

### Application Note 516<sup>†</sup>

# The identification of hydrocarbons in highly complex petrochemical samples by GC×GC–TOF MS

## Summary

This Application Note shows that GC×GC–TOF MS provides a high-performance solution for analysing highly complex petrochemical products. In particular, the high degree of separation of GC×GC combined with the sensitivity of BenchTOF instruments maximises the number of compounds detected, while the production of ‘reference-quality’ spectra aids automated comparison against commercial spectral databases.



## Introduction

Precise characterisation of petrochemical samples is crucial for quality control, and also to understand the reactions that take place during refining processes.

Comprehensive two-dimensional gas chromatography (GC×GC) offers significant advantages over conventional chromatography for such analyses, with its vastly expanded separation space and the added benefit of highly structured groupings of compounds.

This Application Note aims to show that BenchTOF instruments are excellent detectors for use alongside GC×GC for the analysis of a complex diesel sample. In addition, we demonstrate that the GC×GC–TOF MS method can be easily transposed to FID to allow compound quantitation, as demanded by current best-practice in the petrochemical industry.

## Background to BenchTOF instruments

Markes’ BenchTOF™ instruments are particularly appropriate for the GC×GC analysis of complex samples such as petrochemicals, for the following reasons:

- **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.
- **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 applications, as demonstrated by this work.

## Experimental

A conventional apolar–polar column set with no secondary oven was used, as stipulated in Method UOP990.

### GC:

|               |  |
|---------------|--|
| Injector:     | Split/splitless, 4.0 mm i.d. liner, 0.1 µL injection TOF, 1 µL for FID |
| Carrier gas:  | He, constant flow at 1.0 mL/min  |
| Mode:         | Split  |
| Temperature:  | 280 °C   |
| Septum purge: | On, 3 mL/min   |

#### Column set:

1st dimension: Agilent HP-PONA, 50 m × 0.2 mm × 0.5 μm  
 2nd dimension: SGE SolGelWax, 2.5 m × 0.1 mm × 0.1 μm  
 Modulation loop: As for 2nd dimension  
 Column set: Equivalent pneumatic impedance to 59 m × 0.18 mm (calculated from K factor look-up charts for 1st- and 2nd-dimension columns)

#### FID:

Temperature: 280 °C  
 Hydrogen flow: 40 mL/min  
 Air flow: 500 mL/min  
 Make-up gas: N<sub>2</sub> (flow 25 mL/min)

#### Software:

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

#### Temperature programme:

Main oven: 60 °C (2.0 min), 1.5 °C/min to 153 °C (0 min), 2 °C/min to 280 °C (17.5 min) Not applicable  
 Secondary oven: Hot jet: 160 °C (2.0 min), 1.5 °C/min to 250 °C (0 min), 2 °C/min to 320 °C (hold time matched to total run time)  
 Cold jet: Modulation period: Dewar fill: high, 60%; low, 50%  
 Total run time: 8 s, hot-jet pulse 350 ms  
 145 min

#### MS:

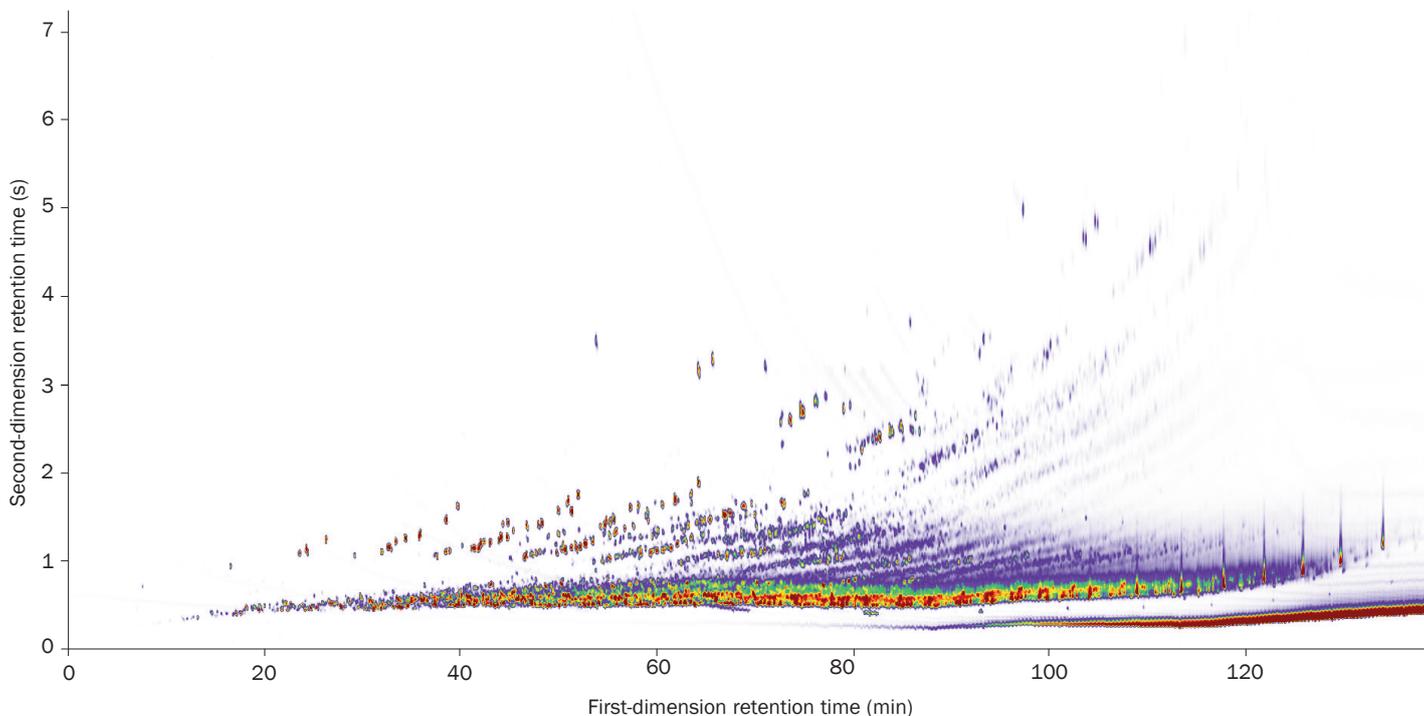
Instrument: BenchTOF (Markes International) 280 °C  
 Ion source: Transfer 285 °C  
 line: Mass range: m/z 40–400  
 Data rate: 50 Hz (200 spectral accumulations per data point)

## Results and discussion

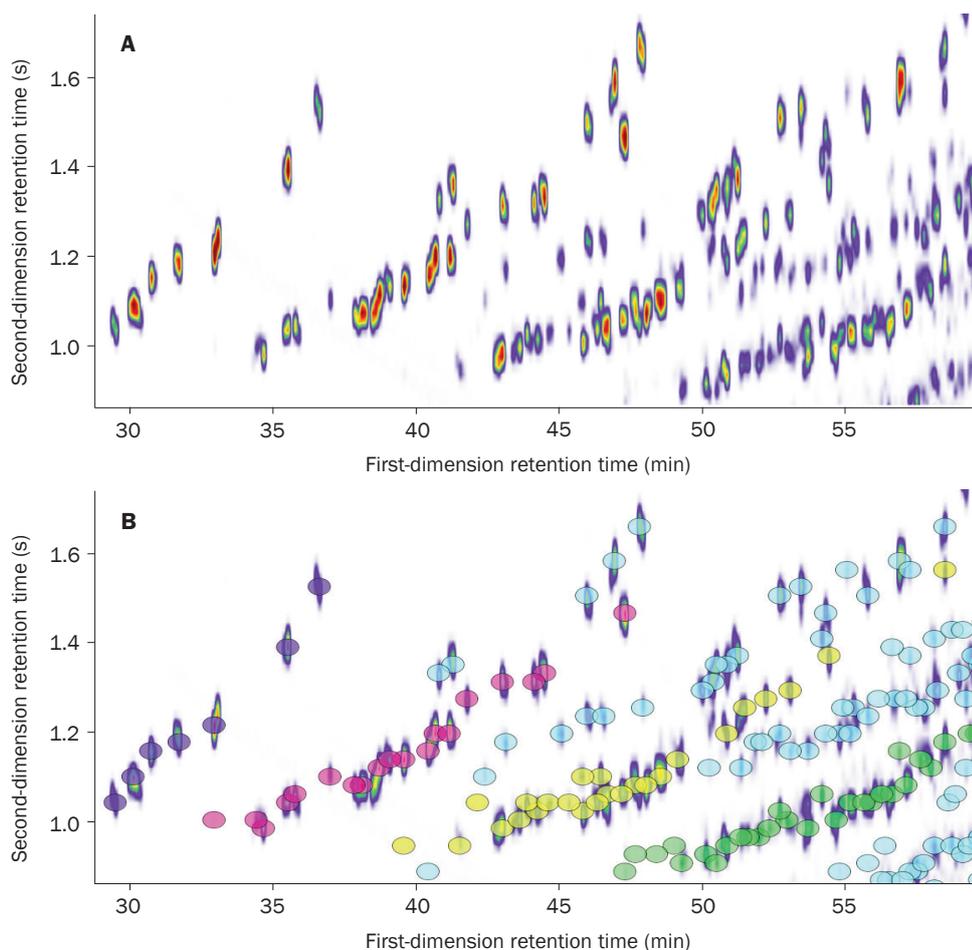
### Compound separation

The chromatogram shown in Figure 1 demonstrates a high degree of compound separation.

In addition to a vastly increased separation space, GC×GC provides a highly ordered chromatogram, with classes of compounds eluting in structured patterns (Figure 2). Compounds were identified by comparison of spectra against the NIST 11 database.



**Figure 1:** Contour plot of diesel sample analysed using BenchTOF.



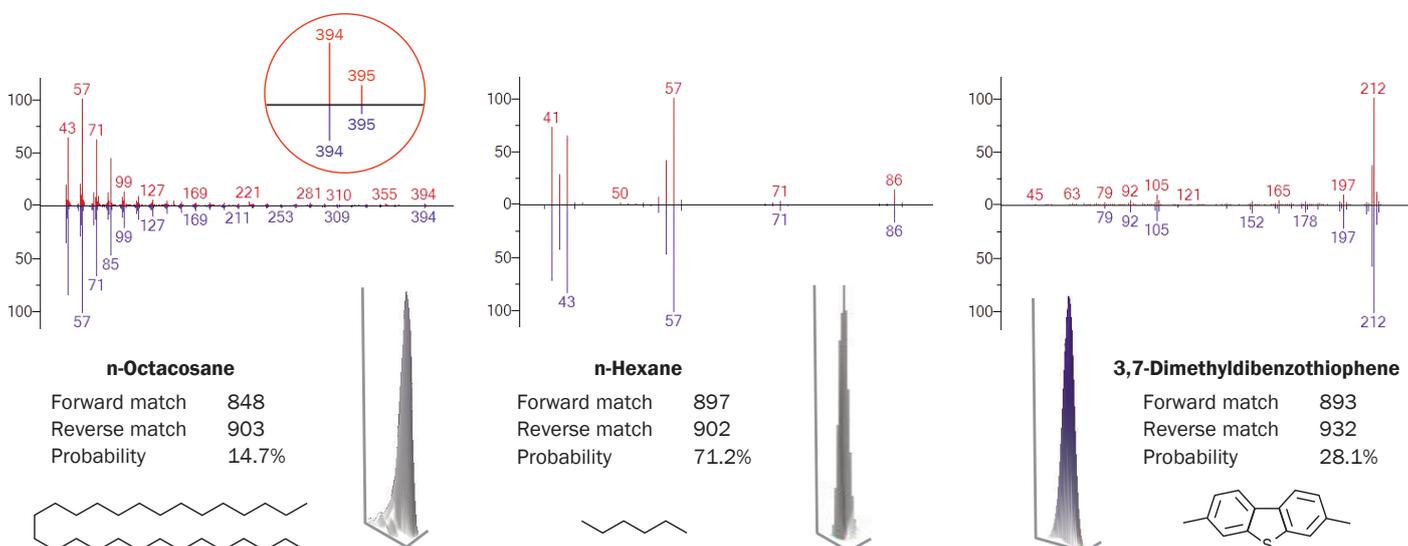
**Figure 2:** (A) Zoomed-in portion of the contour plot of diesel sample analysed using BenchTOF and displayed using *GC Image*. (B) The same portion of the chromatogram overlaid with circles (using the 'blob plot' function of *GC Image*) indicating the following compound groups:

● C<sub>3</sub>-alkylbenzenes; ● C<sub>4</sub>-alkylbenzenes; ● C<sub>5</sub>-alkylbenzenes; ● alkylbenzenes; ○ o-rs.

### Spectral quality

Figure 3 highlights the quality of the spectra delivered by BenchTOF instruments across a range of compound abundances and classes – note in particular that the spectra are directly comparable with those in the NIST 11 database.

The combination of the thermal modulator and BenchTOF ensures the peaks are highly symmetrical, and that they contain high-quality spectra. Note in particular the library match for n-octacosane, highlighting preservation of the molecular ion.



**Figure 3:** Mass spectra (top) and NIST library match (bottom), alongside the 3D-rendered peak shape, for three compounds in the diesel sample. The inset for n-octacosane shows the quality of the match for the low-abundance molecular ion cluster.

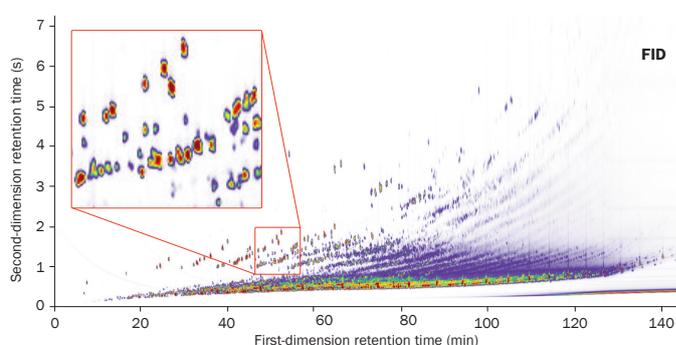
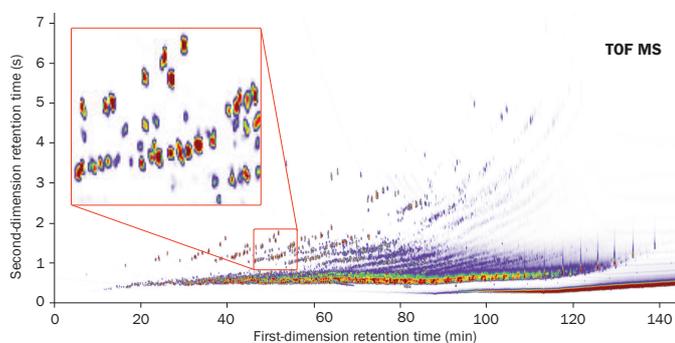


Figure 4: Comparison of contour plots of diesel sample analysed using TOF MS and FID.

### Method transfer to FID

Best-practice in the petrochemical industry<sup>1</sup> demands that FID is used for compound quantitation. With peaks identified using TOF MS, we were in a position to transfer the method to a FID detector. As shown in Figure 4, the GC×GC–FID data corresponds with the GC×GC–TOF MS data to a high degree, allowing easy assignment of peaks to particular target compounds.

### Conclusion

This Application Note demonstrates that GC×GC, in conjunction with a BenchTOF time-of-flight mass spectrometer, provides a high-performance solution for analysing complex petrochemical products.

A number of features of the GC×GC–TOF MS system combine to give excellent performance for this demanding application. Firstly, the vast separation space afforded by GC×GC methodology and the narrow peak widths in the second dimension mean that analytes are grouped by chemical class, simplifying the process of compound identification.

At the same time, the high data-rate and sensitivity of BenchTOF instruments maximises prospects for detecting

trace-level compounds in this complex matrix, while the quality of the spectra produced allows automated comparison with commercial spectral databases.

Finally, easy method transfer from TOF to FID allows quantitation in accordance with current best-practice in the petrochemical industry.

### References

1. UOP990-11: Organic analysis of distillate by comprehensive two-dimensional gas chromatography with flame ionization detection. See <http://www.astm.org/Standards/UOP990.htm>.

### Trademarks

BenchTOF™ is a trademark of Markes International.

GC Image™ is a trademark of GC Image, LLC, NE, USA.

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

## INTERNATIONAL

JSB Group  
Tramstraat 15  
5611 CM Eindhoven  
T +31 (0) 40 251 47 53 F  
+31 (0) 40 251 47 58

INFO@GO-JSB.COM  
WWW.GO-JSB.COM

## SALES AND SERVICE

### NETHERLANDS

Apolloweg 2B  
8239 DA Lelystad  
T +31 (0) 32 087 00 18  
F +31 (0) 32 087 00 19

### GERMANY, AUSTRIA, SWITZERLAND

Max-Planck-Strasse 4  
D-47475 Kamp-Lintfort  
T +49 (0) 28 42 9280 799  
F +49 (0) 28 42 9732 638

### BELGIUM

Grensstraat 7, Box 3  
1831 Diegem  
T +32 (0) 27219211  
F +32 (0) 27207622

### UK & IRELAND

Cedar Court, Grove Park Business Est. White  
Waltham, Maidenhead, Berks, SL6 3LW T +44  
(0) 16 288 220 48  
F +44 (0) 70 394 006 78

