Dual-channel GC×GC–FID for routine analysis of total petroleum hydrocarbons (TPH-CWG)

Laura McGregor
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Who is SepSolve Analytical?

Experts in analytical chemistry

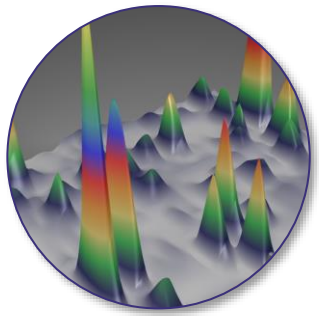
SCHAUENBURG Analytics

MARKES international



Sample preparation

SepSolve Analytical

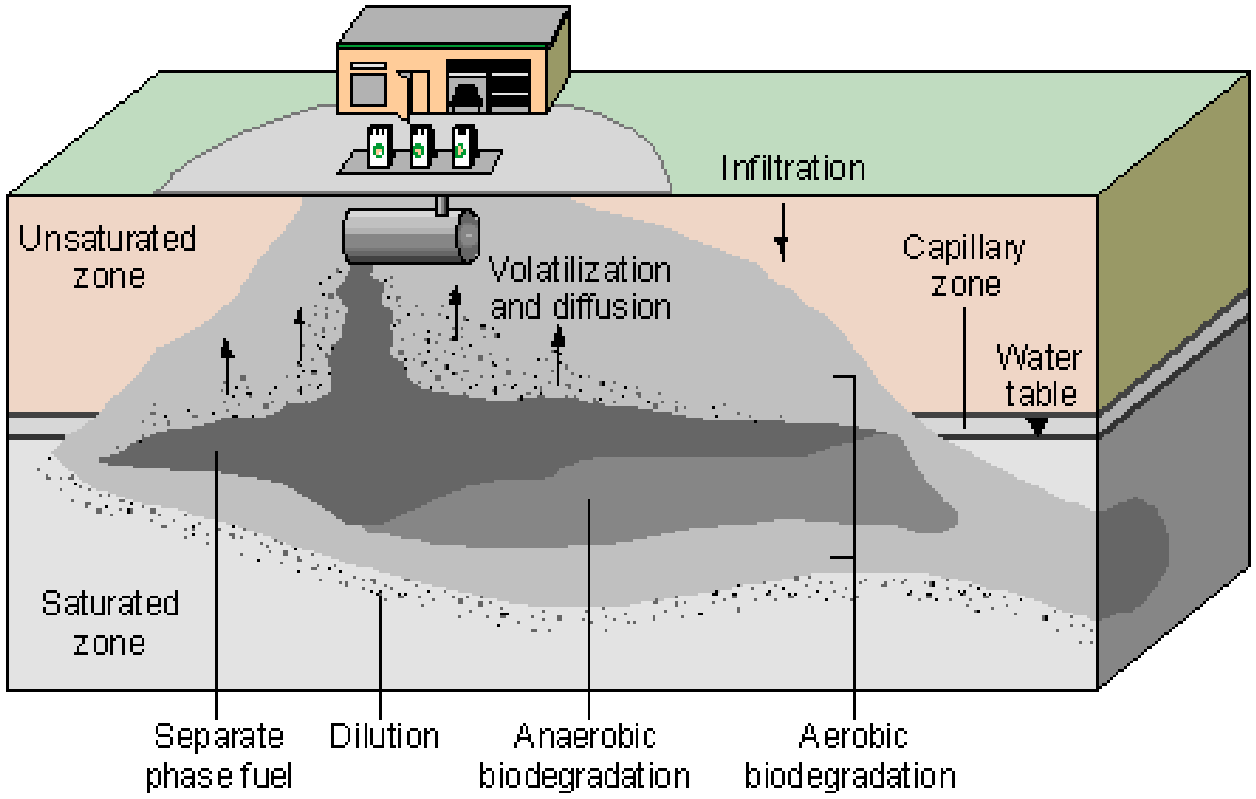

Separation

Identification


Data analysis

Background information

Soil and water contamination



Source: California Environmental Protection Agency

- Leaking underground storage tanks (UST) are the most frequent causes of petroleum hydrocarbon problems.
- Soil contamination can lead to:
  - Groundwater/drinking water contamination
  - Reduce the usability of land
- Weathered petroleum residuals can stay bound to soils for years

Standard methods

Analysis of Petroleum Hydrocarbons in Environmental Media, Volume 1, 1998

MassDEP
Commonwealth of Massachusetts
Department of Environmental Protection

MADEP-EPH-04. Method for the determination of extractable petroleum hydrocarbons, May 2004 revision 1.1

ISO

ISO/TS 16558-2:2015 Soil quality - Risk-based petroleum hydrocarbons - Part 2: Determination of aliphatic and aromatic fractions of semi-volatile petroleum hydrocarbons using gas chromatography with flame ionization detection (GC/FID).

Environment Agency

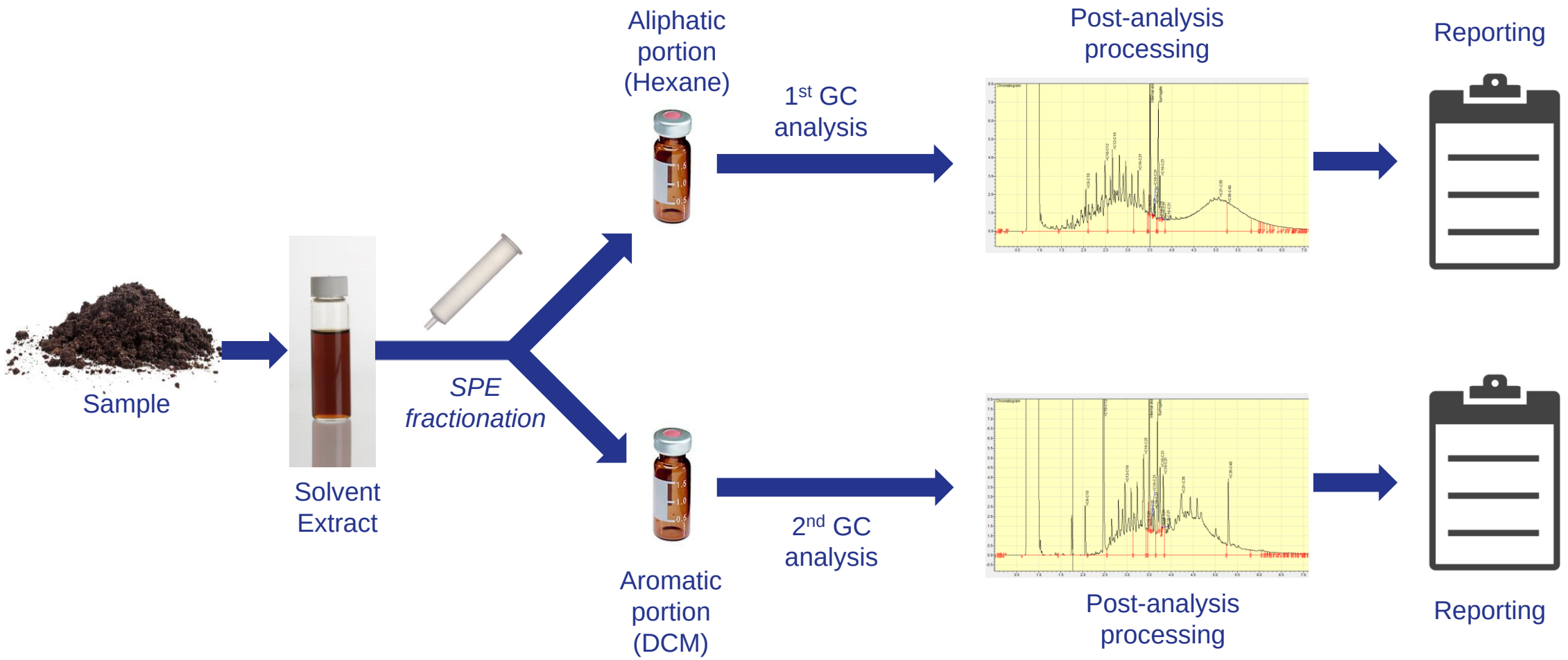
Performance standard for laboratories undertaking chemical testing of soil, version 4, March 2012

Total Petroleum Hydrocarbon (TPH) analysis

- Commonly split into the Volatile Petroleum Hydrocarbons (VPH) and the Extractable Petroleum Hydrocarbons (EPH)
- EPH monitors hydrocarbons from an equivalent carbon number of C_{10}-C_{40} (sometimes C_{44})
- For environmental fate and risk-based analysis the aliphatic and aromatic hydrocarbons must be separated
- Compounds are reported as groups (>C_{10}-C_{12}, >C_{12}-C_{16}…etc) rather than individually

Extractable Petroleum Hydrocarbons

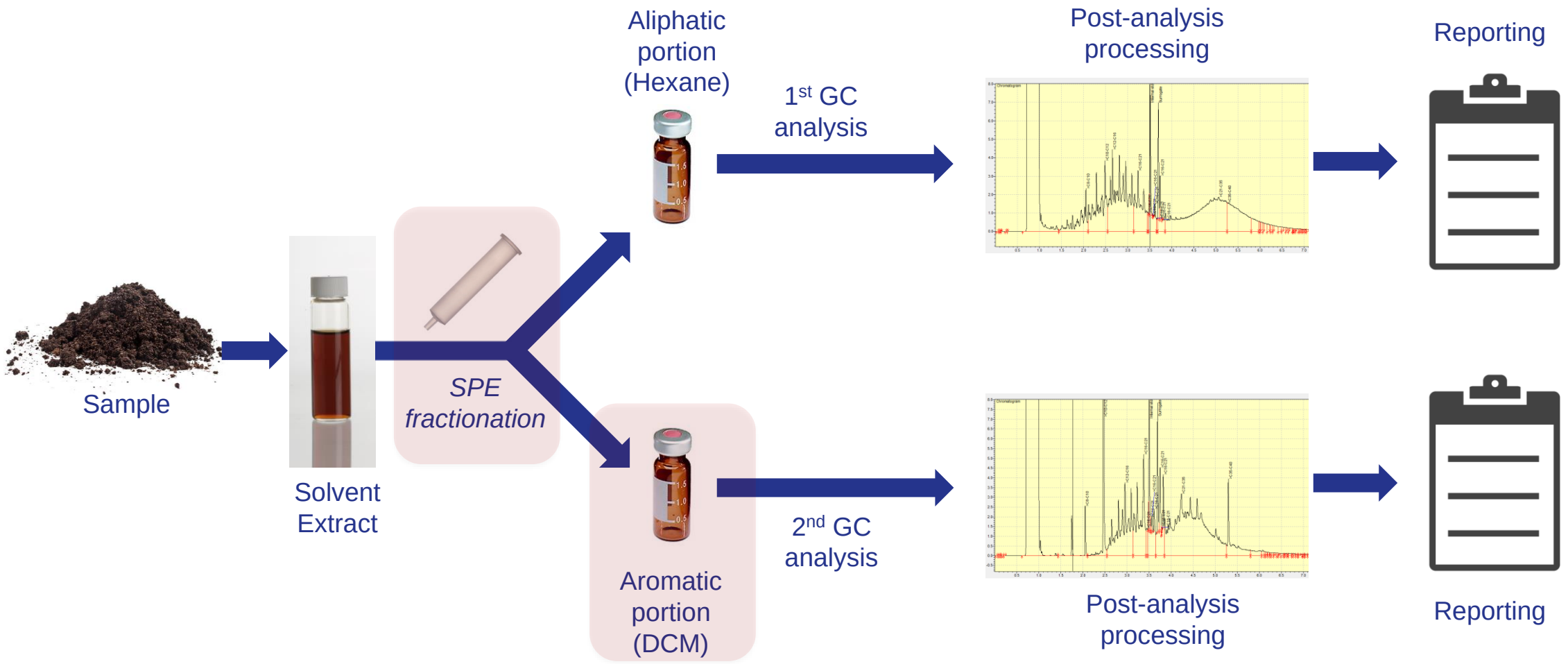
The Traditional Method



Extractable Petroleum Hydrocarbons

What can we change?

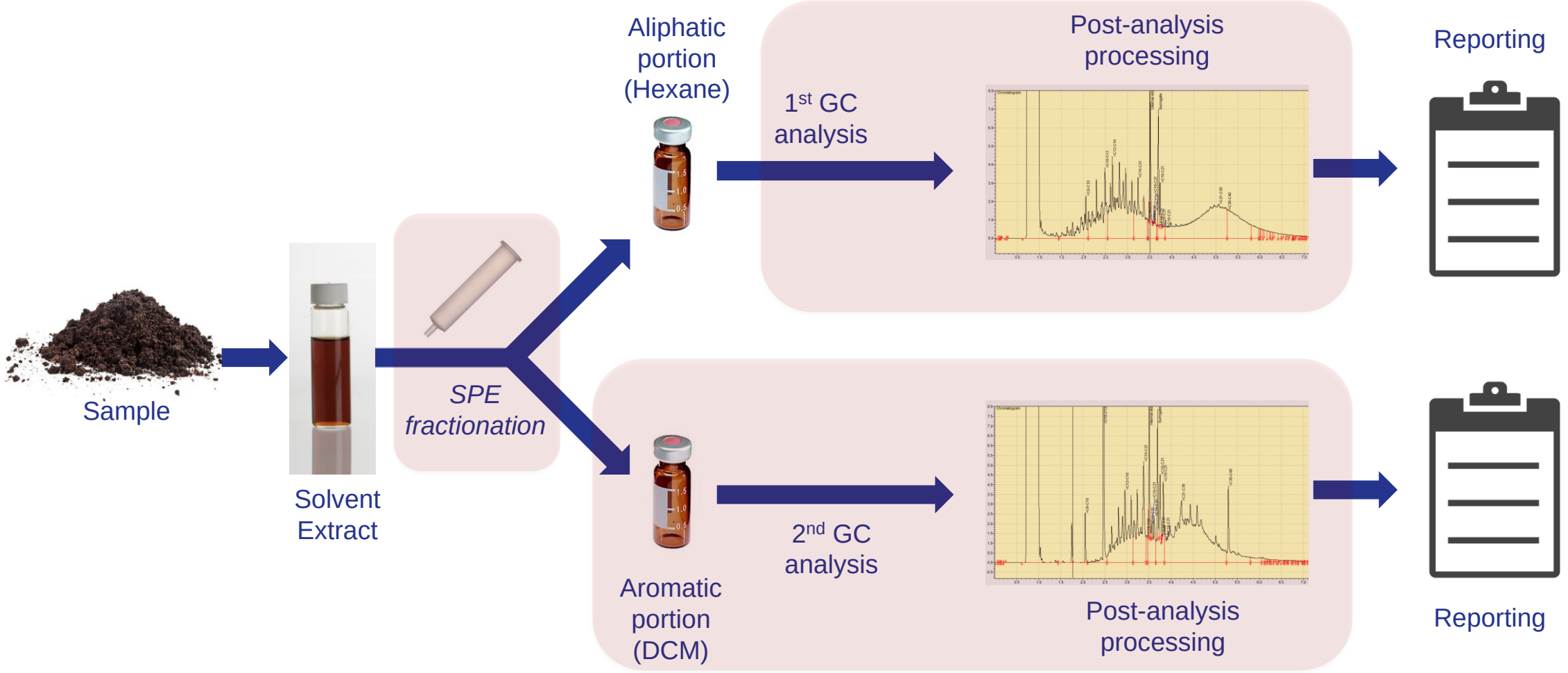
Expensive consumables and waste disposal



Extractable Petroleum Hydrocarbons

What can we change?

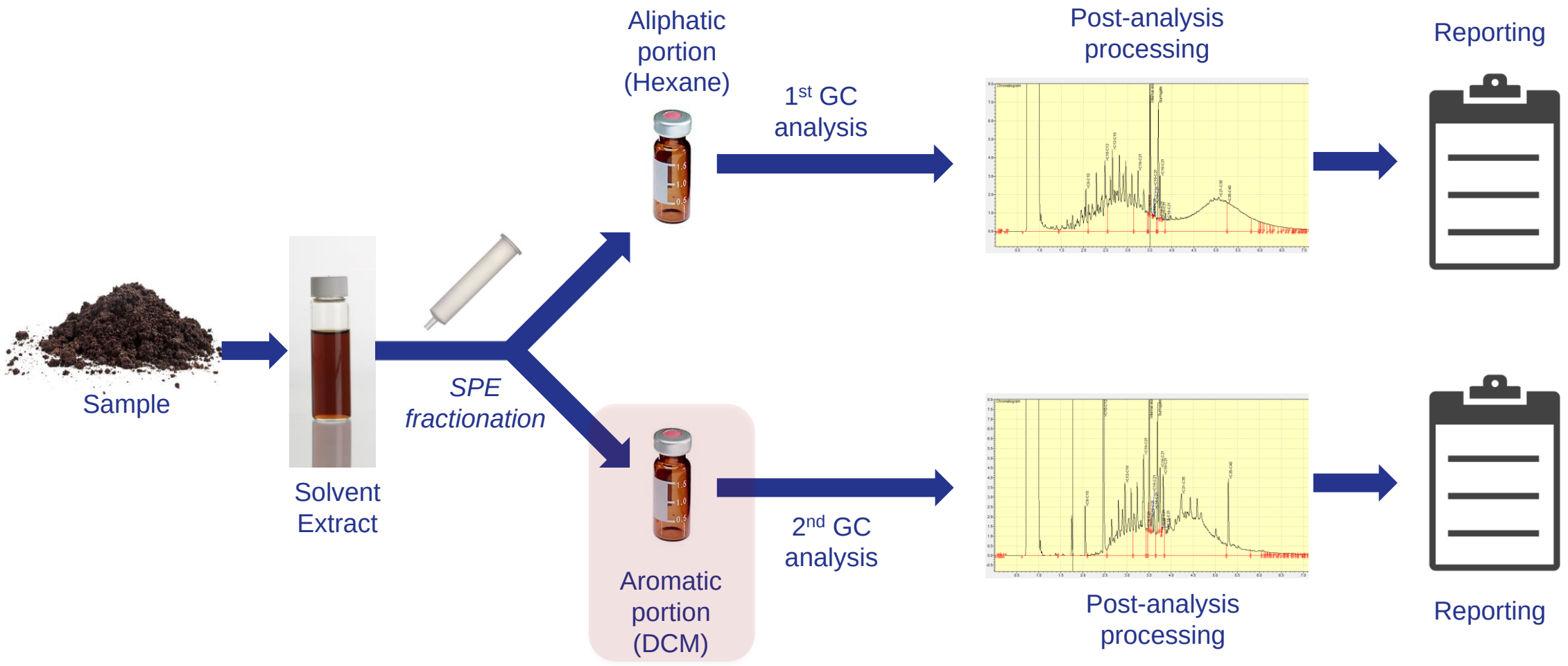
Labour-intensive process



Extractable Petroleum Hydrocarbons

What can we change?

Health and safety concerns



A new approach to EPH…

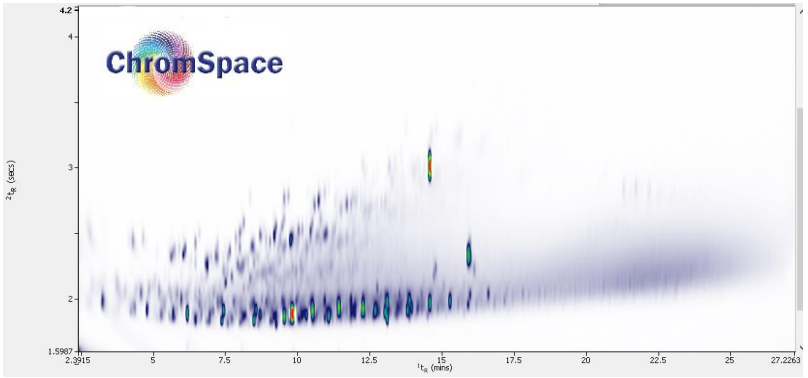
…using GC×GC-FID

- Chromatographic separation of aliphatic and aromatic hydrocarbons in a single run, eliminating sample fractionation and reducing processing time

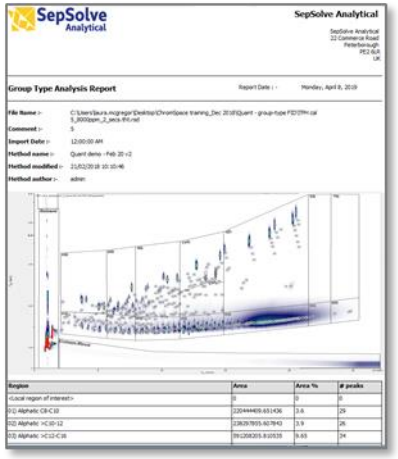
Sample

Traditional solvent extract

Single transfer

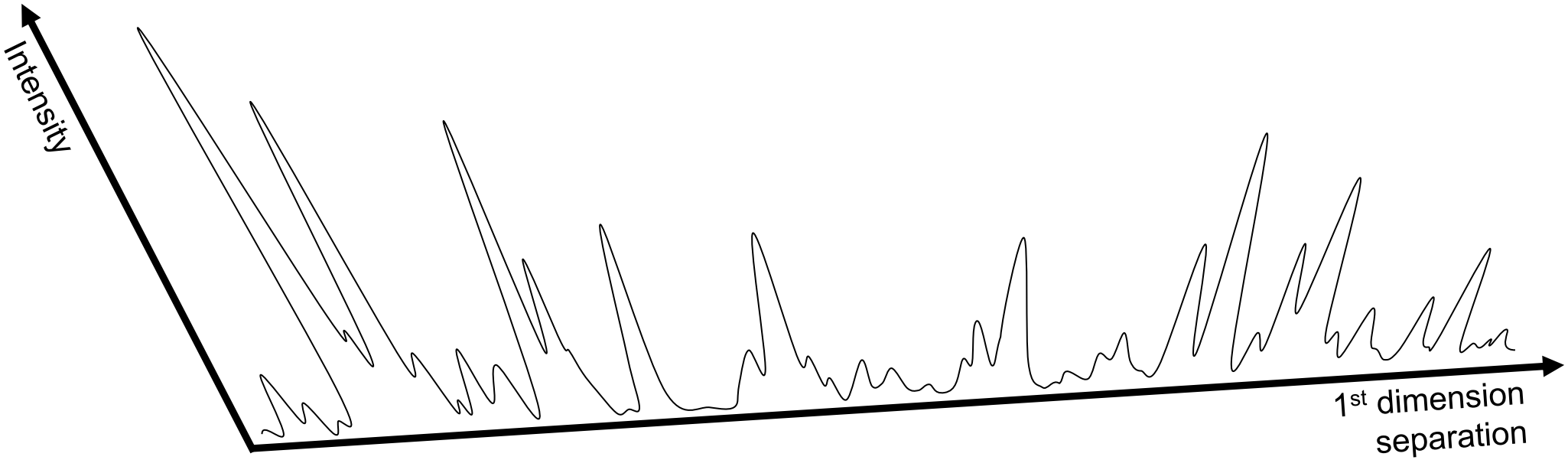


Single analysis AND automated real-time data processing



Reporting

What is GC×GC?



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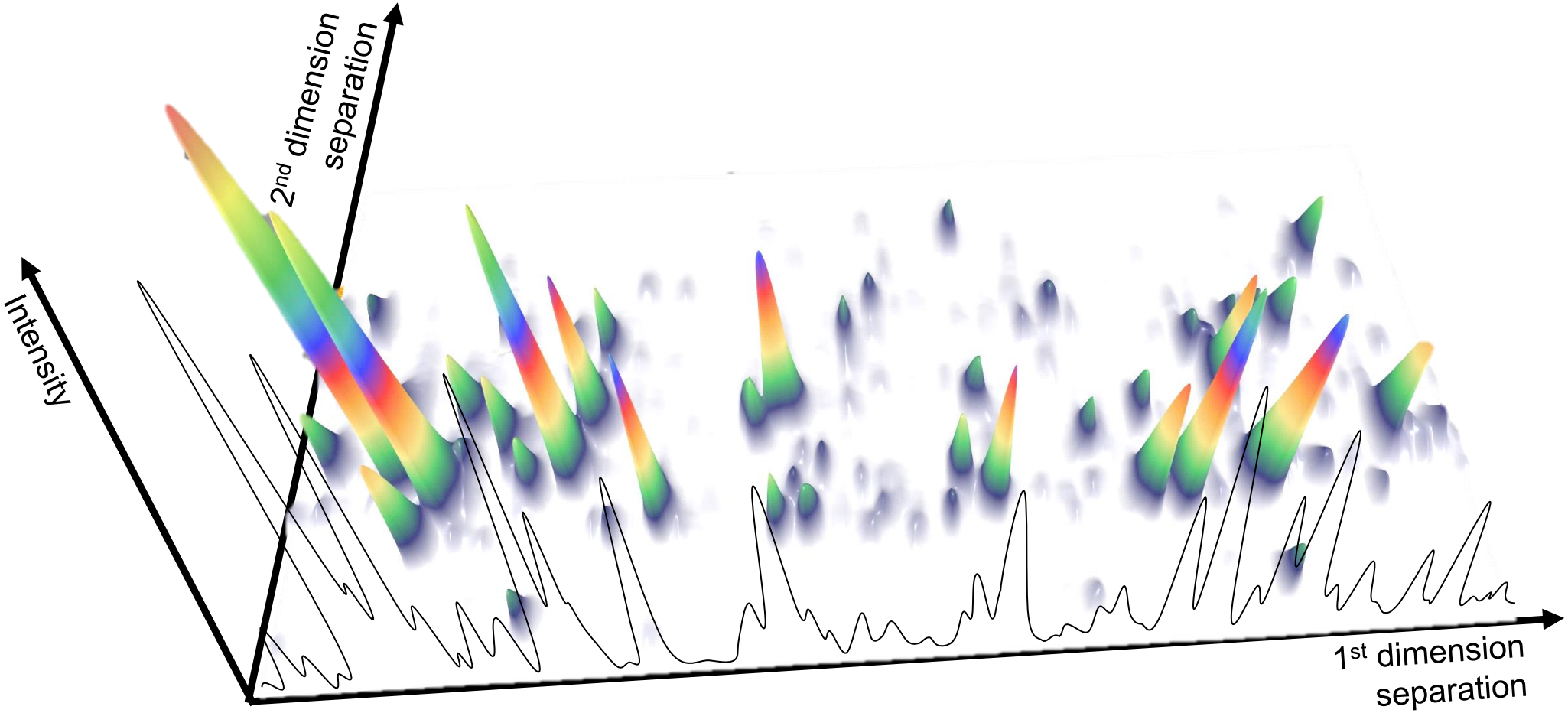
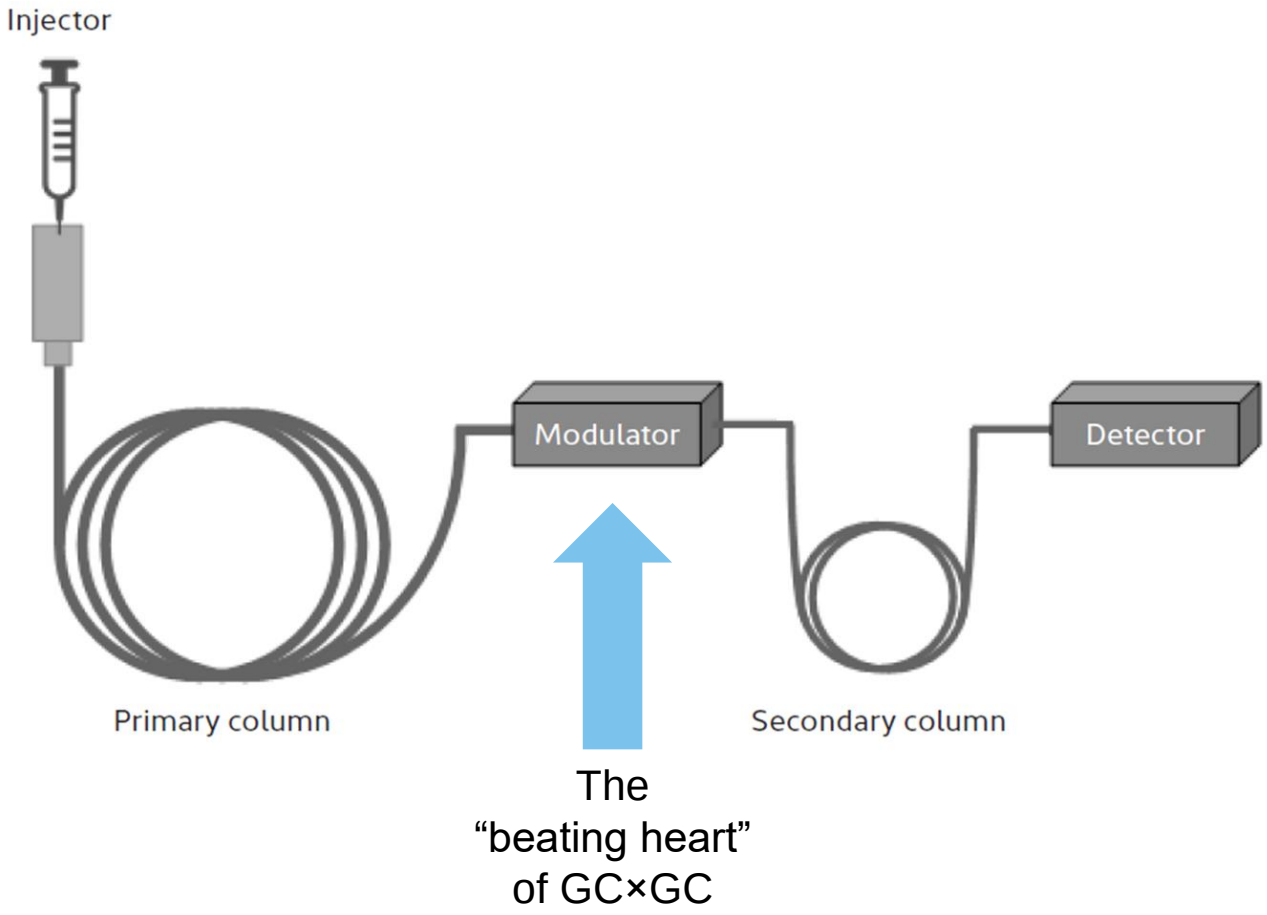

2nd dimension separation
Intensity
1st dimension separation

How does GC×GC work?

Analytical system



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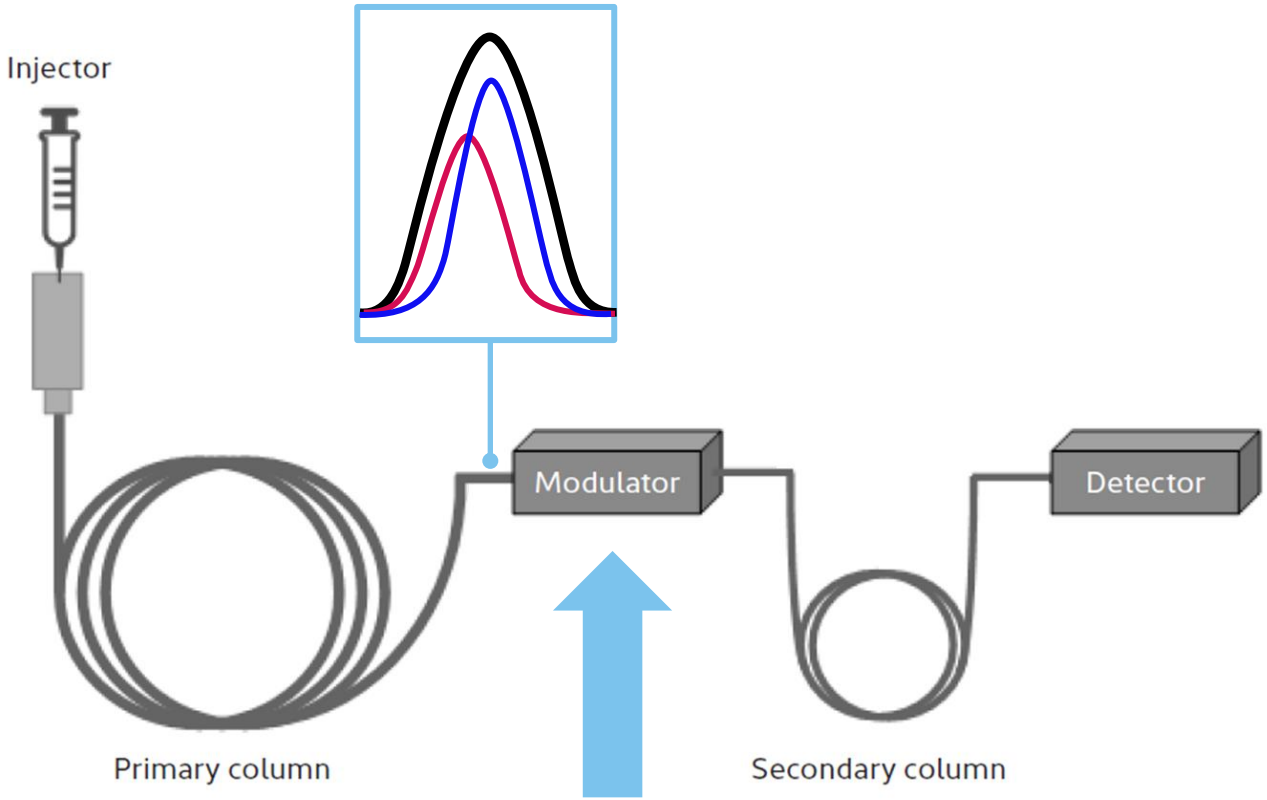

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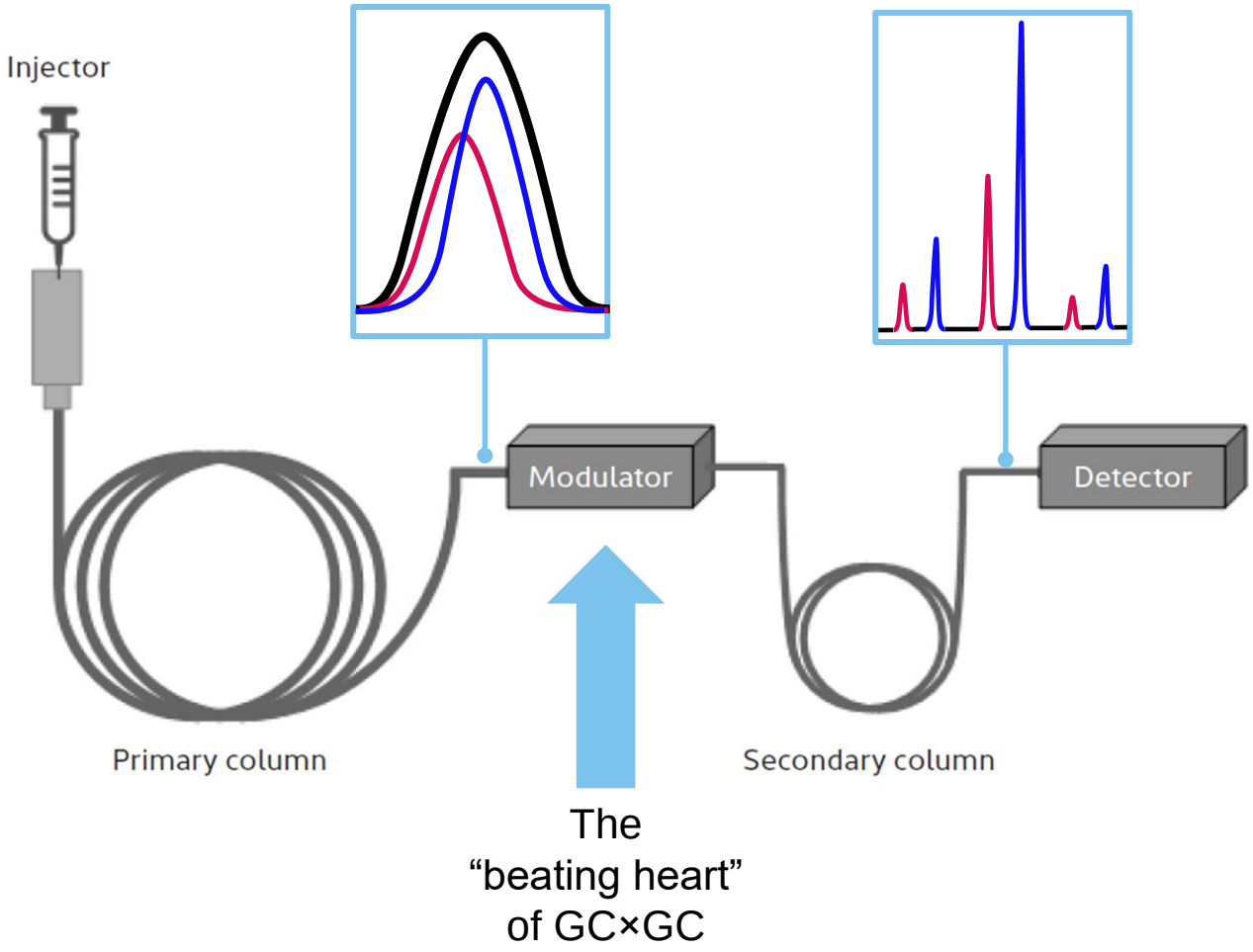
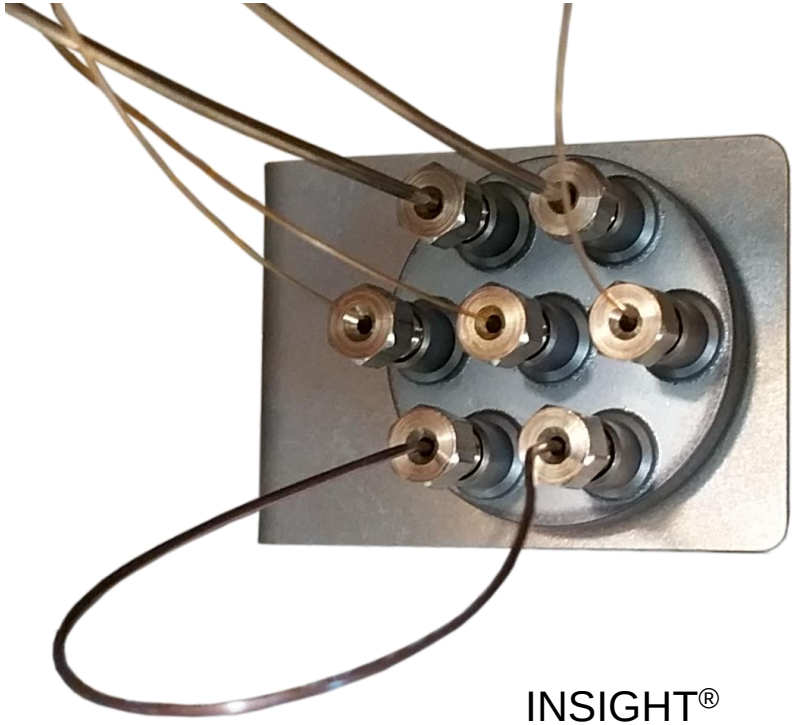


Benefits of flow modulation

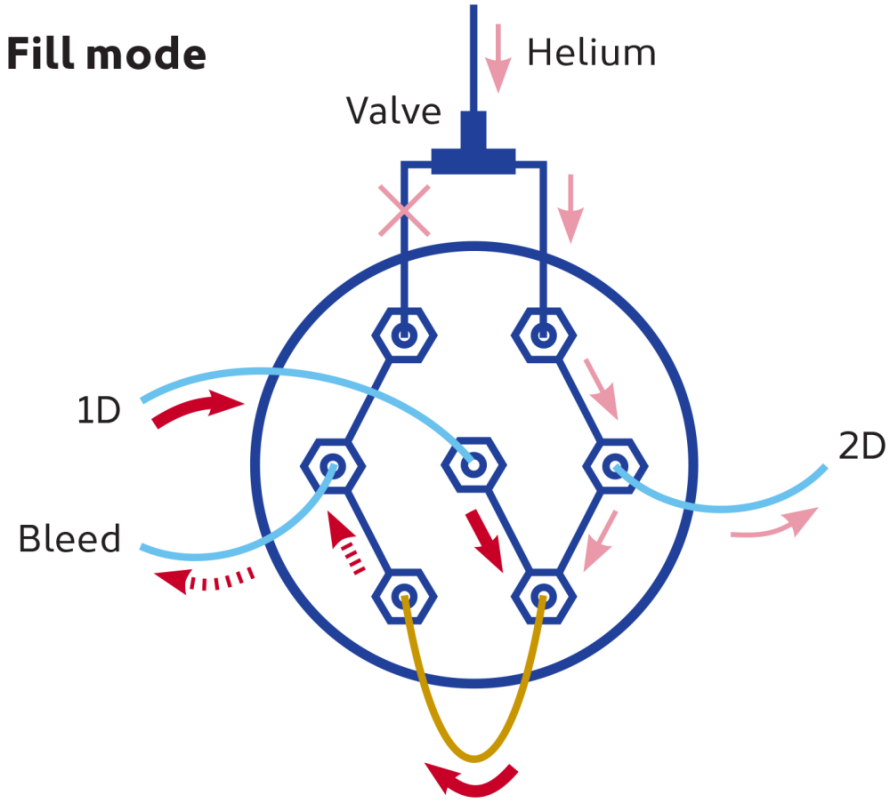
- Consumable-free operation
  - Low running costs
- Efficient modulation of volatiles
  - Extends application range
- Excellent repeatability
  - For routine analyses and large sample batches



INSIGHT®
(SepSolve Analytical)

Reverse fill/flush flow modulation

How does it work?



Further reading: Griffith et al, J. Chromatogr. A, 1226 (2012) 116– 123

Reverse fill/flush flow modulation

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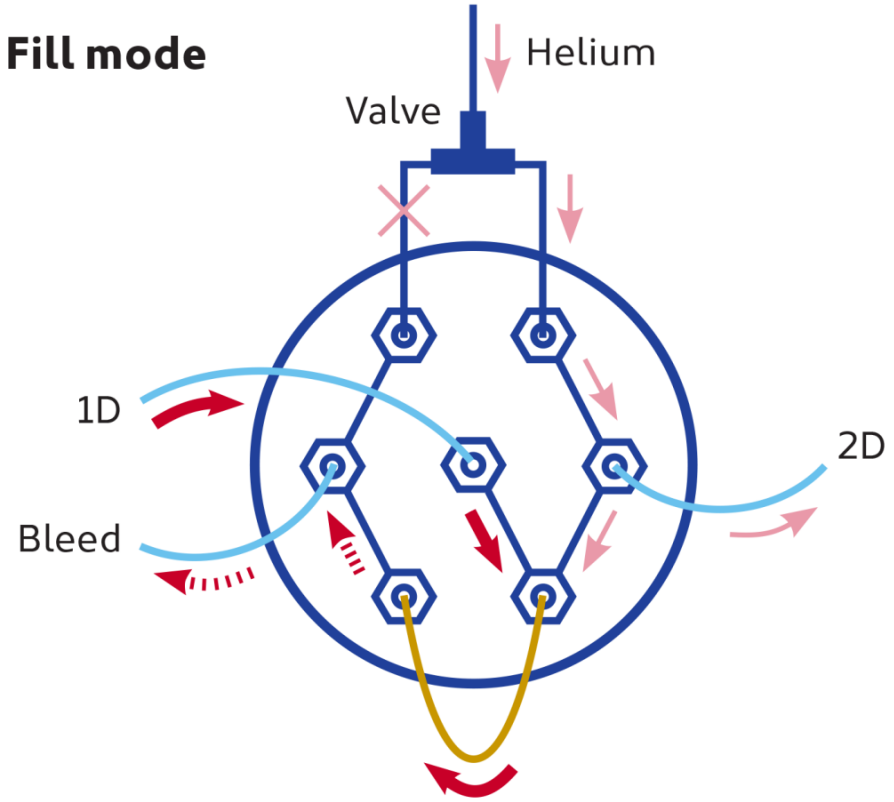

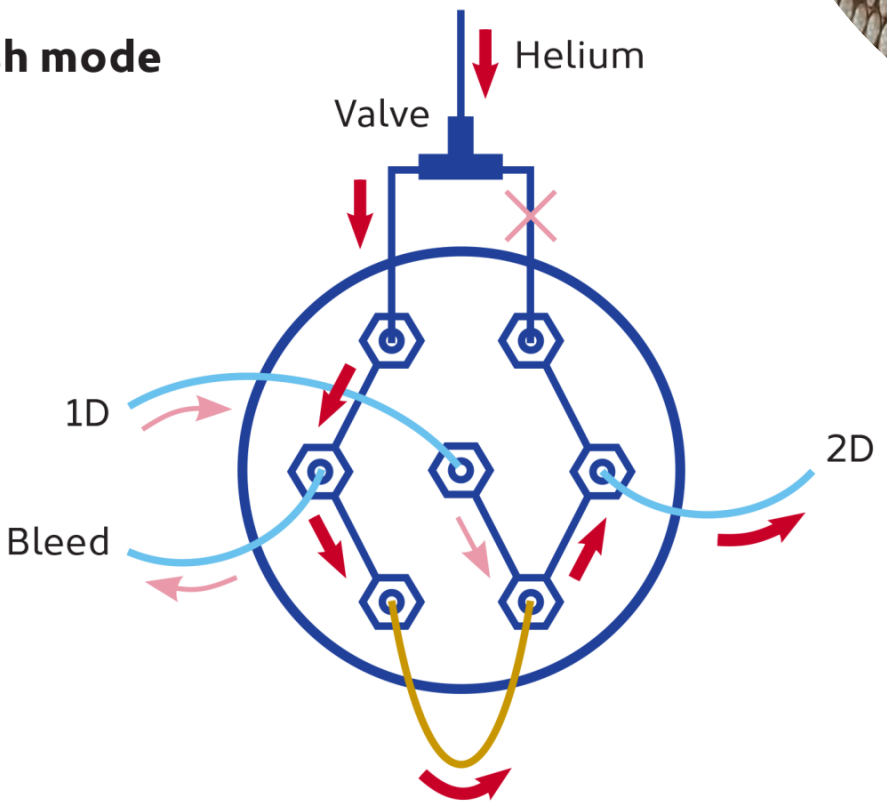

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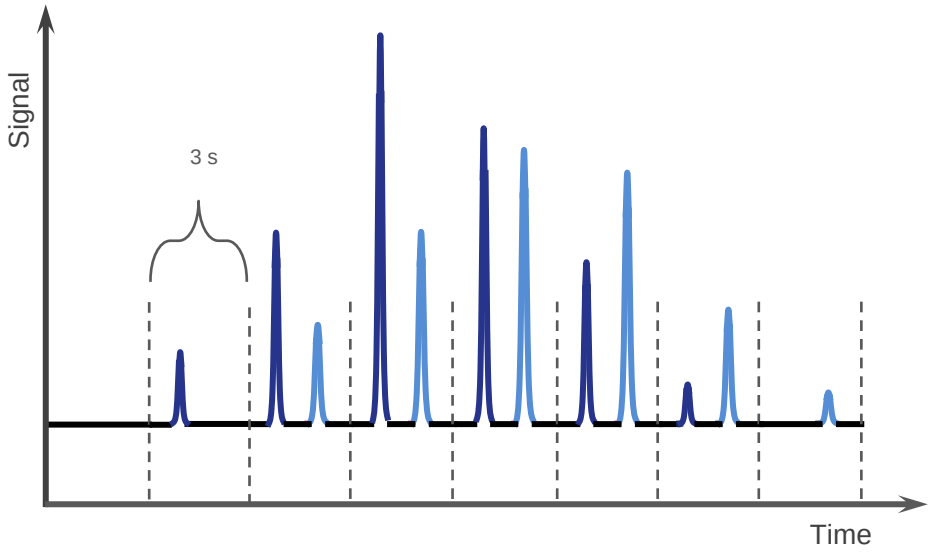
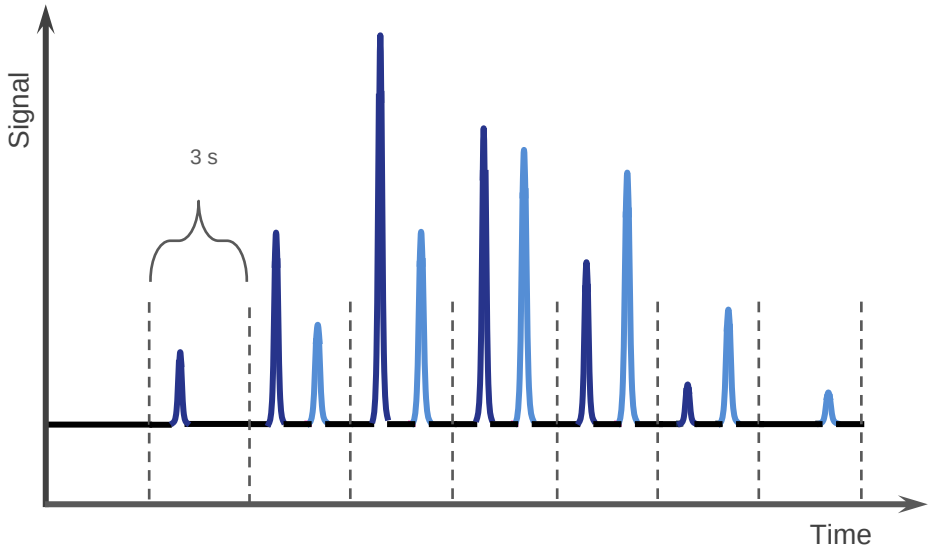
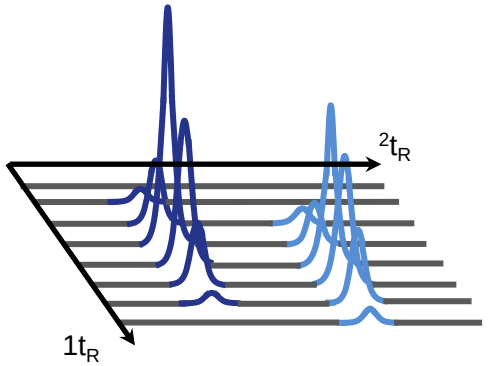
GC×GC detection and the role of software



- GC×GC software must merge the sub-peaks for easy visualisation of the data

GC×GC detection and the role of software



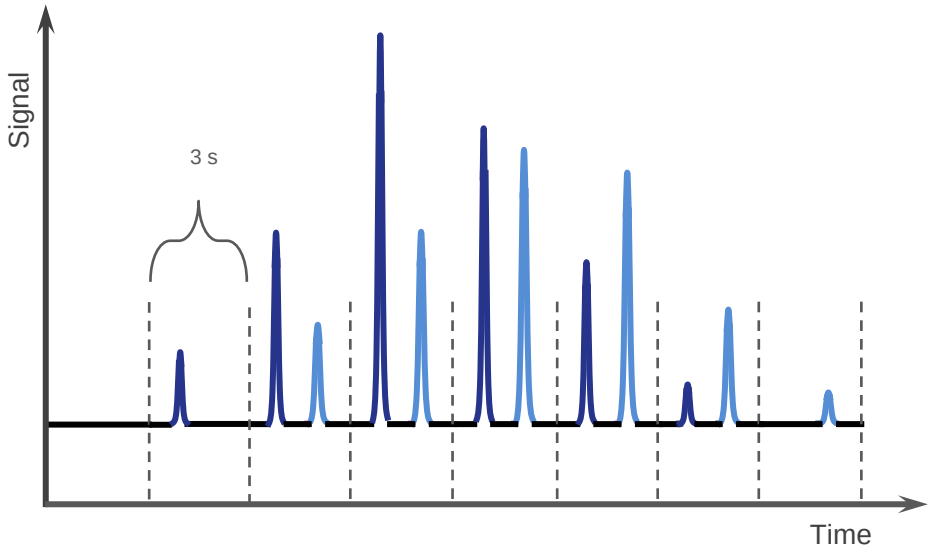


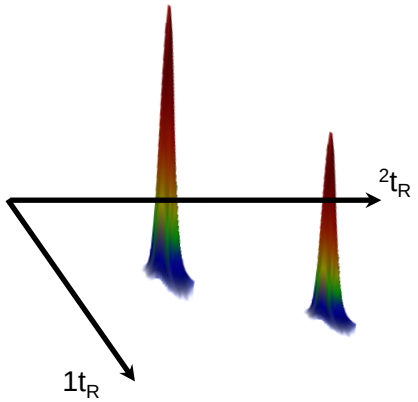
3D Surface chart

Stacked modulation slices

- GC×GC software must merge the sub-peaks for easy visualisation of the data

GC×GC detection and the role of software





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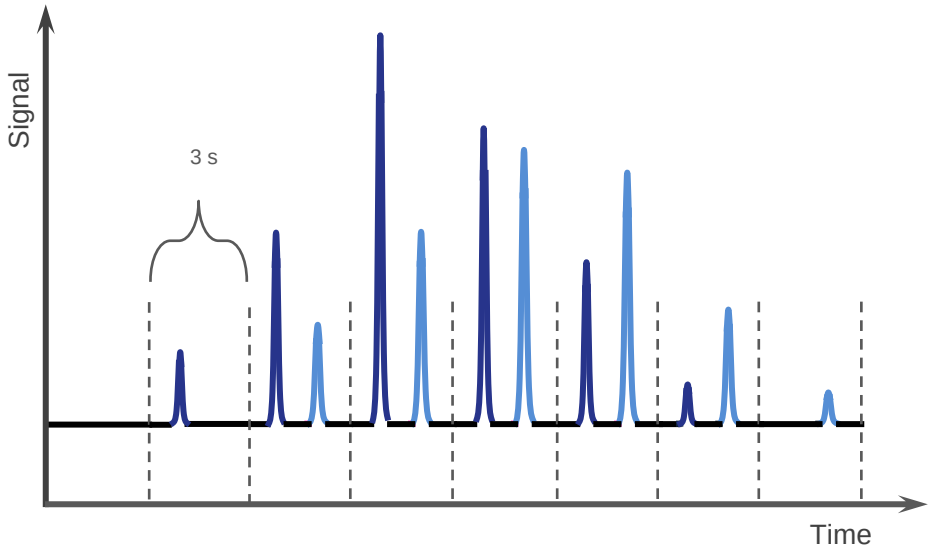
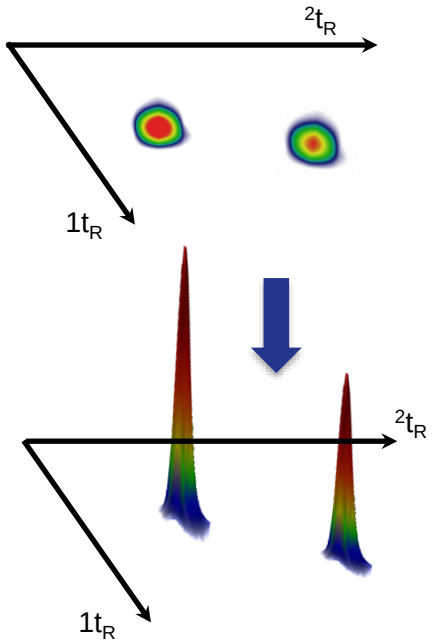




Colour plot

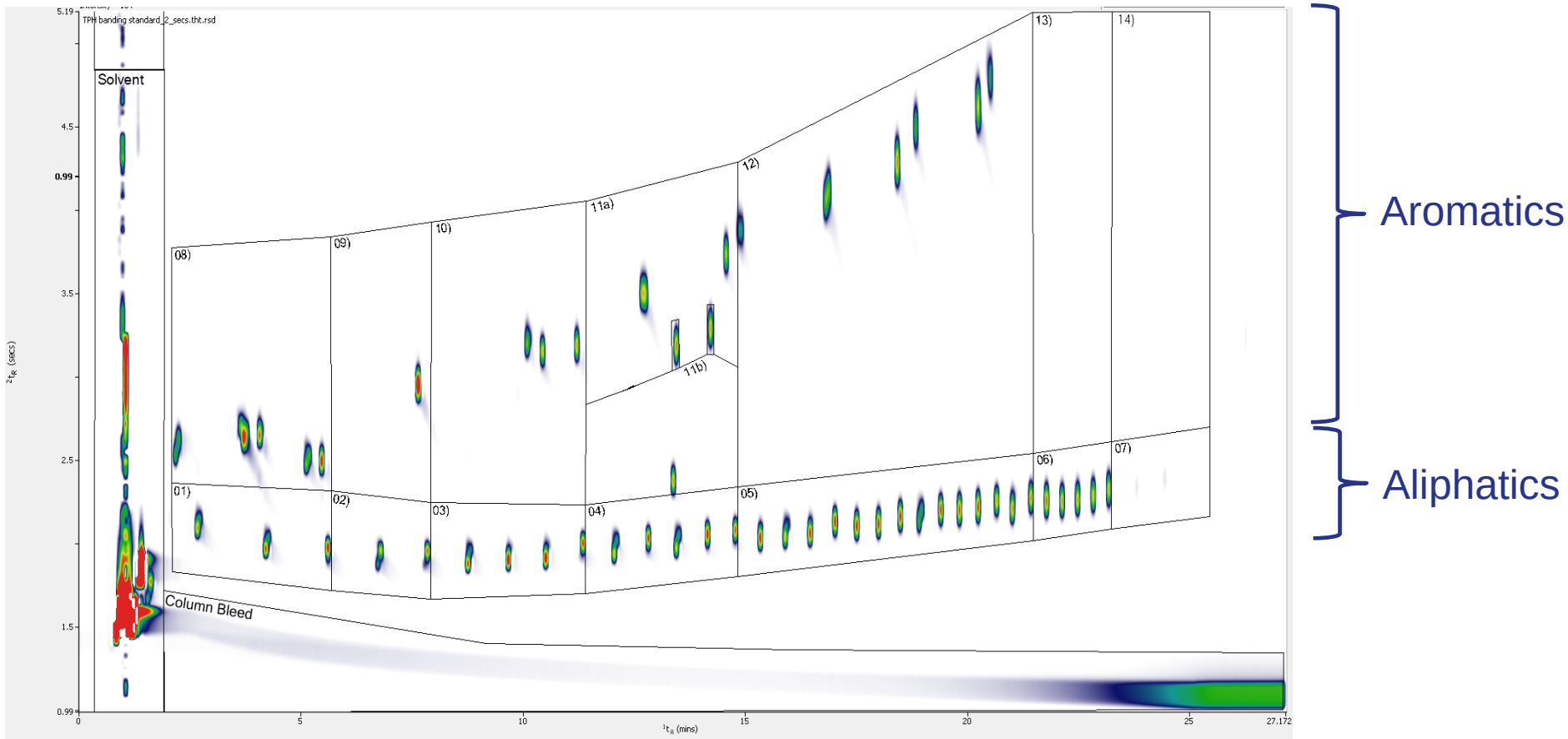
3D Surface chart

Stacked modulation slices

- GC×GC software must merge the sub-peaks for easy visualisation of the data

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

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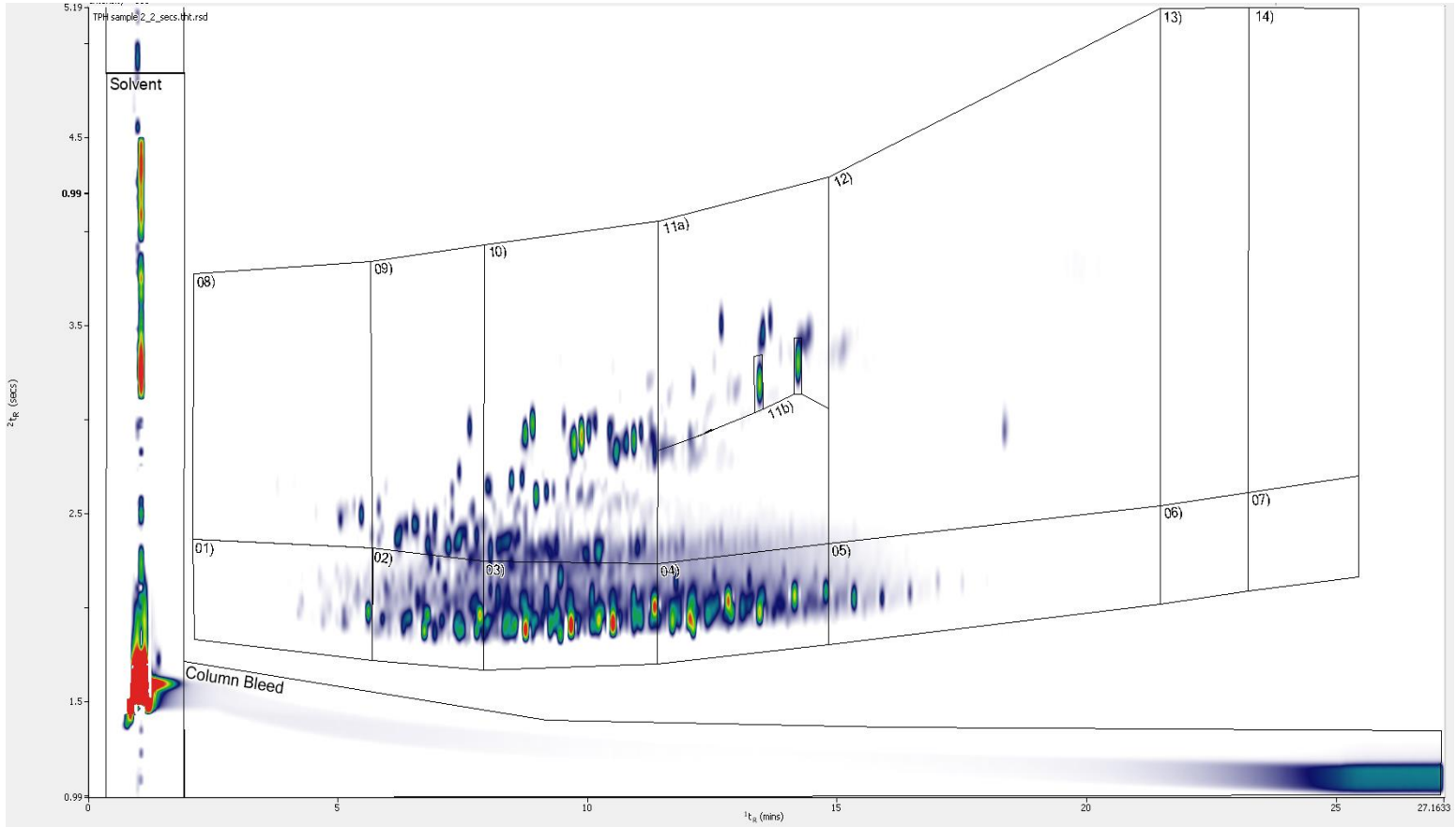
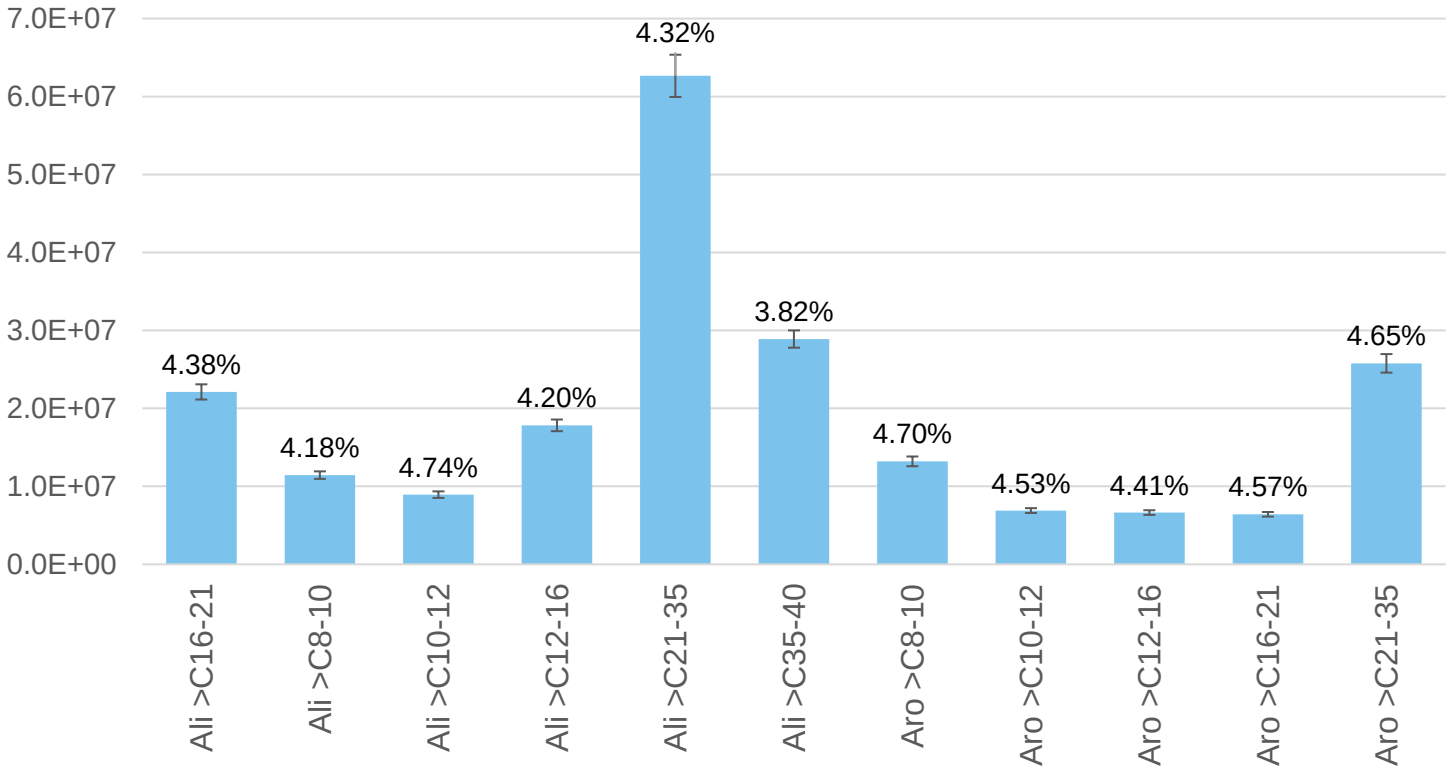
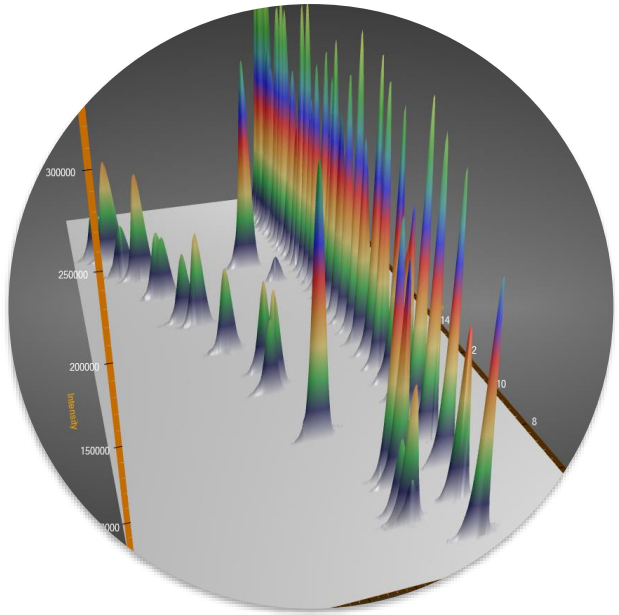


- Stencils are then applied to real samples

Repeatability for EPH analysis





- 15 injections of the TPH marker standard over a 5 day period
- All RSD <5%

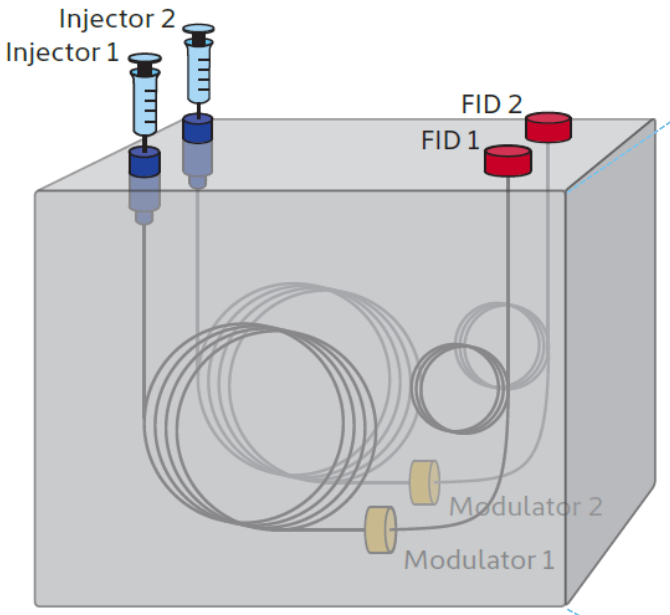
Benefits of eliminating sample fractionation

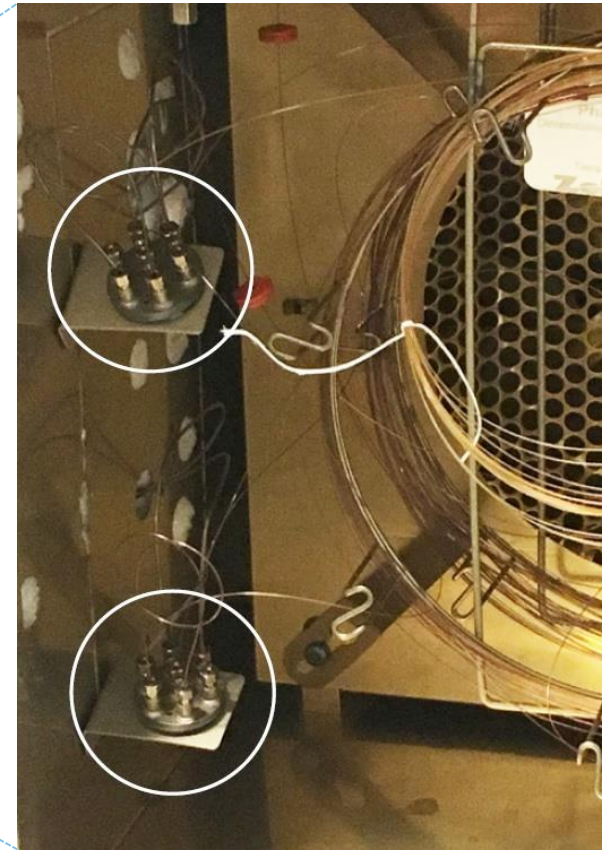
- Improved reliability – fewer QC failures

- Cost savings associated with consumables

	Small lab	Large lab
Samples per week	100	500
Weekly saving	£250 / $310	£1,250 / $1,550
Monthly saving	£1,080 / $1,340	£5,410 / $6,710
Annual saving	£12,980 / $16,100	£64,910 / $80,490

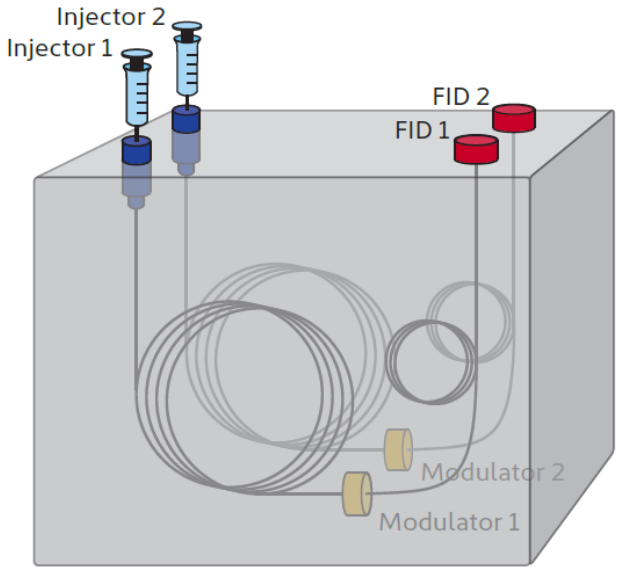
Dual-channel GC×GC

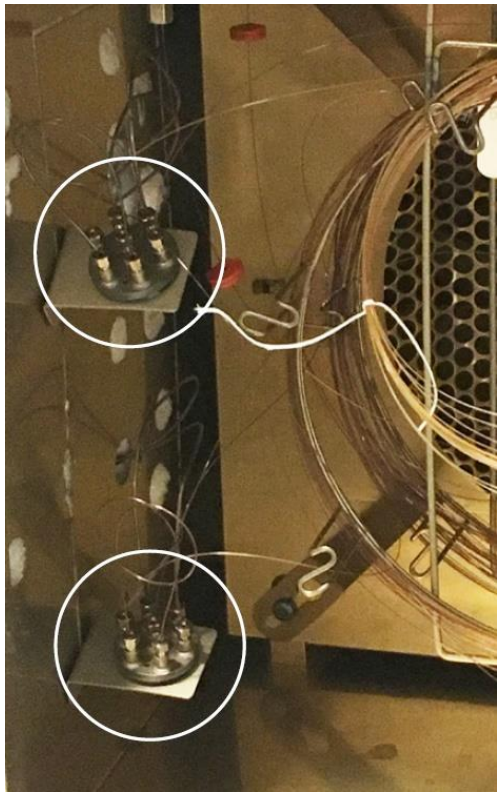


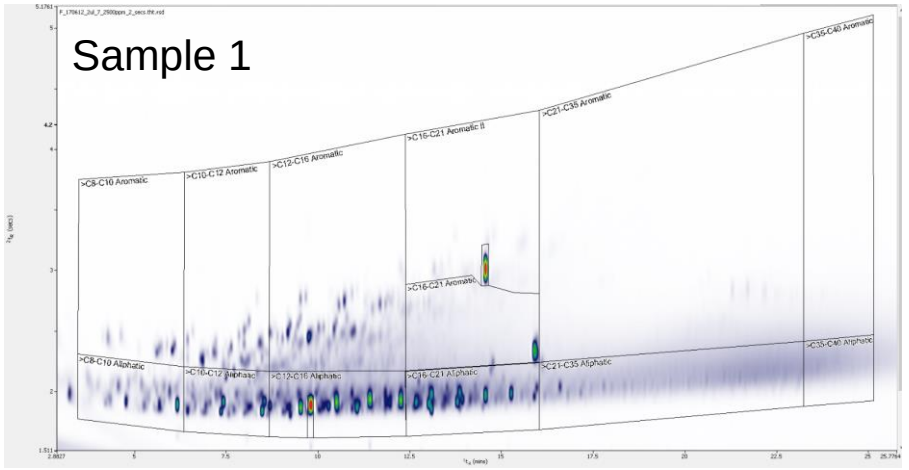


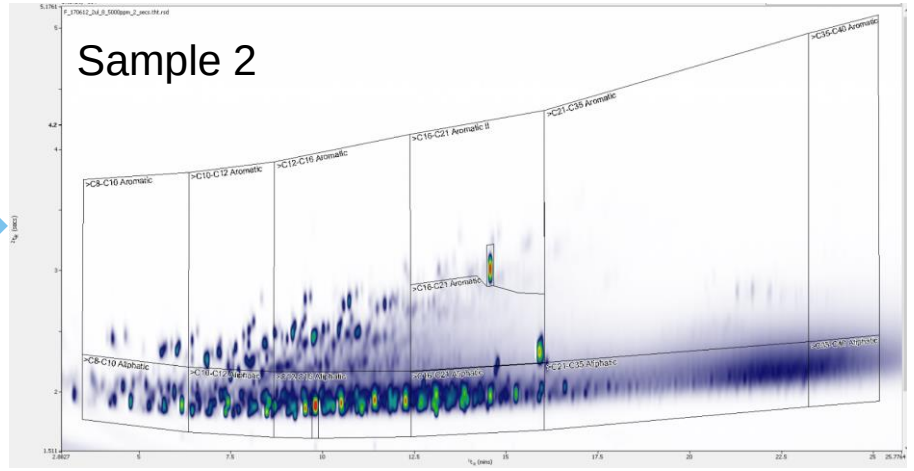
- Two flow modulators configured in a single oven
- Doubles productivity

Dual-channel GC×GC





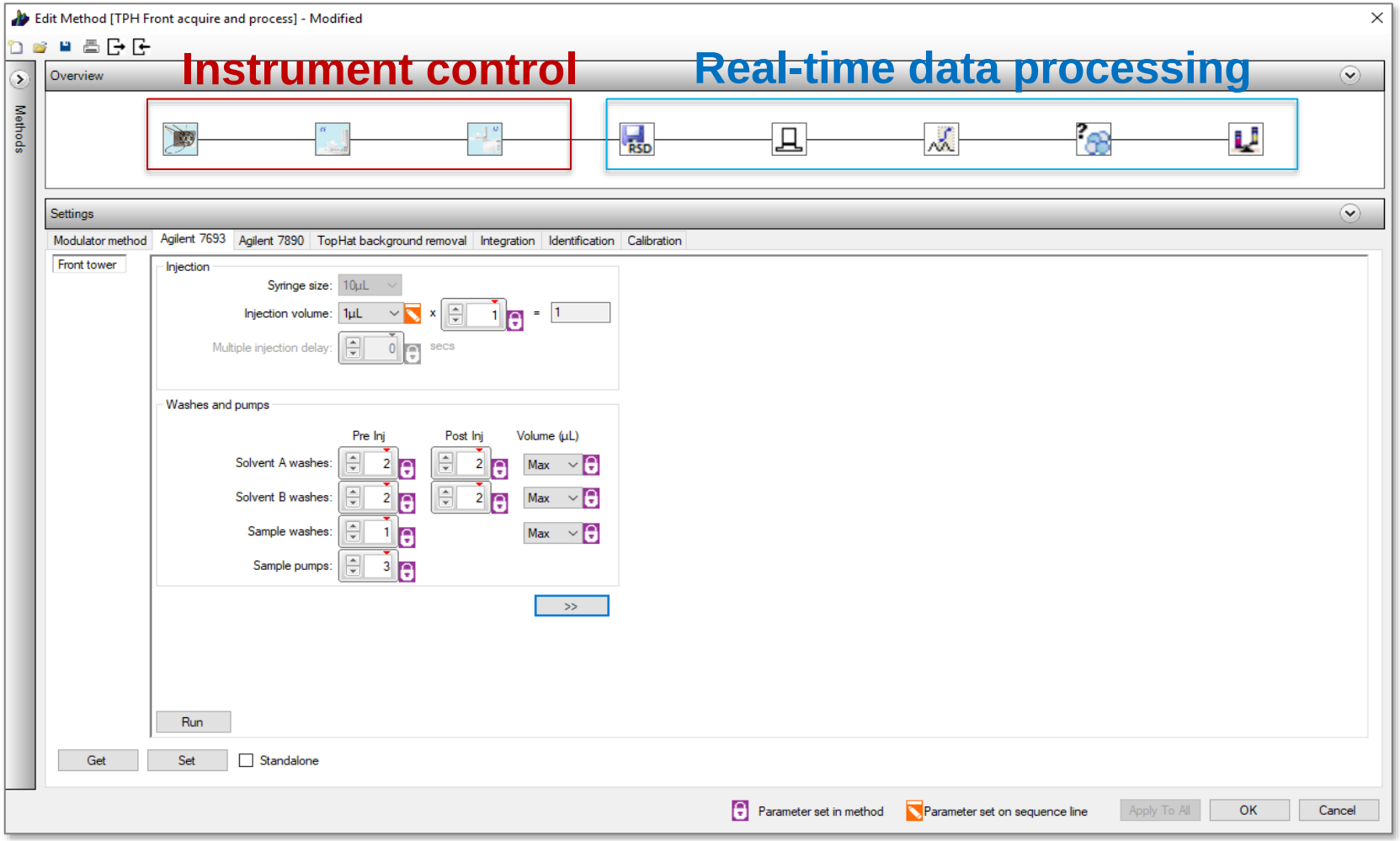




- Run two samples simultaneously for highest productivity

Reporting of results

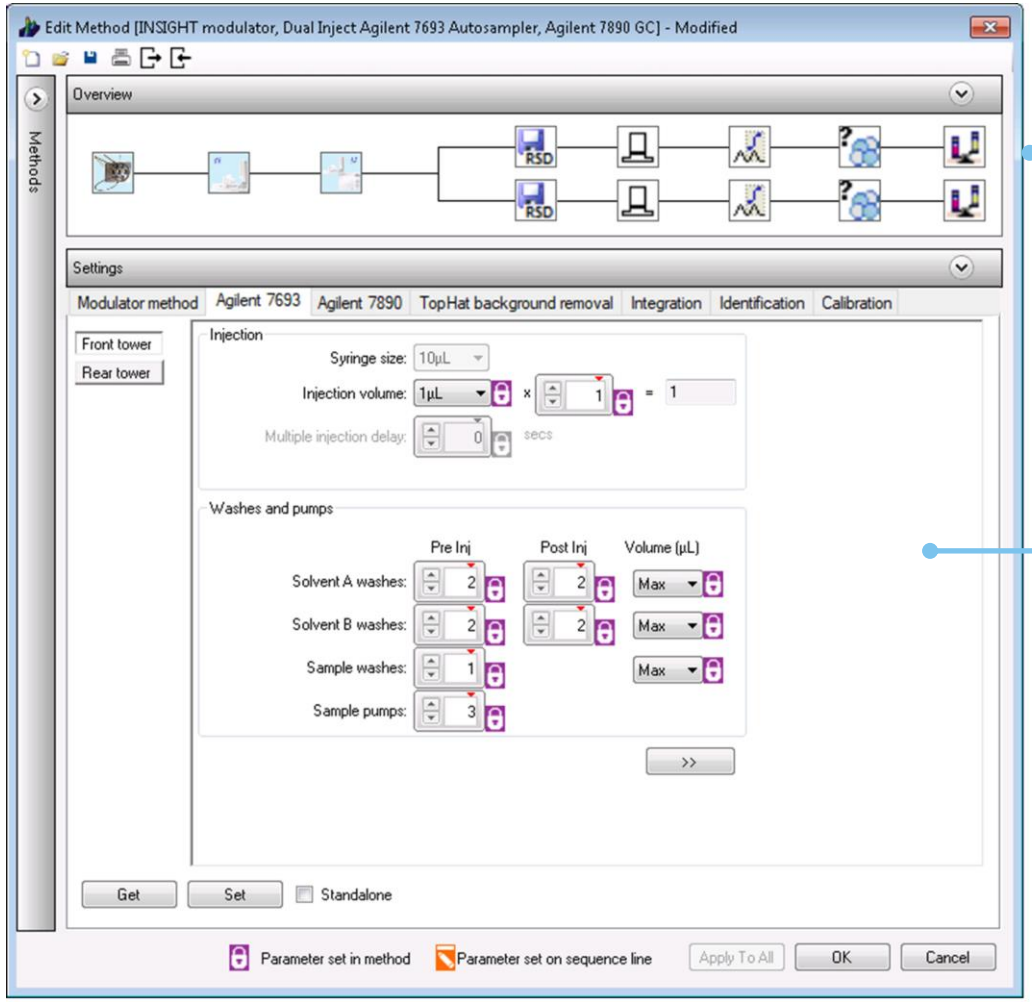
Real-time data processing



- ChromSpace provides both instrument control and data processing
- Data processing (e.g. stencil, integration, quantitation) can be stored as part of the global method
- Processing begins while the sample is running, with no user intervention

Reporting of results

Dual-channel GC×GC



Real-time data processing for both channels

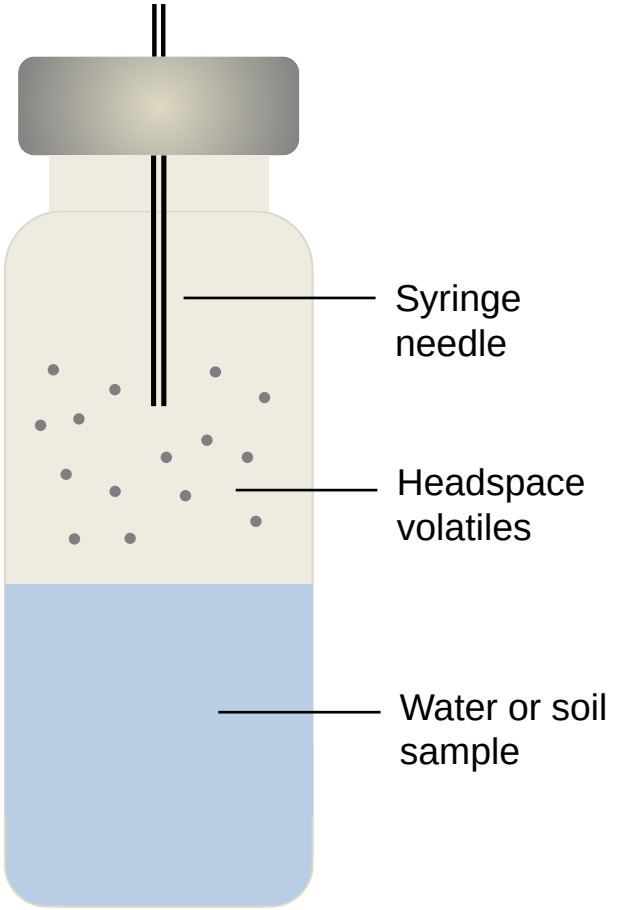
Template methods already configured

Beyond EPH…

Volatile petroleum hydrocarbons (VPH)

- TPH is commonly split into the **Volatile** Petroleum Hydrocarbons (VPH) and the **Extractable** Petroleum Hydrocarbons (EPH)

- VPH monitors hydrocarbons from an equivalent carbon number of C_5–C_{10}



Challenges in VPH analysis

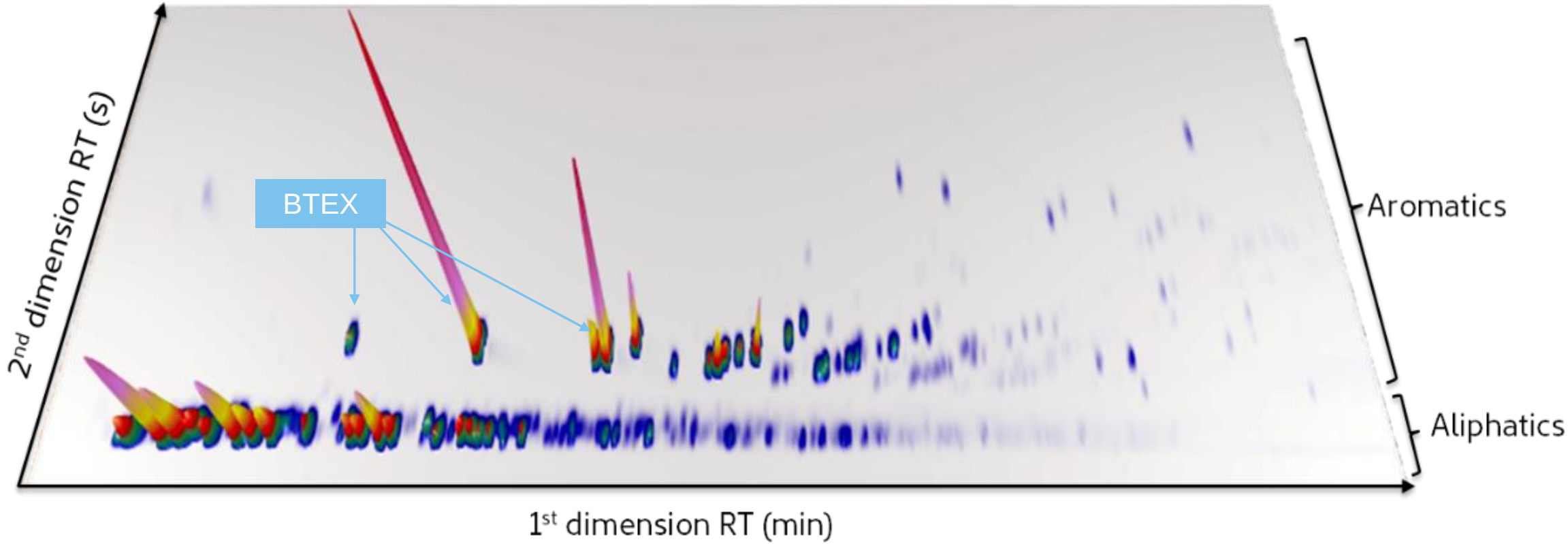
- Current methods are subject to inherent bias due to coelutions between non-petroleum hydrocarbons and the petroleum hydrocarbons of interest
- Quantitative values that either over-estimate or under-estimate the target compounds.

Targets	Potential instrument bias	
	GC–PID/FID	GC–MS
Individual target analytes (e.g., BTEX)	High	No bias
C_5-C_8 aliphatics	Low	No significant bias
C_9-C_{12} aliphatics	Low	High
C_9-C_{10} aromatics	High	No significant bias

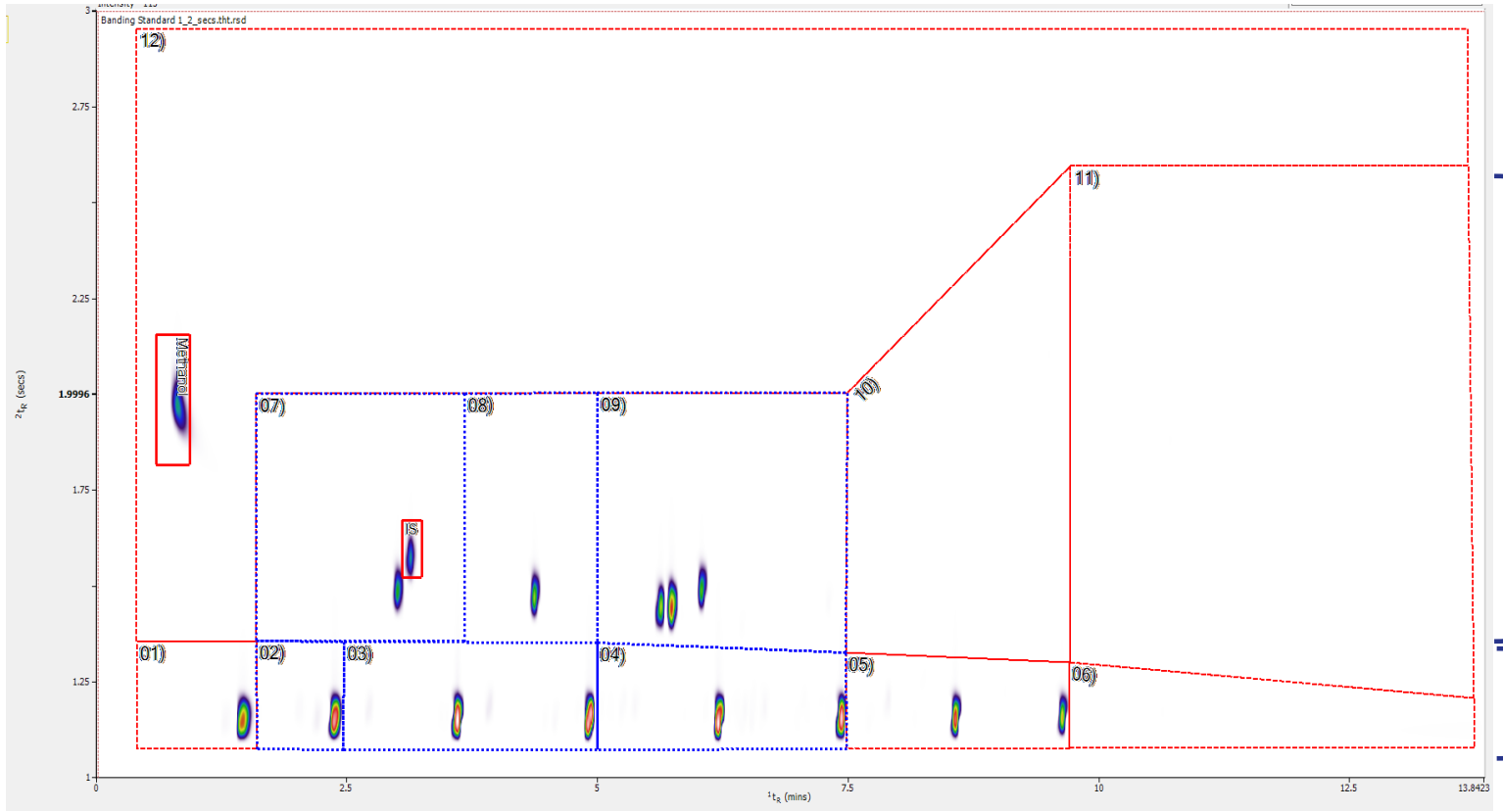
Source: www.mass.gov/doc/evaluation-of-massdep-volatile-petroleum-hydrocarbon-vph-methods-vph-by-gcpidfid-and-vph-by/download

Solving the challenges in VPH analysis…

…with headspace(HS)–GC×GC–FID



Simplified data processing



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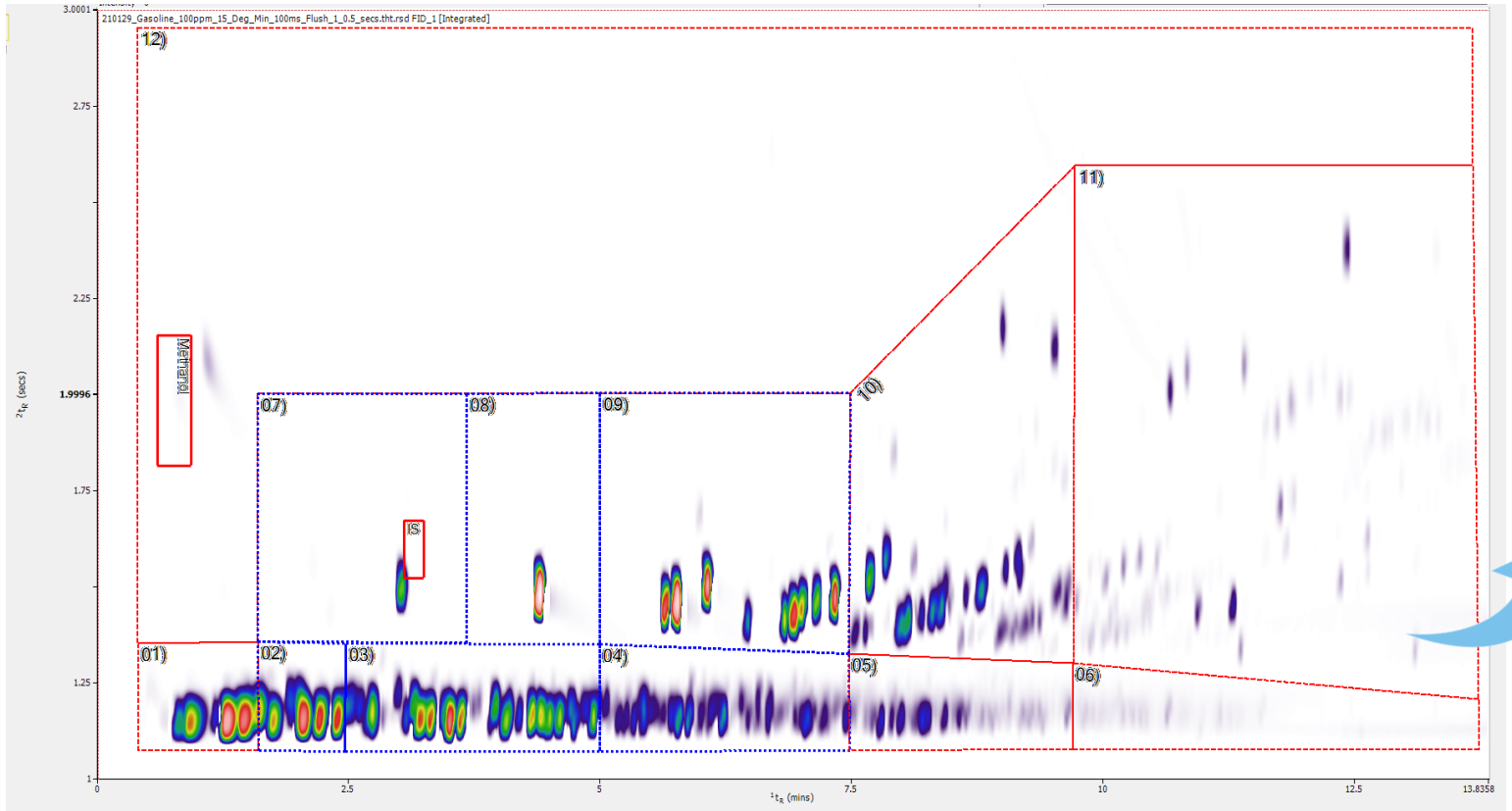
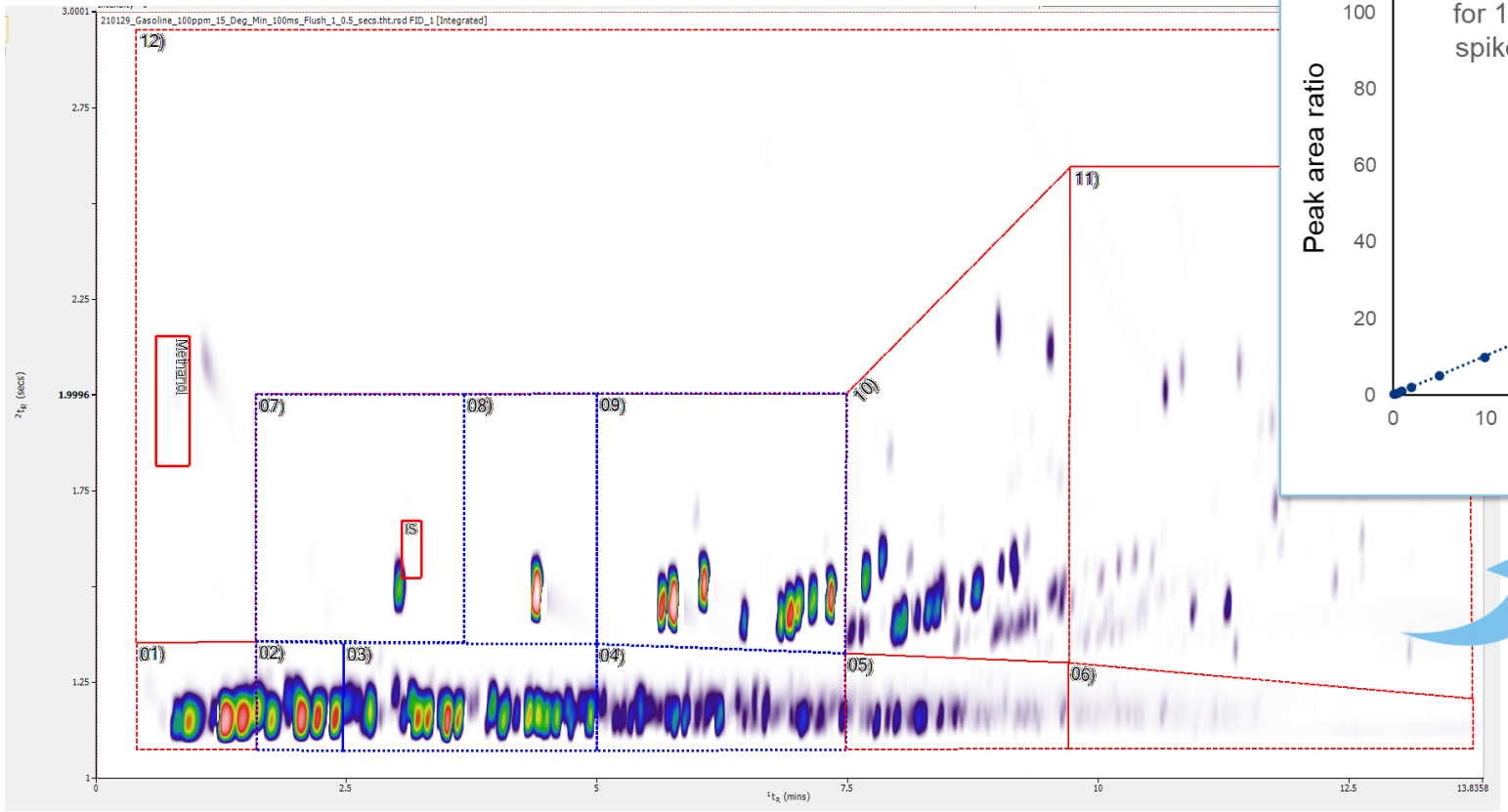


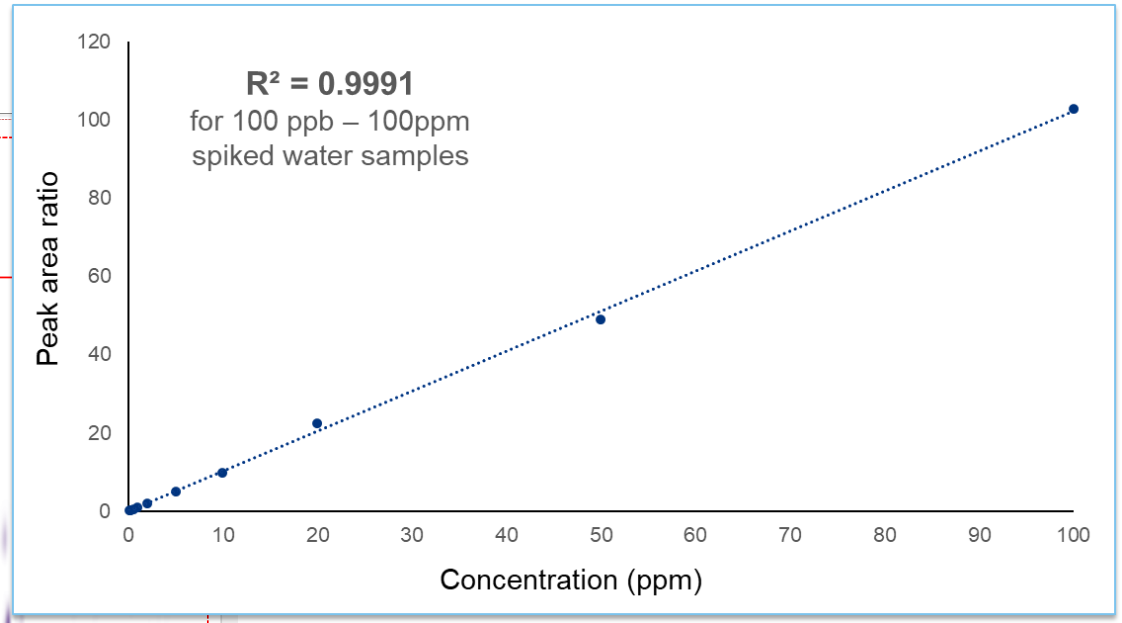
Area Percent

Source	Area	Area %	Status
01) < C5 Aliphatics	1.72324E+09	19.3	Included
02) > C5 - C6 Aliphatics	1.39629E+09	15.64	Included
03) > C6 - C8 Aliphatics	1.56501E+09	17.53	Included
04) > C8 - C10 Aliphatics	2.05826E+08	2.31	Included
05) > C10 - C12 aliphatics	5.95305E+07	0.67	Included
06) > C12 Aliphatics	9.23373E+06	0.1	Included
07) > C5 - C7 Aromatics	6.25803E+07	0.7	Included
08) > C7 - C8 Aromatics	1.27524E+09	14.28	Included
09) > C8 - C10 Aromatics	2.33965E+09	26.21	Included
10) > C10 - C12 Aromatics	2.56539E+08	2.87	Included
11) > C12 Aromatics	3.21594E+07	0.36	Included
12) Non-petroleum compounds	2.42217E+06	0.03	Included
Aliphatics	4.95913E+09	55.55	Included
Aromatics	3.96617E+09	44.43	Included

- Stencils are then applied to real samples for a fast overview of sample composition, as well as full quantitative analysis

Simplified data processing





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Summary

TPH analysis using GC×GC–FID

- GC×GC provides enhanced chromatographic resolution for more robust methods
- Huge cost savings due to the elimination of offline sample fractionation
- Flow modulation is simple, repeatable and affordable, and adds no additional lab space
- Faster reporting times with full instrument control and reliable, automated processing
- Enhanced productivity with dual injection
- Proven, fully optimised methods with step-by-step protocols

Contact SepSolve

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