

## Application Note 505<sup>†</sup>

# Fingerprinting of crude oil by GC×GC–TOF MS

### Summary

This study demonstrates that GC×GC in conjunction with the BenchTOF time-of-flight mass spectrometer allows the high-resolution analysis of a complex crude oil distillate. In particular, we show how the ability to generate 'classical' spectra aids the confident identification of compounds used as petrochemical markers.



### Introduction

Crude oil contains vast numbers of organic compounds ranging from light hydrocarbons to complex biomolecules. The compounds of most interest to the petroleum industry are relatively volatile (boiling points generally below 400 °C) and non-polar, so separations are predominantly performed by GC using a non-polar column. The resulting chromatograms are highly convoluted, and usually characterised by a matrix of unresolved material that appears as a significant background 'hump' beneath the partially resolved non-polar compound peaks.

Although methods involving background subtraction and/or library searching can help in such cases, the only way of obtaining a thorough understanding of the oil sample's constituents is to subject it to two-dimensional chromatography<sup>1,2</sup>. This is becoming increasingly important as the more easily extracted 'light' crude oils become depleted, and oil companies move to reservoirs containing 'heavier' crudes, bituminous shales and tar sands, with their higher proportions of involatile polar compounds.

This Application Note illustrates the separating power of GC×GC, and how use of a BenchTOF instrument as the detector provides information-rich datasets that greatly simplify the process of compound identification.

### Background to BenchTOF instruments

Several of the key features of Markes' BenchTOF<sup>™</sup> instruments make them particularly appropriate for the GC×GC analysis of complex samples such as petrochemicals. These include:

- **Sensitivity:** Highly efficient direct-extraction technology allows BenchTOF instruments to acquire full-range spectra with SIM-like sensitivity, allowing them to reliably detect trace-level analytes in a single run, which would be difficult or impossible on a quadrupole system.
- **Selectivity:** Sub-unit mass resolution allows selective elimination of interferences, dramatic improvement of signal-to-noise ratios, and discrimination between hydrocarbons, which can have very similar mass spectra.
- **Spectral quality:** The 'reference-quality' spectra produced by BenchTOF are a close match for those in commercial libraries such as NIST or Wiley. This enables quick and confident matching of both targets and unknowns. BenchTOF instruments are also particularly good at maintaining the correct abundance of higher-mass ions (including the molecular ion), greatly aiding the identification of hydrocarbons.
- **Speed:** The ability to record full-range mass spectral information to extremely high densities (10,000 transient spectral accumulations per second) enables BenchTOF to handle the narrowest peaks encountered in well-optimised GC×GC couplings. The high stored-to-disk data rate also enables advanced spectral deconvolution and 'data-mining' algorithms to extract maximum information from weak, matrix-masked signals.

The high-definition mass spectrometry delivered by this combination of features makes BenchTOF instruments ideal for the most demanding GC×GC applications, as demonstrated in this work.

<sup>†</sup> Formerly ALMSCO Application Note 005.



## Experimental

GC×GC separations were conducted using a conventional apolar–polar column set, using a 10 mg/mL dilution of crude oil in dichloromethane.

### GC:

Injector: Split/splitless  
 Liner: 4.0 mm i.d. liner, 1 µL injection  
 Carrier gas: He, constant flow at 1.0 mL/min  
 Mode: Split  
 Temperature: 250 °C  
 Septum purge: On, 3 mL/min

### Column set:

1st dimension: SGE BPX5, 30 m × 0.25 mm × 0.25 µm  
 2nd dimension: SGE BPX50, 4 m × 0.1 mm × 0.1 µm  
 Modulation loop: As for 2nd dimension  
 Column set: Equivalent pneumatic impedance to 50 m × 0.18 mm (calculated from K factor look-up charts for 1st- and 2nd-dimension columns used)

### Temperature programme:

Main oven: 40 °C (1.0 min), 2.5 °C/min to 350 °C (15 min)

Secondary oven: 60 °C (1.0 min), 2.5 °C/min to 150 °C (0 min), 2.9 °C/min to 350 °C (hold time matched to total run time)  
 Hot jet: 150 °C (1.0 min), 2.5 °C/min to 400 °C (hold time matched to total run time)  
 Cold jet: Dewar fill: high, 50%; low, 40%  
 Modulation period: 10 s, hot-jet pulse 400 ms  
 Total run time: 140 min

### TOF MS:

Instrument: BenchTOF (Markes International)  
 Filament voltage: 1.8 V  
 Ion source: 280 °C  
 Transfer line: 310 °C  
 Mass range: m/z 40–600  
 Data rate: 50 Hz (200 spectral accumulations per data point)

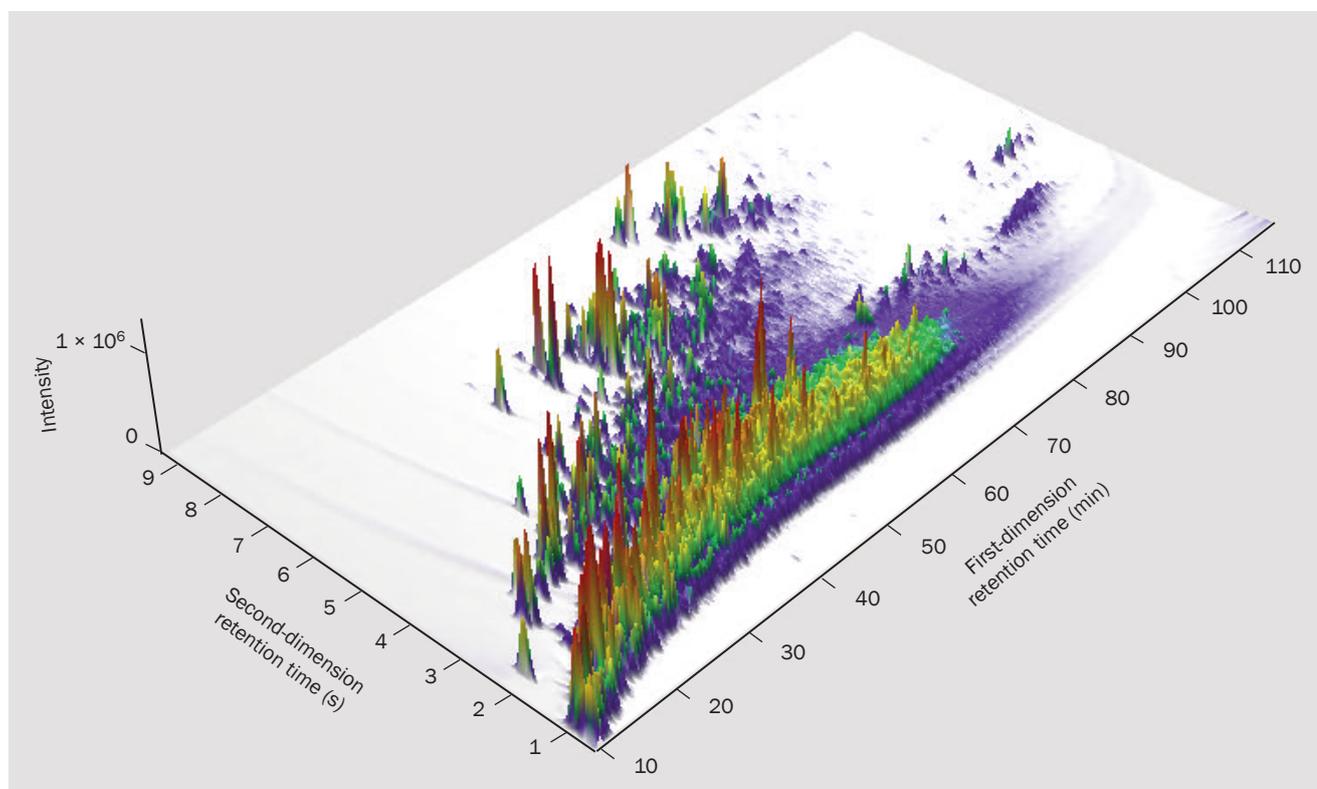
### Software:

Image processing: GC Image™ (GC Image, LLC)

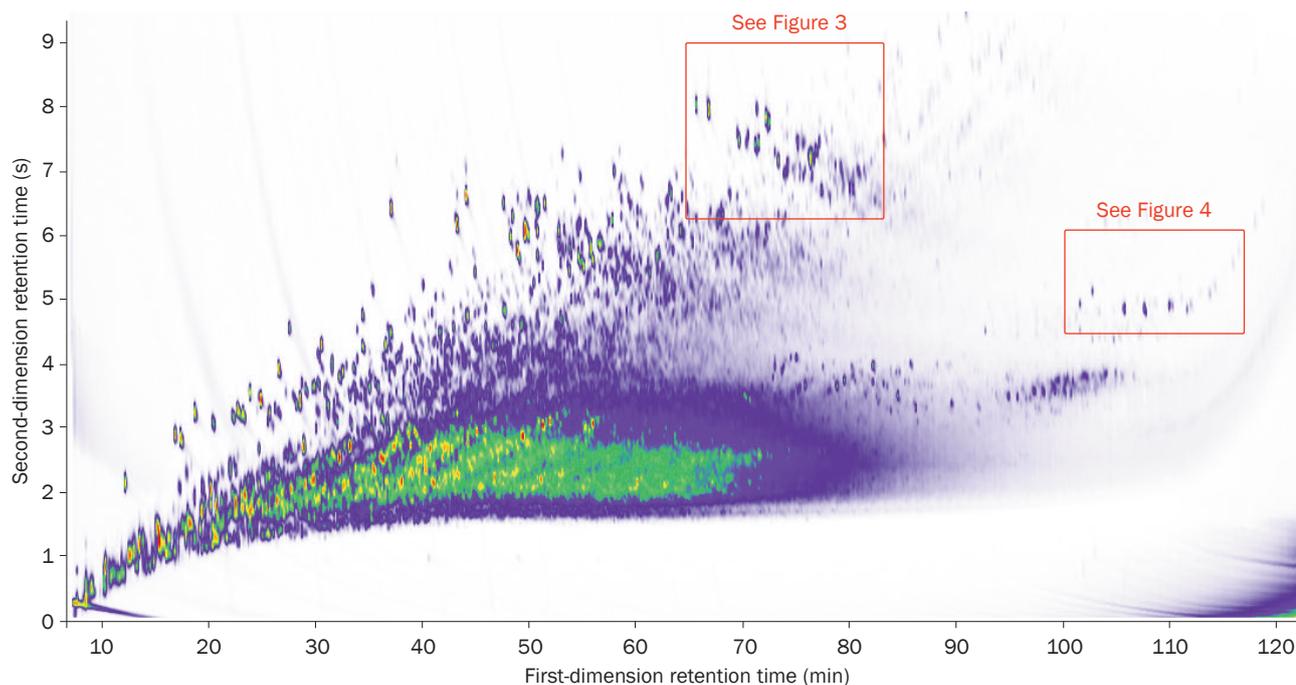
## Results and discussion

Figure 1 shows a 3D surface plot of a GC×GC separation of a crude oil. The increased resolution resulting from separation in two dimensions allows the visualisation of compound peaks that would have co-eluted in a one-dimensional setup.

The GC×GC separation shown in Figure 1 can also be represented by a 2D contour plot (Figure 2).



**Figure 1:** 3D surface plot of a GC×GC separation of crude oil.

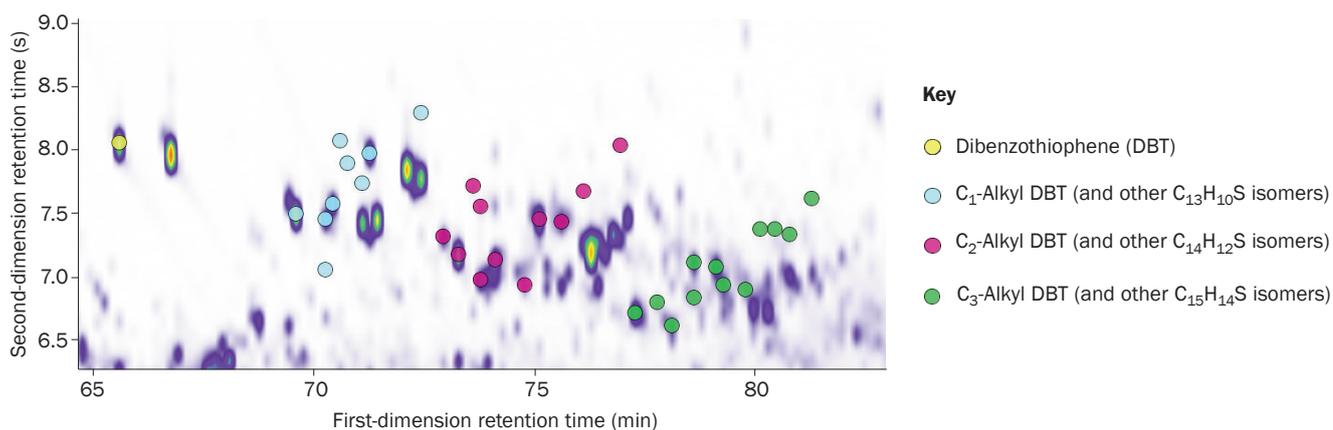


**Figure 2:** 2D contour plot of a GCxGC separation of crude oil (the same sample as shown in Figure 1). The boxes indicate the areas expanded in Figures 3 and 4.

### Identification of dibenzothiophenes

The *GC Image* software used here is set to automatically detect compound peaks and flag them up as 'blobs'. Filtering of these blobs can be performed using simple generic templates that make use of chromatographic and mass spectral expressions, using Computer Language for the Identification of Chemicals (CLIC)<sup>3</sup>. This allows classification of the compounds according to structural features, vastly reducing data processing time.

Sulfur compounds can cause corrosion of refinery equipment or deactivation of refinery catalysts, and so it is important that they are reliably characterised in crude oils<sup>4</sup>. Figure 3 illustrates this for the dibenzothiophenes (three-ring sulfur-containing heterocycles), which were distinguished from other closely-eluting aromatic compounds using characteristic mass spectral qualifiers.



**Figure 3:** Expansion of Figure 2 showing identification of sulfur-containing three-ring heterocycles.

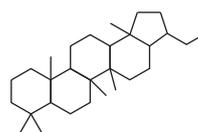
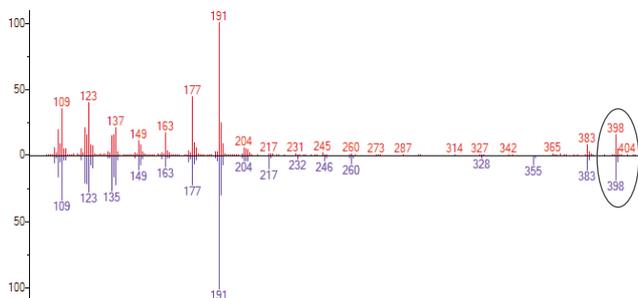
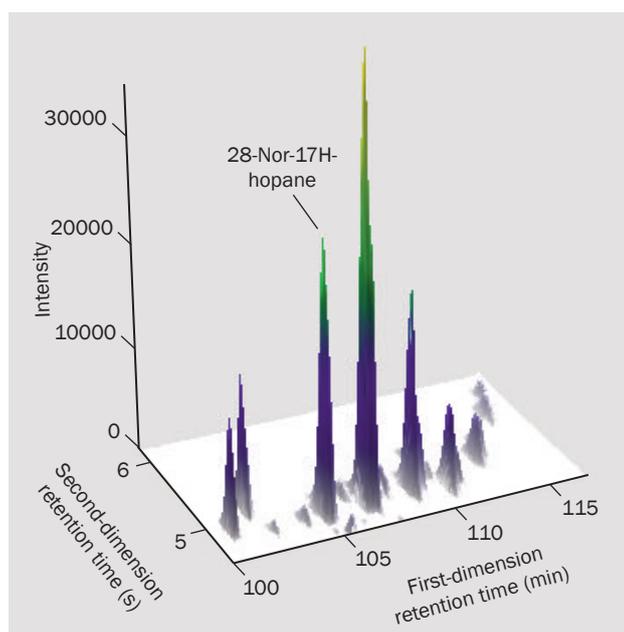
### Detection of oil 'markers'

Hopanes are a class of compounds widely used as markers for characterisation of oil, and the ability to analyse them in a single run with minimal sample preparation is clearly advantageous. An extracted-ion chromatogram for  $m/z$  191 displays the hopanes as highly resolved peaks (Figure 4). Transmission of these high-boiling components as sharp peaks proves that a uniform thermal path exists between the GC oven and ion source, resulting in no analyte recovery issues.

The spectra obtained included accurate representations up to  $C_{34}$ , and possessed molecular ions of correct abundance

relative to their common base peak ( $m/z$  191). This, and the generation of classical spectra, enabled confident identification of the individual hopanes using the NIST mass spectral library.

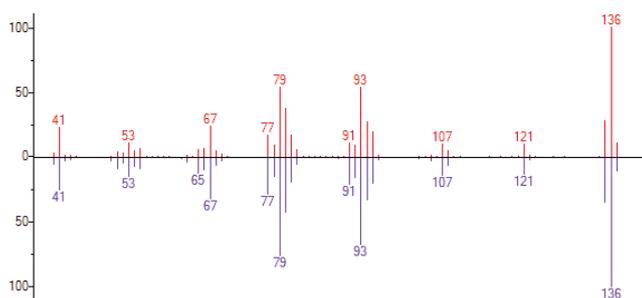
Diamondoids are cage-like hydrocarbons that, unlike the high-MW hopanes and steranes, are not removed during the refining process. As a result they are found in most petroleum products, and have been considered as a diagnostic tool for the environmental forensic investigation of oil spills<sup>5</sup>. The mass spectral library matches for two such compounds are provided in Figure 5, and again demonstrate the ability of BenchTOF instruments to provide mass spectra matching those in commercial libraries.



**28-Nor-17H-hopane**

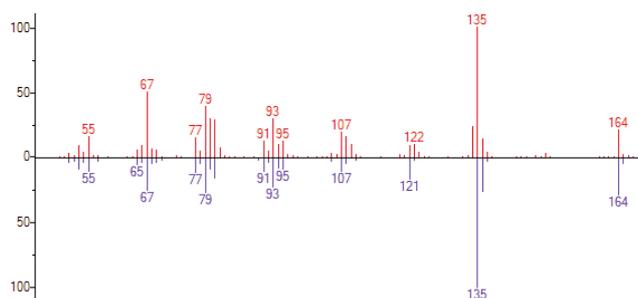
Forward match 825  
Reverse match 874  
Probability 57.8%

**Figure 4:** 3D expansion of Figure 2 showing the  $m/z$  191 extracted-ion chromatogram for the  $C_{27}$ - $C_{34}$  hopanes, and comparison of the obtained mass spectrum of a  $C_{29}$  hopane (top, red) with that in the NIST database (bottom, blue). Note the preservation of the molecular ion (circled).



**Adamantane**

Forward match 949  
Reverse match 955  
Probability 74.4%



**2-Ethyladamantane**

Forward match 790  
Reverse match 875  
Probability 15.6%

**Figure 5:** Comparison of the obtained mass spectra of two diamondoids (top, red) with those in the NIST database (bottom, blue).

## Conclusion

The ability of BenchTOF to produce 'reference-quality' spectra, combined with its high sampling frequency, makes it ideal for use with GC×GC, allowing the analyst to benefit from the resolving power of GC×GC without the need to develop TOF-specific spectral libraries.

Furthermore, the use of automated compound identification, in conjunction with the structural ordering of the GC×GC chromatogram, allows initial assignment of key compound classes at a glance.

## Acknowledgements

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## References

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## Trademarks

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