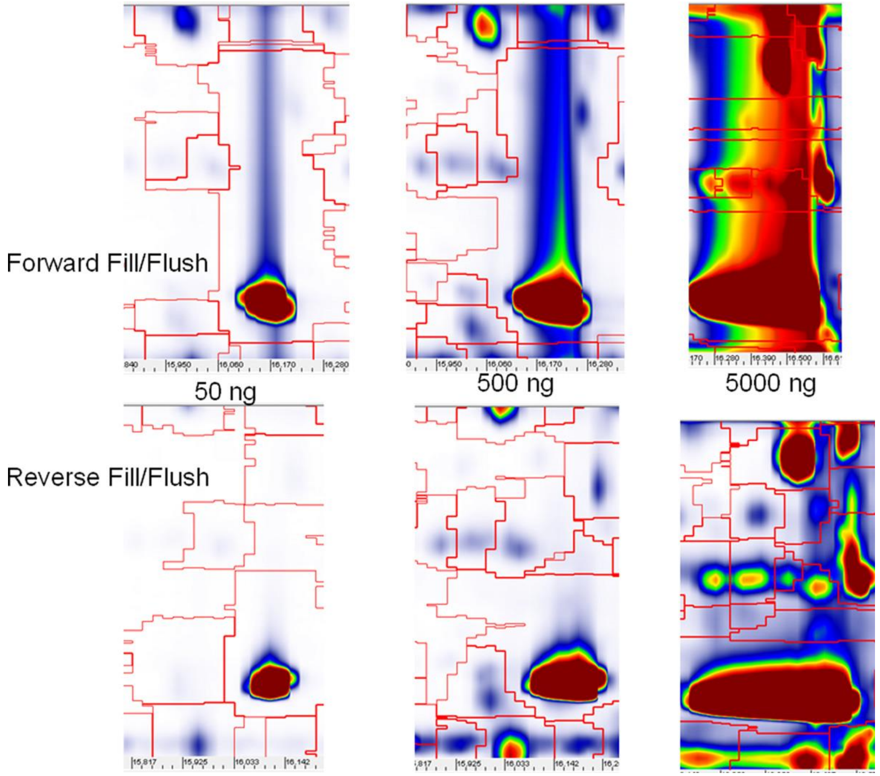


INSIGHT™
flow modulator

Reverse fill/flush modulation

Performance summary

- Flexible collection channel volume
  - Offers flexibility in column and flow rate selection
- Overfilling the loop is OK – eluate is directed to the bleed line
  - Monitor the bleed line with an additional detector (FID)
  - Activate the valve during specific intervals – heart cutting
- Reverse fill/flush improves peak shape
  - Breakthrough eliminated
  - Tailing is greatly reduced

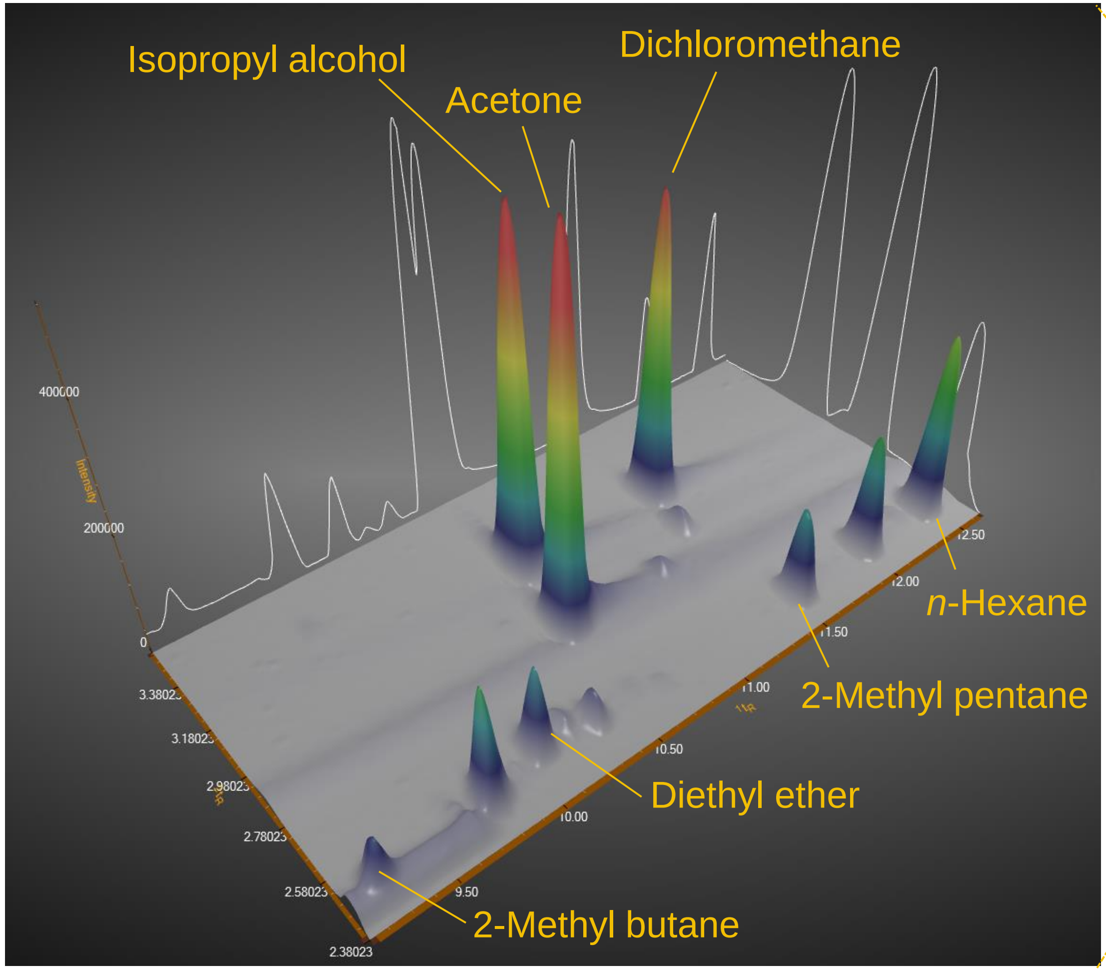


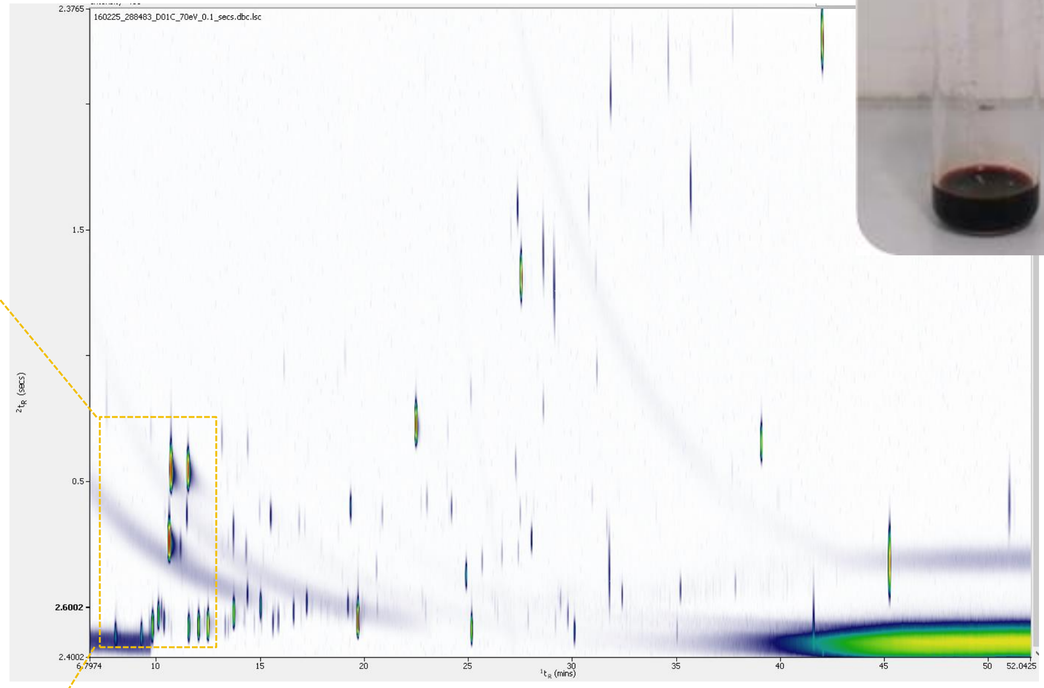
Journal of Chromatography A, 1226 (2012) 116– 123

SepSolve Analytical

Efficient modulation of volatiles

VOCs from blood



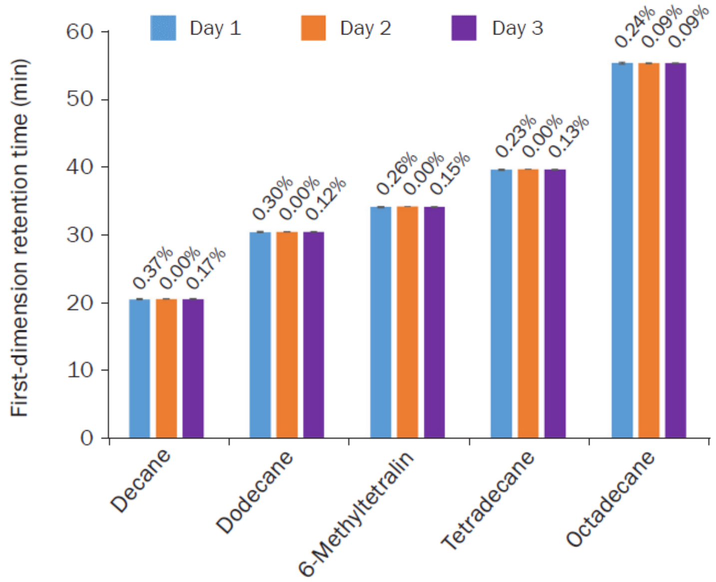


- Modulate volatiles <C_6
- Expand application range for GC×GC

Courtesy of University of Liège

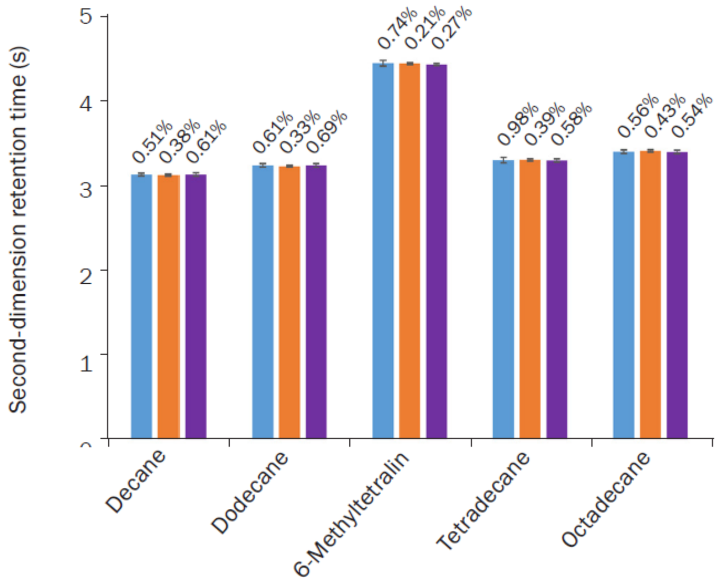
Repeatability

- Replicate injections of diesel (*n*=8/day for 3 days)
- This level of time precision is due to a dedicated EPC for each column



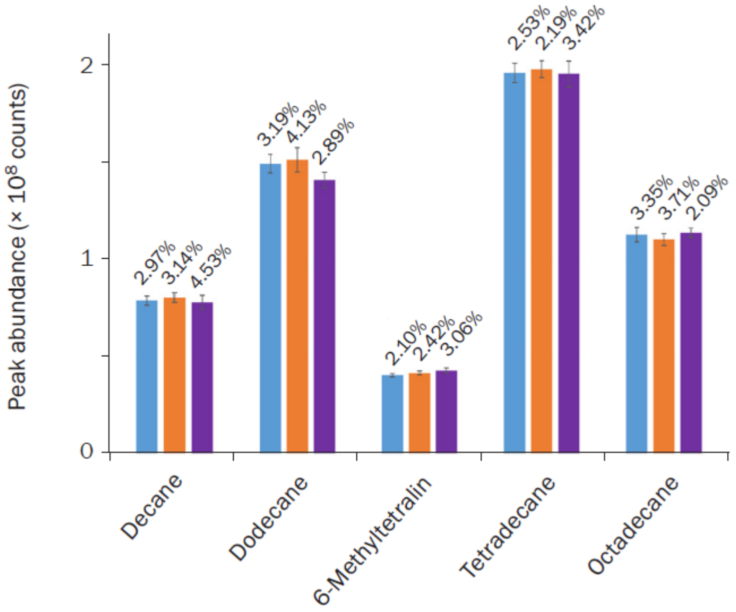
1st dimension retention time ($^{1}t_R$)

Mean RSD = 0.14%



2nd dimension retention time ($^{2}t_R$)

Mean RSD = 0.52%

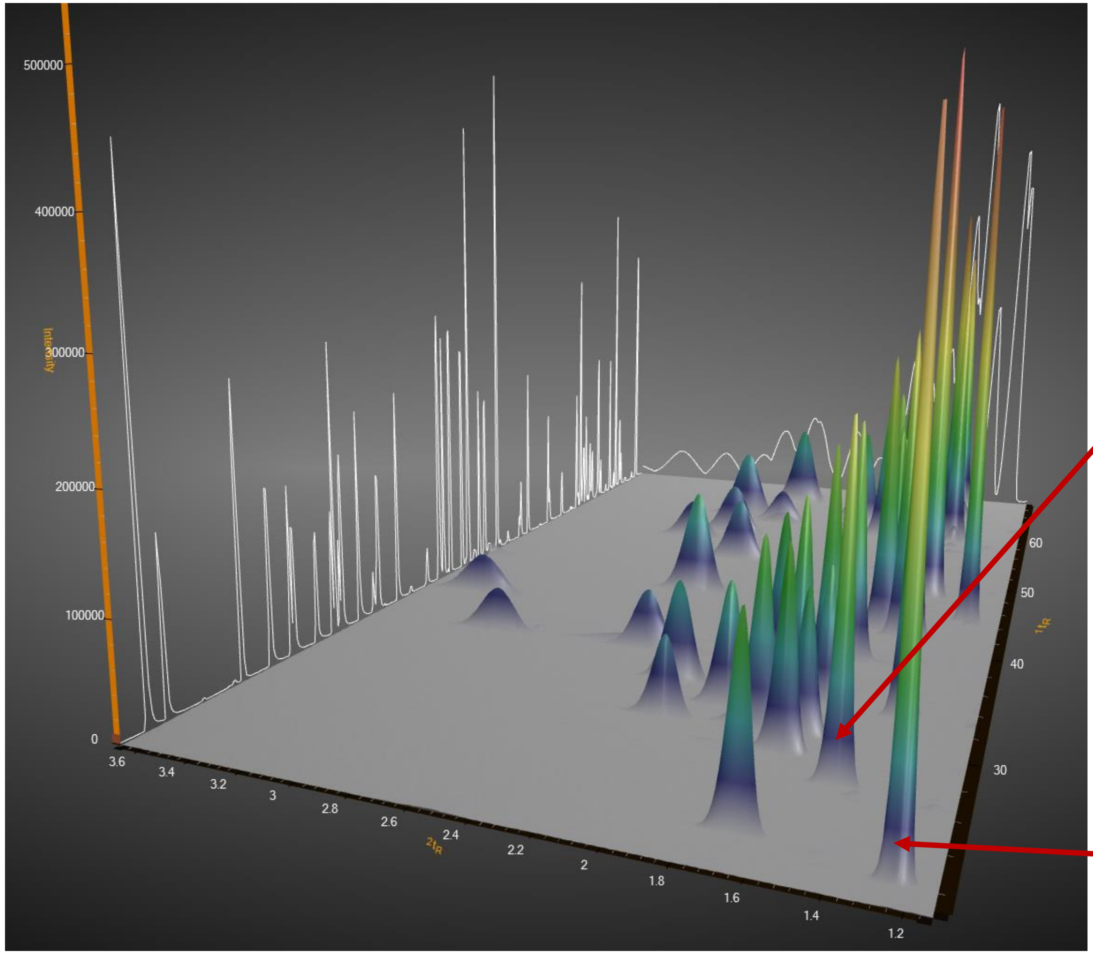


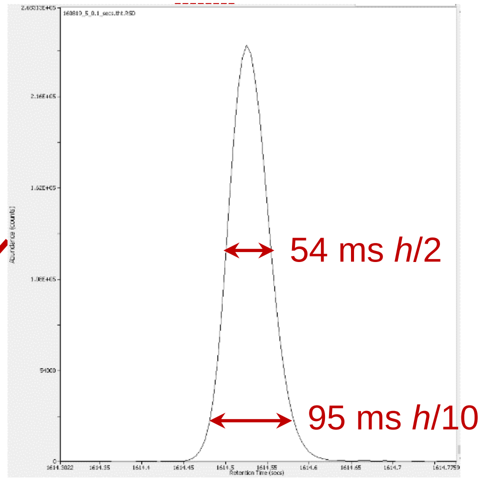
Peak abundance

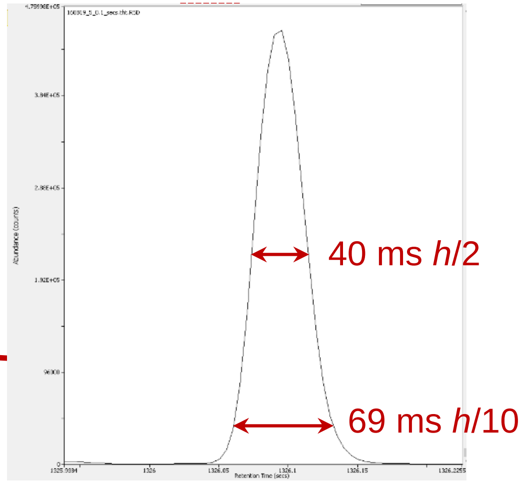
Mean RSD = 2.98%

Improved peak shape

^{2}D peak width is a function of loop volume and ^{2}D flow rate

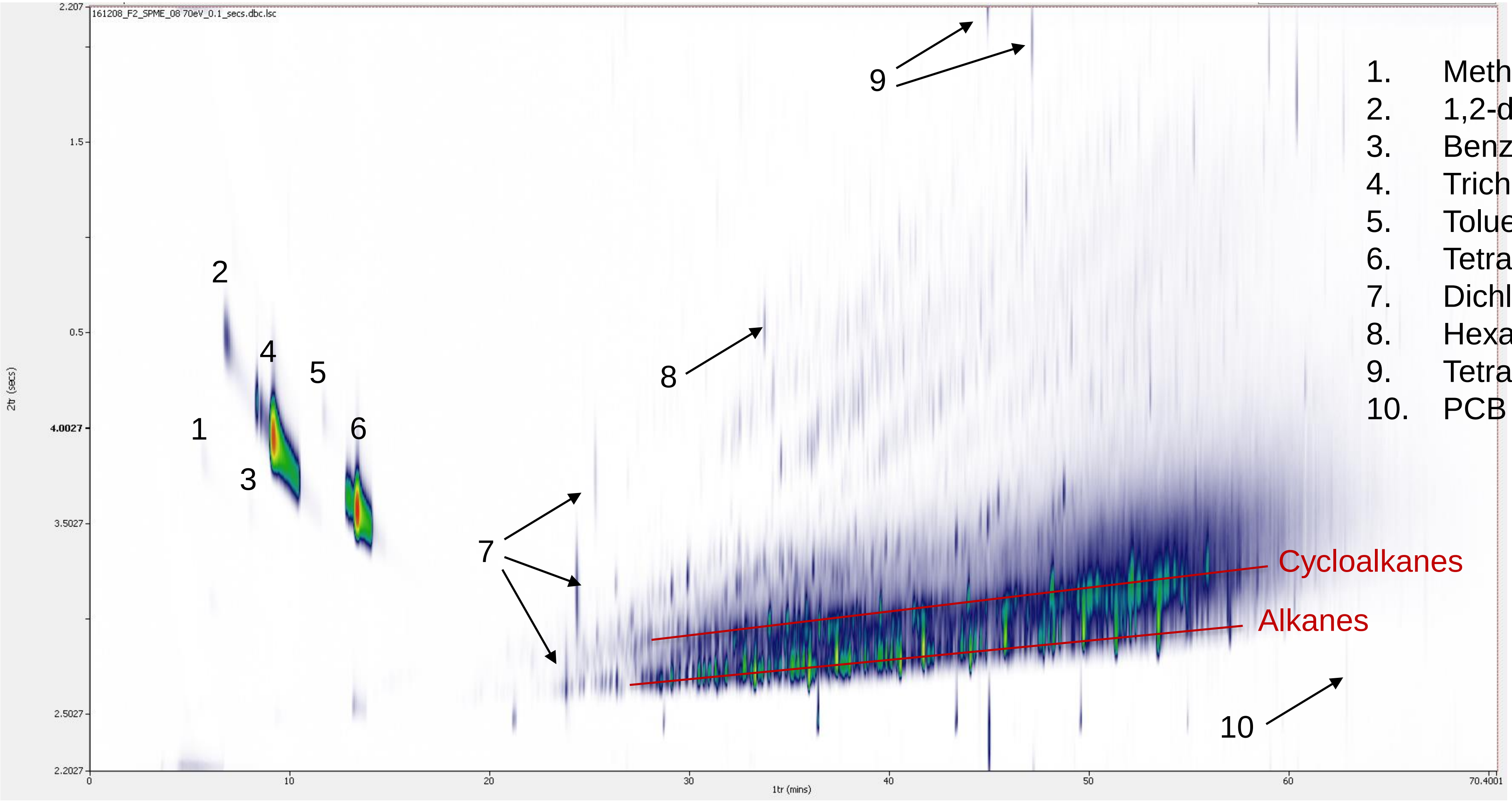






Analysis of water from a contaminated aquifer…

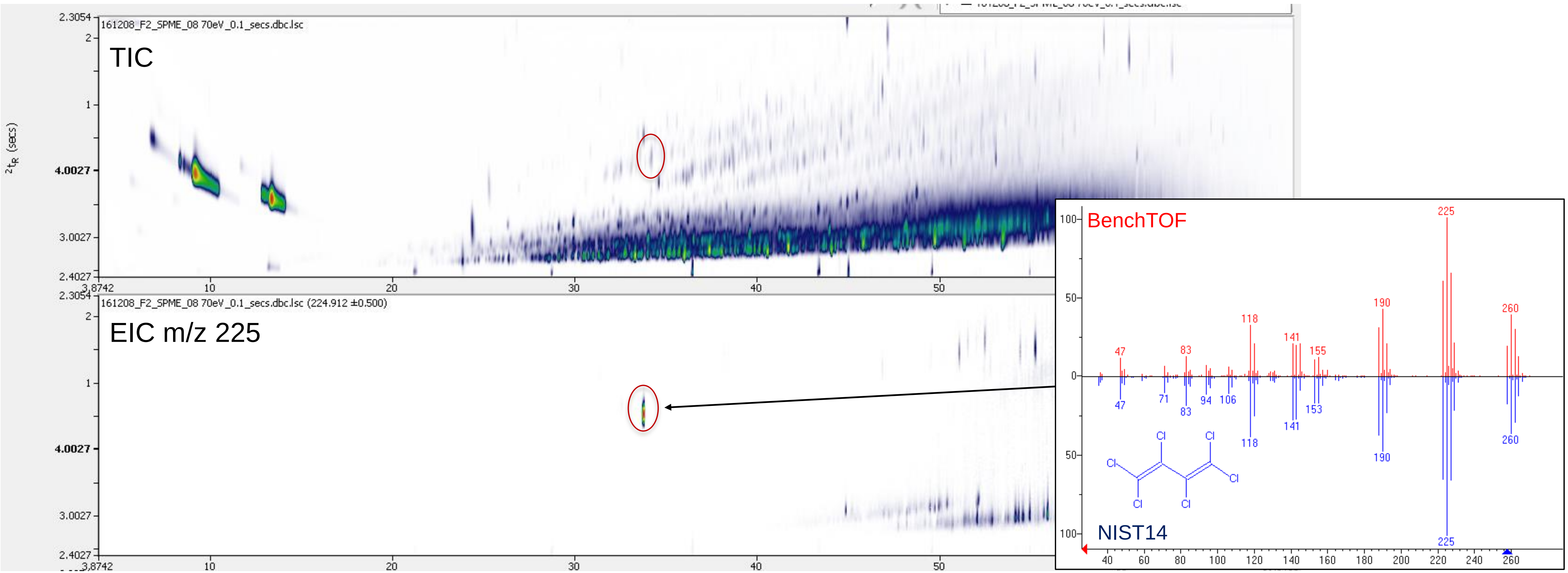
…by SPME-GC×GC-TOF MS



1. Methylene chloride
2. 1,2-dichloroethylene
3. Benzene
4. Trichloroethylene
5. Toluene
6. Tetrachloroethylene
7. Dichlorobenzenes
8. Hexachlorobutadiene
9. Tetrachlorobenzenes
10. PCB 57

Analysis of water from a contaminated aquifer…

…by SPME-GC×GC-TOF MS

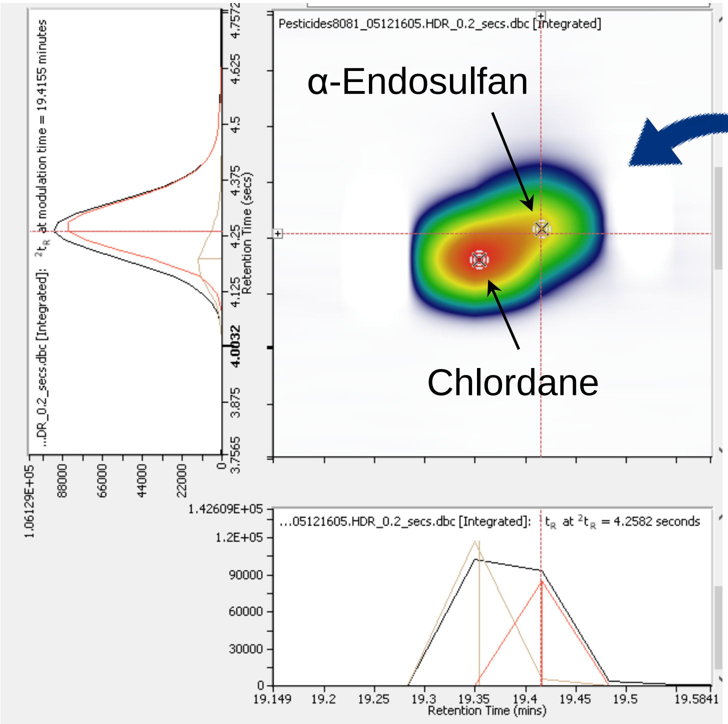


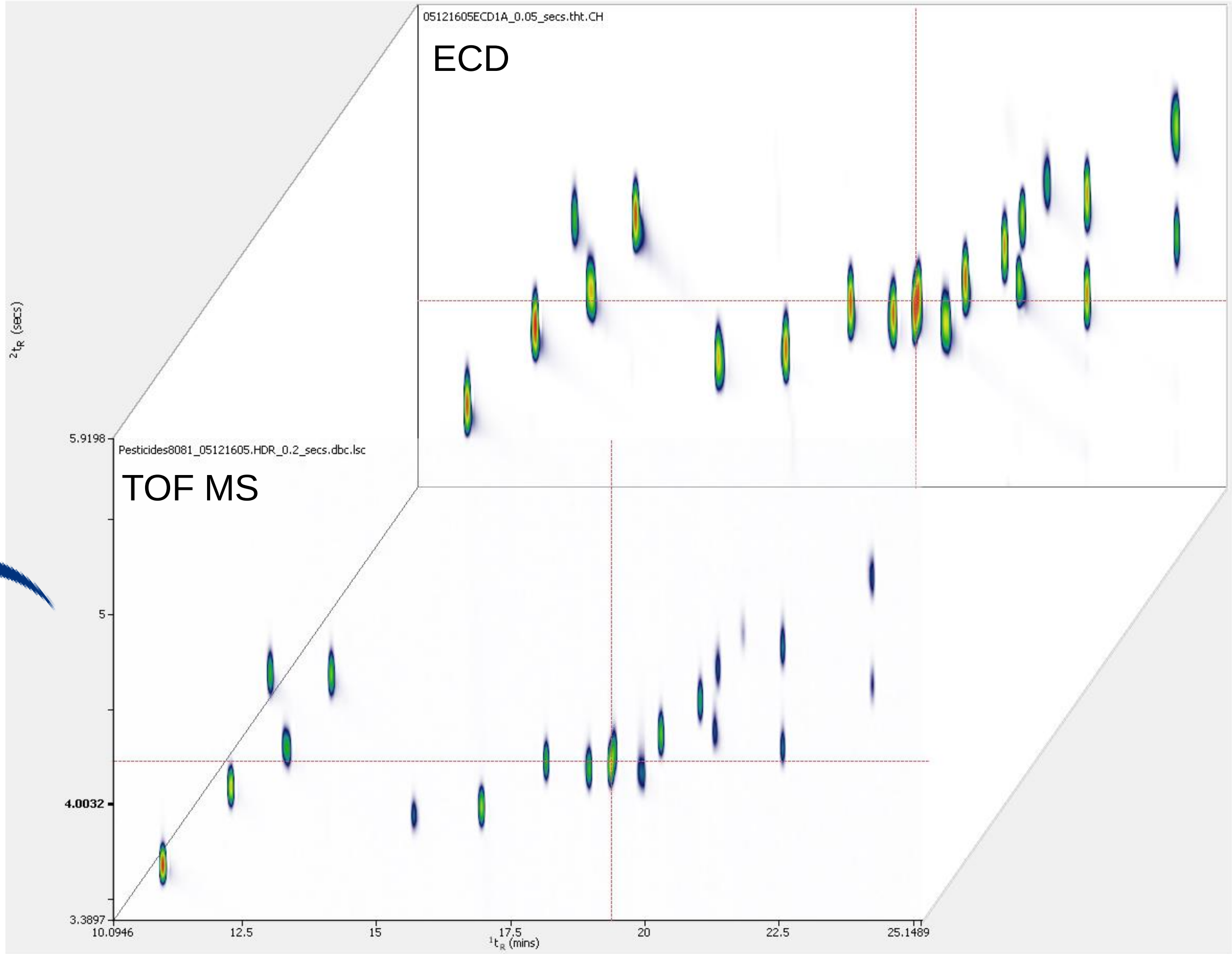
- Hexachlorobutadiene would have coeluted with numerous hydrocarbons in 1D GC.

Parallel detection ECD/TOF MS

Organochlorine pesticides

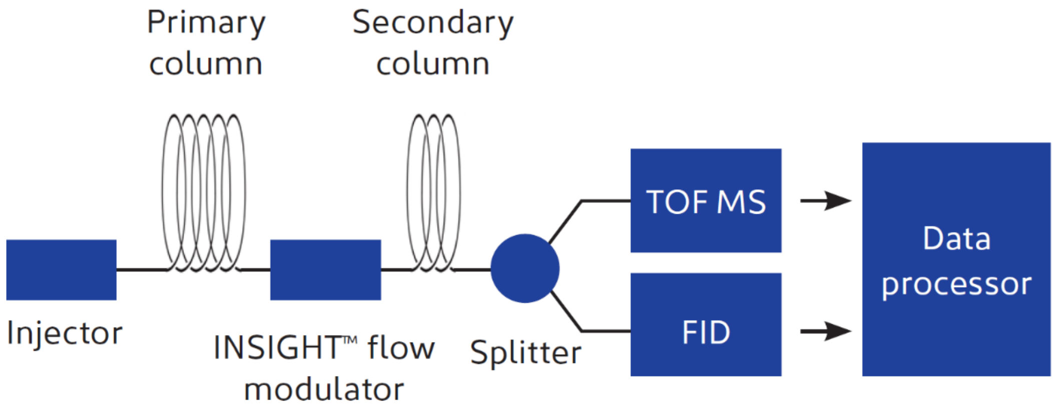
- Excellent $^1t_R/^2t_R$ correspondence
- Confirmation of peak purity by MS

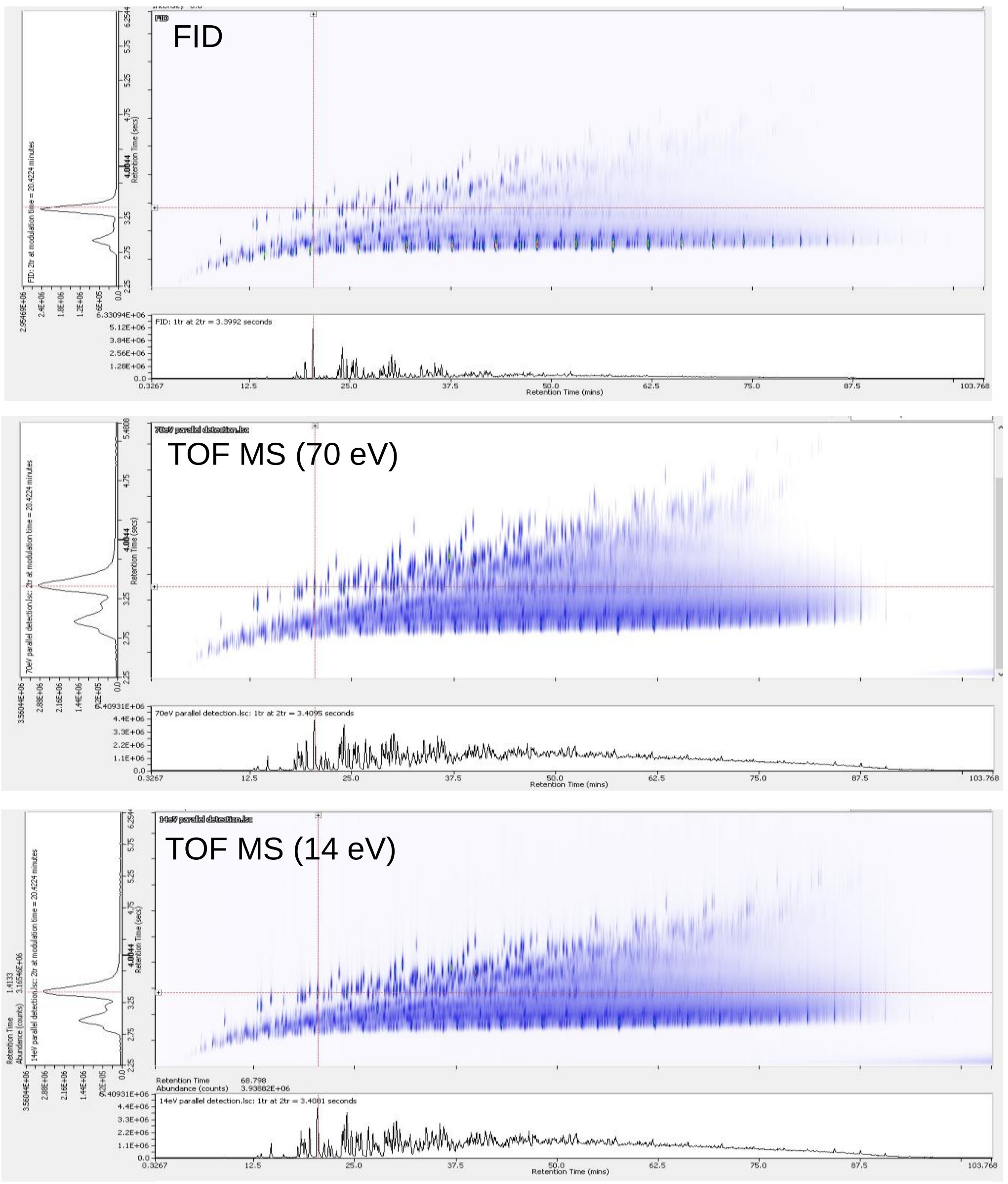




3 information-rich datasets…

…with Tandem Ionisation

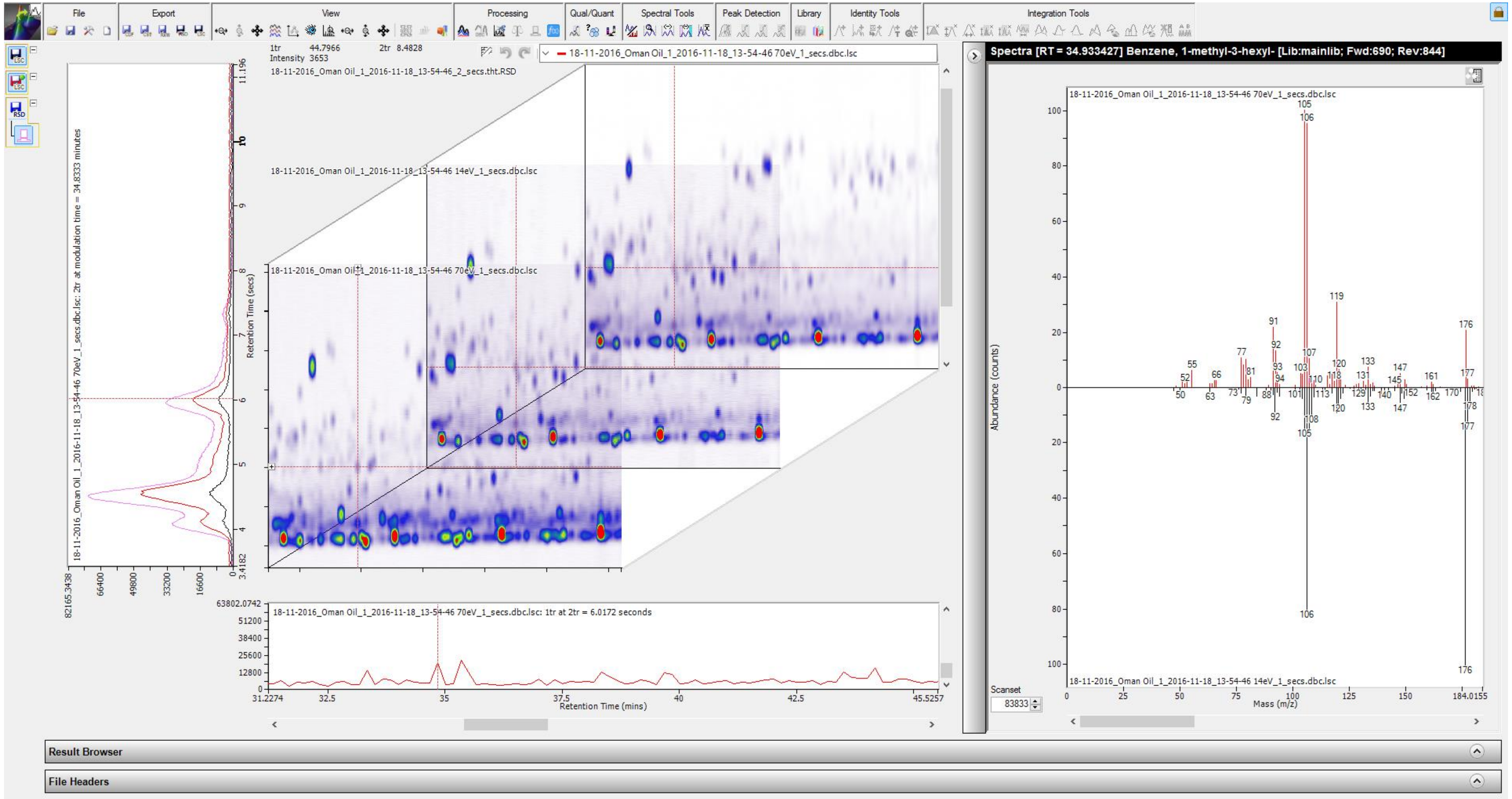




- Analysis of diesel by dual detection GC×GC-FID/TOF MS
- Cross-validation and confirmation of peak purity by TOF MS
- Gain another dimension with Tandem Ionisation

Parallel detection FID/TOF MS

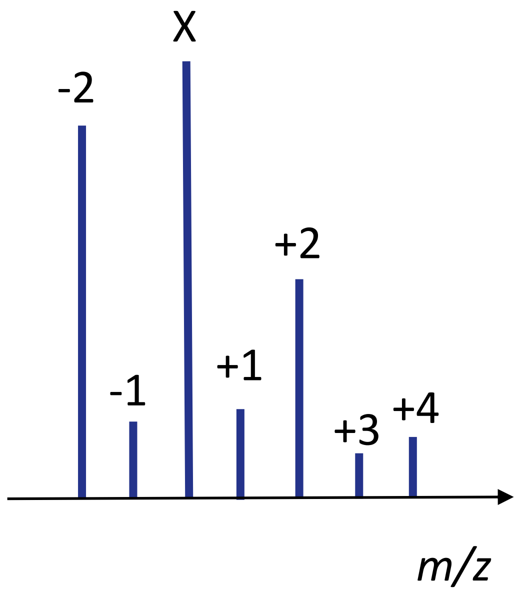
Crude oil with 70 eV, 14 eV, FID

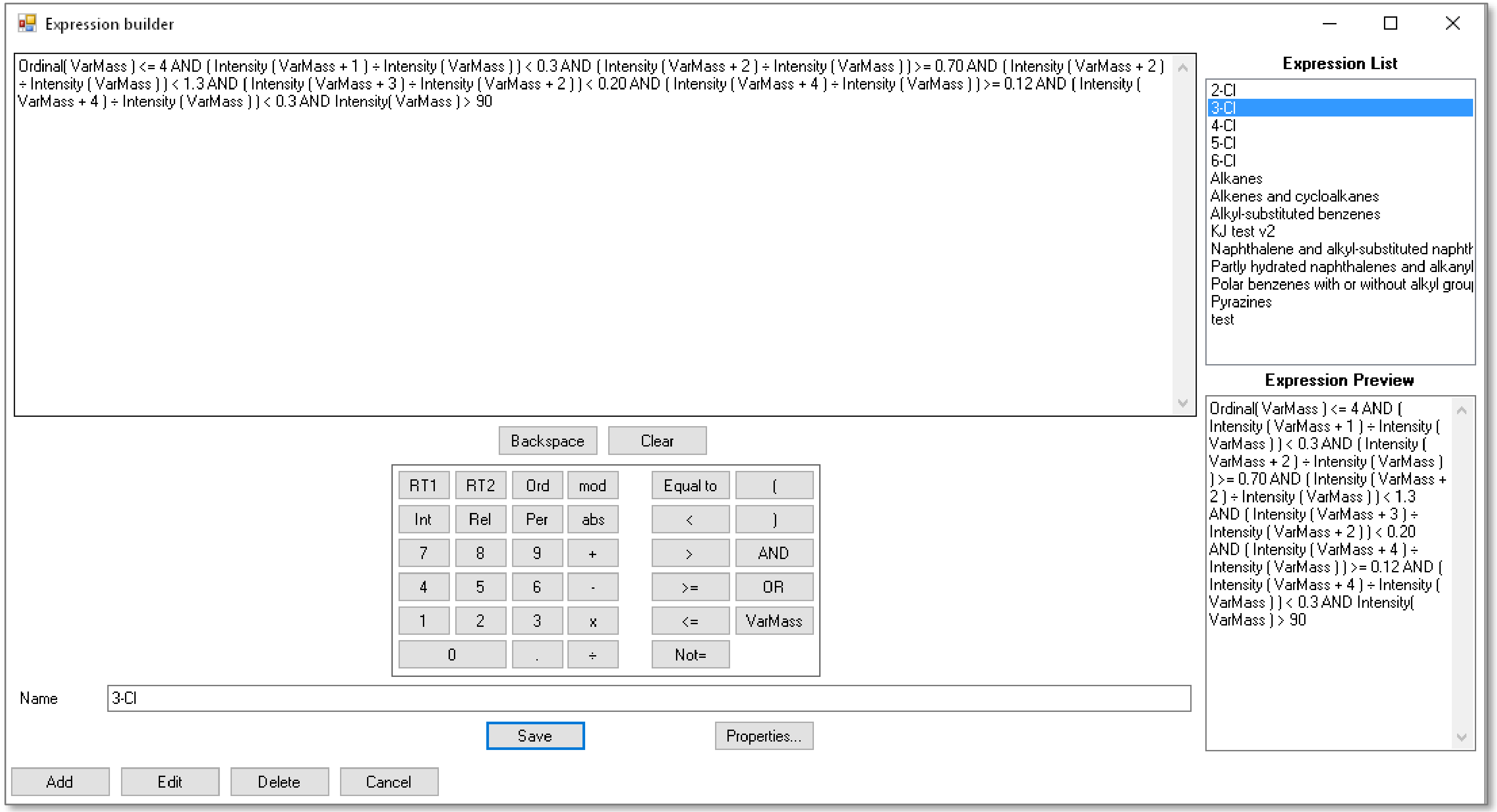


Solving the *“needle in a haystack”* problem…

…using simple scripting expressions

- Search for compounds with specific spectral features
  - e.g. Isotopic fingerprint of Cl

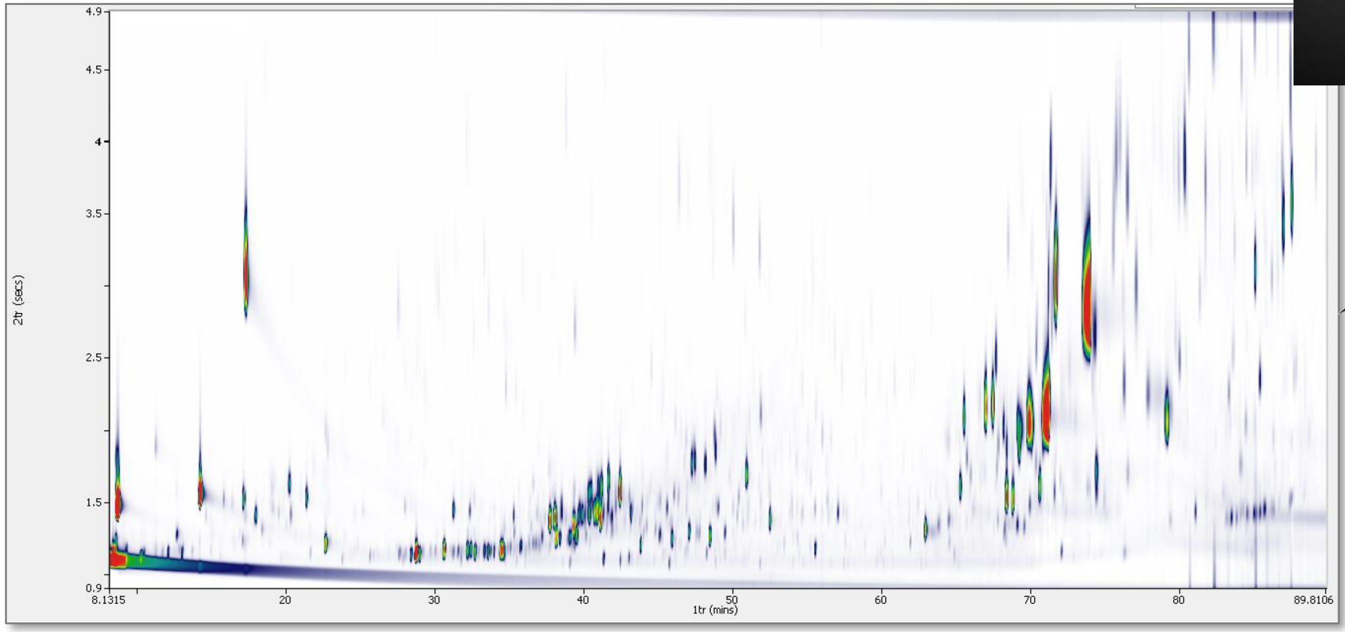


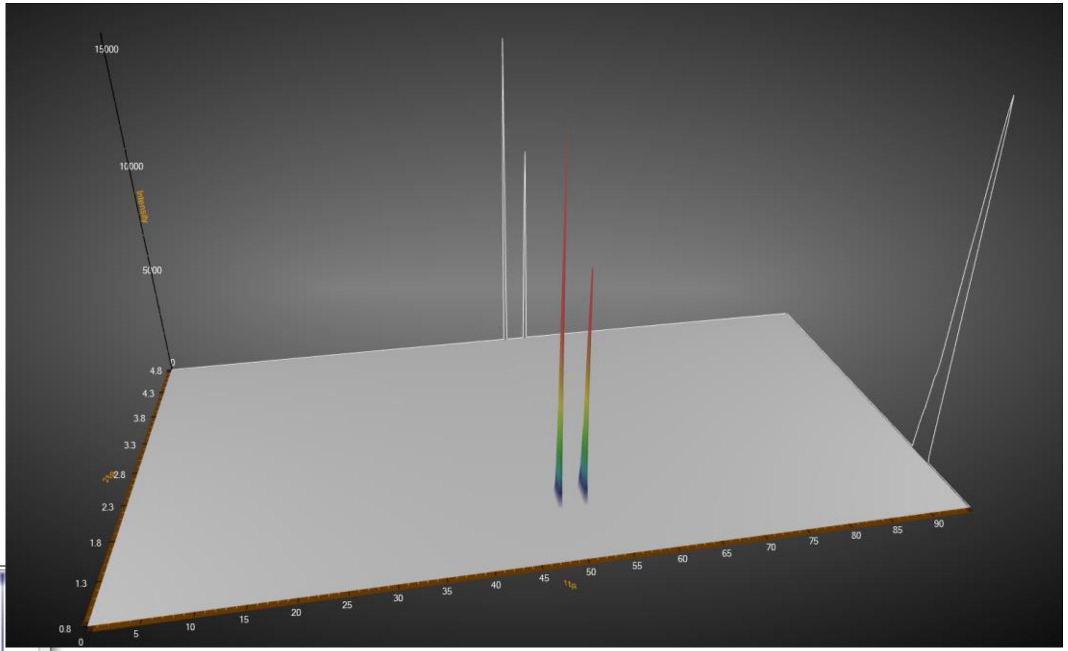


Organochlorines in cannabis…

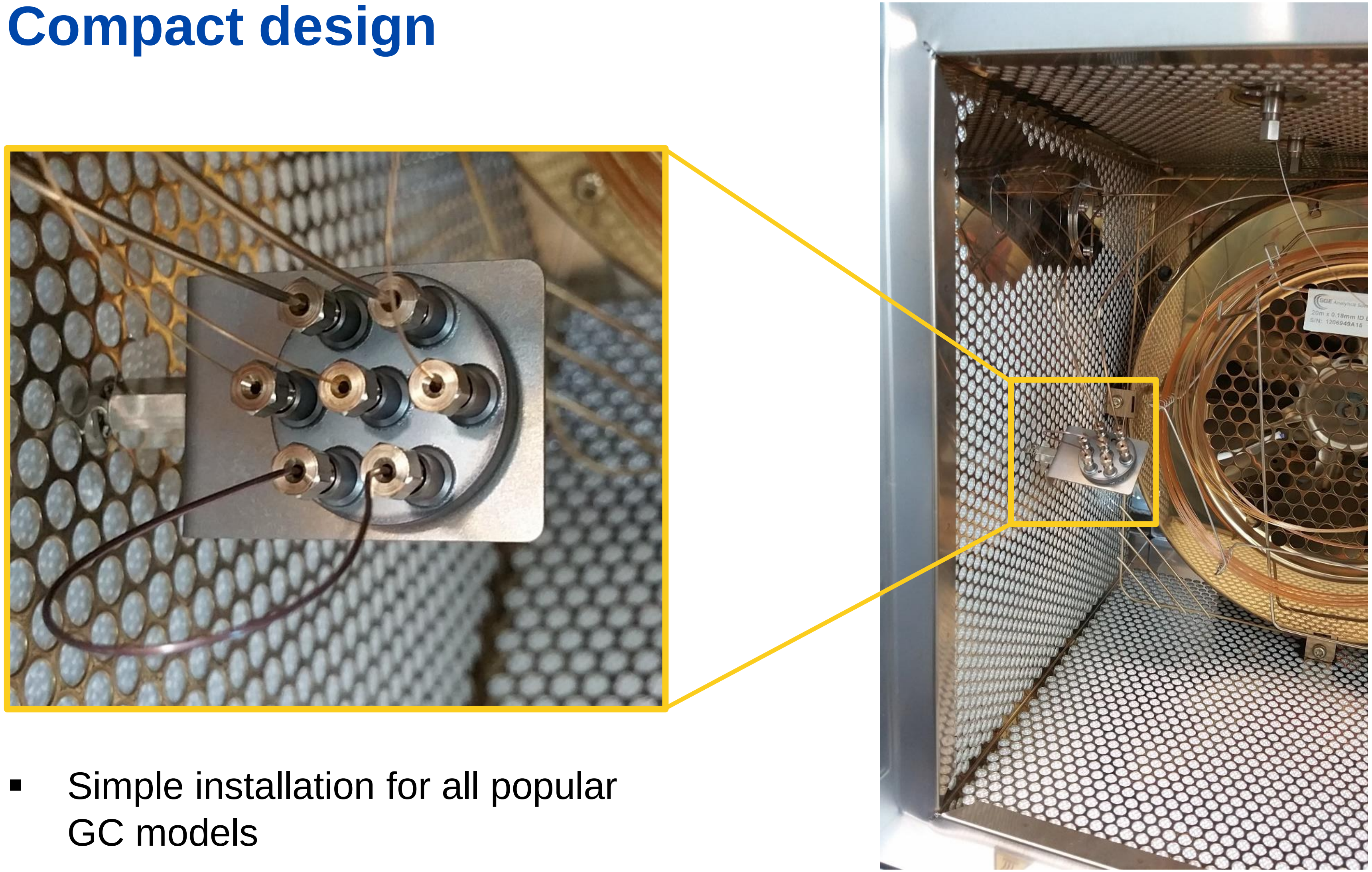
…using simple scripting expressions

- Scripting expressions generate clean images containing only the peaks that “pass”
- Multiple scripts can be run at once



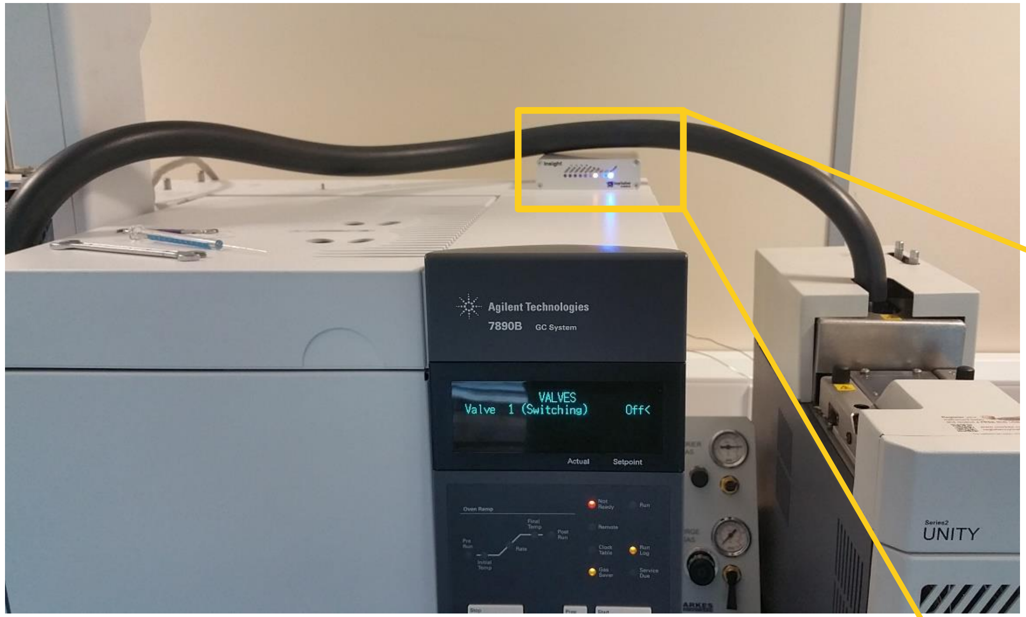


Compact design



- Simple installation for all popular GC models

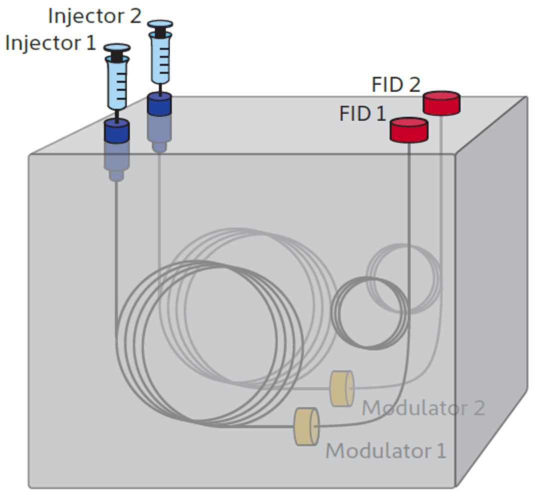
Compact design

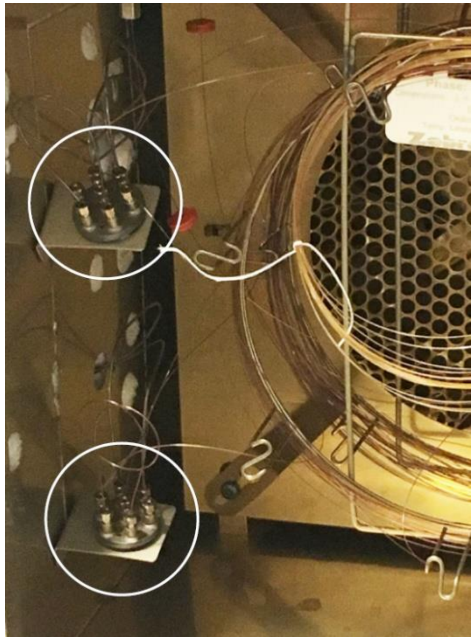


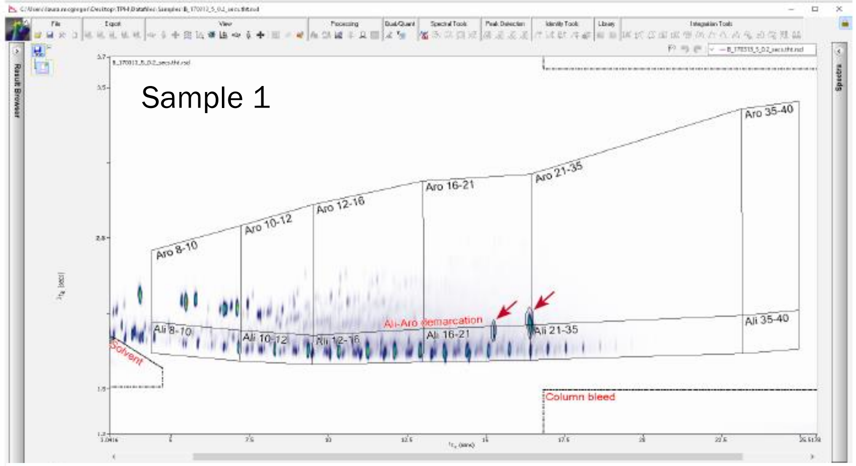
- Simple installation for all popular GC models

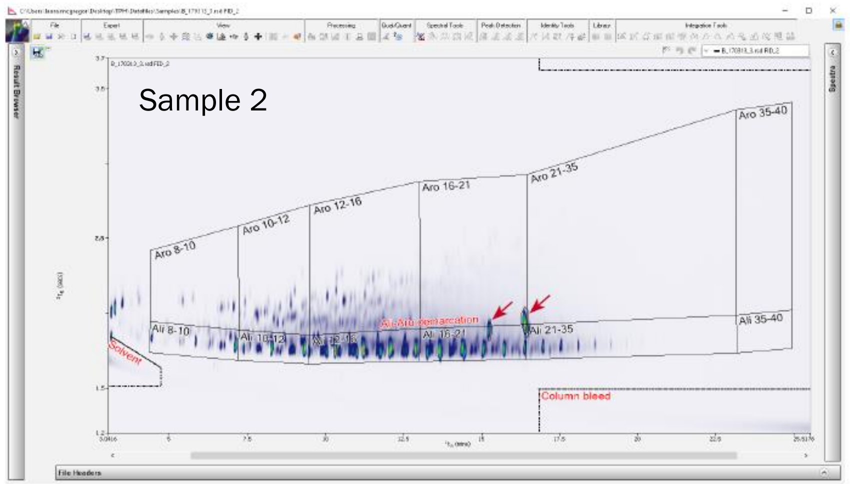
Dual-channel configuration

Total Petroleum Hydrocarbons (TPH)





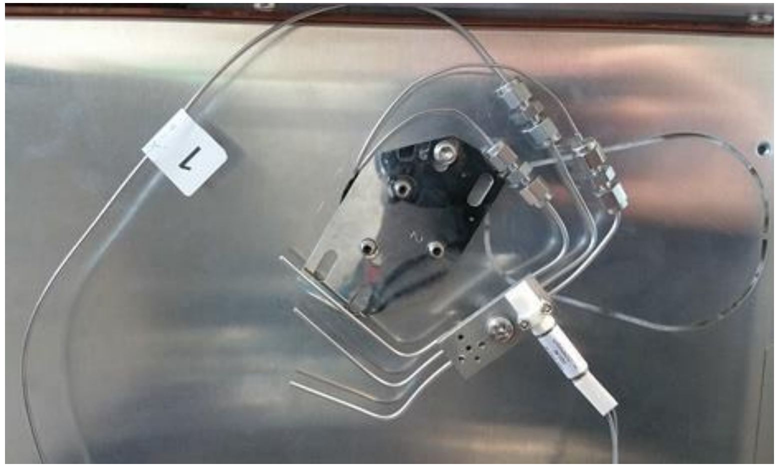


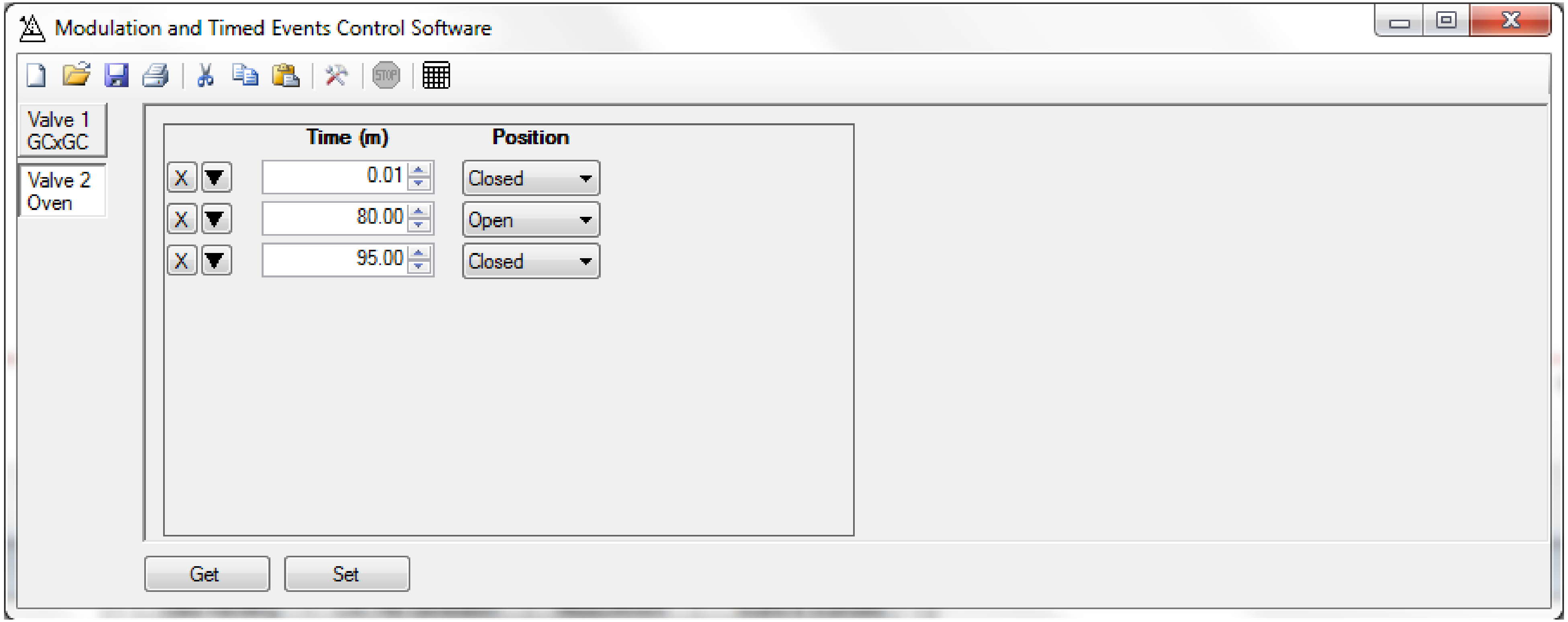


- Run two samples simultaneously
- Simple stencils for fast group-type quantitation in ChromSpace software

Valve control

Control up to 4 valves in various configurations

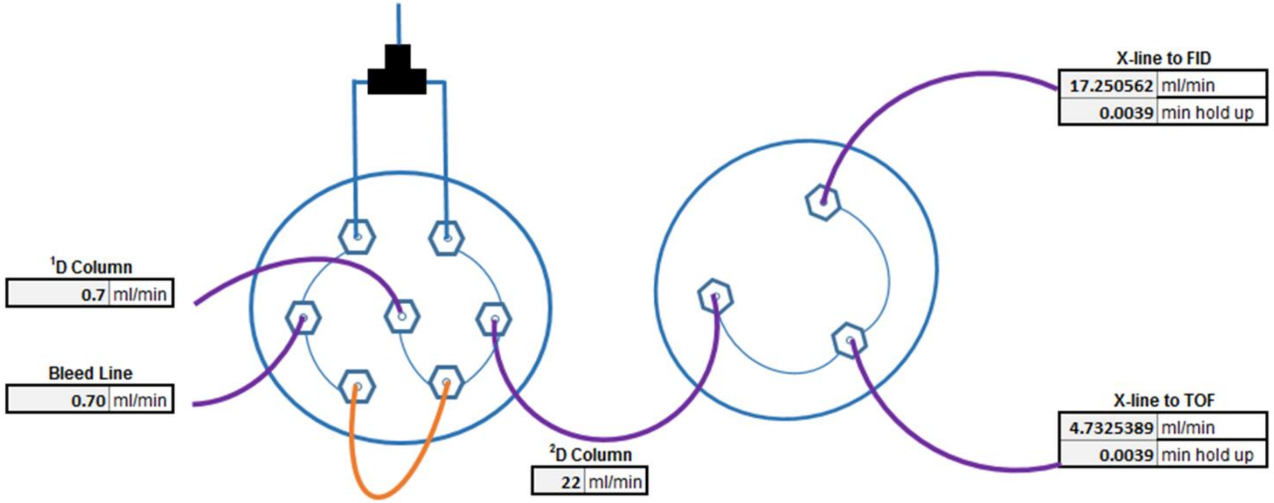




Flow calculator…

…for simplified method set-up

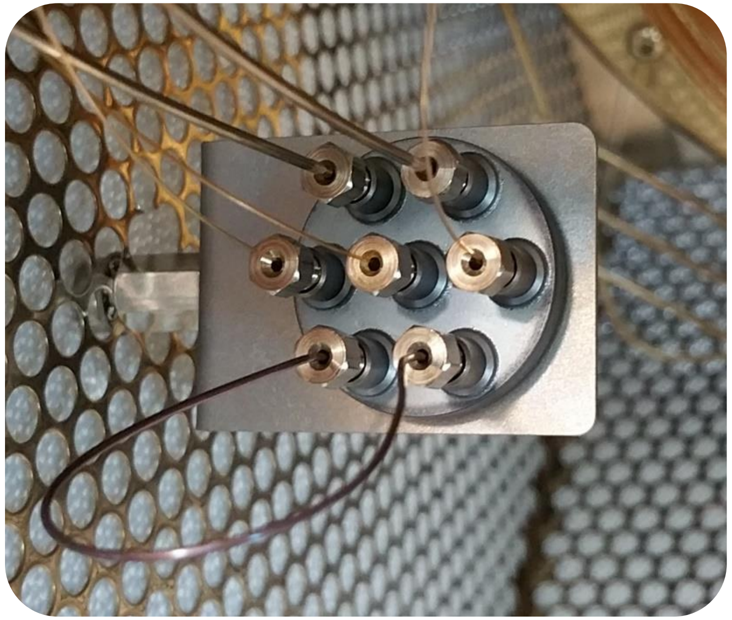
INSIGHT Flow Calculator	
Column flows and bleed line	
Carrier Gas	Helium
Oven Temp (Deg. C)	60
PCM Pressure (psig)	21.05
Secondary column length (m)	2.48
Secondary column diameter (mm)	0.25
Bleed line length (m)	2.42
Bleed line diameter (mm)	0.1026
2D Effluent Splitter	
X-line to TOF length (m)	1
X-line to TOF diameter (mm)	0.18
X-line to FID length (m)	0.84
X-line to FID diameter (mm)	0.32
Loop Fill and Flush	
alues valid for 0.530 mm ID tubing only. Calculations are for He carrier gas	
LOOP VOLUME	
Loop Length (cm)	23
Loop Internal diameter (mm)	0.53
Volume (µl)	50.74
FILL	
^{1}D Column volumetric flow rate (ml/min, He)	0.7
^{1}D Column Average linear velocity (cm/sec, He)	5.60
Loop fill time by volumetric flow rate (seconds)	4.349329
Loop fill time by average linear velocity (seconds)	4.107143
75% capacity fill time (by volume)	3.26
75% capacity fill time (by velocity)	3.08
FLUSH	
^{2}D Column volumetric flow rate (ml/min, He)	22
^{2}D Column Average linear velocity (cm/sec, He)	173.12
Loop flush time by volumetric flow rate (milliseconds)	138.3878
Loop flush time by average linear velocity (milliseconds)	132.8568
Loop flushed 1.5 times in milliseconds (by volume)	208
Loop flushed 1.5 times in milliseconds (by velocity)	199



Summary

Reverse fill/flush flow modulation provides:

- Improved peak shape and peak capacity
- Efficient modulation of both volatiles and semi-volatiles (CH_4 to n-C_{60})
- Excellent repeatability for large sample batches
  - Rigid retention times
  - Area %RSD routinely <5%
- Simple configuration of:
  - Parallel detection (e.g. FID/TOF MS)
  - Heart-cutting
  - Backflushing
  - Dual injection



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