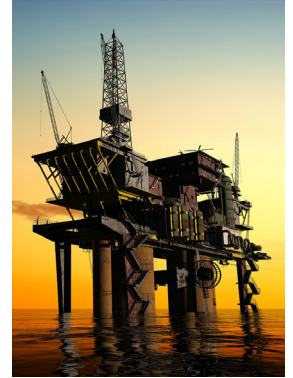


Determining petrochemical composition by GC×GC–TOF MS/FID: The benefits of flow modulation and Tandem Ionisation

This study demonstrates the performance of a flow-modulated GC×GC system for the analysis of complex petrochemicals, with the INSIGHT modulator providing efficient and repeatable modulation without the need for expensive liquid cryogen. Analyte speciation is also aided by Tandem Ionisation for simultaneous acquisition of hard and soft EI data.



Introduction

Precise characterisation of petroleum-derived fuels is crucial for quality control, to understand the reactions that take place during refining processes, and also for environmental monitoring. However, it can be challenging as well as tedious to identify the individual components present in these complex samples. Comprehensive 2D gas chromatography (GC×GC) offers significant advantages over 1D chromatography for such analyses, with its vastly expanded separation space and the added benefit of highly structured groupings of compounds (for examples on the use of software tools to assist group-type analysis of petrochemicals, see the [companion white paper](#)).

The key component in the GC×GC system is the modulator – the device that samples and re-injects the first-column effluent on to the second column in narrow bands to ensure that the first-dimension separation is retained and that the short second-dimension column does not become overloaded.

Thermal modulation is the most commonly used technique, but this often requires expensive liquid cryogen and can make it difficult to achieve precise replication of results across multiple instruments. An alternative approach is flow modulation, which avoids the inconvenience and expense of liquid cryogen, and offers much better between-sample and between-instrument repeatability.

Fast acquisition speeds and sensitive detection make time-of-flight mass spectrometry (TOF MS) the ideal partner to GC×GC. However, best-practice in the petrochemical industry recommends flame ionisation detection (FID) for target compound quantitation.

This study explores the use of INSIGHT™ flow modulation with parallel-detection GC×GC by TOF MS and FID, for confident classification and quantitation of hydrocarbon groupings respectively. Tandem Ionisation® technology is also shown to add another dimension of information to GC×GC, by providing soft EI spectra for improved isomer speciation.

Experimental

A schematic of the analytical system is shown in Figure 1.

Sample: Pump diesel (undiluted).

GC×GC: Injector: Split/splitless; Liner: Single taper with

wool, 4 mm (i.d.); Carrier gas: Helium, constant-flow at 0.5 mL/min; Mode: Split 300:1; Temperature: 280°C; Septum purge: On, 3 mL/min. Modulator: INSIGHT™ flow modulator (SepSolve Analytical). **Repeatability study:** 2D column set: 1st dimension: BPX5™, 20 m × 0.18 mm × 0.18 µm; 2nd dimension: DB-17™, 2 m × 0.25 mm × 0.15 µm. Temperature program: Main oven: 50°C (1 min), 3°C/min to 320°C (hold 10 min). Loop dimensions: 30 cm × 0.32 mm i.d.; Loop volume: 24 µL; Fill time: 5800 ms; Flush time: 200 ms; PM: 6.0 s. **Dual detection study:** 2D column set: 1st dimension: BPX5™, 25 m × 0.15 mm × 0.25 µm; 2nd dimension: ZB-50™, 5 m × 0.25 mm × 0.15 µm. Temperature program: Main oven: 50°C (1 min), 2.5°C/min to 320°C (hold 20 min). Loop dimensions: 10 cm × 0.53 mm i.d. (loop volume: 22 µL); Fill time: 3900 ms; Flush time: 100 ms; PM: 4.0 s.

TOF MS: Instrument: BenchTOF-Select™; Filament voltage: 1.7 V; Ion source: 320°C; Transfer line: 300°C; Mass range: m/z 45–450; Data rate: 100 Hz in Tandem Ionisation® mode at 70 eV and 14 eV.

FID: H₂ flow: 30 mL/min; N₂ flow: 25 mL/min; Air flow: 400 mL/min; Data rate: 100 Hz.

Software: Instrument control and GC×GC data processing was carried out using TOF-DS™ with ChromSpace® (SepSolve Analytical).

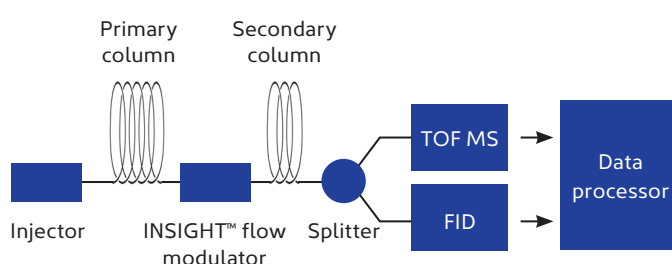


Figure 1

Schematic of the GC×GC–TOF MS/FID analytical system.

Results and discussion

1. Repeatability of flow modulation

A major advantage of flow-modulated GC×GC over thermally-modulated systems (aside from the reduction in running costs) is their superior repeatability. INSIGHT's precisely-defined microfluidic design (Figure 2) allows identical configurations to be installed across multiple instruments, unlike in thermal devices, where small variations in column position can have a large impact on results.

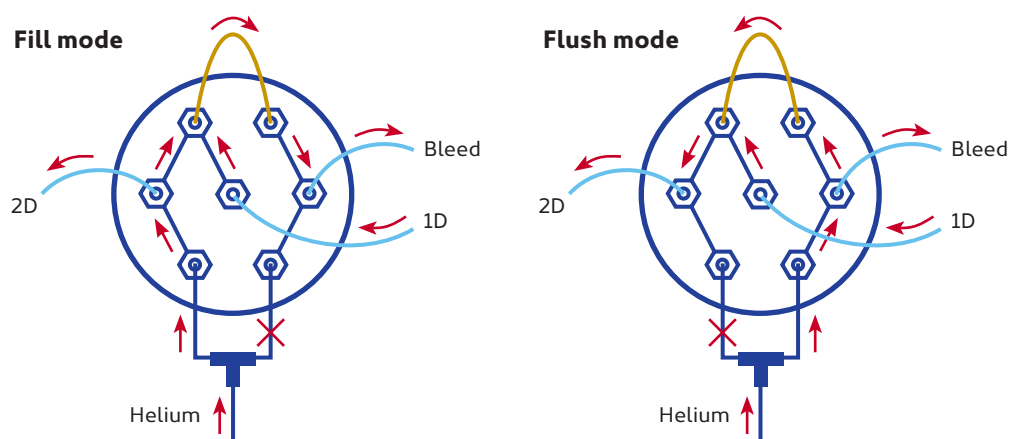


Figure 2

The valve-based INSIGHT modulator uses differential flows to 'fill' and 'flush' a sample loop (orange), meaning that running costs for routine GC×GC are low, and that drawbacks associated with liquid cryogen are avoided.

In this study, the repeatability of the flow modulation device was first evaluated using the GC×GC–FID results for 24 replicate injections over the course of three days. Figures 3 and 4 illustrate the excellent repeatability of the technique, with calculated RSDs less than 0.14%, 0.52% and 2.98% for $t_{R,1}$, $t_{R,2}$ and peak abundance,

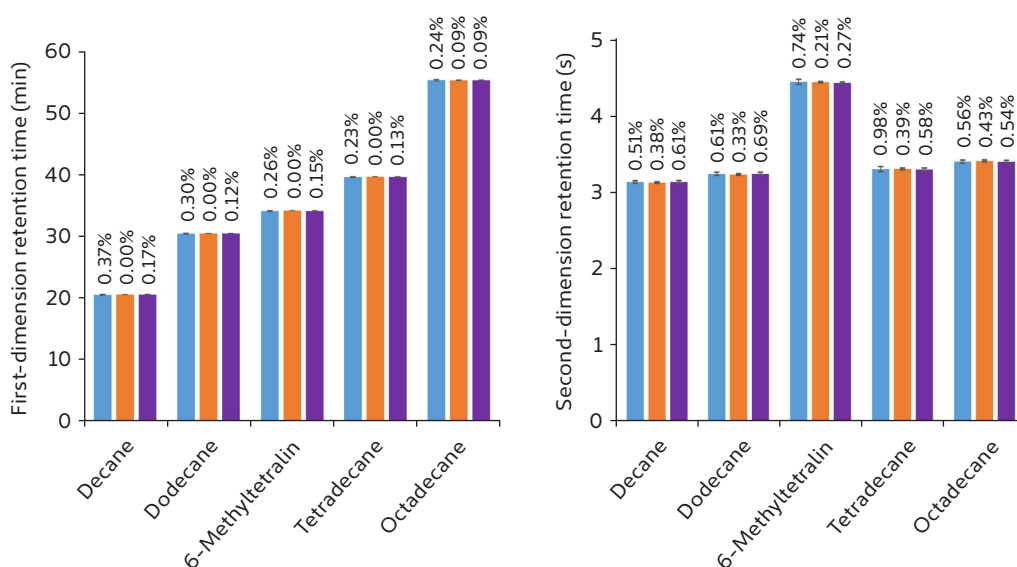


Figure 3

Retention-time repeatability of GC×GC–FID using the INSIGHT modulator during a three-day study ($n = 8$ per day). The RSDs for each day are indicated.

■ Day 1 ■ Day 2 ■ Day 3

respectively. This high precision of time response is aided by having a dedicated EPC unit for each column, and enables simple comparison of large sample batches and confident interpretation of results.

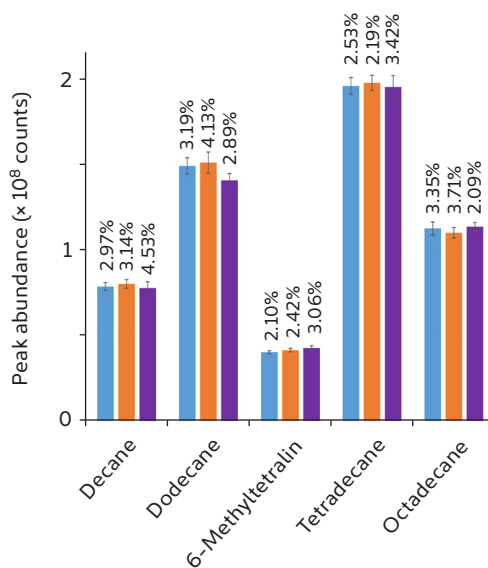


Figure 4

Peak abundance repeatability of GC×GC–FID using the INSIGHT modulator during a three-day study (n = 8 per day). The RSDs for each day are indicated.

Day 1 Day 2 Day 3

2. Evaluation of GC×GC with parallel MS/FID detection

FID is the gold standard for quantitative GC and GC×GC applications in the petrochemical industry for many reasons, including negligible band broadening, wide linear range, fast data capture and mass-dependent response. At the same time, MS detection (especially high-performance TOF MS), offers the advantage of robust analyte identification, and options for peak deconvolution and retrospective data-searching.

The use of GC×GC with parallel detection by MS and FID is therefore an ideal approach for achieving qualitative and quantitative analysis of petrochemicals in a single run. Targeted quantitative analysis can be performed across the widest concentration ranges, with dual-detector cross-validation and confirmation of peak purity.

However, thermally-modulated systems can be troublesome to configure for such dual-detector setups, but this is not an issue with flow modulation. Figure 5 compares colour plots obtained by simultaneous detection by TOF MS and FID, using chromatographic conditions for optimum separation and alignment of retention times in both the first and second dimensions. Figure 6 further illustrates the excellent retention time alignment, using the linear TOF MS and FID traces.

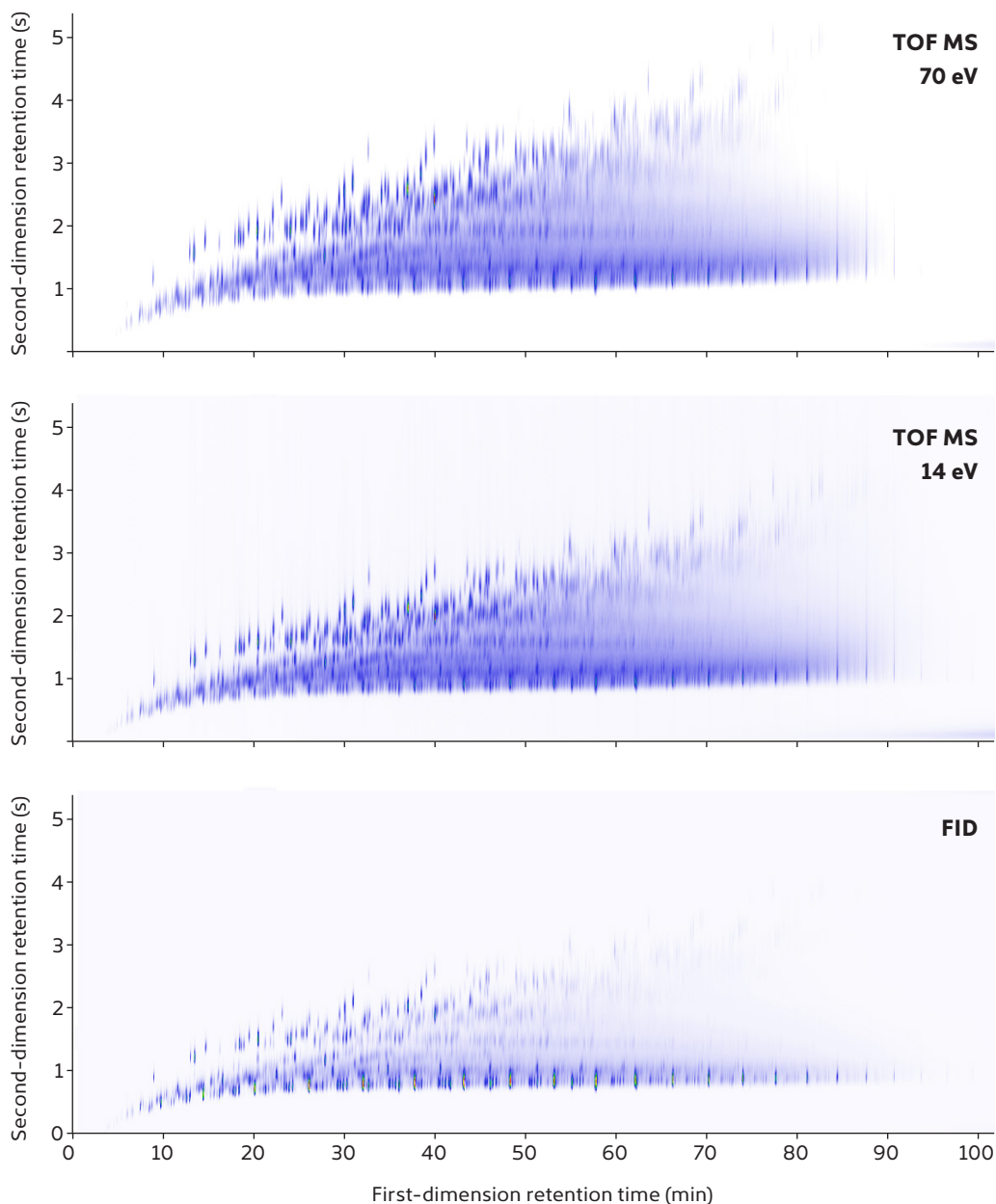


Figure 5

GCxGC colour plots of diesel, generated by simultaneous detection by TOF MS (with Tandem Ionisation at 70 eV and 14 eV) and FID.

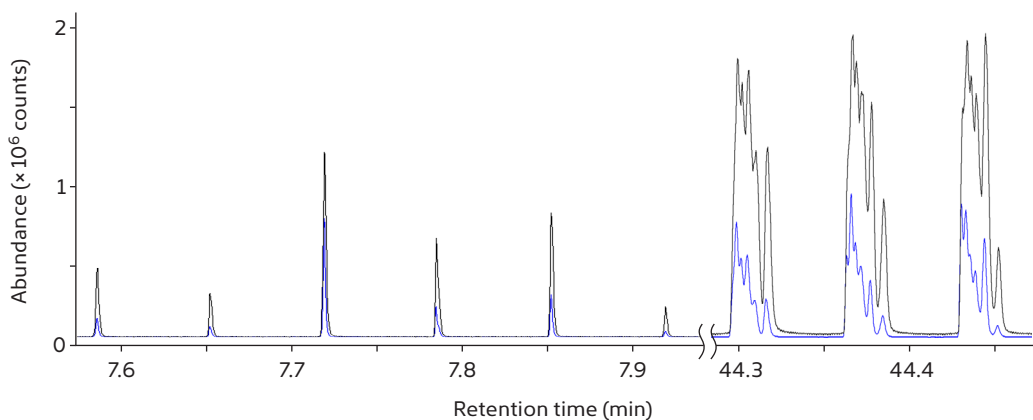


Figure 6

Overlays of the FID (blue) and TOF MS (black) linear traces, showing the excellent retention time alignment achieved throughout the run, using the INSIGHT modulator.

3. Improved isomer speciation using Tandem Ionisation

The use of simultaneous detection by TOF MS and FID provides a wealth of information for petrochemical analyses, but the challenge of identifying individual hydrocarbon isomers remains. At conventional 70 eV ionisation, the spectra of these isomers are virtually indistinguishable, meaning it is impossible to make confident assignments. Such identifications are of great importance to the petrochemical industry, because individual isomers can provide different characteristics to the final fuel (e.g. octane number, flash point and viscosity).

Addressing this challenge, the use of soft electron ionisation (EI) has been shown to provide increased confidence in the identification of branched alkanes,^[1] by providing enhancement of the molecular ion and other structurally-significant ions. A further advance in this area is Tandem Ionisation[®], which involves fast switching between conventional 70 eV ionisation and lower-energy 'soft' EI. This allows two complementary MS datasets to be simultaneously acquired, without impacting laboratory workflow and with perfectly aligned peaks for easy navigation of the soft EI data.

Figure 7 shows the speciation of three hydrocarbon isomers using soft EI. The 14 eV spectra exhibit clear spectral differences that enable confident identification – which would not have been achievable based solely on 70 eV analyses.

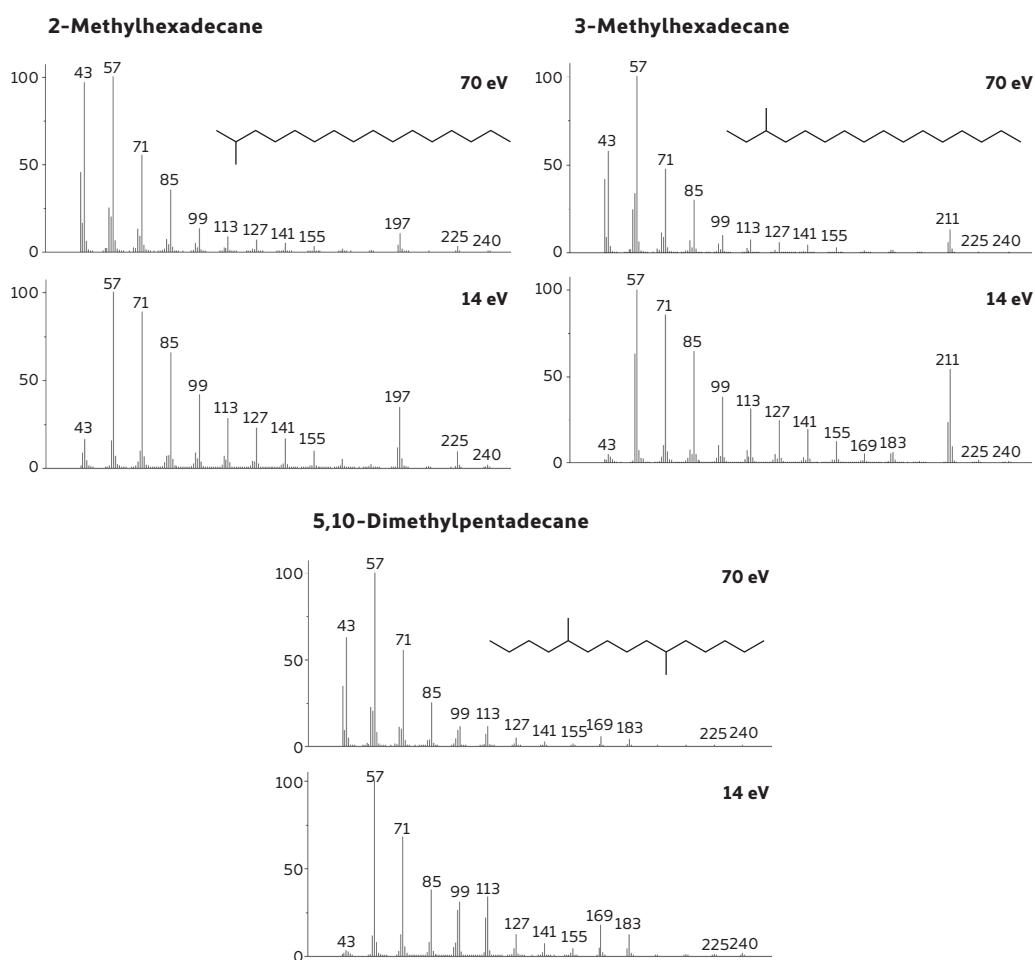


Figure 7

Spectral comparisons at 70 eV and 14 eV for three hydrocarbon isomers.

Conclusions

This study has illustrated the power of flow-modulated GC×GC to provide structured chromatograms that greatly simplify the process of compound identification, as well as the ability of the INSIGHT™ flow modulator to provide robust, repeatable analysis of petrochemicals, without the inconvenience or running costs associated with thermal modulation. In addition, the excellent retention-time repeatability in both dimensions enables fast and confident data processing of large sample batches, while the retention-time alignment between FID and TOF MS during parallel detection enables two-fold validation of measured peaks.

The analytical approach detailed here has also been shown to push the boundaries of hyphenated systems by providing three information-rich datasets per acquisition – namely, robust quantitation by FID, untargeted screening by TOF MS with electron ionisation (EI) at 70 eV, and confirmatory identification by TOF MS with soft EI.

For more information on this application, or any of the techniques or products used, please contact SepSolve.

References

- [1] M.S. Alam, C. Stark and R.M. Harrison, Using variable ionisation energy time-of-flight mass spectrometry with comprehensive GC×GC to identify isomeric species, *Analytical Chemistry*, 2016, 88: 4211–4220, <http://dx.doi.org/10.1021/acs.analchem.5b03122>.

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