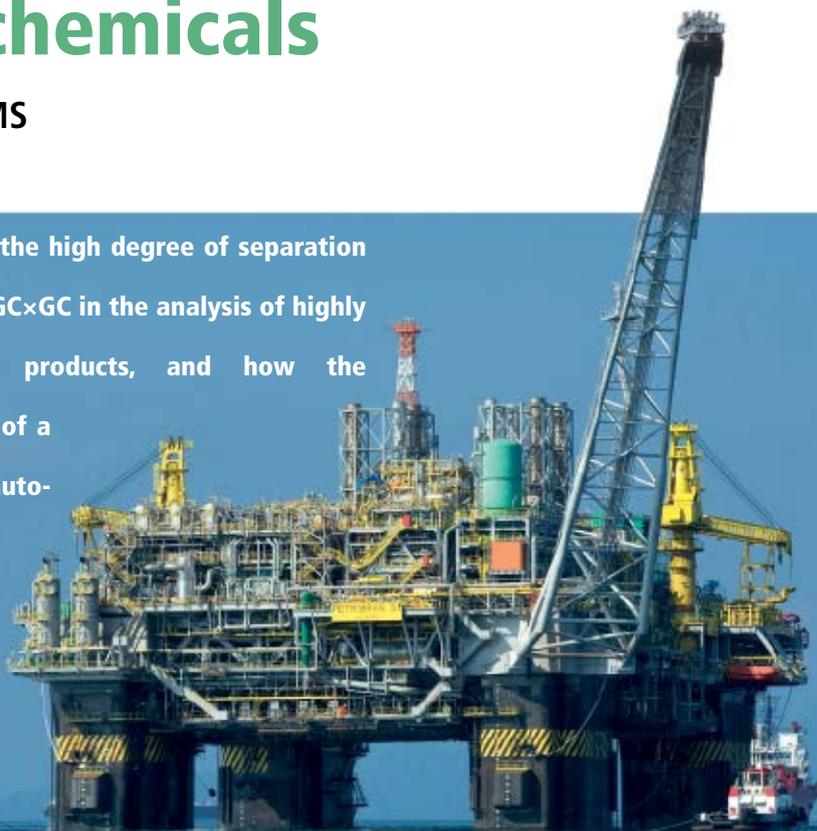# Identifying Hydrocarbons in Petrochemicals

Using GC×GC/TOF MS

This paper demonstrates the high degree of separation that is possible by using GC×GC in the analysis of highly complex petrochemical products, and how the 'quadrupole-like' spectra of a modern TOF MS allows automated searching against large commercial databases.

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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.

However, the very fast second-dimension runs required for GC×GC demand a detector with high acquisition rates, and time-of-flight mass spectrometry (TOF MS) is now widely recognized as being superior to quadrupole instruments for this purpose. Nevertheless, until recently all TOF instruments suffered from the production of distorted spectra, demanding the laborious creation of TOF-specific libraries. Fortunately, this problem has now been overcome by TOF instruments able to produce spectra closely matching those in commercial libraries. In this short paper we report the application of one such instrument to the GC×GC analysis of a complex diesel sample.

Experimental

A sample of diesel was analyzed using a conventional apolar–polar column set with thermal modulation and no secondary oven, as stipulated in Method UOP990. Spectra were queried against the NIST 11 database, and image processing was carried out with GC Image (GC Image, LLC, NE, USA).

GC

Split/splitless injector: 4.0 mm i.d. liner, 0.1 µl injection
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)

Temperature Program

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)
Secondary oven: Not applicable
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: Dewar fill: high, 60%; low, 50%
Modulation period: 8 s, hot-jet pulse 350 ms
Total run time: 145 min

TOF MS

Instrument: BenchTOF-dx (Almsco International)
Ion source: 280°C
Transfer line: 285°C
Mass range: 40–400 amu
Data rate: 50 Hz with 200 spectra per data point

Results

The chromatogram shown in Figure 1 demonstrates the compound separation and the high degree of ordering achievable with GC×GC. The inset shows the outcome of automated processing of the spectral data against library spectra according to user-defined criteria, giving a 'blob plot' that identifies alkylbenzene structural groupings.

Figure 2 gives examples of the spectra that underlie this capability. Note the symmetrical peaks, the similarity of the spectra to those in the NIST 11 database, and in particular the li-
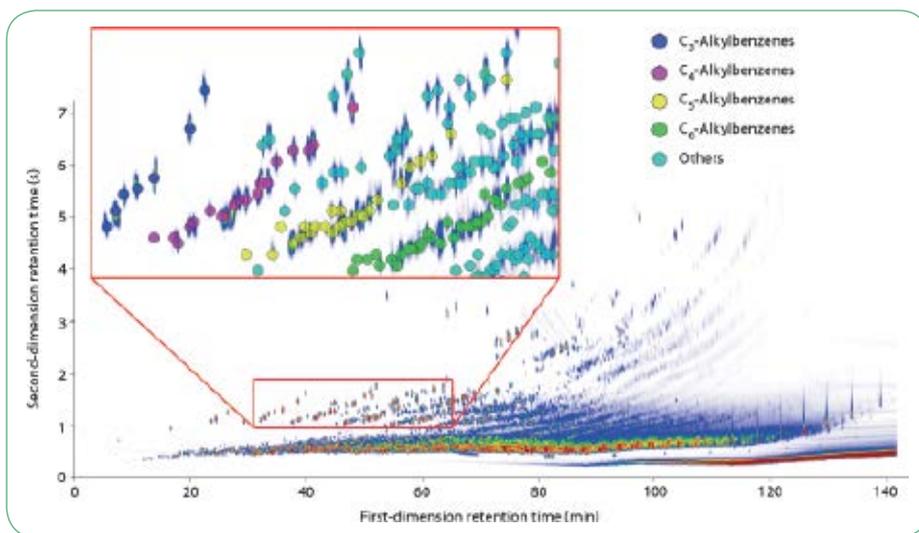
Fig. 1: Contour plot of diesel sample analysed by GC×GC/TOF MS, with the inset showing a portion of the chromatogram overlaid with a 'blob plot' indicating compound groupings.
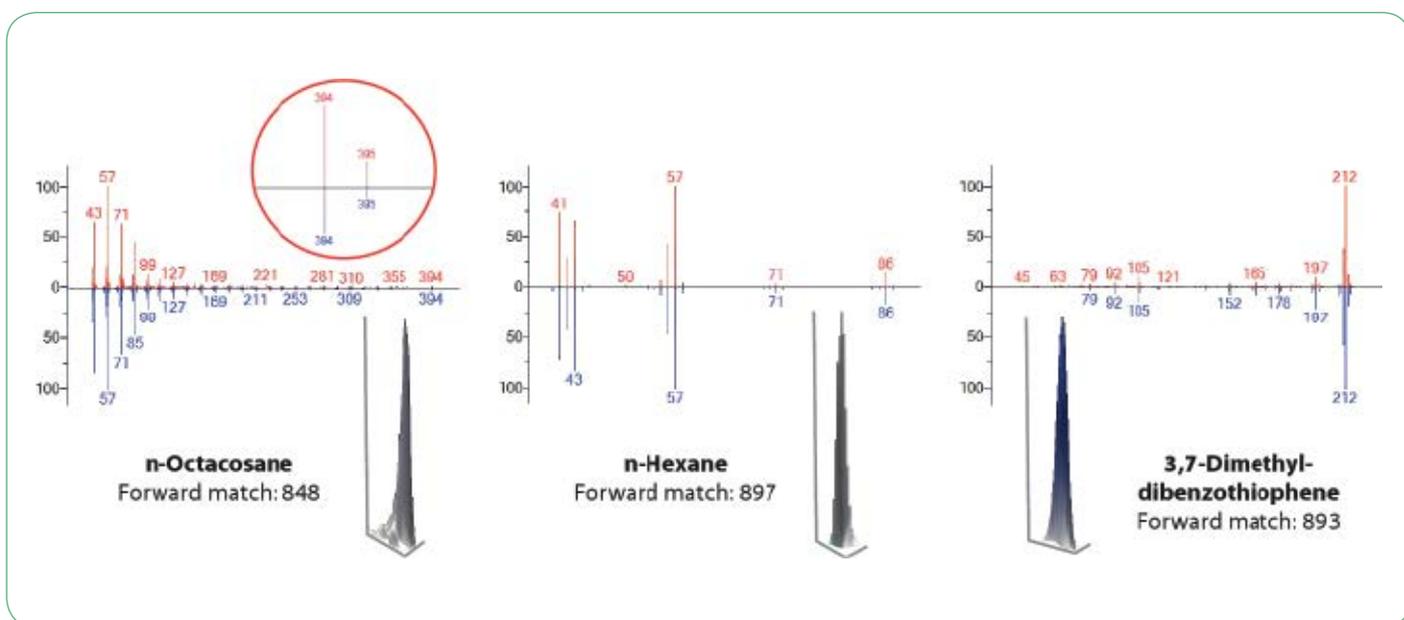

Fig. 2: Mass spectra (top) and NIST library match (bottom), alongside the 3D-rendered peak shape, for n-octacosane, n-hexane, and 3,7-dimethyldibenzothiophene (a sulfur-containing three-ring heterocycle) in the diesel sample. The inset for n-octacosane shows the quality of the match for the low-abundance molecular ion cluster.

brary match for n-octacosane, with preservation of the low-abundance molecular ion.

Discussion

The above examples show that GC×GC, in conjunction with a TOF MS able to produce 'reference-quality' spectra, is a powerful technique for analysing highly complex petrochemical products. A key aspect of this is the groupings of structural isomers produced by GC×GC. These are a familiar feature of petrochemical analyses, and can greatly simplify the process of compound identification even without the benefit of spectral information (e.g. if FID is used as the detector). However, in less intensively refined

samples such as these, the presence of additional compounds obscures such groupings, making the patterns difficult to interpret and increasing the likelihood of error.

In such cases, therefore, the ability to extract high-quality spectral information from each peak is of great value, and in this example we have shown that modern TOF instruments can achieve this, by overcoming the historical disadvantage of distorted mass spectra. This issue of spectral quality is of particular relevance for compounds such as hydrocarbons, where the presence of the molecular ion is essential for reliable compound identification.

In summary, the combination of GC×GC and TOF MS is an appealing technique for the analy-

sis of petrochemicals, with the latest advances in TOF MS and associated software allowing a significant reduction of the burden on the analyst, especially for routine processing.

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