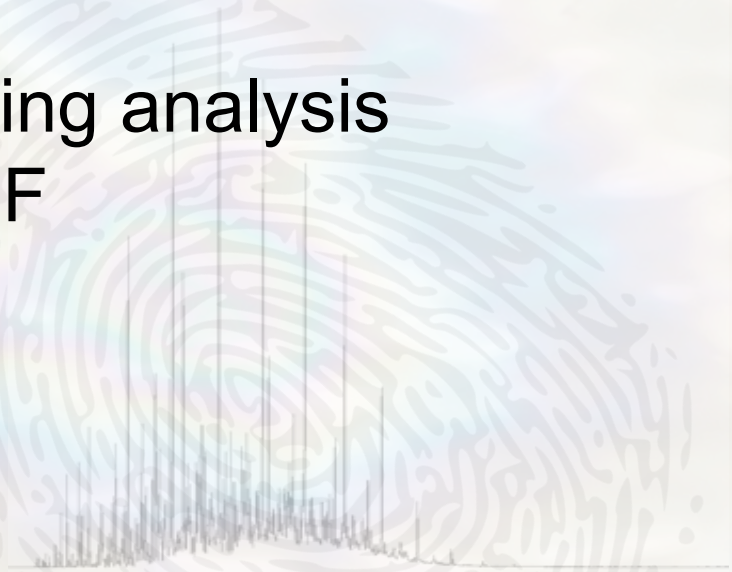
# Petrochemical fingerprinting analysis by GCxGC-TOF



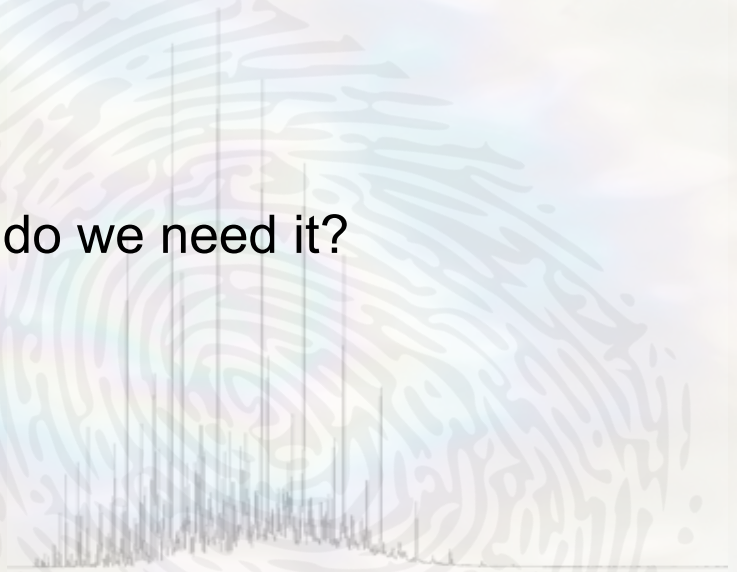
Ratimarth Bunlorm
GC GCMS Product Specialist

# Topic

- GC×GC system
- Petrochemical analysis
- Petrochemical fingerprinting analysis

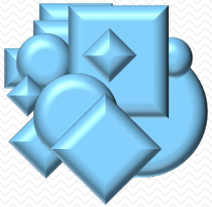
# GC×GC:

## What is it, how does it work & why do we need it?



# What is GC×GC?

The challenge…



A complex mixture

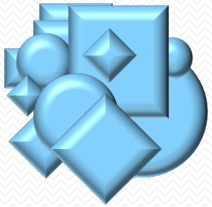
1D by size

1D by shape

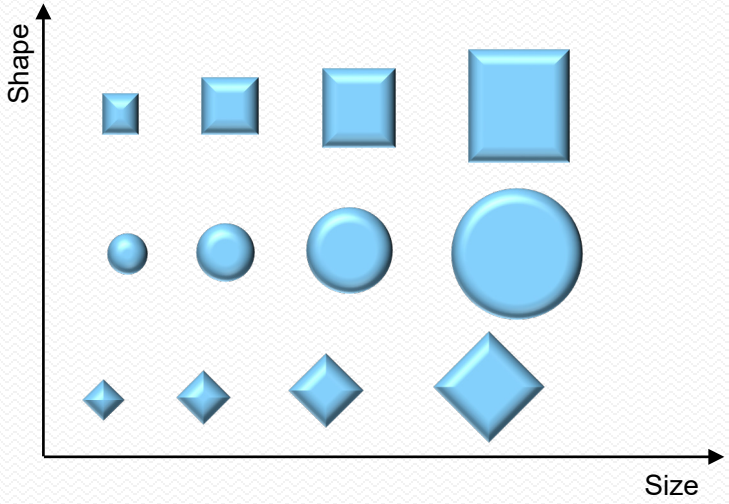
*Both options have potential coelutions*

# What is GC×GC?

The solution…



A complex mixture

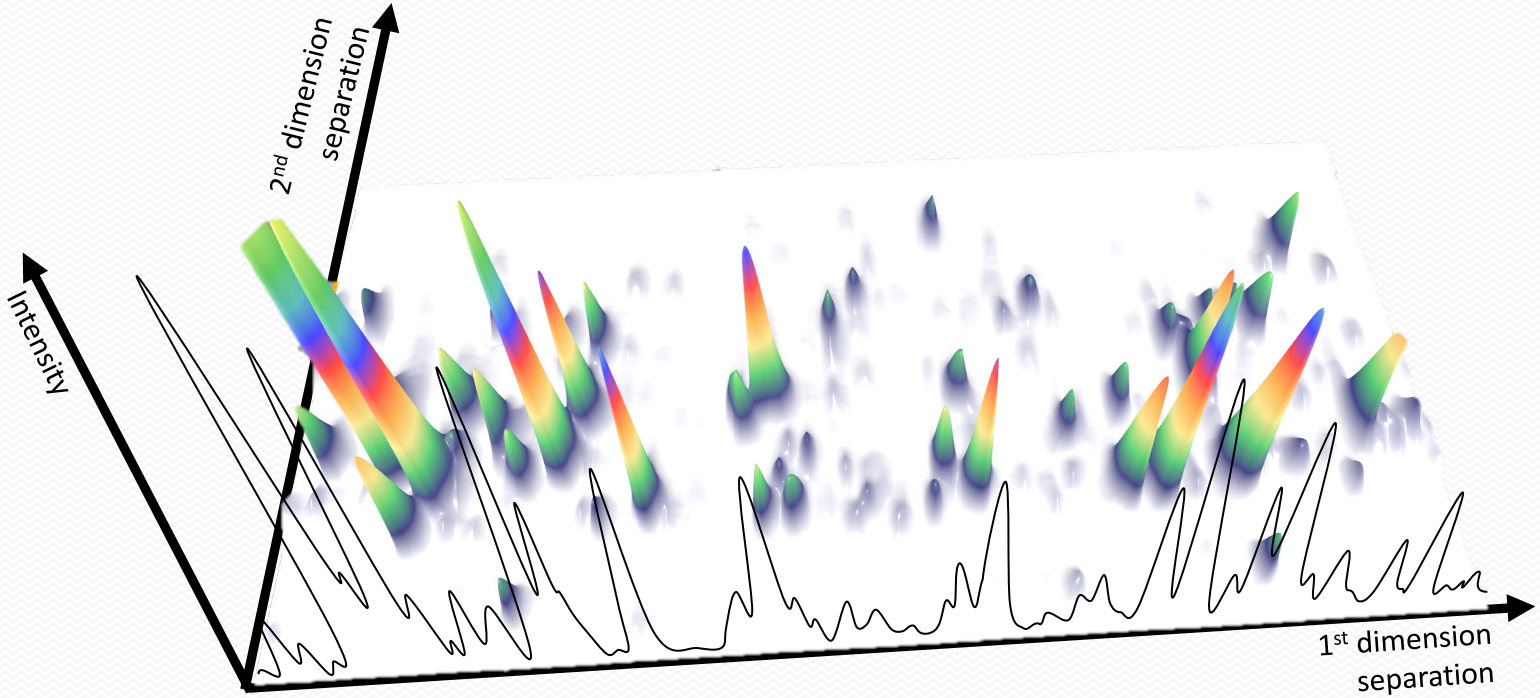



2D by size **AND** shape

*Improved separation of the mixture*

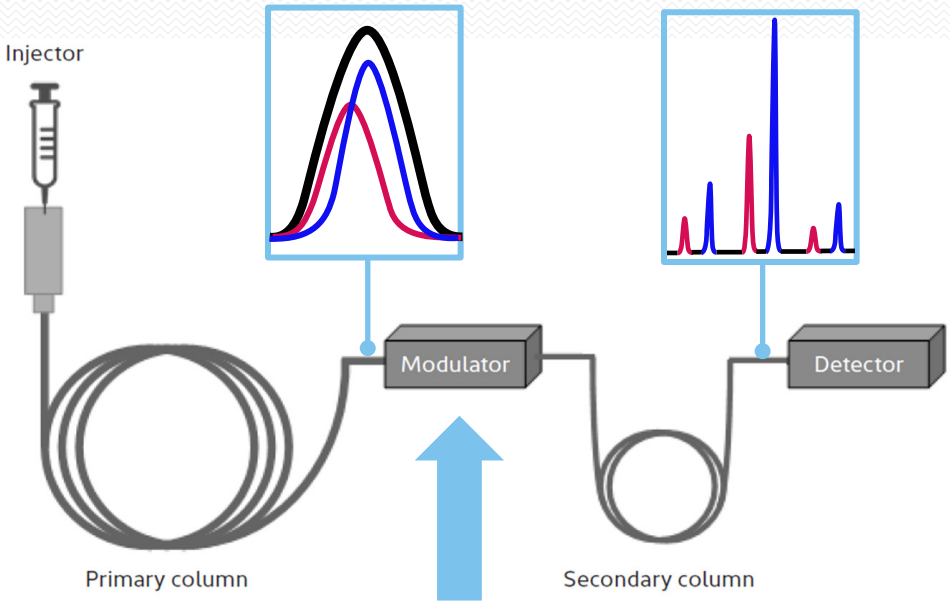
# Chromatogram

Discover more…



# How does GC×GC work?

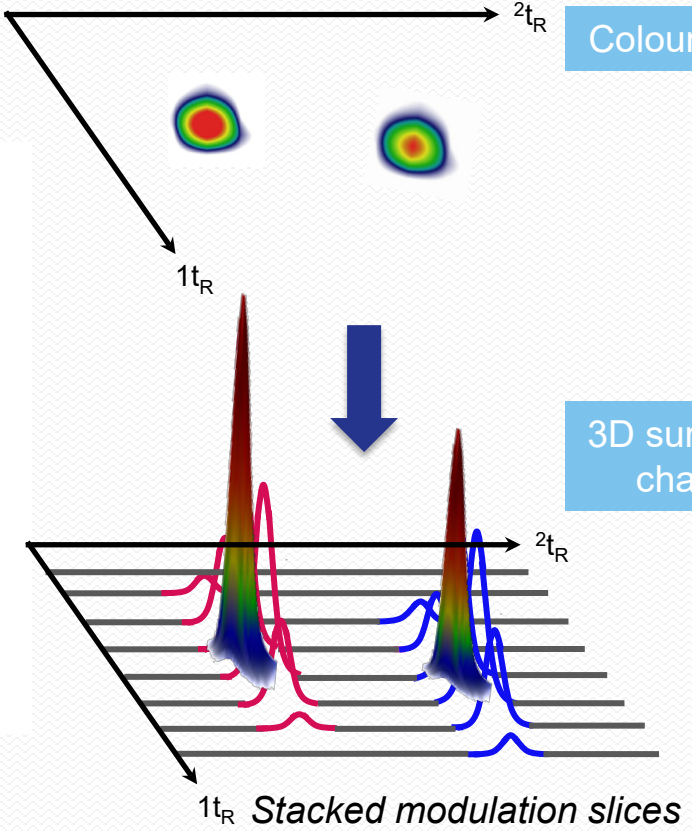
## Analytical system




The
“beating heart”
of GC×GC

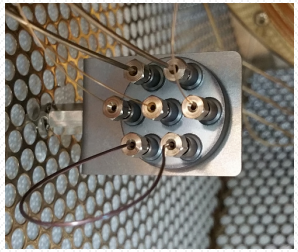
Colour plot

3D surface chart



# Types of modulator

- Commercial devices use:
  - Flow modulation
    e.g. INSIGHT modulator (SepSolve Analytical)

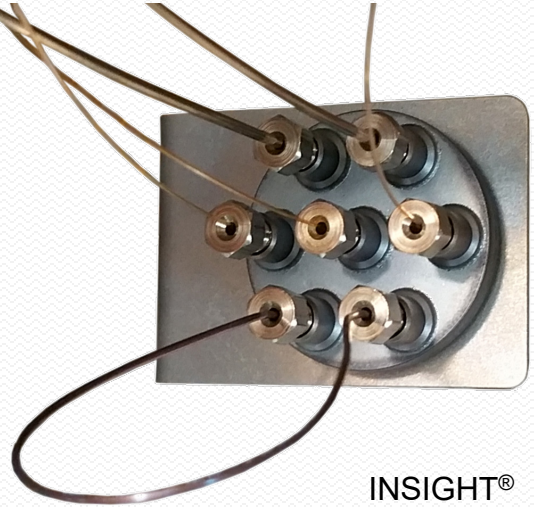


  - Thermal modulation
    e.g. Delay loop modulator (Zoex)

- Both have their own pros and cons – the choice will depend on the application

# Benefits of flow modulation

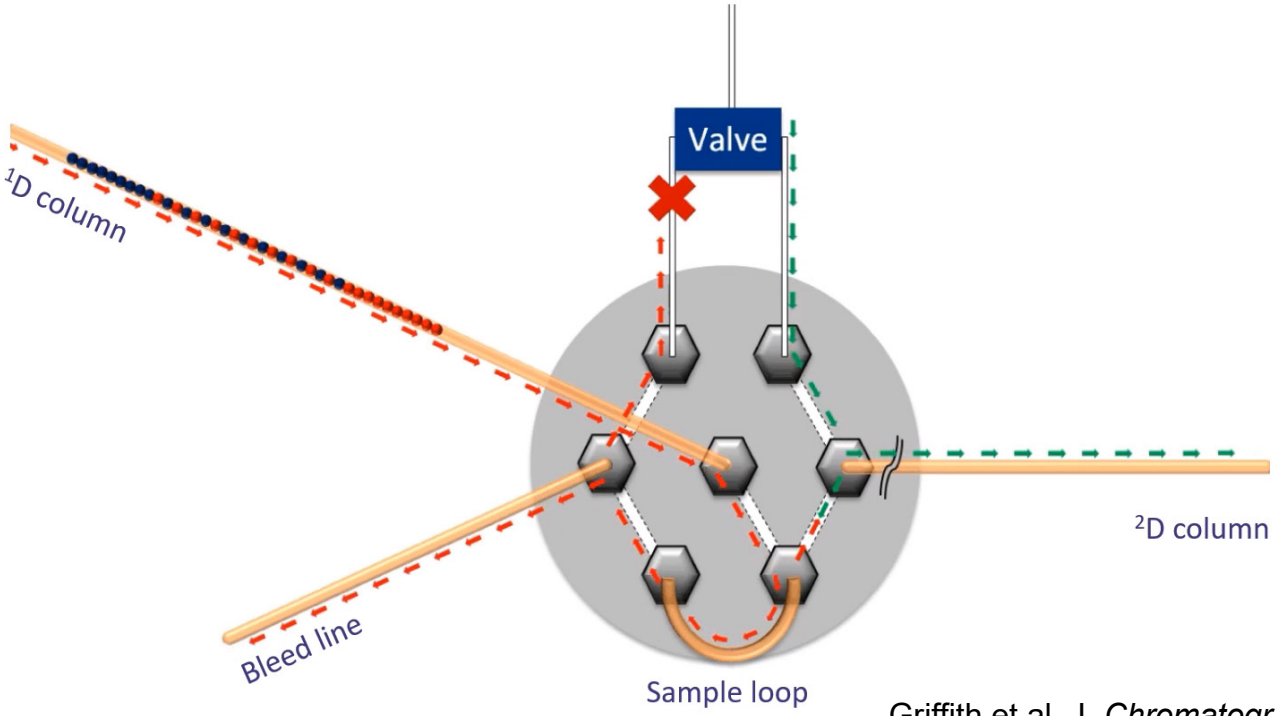
- Consumable-free operation
  - Low running costs
- Efficient modulation of volatiles
  - Extends application range
- Excellent repeatability
  - For routine analyses and large sample batches



INSIGHT®
(SepSolve Analytical)

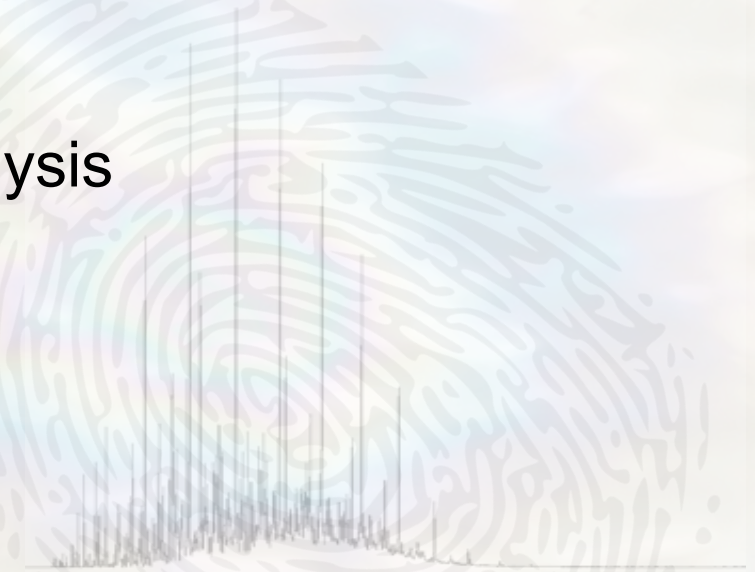
# INSIGHT reverse fill/flush (RFF) modulator

## How does it work?



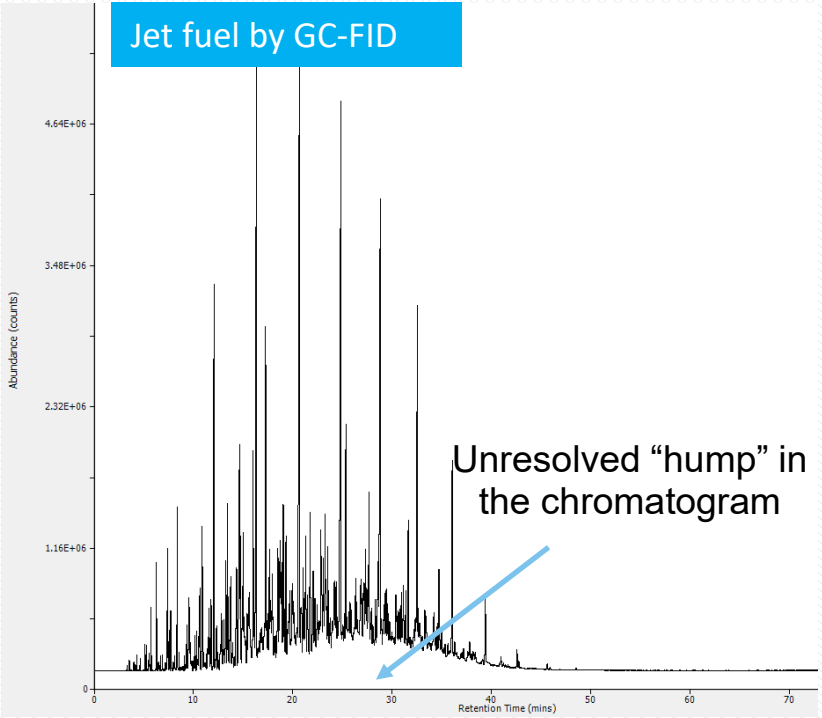

Griffith et al, J. *Chromatogr. A,* 1226 (2012) 116– 123

# Petrochemical Analysis

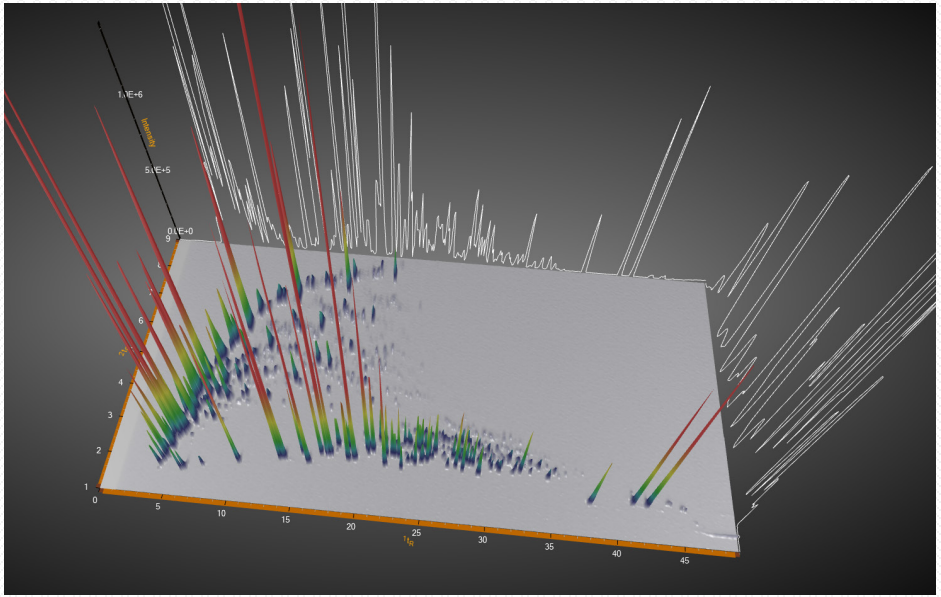


# Why use GC×GC?

Jet fuel by GC-FID

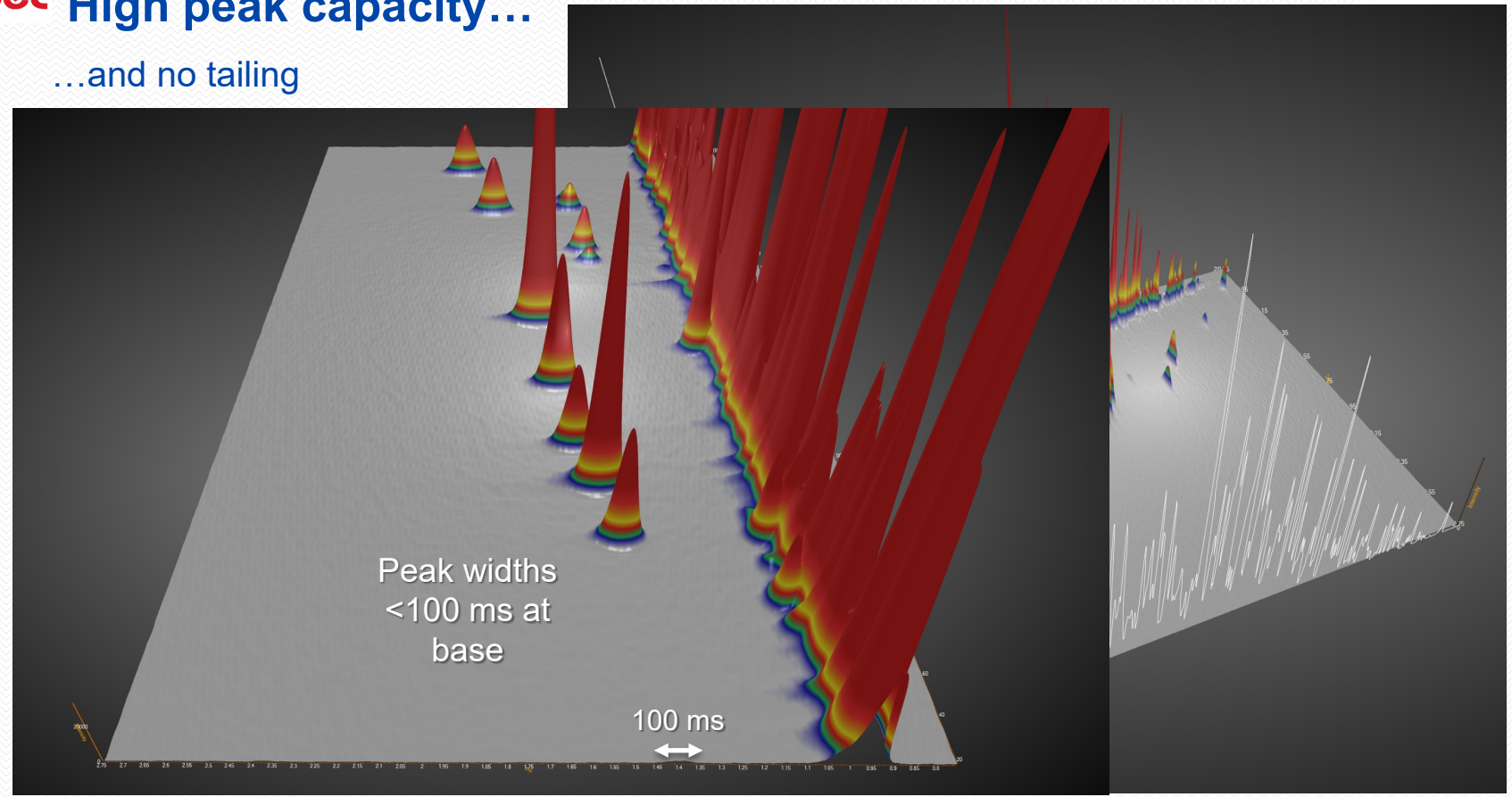



Jet fuel by GC×GC-FID

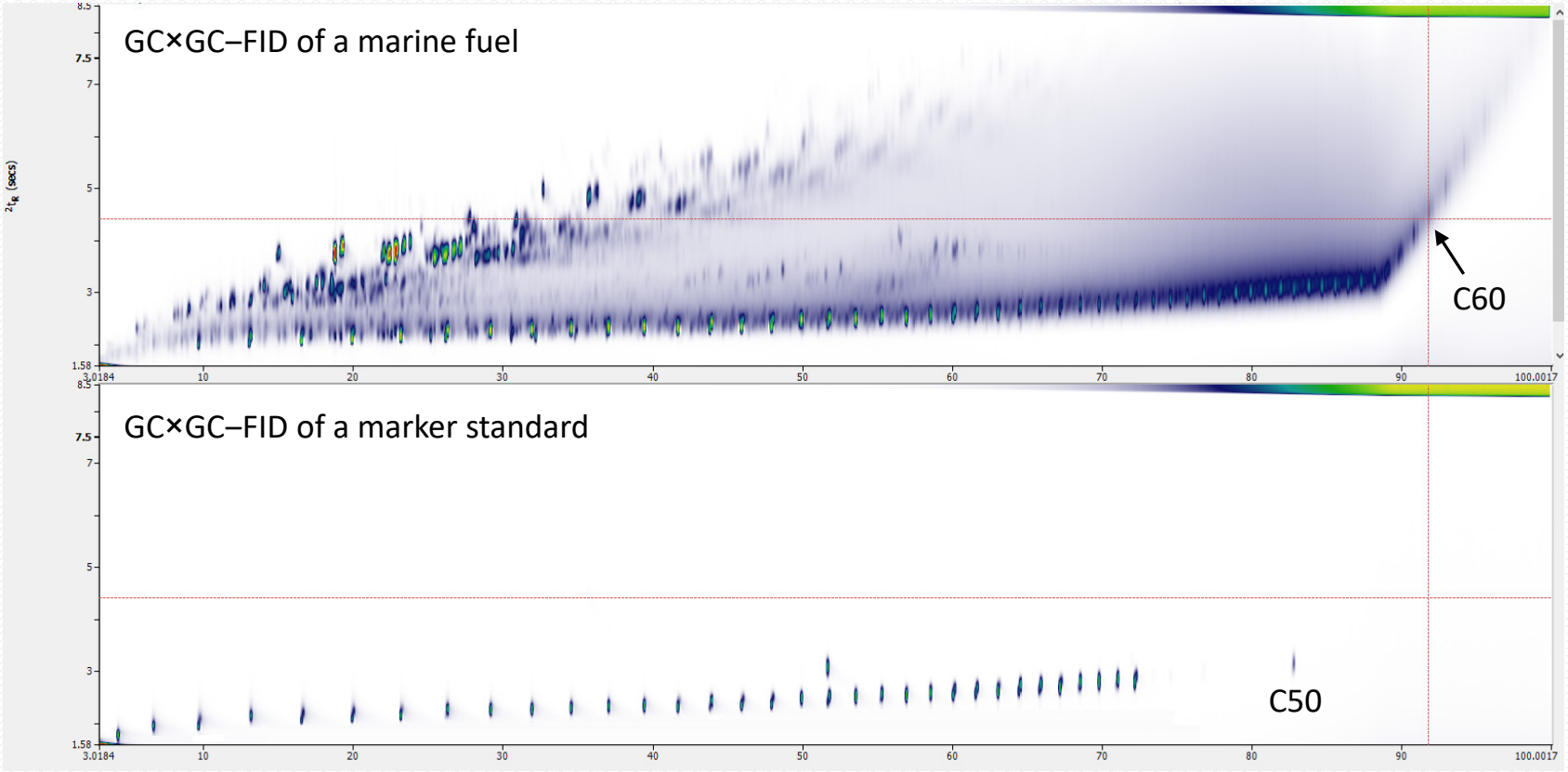


# High peak capacity…

…and no tailing

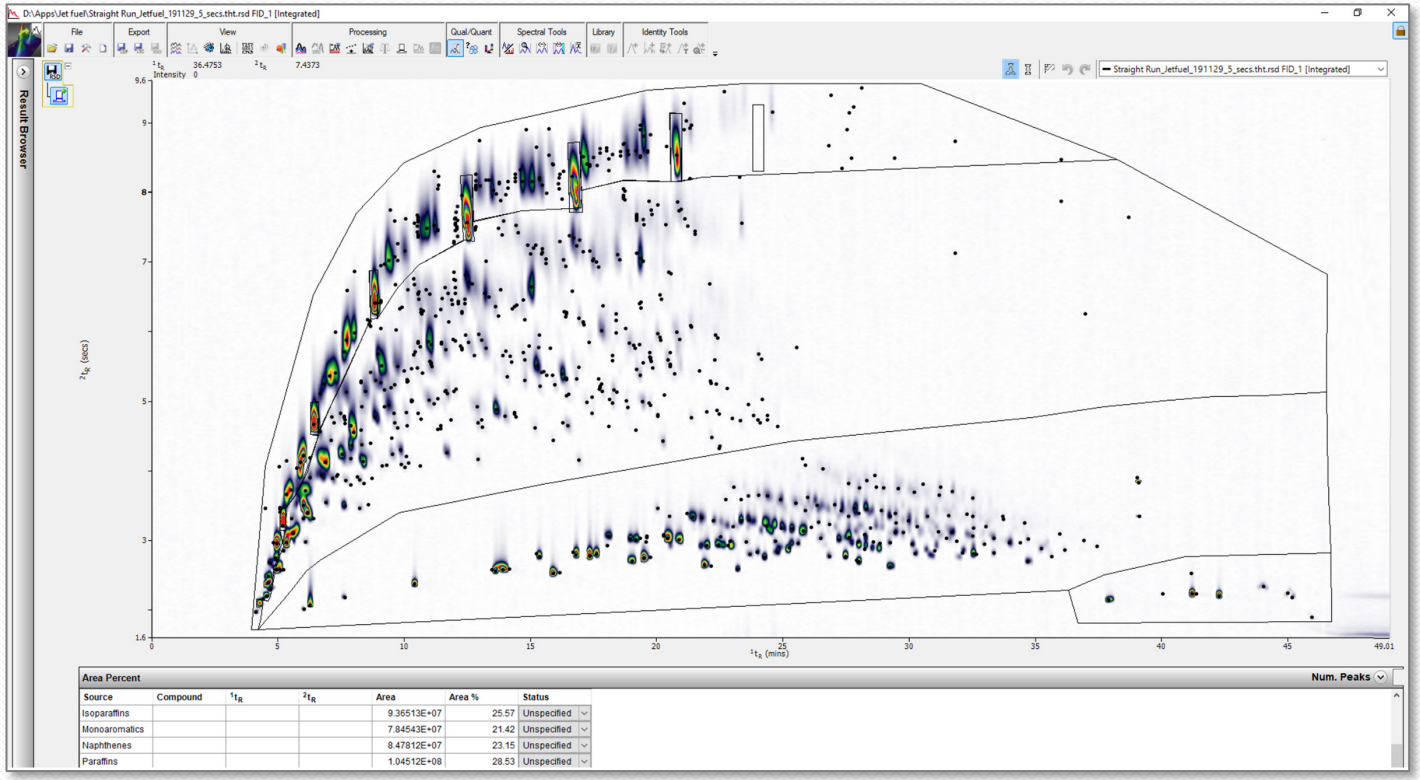


# Wide analyte range



# Group-type analysis of a jet fuel

## Paraffins, iso-Paraffins, Naphthenes and Aromatics (PiPNA)



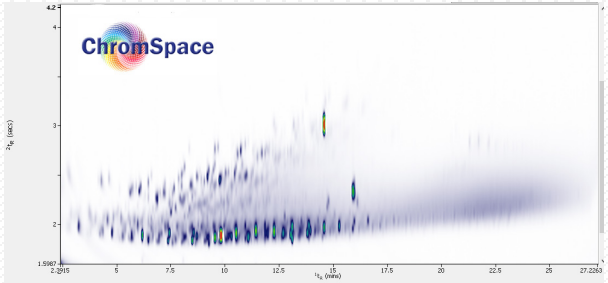
# Example : Extractable Petroleum Hydrocarbons by GC×GC-FID

Chromatographic separation of aliphatic and aromatic hydrocarbons in a single run, reducing processing time

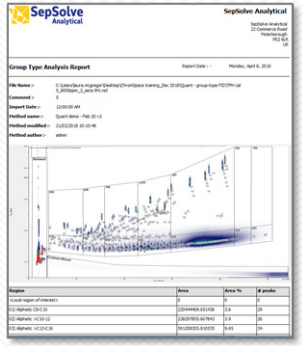
Sample

Traditional solvent extract

Single transfer



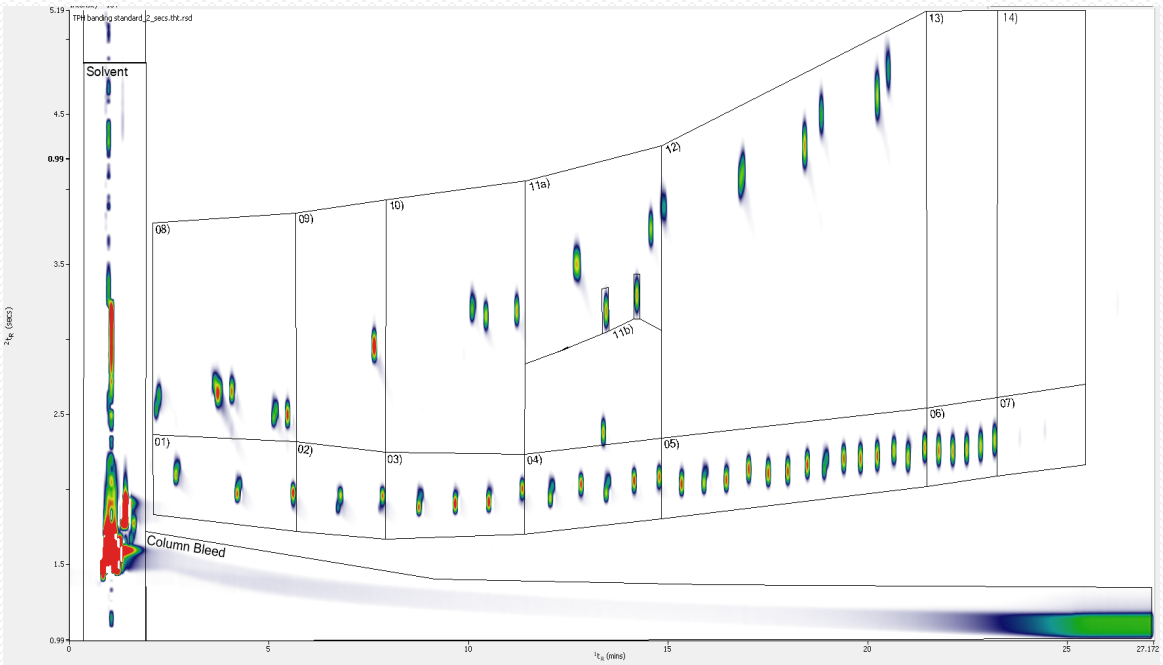

Single analysis AND automated real-time data processing




Reporting

# Simple data processing…

## …using stencils

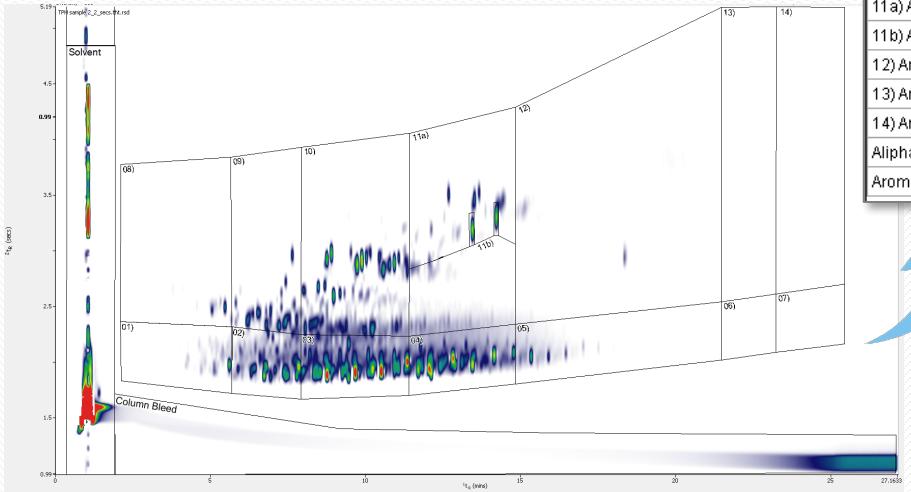



- Regions of interest (Aliphatic >$C_{10}$-$C_{12}$….etc) are identified using a banding standard
- Internal standard and surrogate regions can also be added

# Reporting of results

## Area percent reports

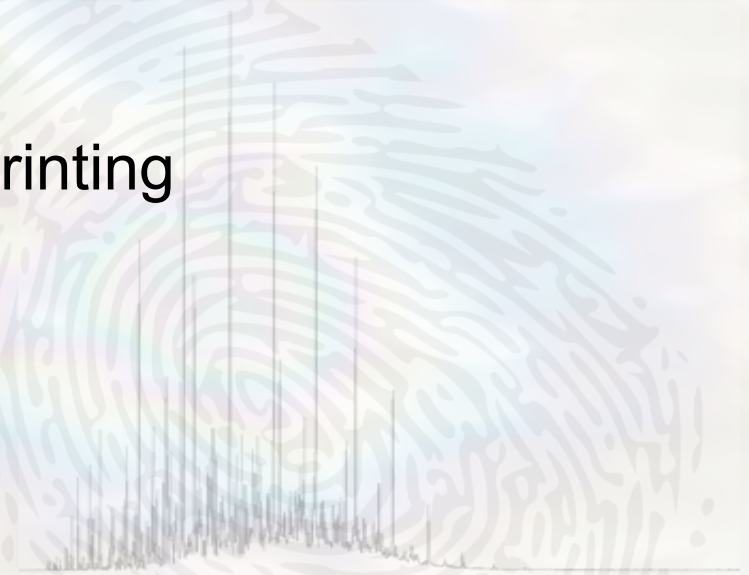
- Flexible stencils can be created in seconds
- Simple area percent reports provide an overview of sample composition




Area Percent

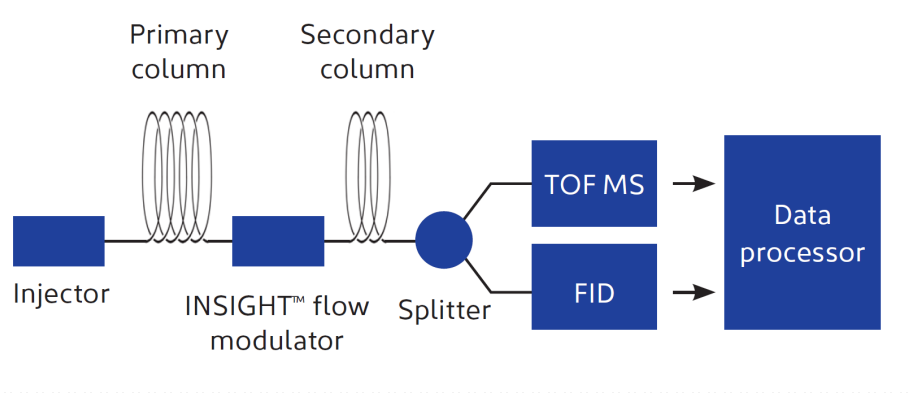
| Source | Area | Area % | Status |
|---|---|---|---|
| 01) Aliphatic C8-C10 | 2.48191E+07 | 1.69 | Included |
| 02) Aliphatic >C10-12 | 1.61797E+08 | 11.04 | Included |
| 03) Aliphatic >C12-C16 | 4.45969E+08 | 30.44 | Included |
| 04) Aliphatic >C16-C21 | 3.16009E+08 | 21.57 | Included |
| 05) Aliphatic >C21-C35 | 4.30518E+07 | 2.94 | Included |
| 06) Aliphatic >C35-C40 | 0 | 0 | Included |
| 07) Aliphatic >C40 | 0 | 0 | Included |
| 08) Aromatic >C8-10 | 1.1219E+07 | 0.77 | Included |
| 09) Aromatic >C10-C12 | 7.15922E+07 | 4.89 | Included |
| 10) Aromatic >C12-C16 | 2.6734E+08 | 18.25 | Included |
| 11a) Aromatic >C16-C21 A | 3.23494E+07 | 2.21 | Included |
| 11b) Aromatic >C16-C21 B | 4.83643E+07 | 3.3 | Included |
| 12) Aromatic >C21-C35 | 1.36035E+07 | 0.93 | Included |
| 13) Aromatic >C35-C40 | 0 | 0 | Included |
| 14) Aromatic >C40 | 0 | 0 | Included |
| Aliphatics | 9.91646E+08 | 67.68 | Included |
| Aromatics | 4.44468E+08 | 30.34 | Included |

# Petrochemical fingerprinting



# Parallel detection…

## …confident identification using GC×GC-FID/TOF MS

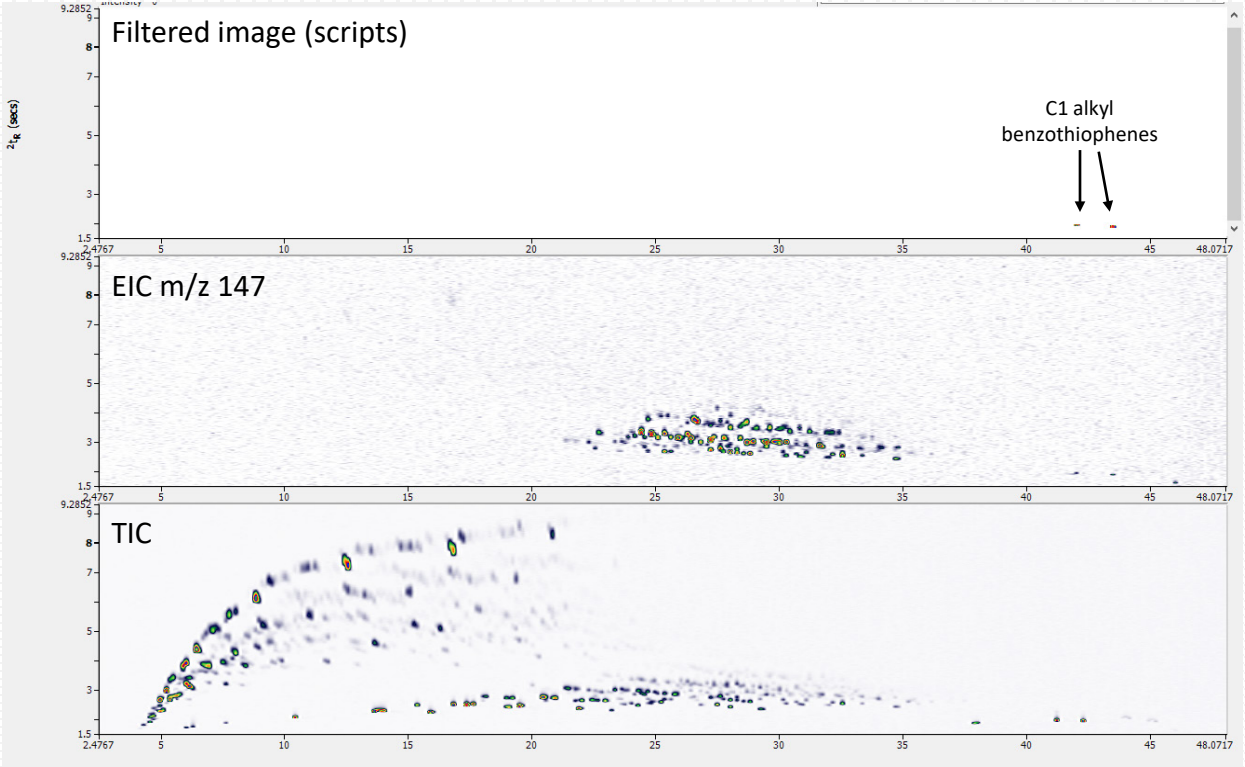




- The **BenchTOF2 mass spectrometer** can be configured in parallel with FID for confident identification of trace contaminants

# Trace contaminants in fuels

## Using scripts to uncover target compounds

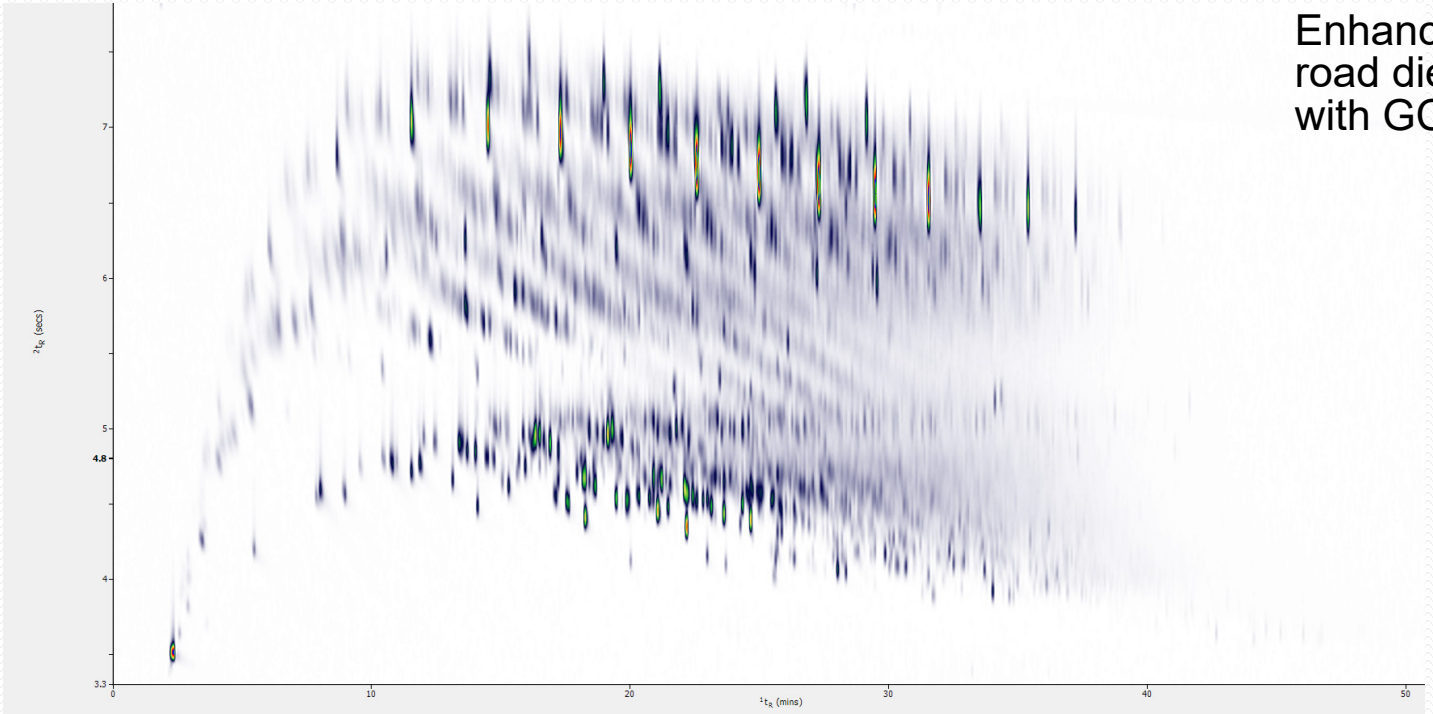



*Clean background - only the peaks which pass the script are shown (in this case, benzothiophenes)*

*Many peaks share the m/z 147 ion*

# Compound Explorer toolkit

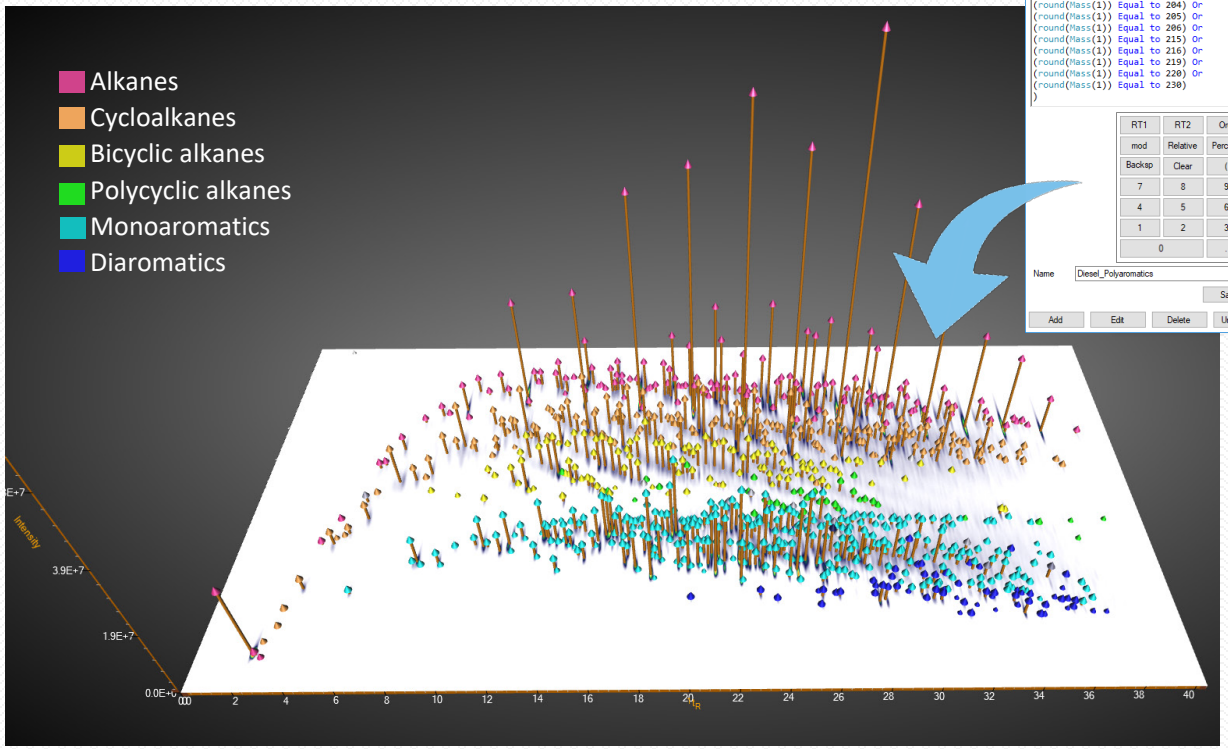
## Classifying complex petrochemicals

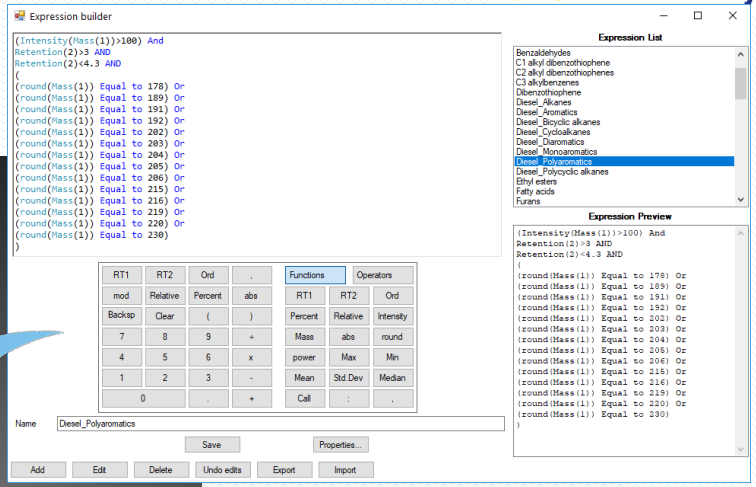



Enhanced separation of a road diesel using INSIGHT® with GC×GC–TOF MS

# Compound Explorer toolkit

## Classifying complex petrochemicals

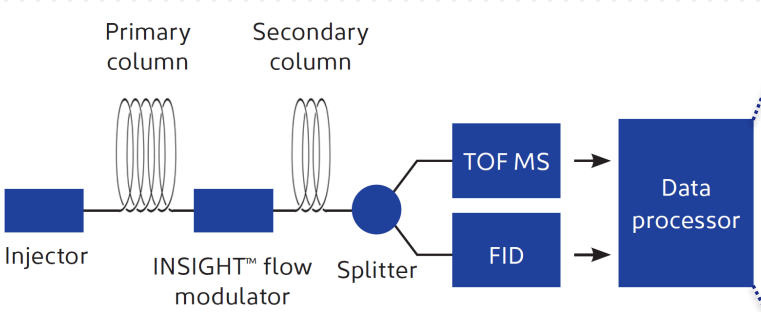


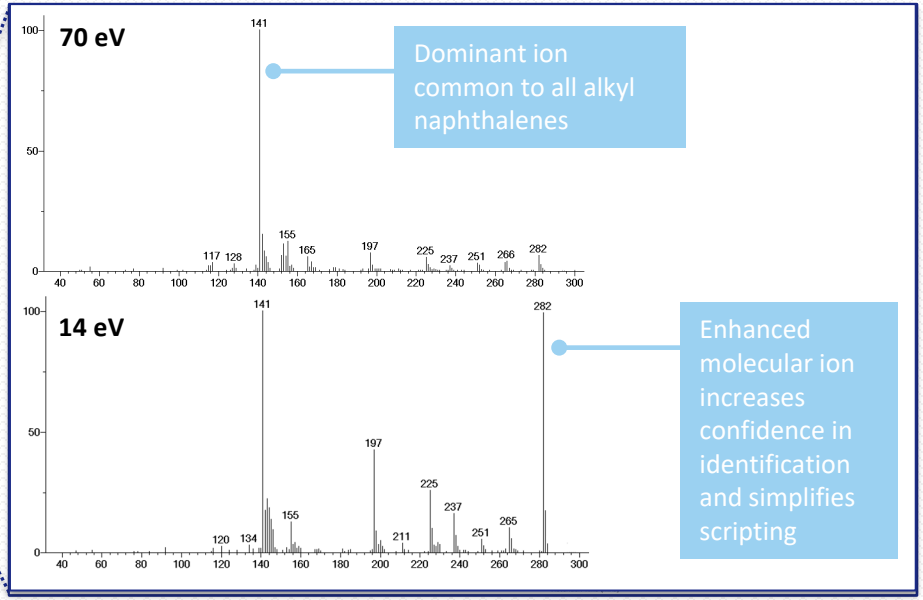




- Easily create and manage expressions using Compound Explorer's Expression Builder
- Apply multiple expressions during integration to quickly classify the entire sample

# Adding extra dimensions…

## …with Tandem Ionisation

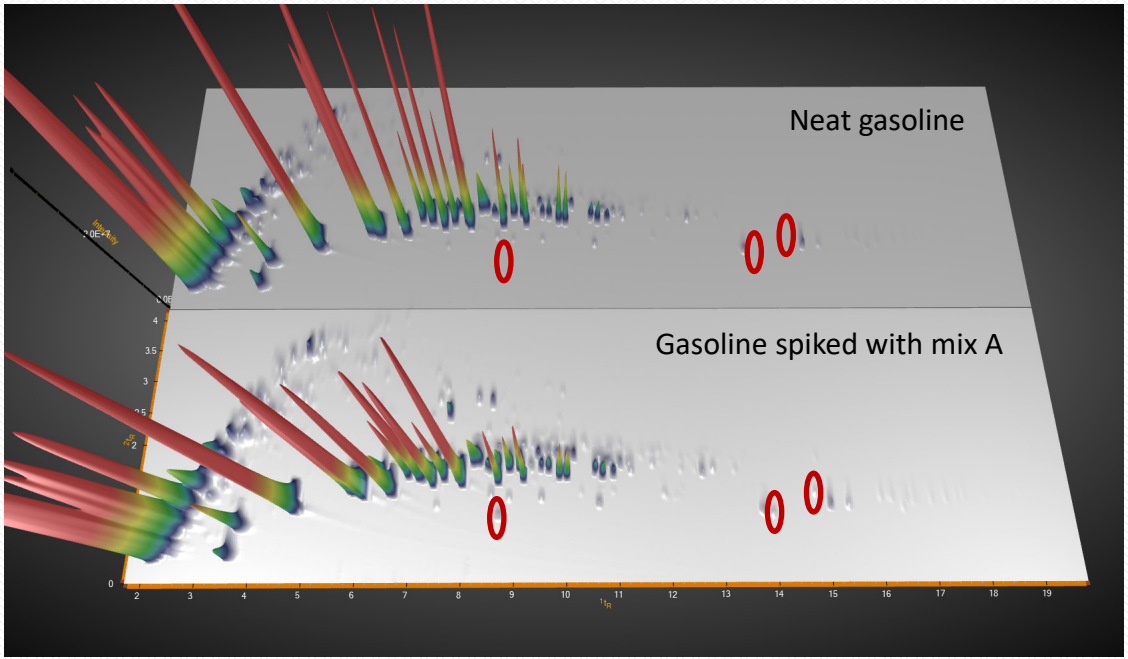



- BenchTOF2 with Tandem Ionisation provides simultaneous hard and soft EI
- Enhanced confidence in identification, as well as robust quantitation with FID

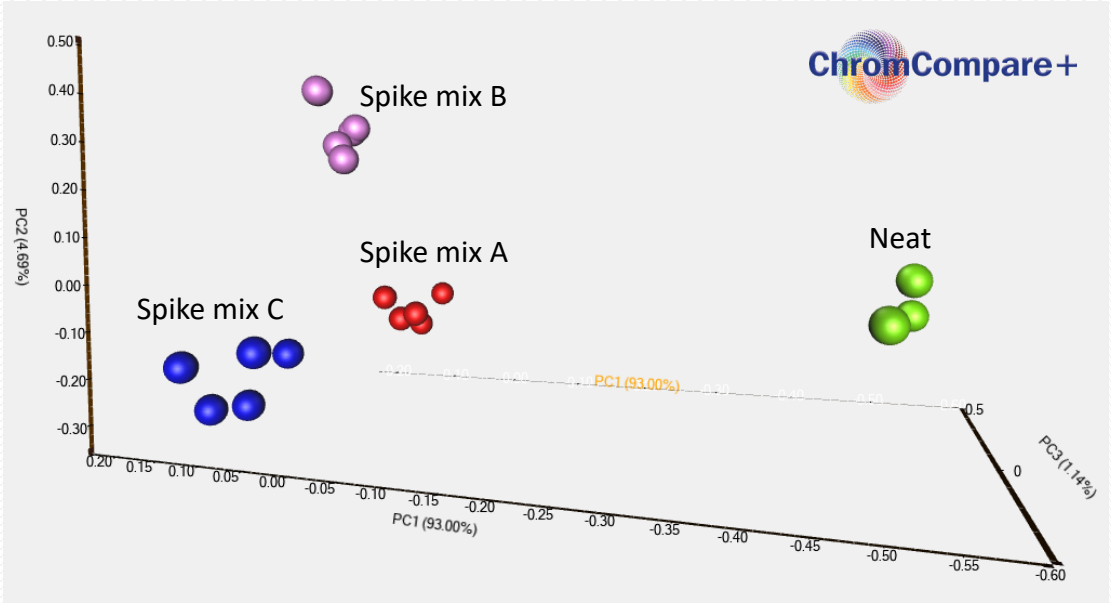
*3 datasets from one run!*

# Uncovering trace additives in gasoline




- Analysis of neat and spiked petrol – using three sets of gasoline additives (mix A, B and C)

# Uncovering trace additives in gasoline




| Spiking compounds | Datasets | |
|---|---|---|
| | 70 eV only | TI at 70/14eV |
| D6-Acetone | ✓ | ✓ |
| 2-Methylfuran | ✓ | ✓ |
| Ethyl acetate | × | ✓ |
| 2-Butanone | ✓ | ✓ |
| D6-Benzene | ✓ | ✓ |
| 2-Pentanone | ✓ | ✓ |
| 4-Methyl-2-Pentanone | ✓ | ✓ |
| 3-Hexanone | × | ✓ |
| Cyclopentanone | × | ✓ |
| Anisole | ✓ | ✓ |
| MMT | ✓ | ✓ |
| Ferrocene | ✓ | ✓ |

- Subtle differences are easily uncovered by ChromCompare+
- Tandem Ionisation data suppresses false positives to enable true differences to be found more easily

# Summary

- Flow-modulated GC×GC with flexible parallel detection is the ideal platform for the analysis of complex petrochemicals
- ChromSpace software enables fast and efficient group-type analysis using stencils, while ChromCompare+ add the ability to automatically find differences between complex chromatograms
- BenchTOF2 provides improved precision of group boundaries using EICs or filtering scripts.
- Tandem Ionisation adds another dimension of information to GC×GC, with soft EI spectra for enhanced confidence in identification