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Fast and efficient group-type (PiPNA) classification of jet fuels

This study demonstrates the performance of flow-modulated GC×GC for robust group-type characterisation of jet fuels, with quantitative analysis by flame ionisation detection (FID) and confident identification of trace-level contaminants by mass spectrometry.

Introduction

Jet fuels typically consist of simple blends of different kerosene streams – such as straight run kerosene from the crude tower, hydrotreated kerosene and hydrocracked kerosene.[1] Kerosene is known as a middle distillate, typically in the range of C_9 to C_{16} hydrocarbons, but the precise composition will be dependent on the original crude oil from which it was derived.

Fuels, like kerosene, are among the most complex of samples to be analysed by gas chromatography, typically containing thousands of individual components that result in an unresolved hump in a 1D GC chromatogram. Therefore, their analysis is now typically performed by two-dimensional GC (or GC×GC) for enhanced separation in a realistic run time.

However, in petrochemical analyses, it is not necessary nor even possible to identify every individual component – rather, the responses for key chemical classes are summed, in what is known as group-type analysis. Most commonly, this follows 'PiPNA' classification, whereby the Paraffins, iso-Paraffins, Naphthenes and Aromatics are reported and other compound classes, like olefins, are either known or assumed to be unrepresented in the sample.

In this study, we will demonstrate the use of a flow-modulated GC×GC system for group-type (PiPNA) classification of jet fuels. We will also show the added value of parallel detection by FID and TOF MS. FID is the gold standard for the petrochemical industry, providing robust quantitative analysis. TOF MS ensures accurate group-type boundaries are delineated while allowing for identification of trace adulterants or contaminants, such as sulfur species.

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Experimental

Samples: Three jet fuel samples – straight run kerosene, hydrotreated kerosene and hydrocracked kerosene.

GC×GC: Modulator: INSIGHT® flow modulator (SepSolve Analytical); Modulation period (P_M): 8 s. Parallel detection to FID and TOF MS.

FID: H_2 flow: 30 mL/min; Air flow: 300 mL/min; Temperature: 300°C.

TOF MS: Instrument: BenchTOF-Select™; Mass range: m/z 45–600; Acquisition speed: 100 Hz in Tandem Ionisation® mode for simultaneous 70 eV and 12 eV ionisation.

Software: ChromSpace® GC×GC software for full instrument control and data processing.

Please contact SepSolve for full analytical parameters.

Results

Separation by GC×GC–FID/TOF MS

In this study, a reversed-phase column configuration was used to provide necessary separation of the key chemical classes. The reverse fill/flush (RFF) action of the INSIGHT modulator ensures excellent peak shape and high peak capacity are achieved. During method development, the bleed line can even be monitored by connecting to a second FID to ensure that the loop is not overfilled and that a truly 'comprehensive' method is adopted. The GC×GC–FID surface charts for the three kerosene jet fuels are provided in Figure 1 and highlight key differences in sample composition – most significantly, the increased diaromatic content of the straight run kerosene compared to the hydrocracked and hydrotreated versions.

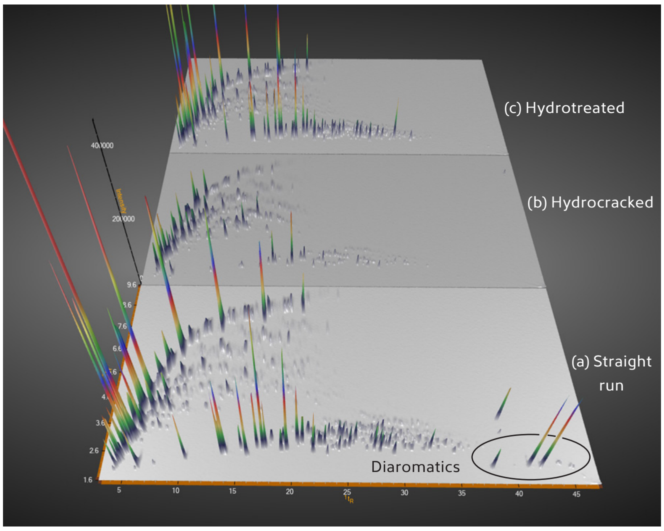

Figure 1

GC×GC–FID surface charts for the three jet fuels analysed in this study: (a) straight run, (b) hydrocracked and (c) hydrotreated kerosene.

Group-type PiPNA classification

Group-type analysis of the paraffins, iso-paraffins, naphthenes and aromatics (PiPNA) was performed using the ChromSpace software platform. ChromSpace enables both the FID and TOF MS data to be opened simultaneously, meaning that the mass spectral data can be used to draw precise boundaries ('stencils') around the classes of interest.

The stencils are simple to use and flexible, and enable user preferences and custom styles to be adopted easily. Figure 2 shows the PiPNA stencil developed in this study, as applied to the straight run kerosene.

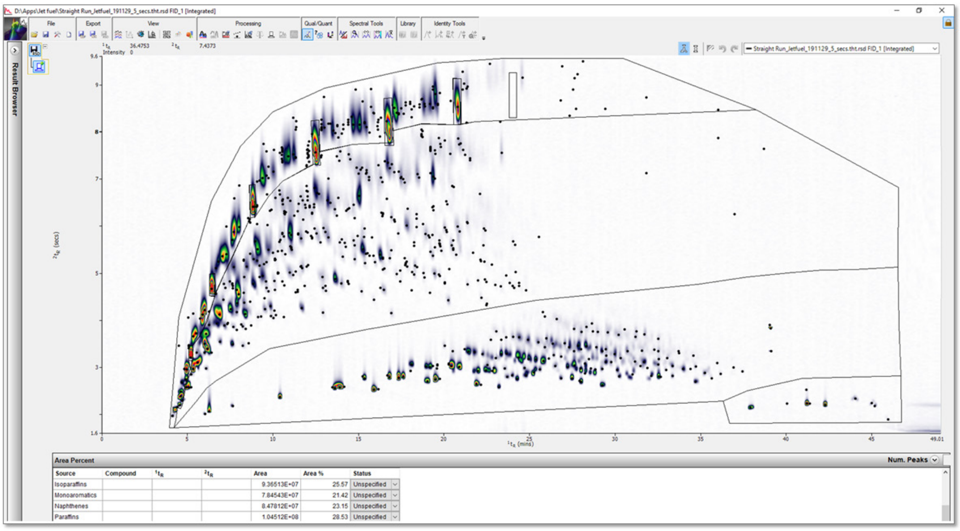

Figure 2

The completed PiPNA stencil applied to the GC×GC–FID colour plot for the straight run kerosene.

Once a stencil is created, it can be saved and applied to multiple data files in an automated batch process to generate area percent reports. This means that the method is then scalable across multiple GCxGC–FID platforms for fast PiPNA classification. In fact, a dual-channel GCxGC–FID configuration can even be adopted to double throughput. A comparison of the area percent values found using the PiPNA stencil for the three jet fuels is provided in Table 1. The chart in Figure 3 highlights the differences in total peak areas for the PiPNA groups across the three samples. The straight run and hydrotreated kerosene have similar compositions, but the hydrocracked kerosene shows a significant increase in the class, potentially from hydrogenation of aromatics to naphthenes during the hydrocracking process.

Group	Area %		
	Straight run	Hydrotreated	Hydrocracked
Paraffins	28.47	29.85	7.53
iso-Paraffins	24.57	25.53	23.84
Naphthenes	23.75	26.69	58.57
Aromatics	23.23	17.93	10.05
Monoaromatics	21.80	17.80	9.80
Diaromatics	1.43	0.13	0.25

Table 1

PiPNA characterisation of three jet fuels.

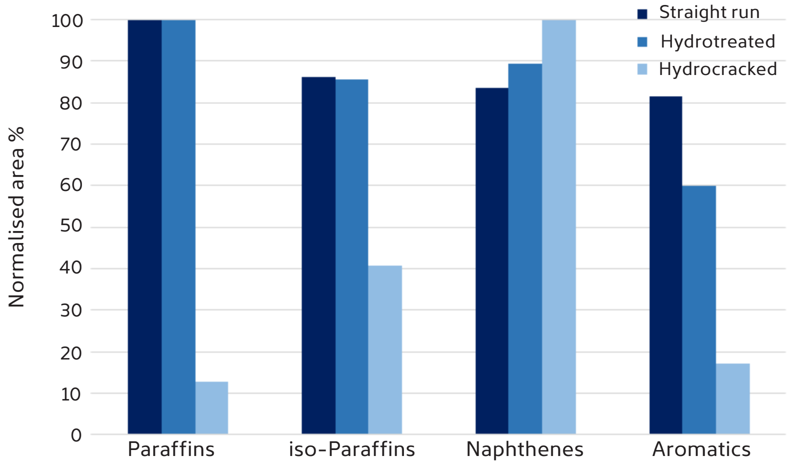

Figure 3

Comparison of the total peak areas for the PiPNA groups across the three kerosene jet fuels.

Identification of trace contaminants

The complexity of jet fuels often makes it a challenge to identify trace adulterants or undesirable components such as sulfur-containing aromatics, which are known to corrode processing pipelines, cause catalyst poisoning and impact product odour.[2]

In this case, the use of parallel detection is imperative, as these trace components typically elute in bands overlapping with the equivalent PAHs and cannot be distinguished by FID alone. Figure 4 shows how scripting in ChromSpace can easily extract trace benzothiophenes from this complex sample using spectral data from BenchTOF. The inset highlights the trace nature of these alkyl benzothiophenes, which are hidden in the baseline of the TIC and have an intensity at least three orders of magnitude lower than the closely-eluting alkyl naphthalenes. It is also worth noting that these sulfur species were not detected in the hydrocracked or hydrotreated kerosenes.

GC×GC with parallel detection by FID and TOF MS ensures that both robust PiPNA classification and identification of trace contaminants can be performed simultaneously on a single platform.

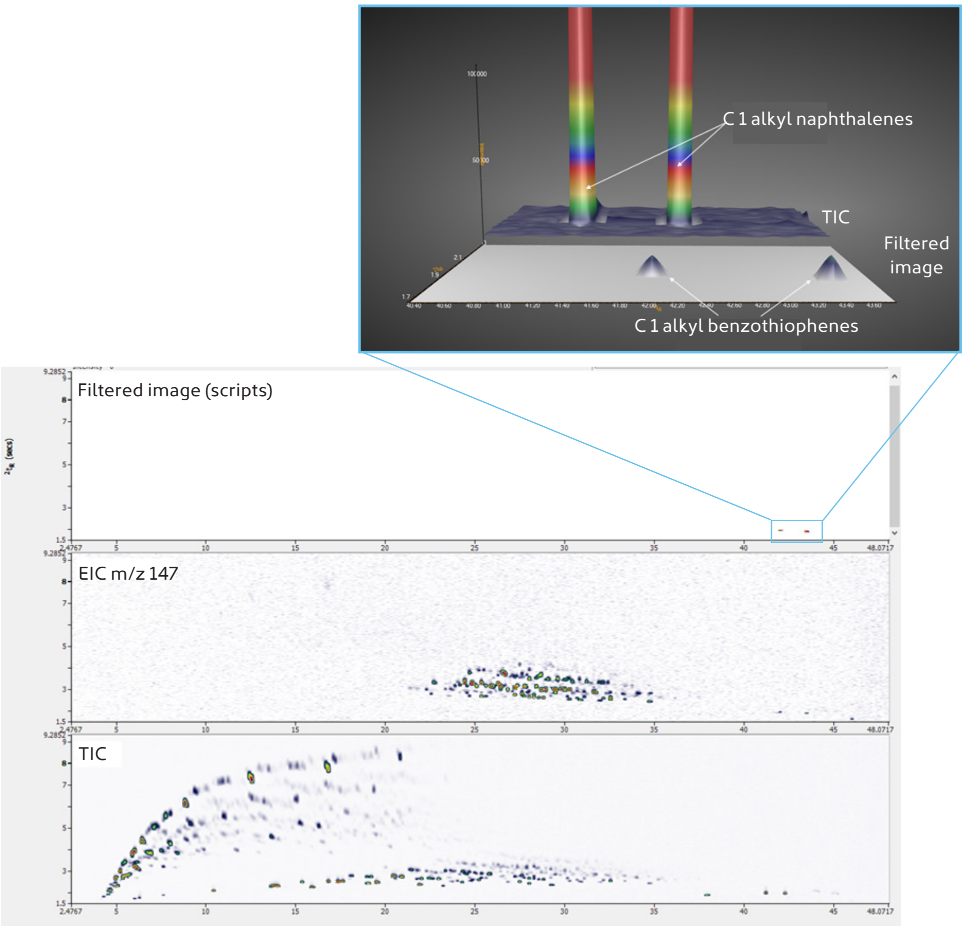

Figure 4

Identification of benzothiophenes in the straight run oil using ChromSpace scripting.

Conclusions

This study has shown:

- Increased separation of the target chemical classes for fast and efficient PiPNA classification by GC×GC–FID.
- Cryogen-free, repeatable GC×GC using the INSIGHT flow modulator.
- Dual-channel GCxGC–FID boosts productivity for PiPNA classification.
- Robust performance from a low maintenance system well-suited to routine applications.
- The addition of parallel detection by TOF MS provides improved precision of group boundaries and confident identification of trace contaminants, such as sulfur species.
- Automated processing workflows with fast and efficient group-type analysis using stencils in ChromSpace.

References

[1] J.G. Speight, *Handbook of Petroleum Product Analysis*, John Wiley & Sons, 2015, p. 127.

[2] A.H. Hegazi and J.T. Andersson, Polycyclic aromatic sulfur heterocycles as source diagnostics of petroleum pollutants in the marine environment, in *Standard Handbook Oil Spill Environmental Forensics*, S. Stout and Z. Wang (eds), Academic Press, 2016.

Applications were performed under the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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