

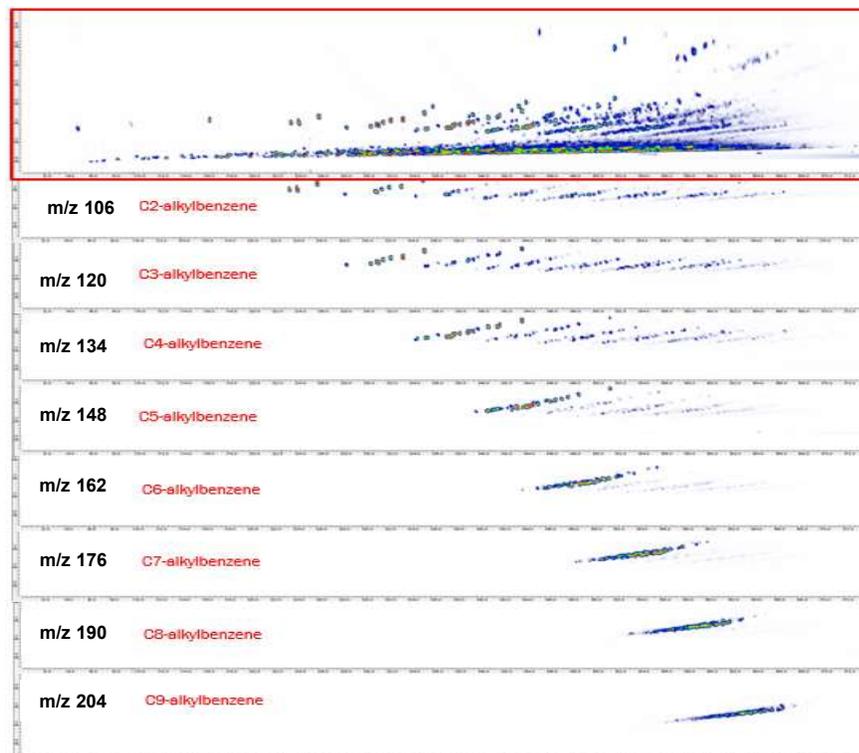
Just Go with the Flow: *The Routine Application of GC × GC-TOF MS to Real-World Analyses*

Dave Wevill, Laura McGregor, Matt Edwards
and Nick Bukowski

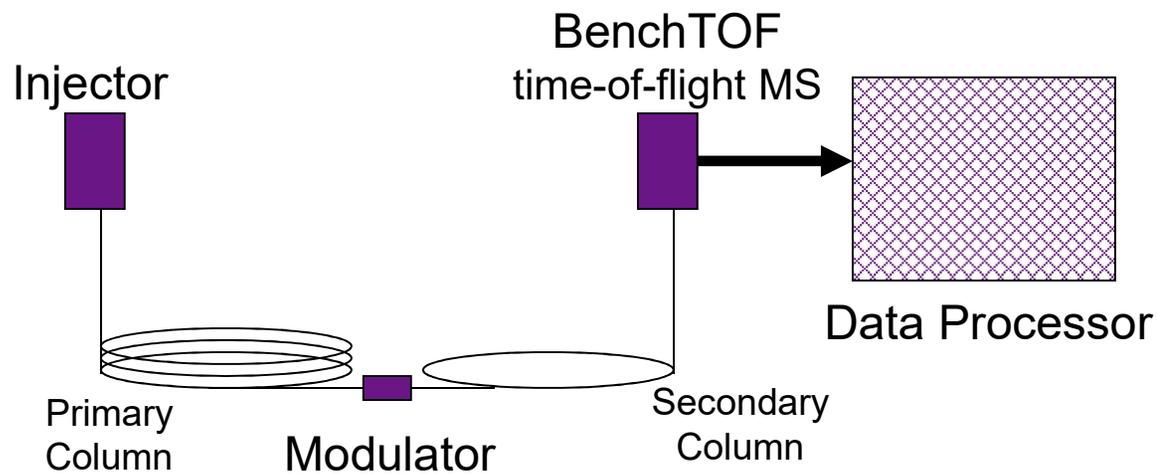


Advantages of GC × GC

- Increased separation capacity
 - Separation using 2 different stationary phases
 - Improved confidence in compound ID
- Structured chromatograms
 - Similar compounds elute together in bands (*“roof-tiling” effect*)
- Enhanced sensitivity
 - Narrow chromatography = improved S/N



Analytical system



The “beating heart”
of GC × GC

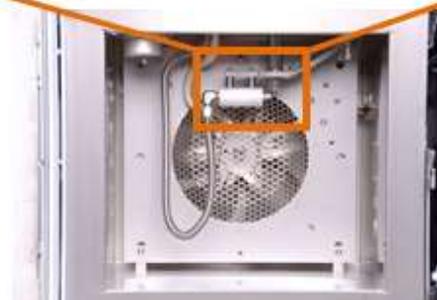
- Purpose of the modulator:
1. Focus 1st column eluent
 2. Injector for 2nd column

Choose the modulator to suit your application



Flow modulators

Valve-based, using differential flows



Thermal modulators

Use hot and cold jets

Both devices have advantages...

Flow modulation...

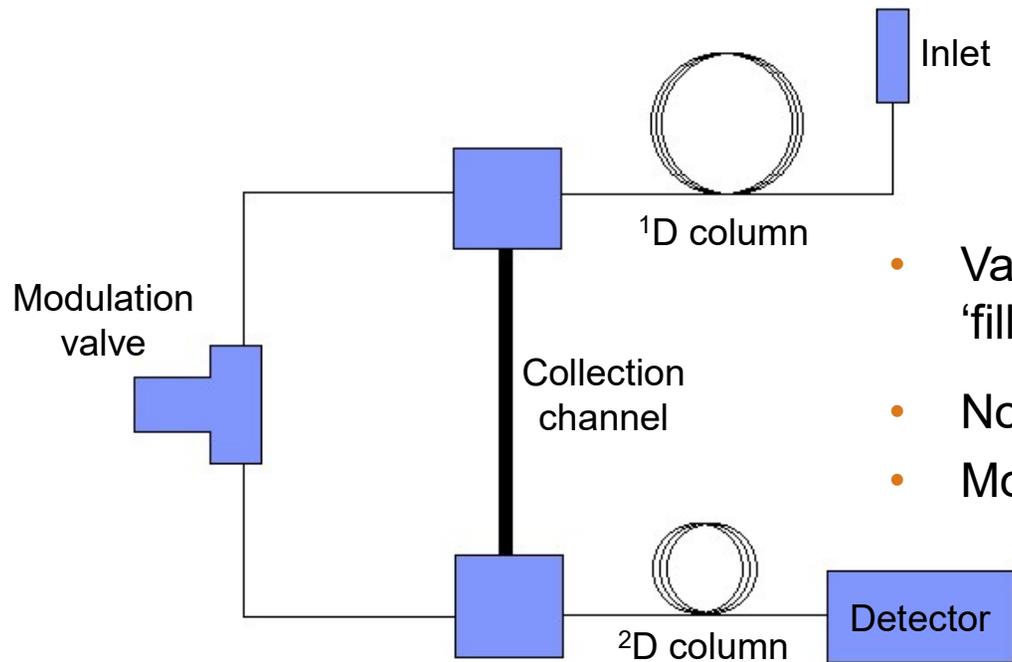
- Has lower running (& capital) costs
- Excellent repeatability
- Enables efficient modulation of volatiles
- Easy implementation of simultaneous detection
- Fewer commercialised designs
- Can also be configured for heart-cutting and back-flushing

Thermal modulation...

- Has higher running costs
- Small changes in loop position impact repeatability
- Restricted volatility range
- Difficult to implement dual detection
- Wide user base
- Has a high peak capacity and enhanced signal-to-noise due to narrower peak widths.

What is flow modulation?

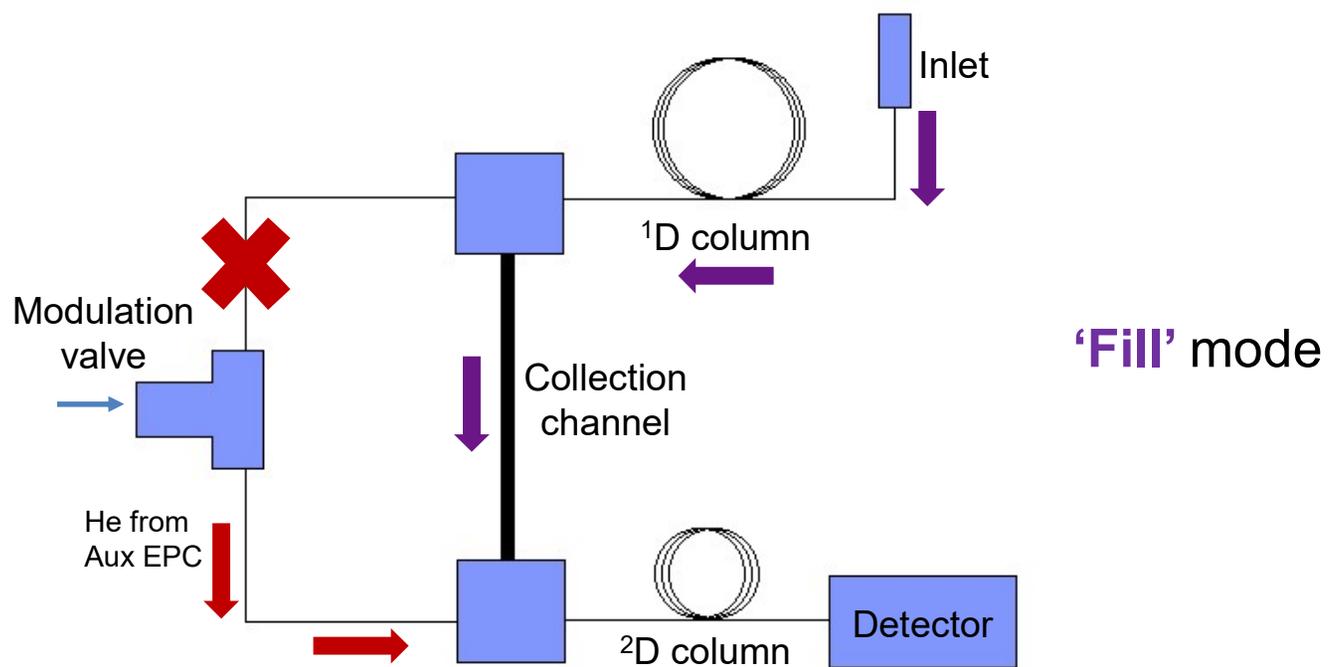
1st generation “forward fill/flush” devices



- Valve design, using differential flows to ‘fill’ and ‘flush’ a sample loop
- No need for expensive liquid cryogen
- Modulation period = fill time + flush time

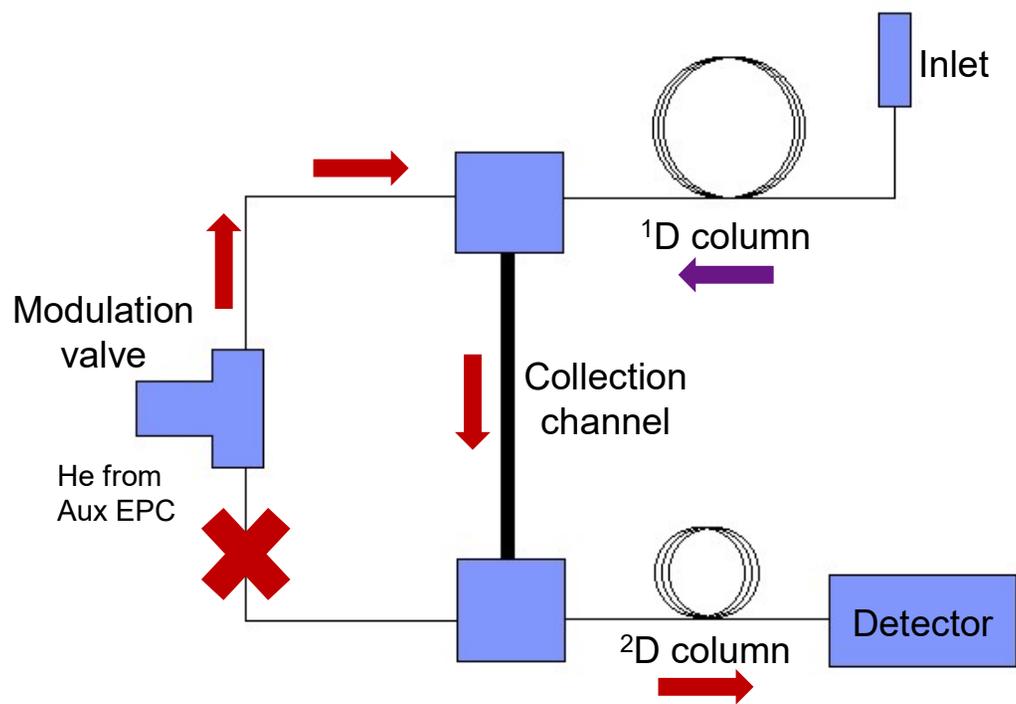
What is flow modulation?

1st generation “forward fill/flush” devices



What is flow modulation?

1st generation “forward fill/flush” devices



‘Flush’ mode

Analytes injected in same direction they entered the channel

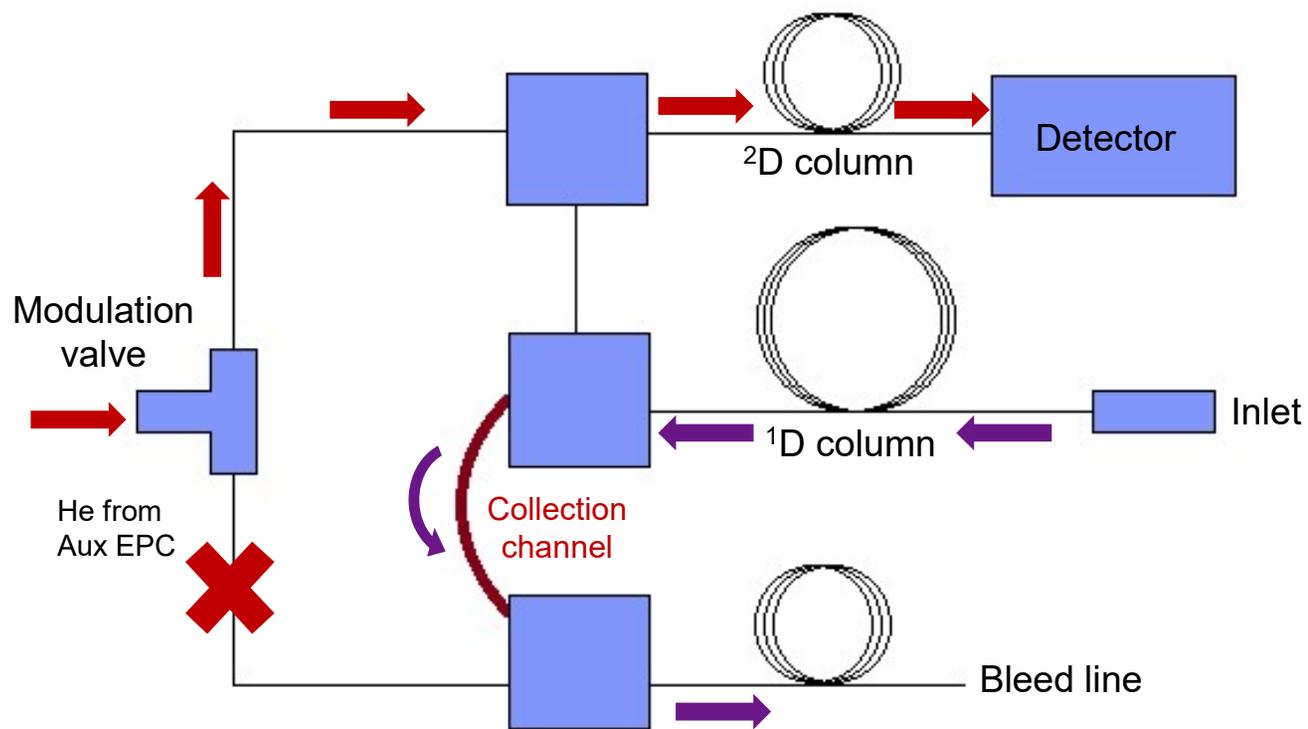
(i.e. forward direction)

Issues with this Forward Fill/Flush device

- Must be precisely timed
 - Overfilling loop = chromatographic tailing/streaking
 - Tailing = loss in peak capacity
- Fixed sample loop
 - Limits applicable column combinations

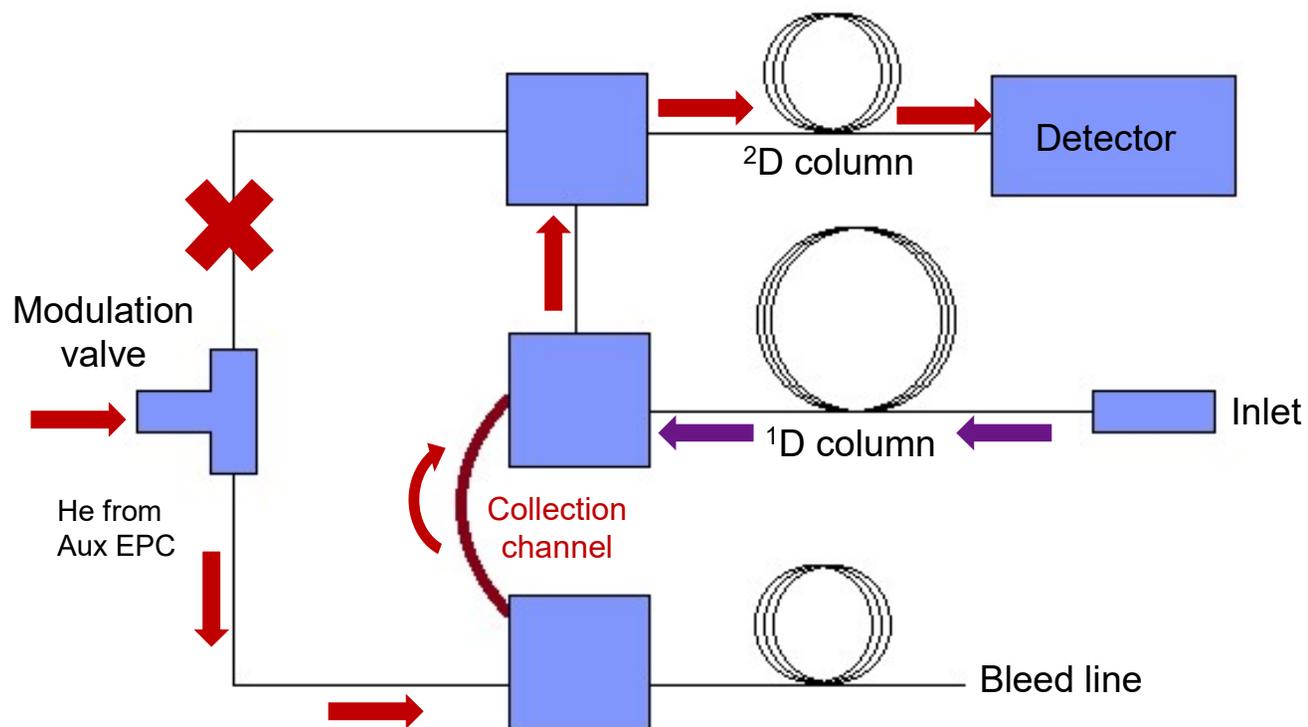
Reverse fill/flush devices

'Fill' mode



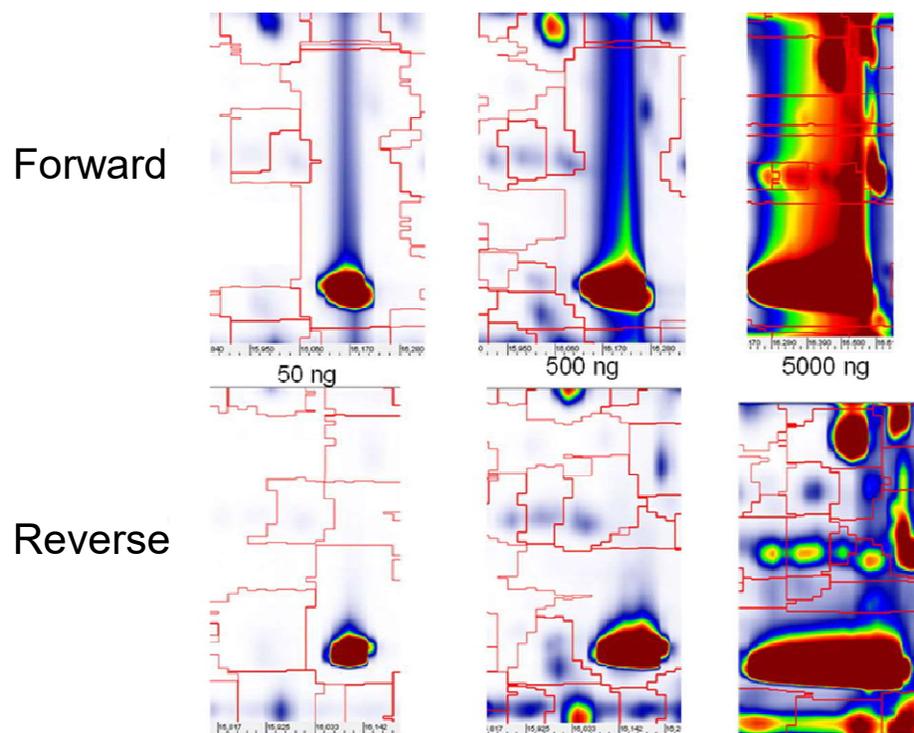
Reverse fill/flush devices

'Flush' mode



Sample loop is flushed in opposite direction

Benefits of Reverse Fill/Flush devices



- Higher efficiency for re-injection
- Improved 2D peak widths and symmetry
- Better handling of overloading
- Flexible sample loop volume

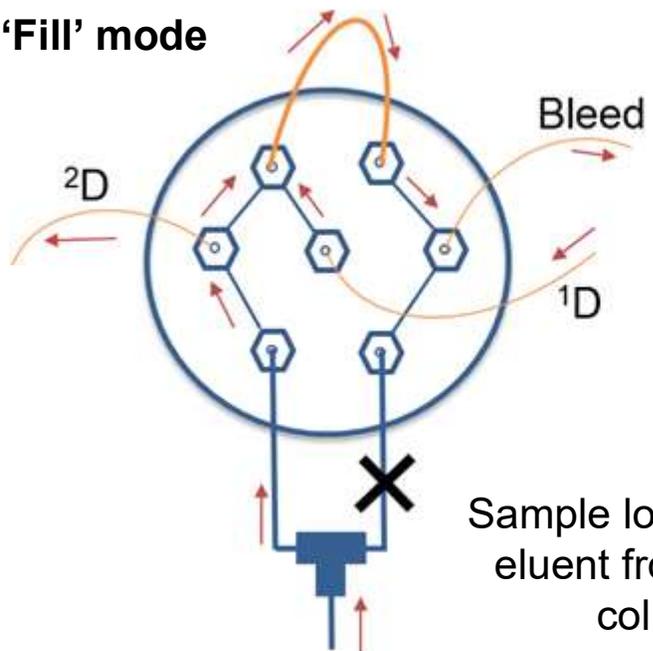
J.F. Griffith et al. / J. Chromatogr. A 1226 (2012) 116–123

Insight modulator

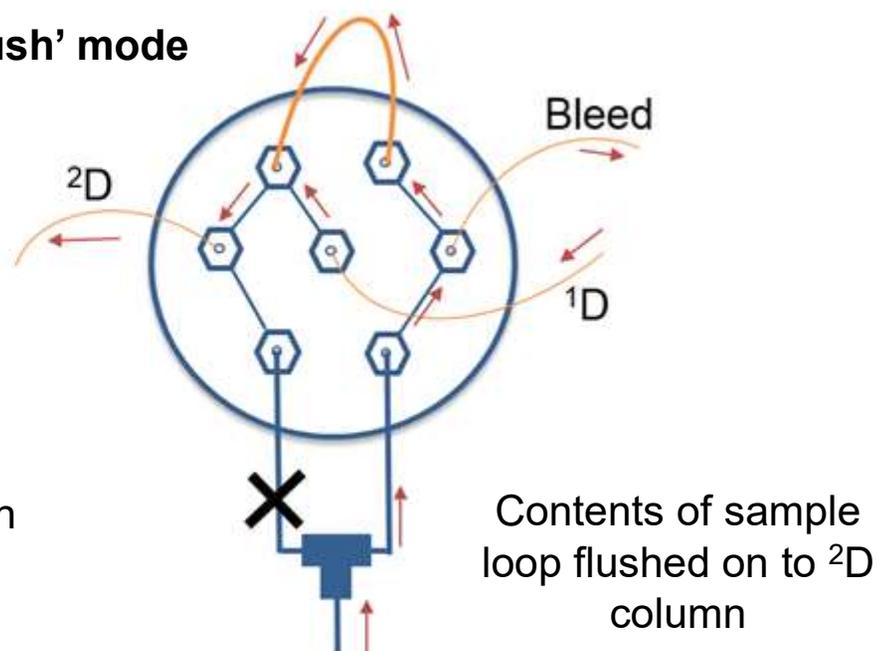
Using reverse fill/flush dynamics



'Fill' mode



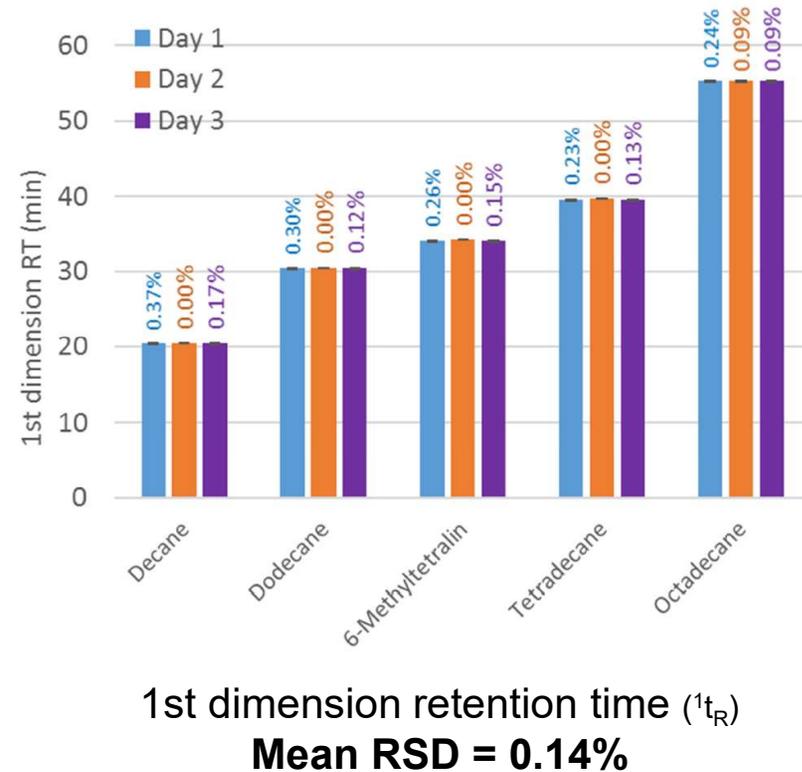
'Flush' mode



Advantages of flow modulation

Repeatability

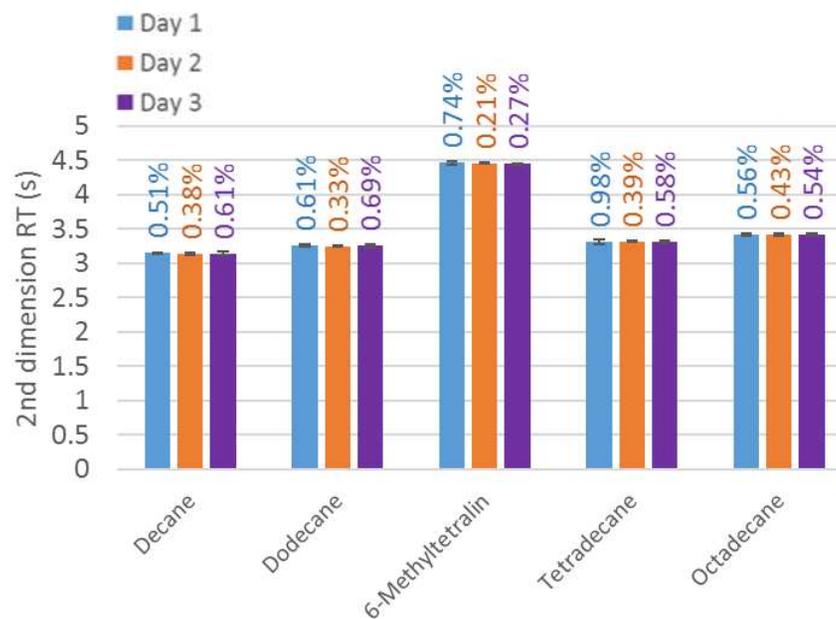
- Replicate injections of diesel ($n=8/\text{day}$)
- This level of time precision is due to a dedicated EPC for each column
- Ideal for comparisons within large sample batches



Advantages of flow modulation

Repeatability

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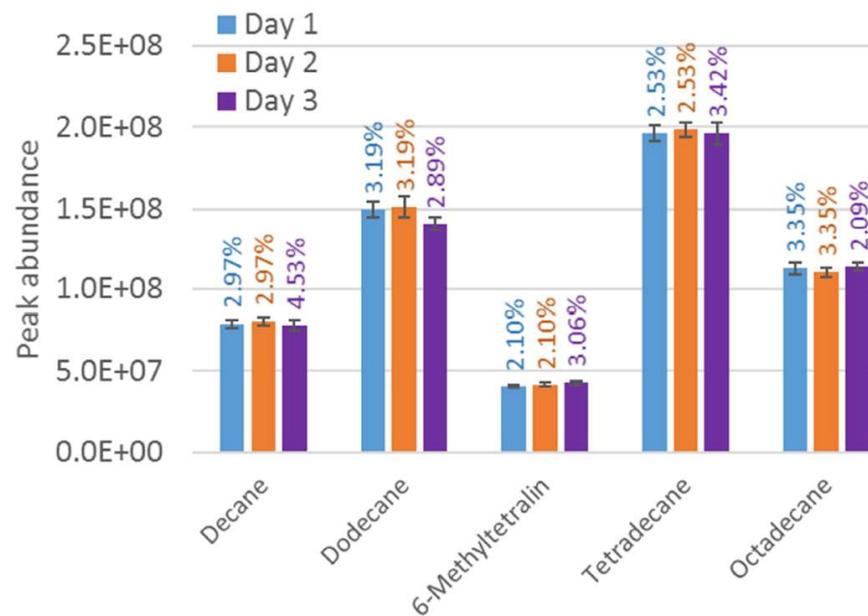


2nd dimension retention time (2t_R)
Mean RSD = 0.52%

Advantages of flow modulation

Repeatability

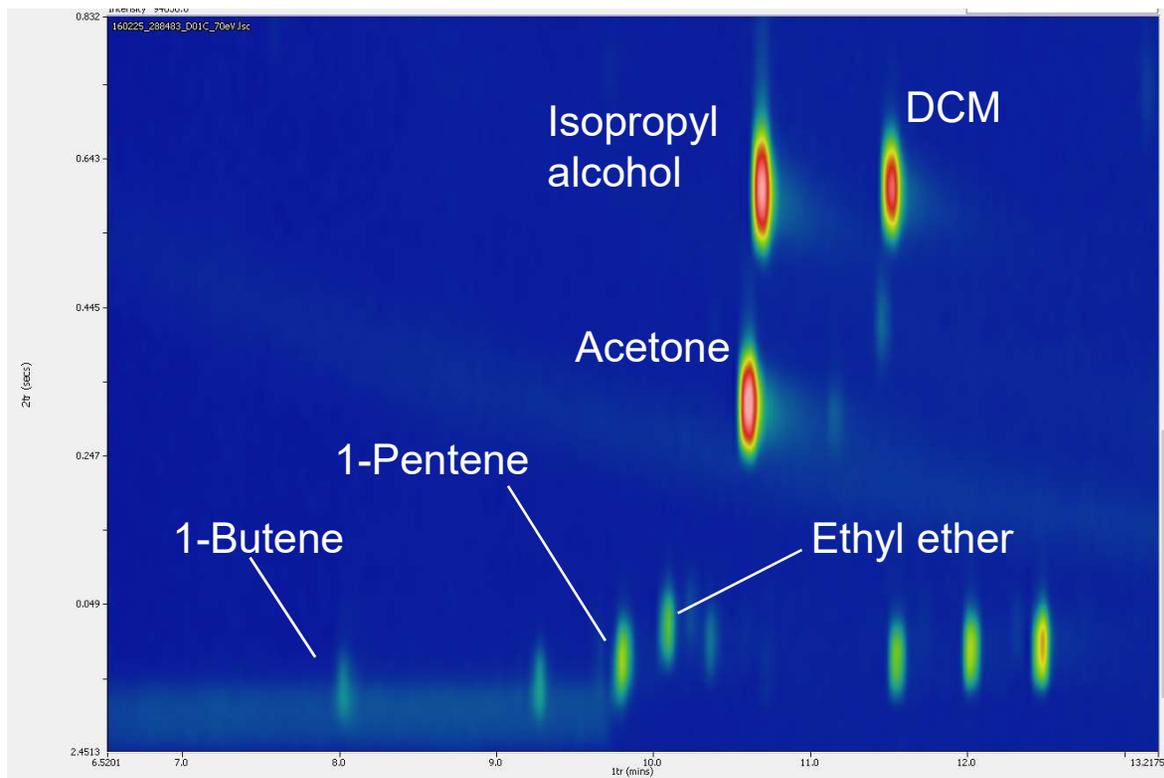
- Replicate injections of diesel ($n=8/\text{day}$)
- Flow modulation is well-suited to comparisons within large sample batches.



Peak abundance
Mean RSD = 2.98%

Advantages of flow modulation

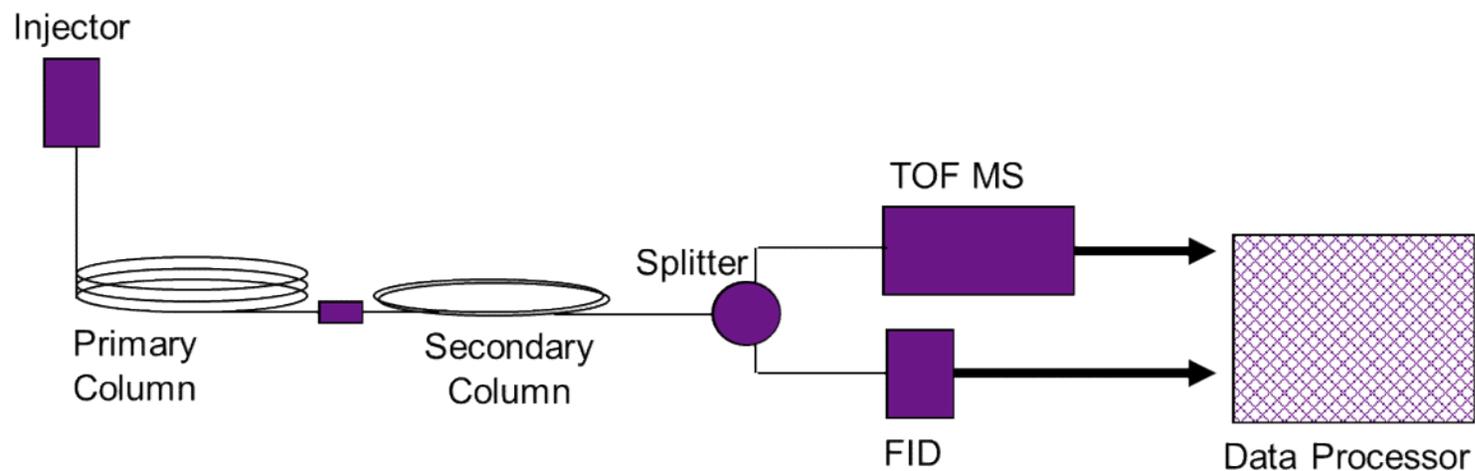
Efficient modulation of volatiles



VOCs from a blood sample

Advantages of flow modulation

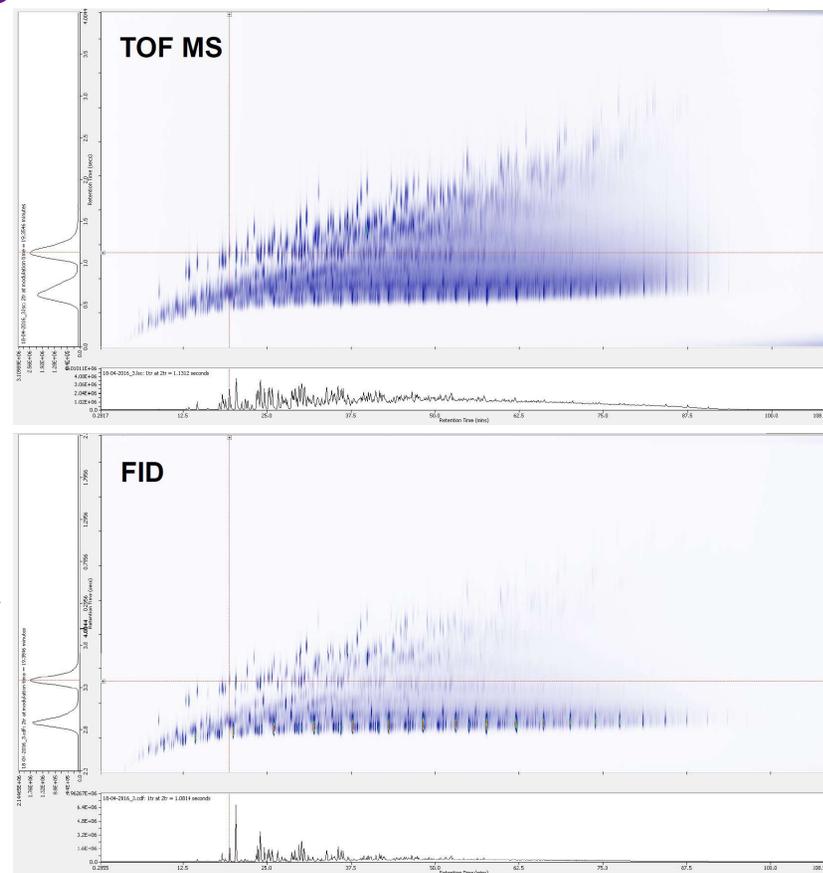
Easy implementation of parallel detection



- 2D column effluent split to two transfer lines
- Goal = equivalent hold up time

Parallel detection FID/TOF MS

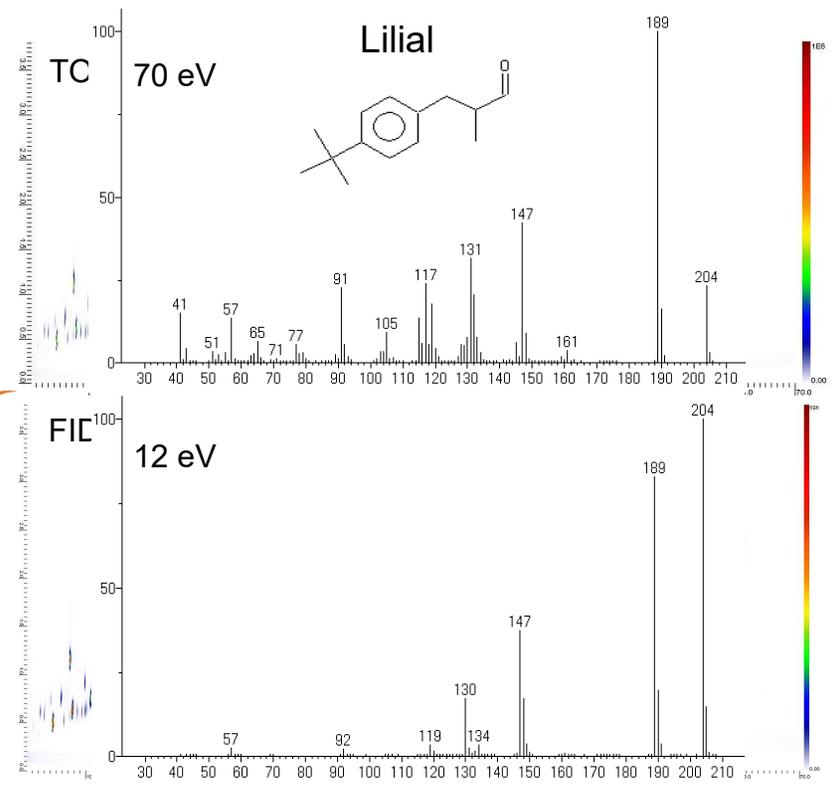
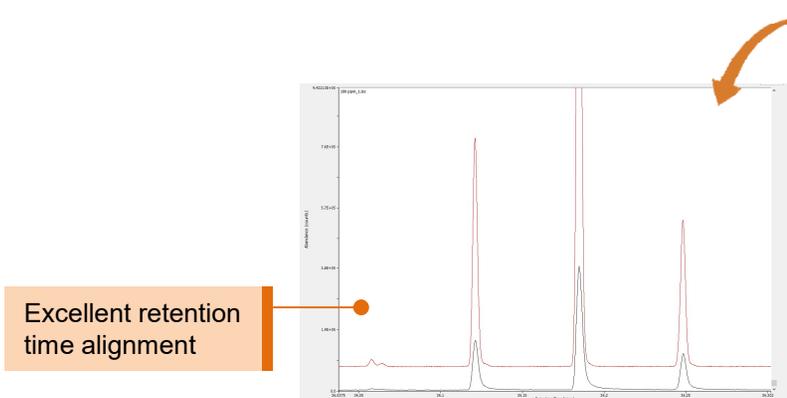
- Analysis of diesel by dual detection GC × GC-FID/TOF MS
- Excellent $1t_R/2t_R$ correspondence
- Robust quant by FID
- Cross-validation and confirmation of peak purity by TOF MS



Parallel detection of fragrance allergens

3 information-rich datasets with Tandem Ionisation

- Robust quant. and validation of compound identity
- Tandem Ionisation adds an extra dimension of information in these applications



Summary

- GCxGC provides confident separation, detection and identification of complex samples
- Flow modulation (using reverse fill/flush dynamics) provides:
 - Improved peak shape and peak capacity
 - Efficient modulation of volatiles
 - Excellent repeatability for large sample batches
 - Both within batches and between instruments
 - Simple configuration of parallel detection (as well as heart-cutting or backflushing)
 - None of the hassle or expense associated with liquid cryogen

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