White Paper 056
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Characterising complex petrochemicals using the enhanced peak capacity of GC×GC–FID with thermal modulation

In this white paper, we demonstrate the performance of the INSIGHT-Thermal modulator for the characterisation of various petrochemicals – including diesel, crude oil and vacuum gas oil – with enhanced peak capacity, streamlined control and ramped cold jet flows to accommodate high boilers (C_{50+}).

Introduction

The analysis of petrochemicals presents unique challenges due to the complexity and diversity of the hydrocarbon mixtures. The enhanced separation offered by comprehensive two-dimensional gas chromatography (GC×GC) tackles this challenge by combining two independent separations, for significantly improved chromatographic resolution compared to conventional GC.

Both flow and thermal modulation have been used successfully in petrochemical applications, but thermal modulation is known as the gold standard for peak capacity in GC×GC due to the refocusing effect of the cold jet and the resulting narrow peak widths achieved. Unfortunately, thermal modulators have also earned a reputation as being more challenging for routine use, as cold jets can be prone to suffer from icicle formation during unattended analysis. Additionally, it has been reported in the literature that excessive cold jet flow rates can cause irreversible trapping of analytes $>C_{26}$.[1]

In this study, we demonstrate the performance of a new thermal modulator designed to address these challenges. INSIGHT®-Thermal is a cryogen-free thermal modulator using delay loop operation, with full jet control integrated into the ChromSpace® software platform. The use of ramped cold jet flow rates ensures efficient release of higher-boiling compounds (C_{50+}), while a minimal standby flow (0.5 L/min) to the cold jet enables confident, unattended analysis by eliminating the use of excessive flow rates between runs or sequences which can lead to icicle formation.

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We showcase the power of GC×GC–FID using the INSIGHT-Thermal modulator for the analysis of various petrochemicals, to help provide the level of detail required for product quality assessment, environmental impact evaluation, and process optimisation within the petrochemical industry.

Experimental

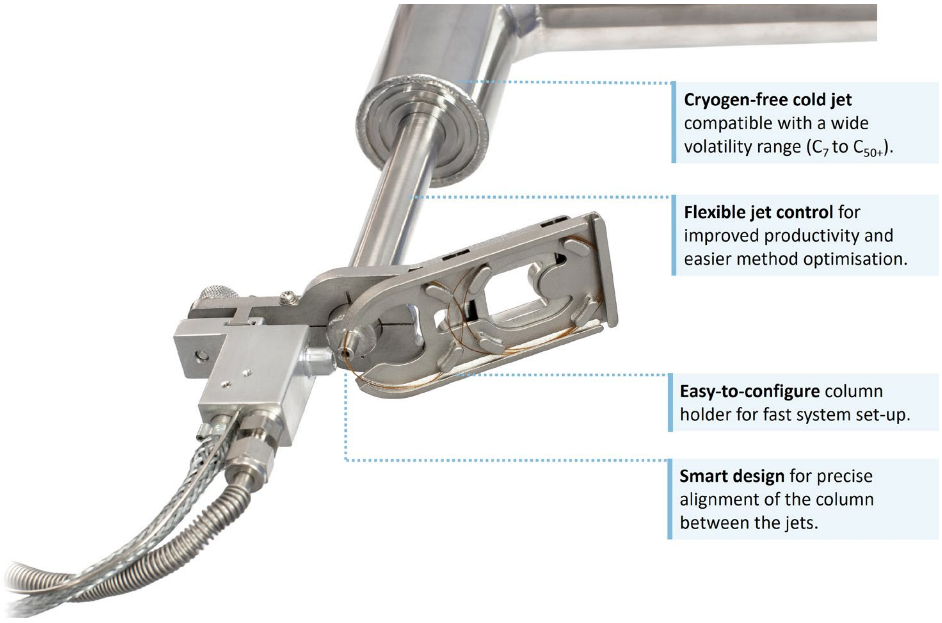

Figure 1

The INSIGHT-Thermal modulator for GC×GC.

Samples: Diesel, light crude oil and vacuum gas oil (VGO).

GC×GC: INSIGHT®-Thermal modulator (SepSolve Analytical); Carrier gas: H_2; Jet gas: Nitrogen (Note: either nitrogen or air can be used to supply the jets).

FID: Temperature: 250°C; Air flow: 350 mL/min; H_2 fuel flow: 35 mL/min; Acquisition rate: 200 Hz.

Software: ChromSpace® software (SepSolve Analytical) for full instrument control and data processing.

Please contact SepSolve for full analytical parameters.

Results and discussion

To demonstrate the performance of the INSIGHT-Thermal modulator for GC×GC, various petrochemical samples were analysed under a range of operating conditions.

Initially, a 'reverse phase' (polar/non-polar) column configuration was used for the analysis of a crude oil and a vacuum gas oil (Figures 2 and 3, respectively).

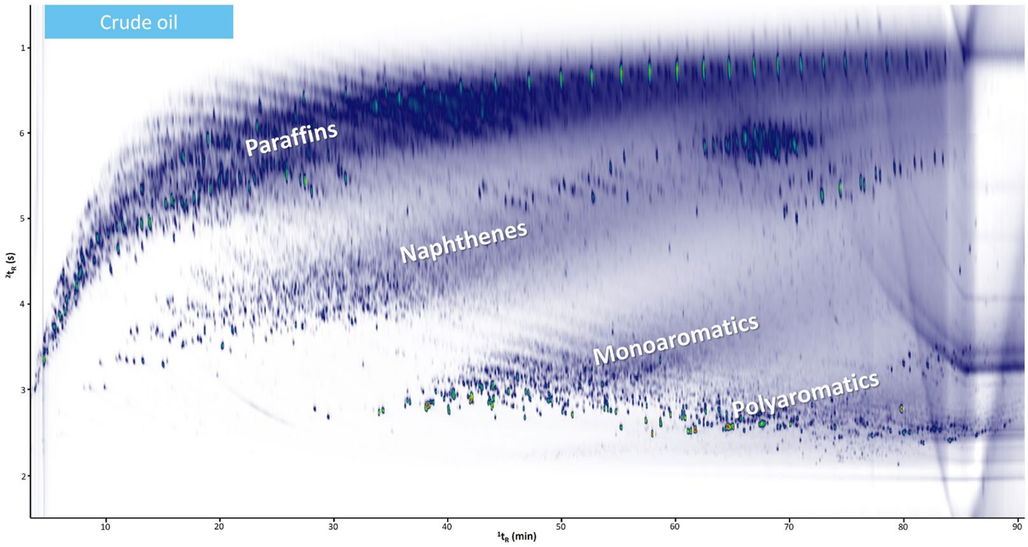

Figure 2

Reverse phase (polar/non-polar) separation of a crude oil using GC×GC–FID, with key chemical classes annotated.

The method parameters were optimised to ensure maximum peak capacity was achieved – which is clearly evident in the distinct class separation observed for the crude oil (Figure 2). Thermal modulators, such as the INSIGHT-Thermal, provide the peak capacity required for detailed characterisation of samples with such extreme complexity.

Both the crude oil and vacuum gas oil also exhibited wide volatility ranges that required additional optimisation of jet parameters. The cold jet flow rate must be high enough to provide sufficient trapping of the more volatile species (C_{10}-C_{15}), but low enough to prevent irreversible trapping of the less volatile species (>C_{26}) - this was achieved by applying a linear ramp to gradually decrease the cold jet flow rate throughout the run.

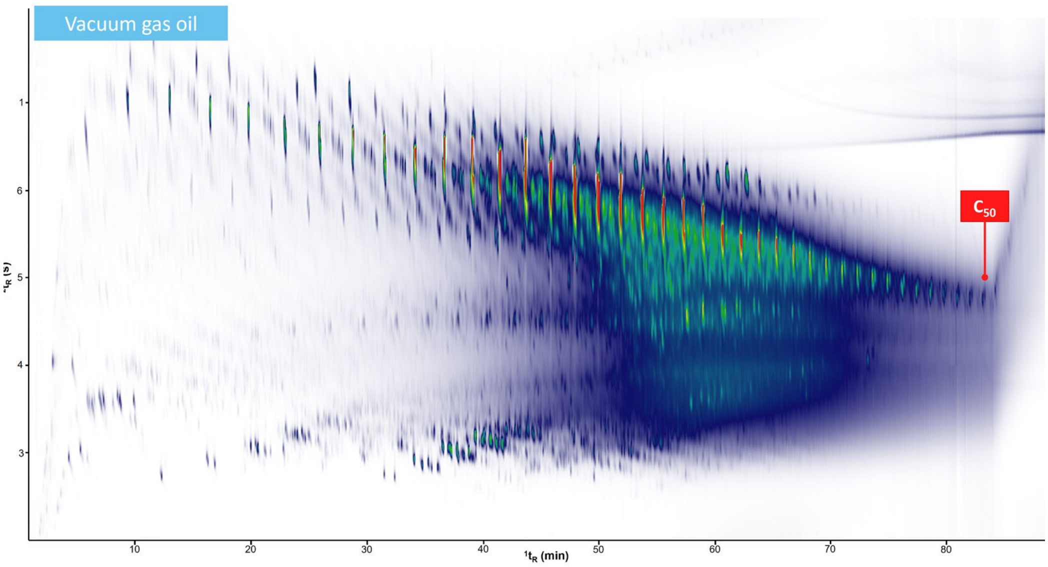

Figure 3

Reverse phase (polar/non-polar) separation of a vacuum gas oil using GC×GC–FID, highlighting efficient modulation of semi-volatiles (C_{50+}).

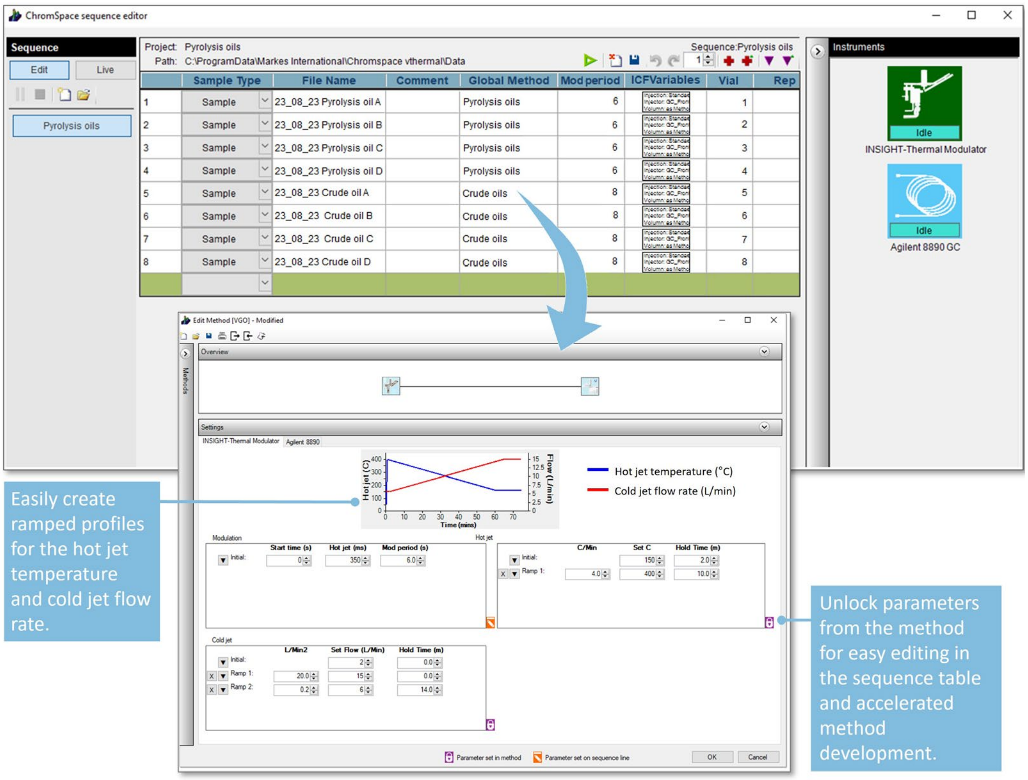

Figure 4

An acquisition sequence and method in ChromSpace showing full instrument control and flexible jet settings, with unlockable parameters that can be easily edited within the sequence.

The results of using such ramped flow rates are clear in Figure 3, where efficient modulation of C_{50} has been achieved for the vacuum gas oil. Analytes >C_{50} can be seen in the isothermal ramp, so it is expected that with a column phase compatible with higher temperatures, the volatility range could be extended even further.

This flexibility in jet control is integrated into the ChromSpace software platform (as shown in the method parameters in Figure 4). The ability to control all jet parameters in named methods means that sequences can be left to run unattended, accelerating the method development process. Additionally, the use of a default standby flow of just 0.5 L/min prevents the formation of icicles at the cold jet throughout such sequences.

Finally, a diesel sample was analysed using a 'normal phase' (or non-polar/polar) column set, as shown in Figure 5 (top). Thanks to the 'roof-tiling' effect of GC×GC, structurally similar compounds elute together in well-defined bands, enabling simple group-type reporting of composition; in this case, using the Stencils tool in ChromSpace.

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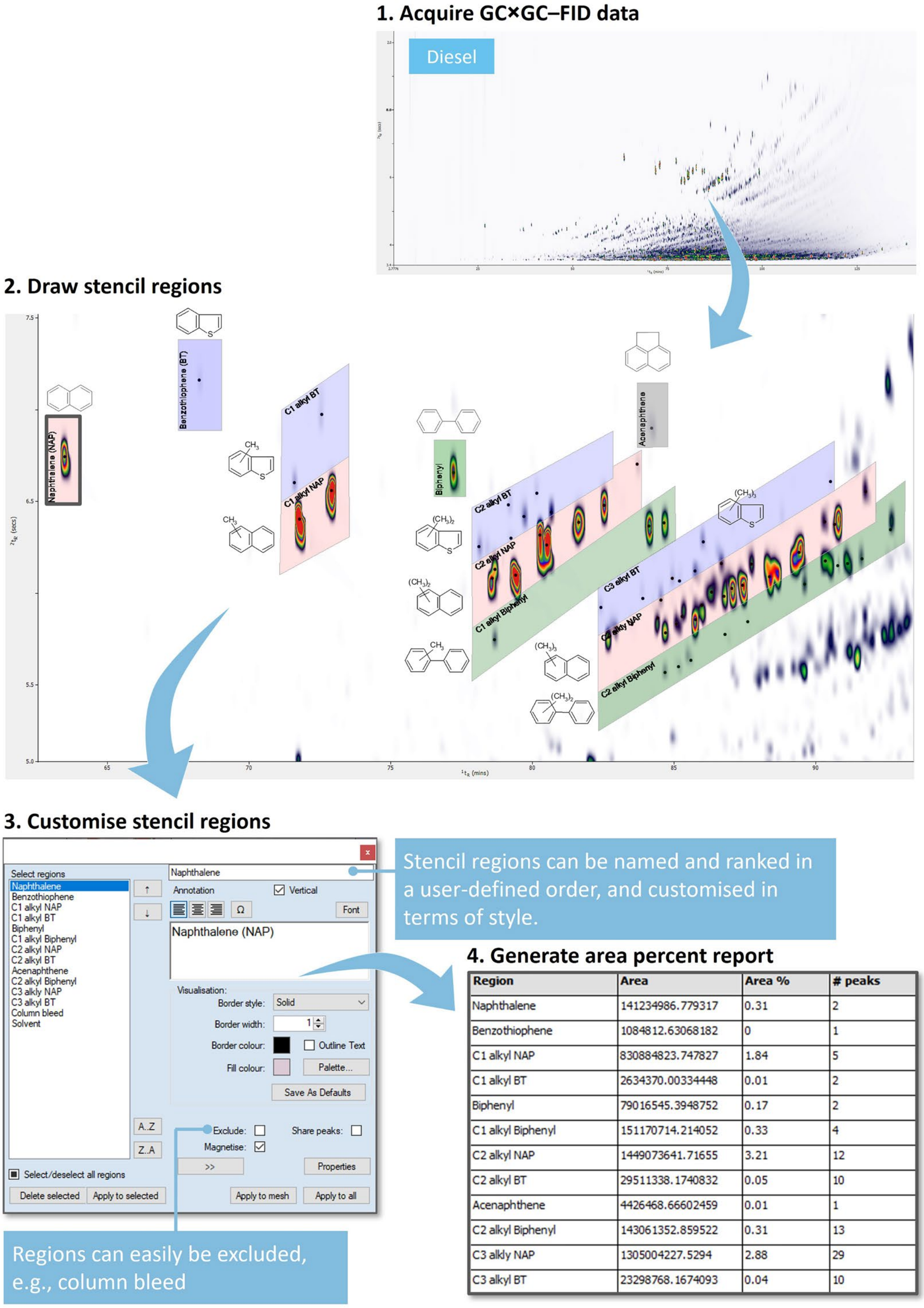

Region	Area	Area %	# peaks
Naphthalene	141234986.779317	0.31	2
Benzothiophene	1084812.63068182	0	1
C1 alkyl NAP	830884823.747827	1.84	5
C1 alkyl BT	2634370.00334448	0.01	2
Biphenyl	79016545.3948752	0.17	2
C1 alkyl Biphenyl	151170714.214052	0.33	4
C2 alkyl NAP	1449073641.71655	3.21	12
C2 alkyl BT	29511338.1740832	0.05	10
Acenaphthene	4426468.66602459	0.01	1
C2 alkyl Biphenyl	143061352.859522	0.31	13
C3 alkly NAP	1305004227.5294	2.88	29
C3 alkyl BT	23298768.1674093	0.04	10

Figure 5

Normal phase (non-polar/polar) separation of diesel using GC×GC–FID, with an example of the group-type analysis workflow in ChromSpace software.

Stencil regions are easily drawn around the target class (Figure 5, middle), altered to the desired shape, and can be connected in contiguous meshes to ensure no areas of the chromatograms are overlooked. Additionally, interferences, such as solvent or column bleed, can be excluded using the tool. Once all regions have been drawn and customised, the complete stencil can be saved and applied to numerous samples in a batch process to generate area percent reports automatically.

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Importantly, in this process, integration is carried out by summing the areas of peaks that have apexes within each region (even if they have tails that extend outside of the boundary) meaning that they do not have to be precisely drawn around each individual peak. This information is then translated into an area percent table that allows a fast overview of sample composition.

Conclusions

In this white paper we have shown that GC×GC–FID using the INSIGHT-Thermal modulator provides unparalleled peak capacity and productivity for group-type characterisation of complex petrochemicals, specifically:

- Ramped cold jet flow rates ensure the efficient release of higher boiling point compounds (C_{50+}), while a minimal standby flow rate (0.5 L/min) enables confident, unattended analysis.
- Fully integrated instrument control within ChromSpace software simplifies operation and accelerates method development.
- Automated group-type analysis using stencil regions provides fast reporting of sample composition.
- Smart column holder design* ensures precise alignment of the column between the hot and cold jets and simplifies system set-up.
- Low running costs are possible with cryogen-free operation, compatibility with hydrogen carrier gas and ability to use either nitrogen or air to supply the jets.
- A platform-neutral design allows existing GC systems to be upgraded to GC×GC capability.

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

References

[1] R.B. Gaines and G.S. Frysinger, Temperature requirements for thermal modulation in comprehensive two-dimensional gas chromatography, *Journal of Separation Science*, 2004, 27: 380–388, https://doi.org/10.1002/jssc.200301651.

* Patent pending

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