

Application Note 524[†]

Analysis of complex petrochemicals by GC×GC–TOF MS with Select-eV variable-energy electron ionisation

Summary

This Application Note shows that BenchTOF instruments, coupled with GC×GC, can provide a high-performance solution for the characterisation of hydrocarbons in complex petrochemical samples. Variable-energy electron ionisation technology is also shown to enhance analyte speciation by providing additional data on both molecular ions and structurally significant fragments in the low-energy mass spectra. The enhanced sensitivity and selectivity stemming from the dramatic reduction in fragmentation at low energies also greatly increases the number of compounds identified, permitting robust statistical comparisons essential for successful chemical fingerprinting.



Introduction

Crude oil contains thousands of organic compounds ranging from light hydrocarbons to complex biomolecules. Speciation of hydrocarbons is of great interest to the petroleum industry, as certain isomers may have an adverse effect on engine performance if present in high quantities in the final fuel. Furthermore, chemical fingerprinting of crude oil has become extremely important for identification of those responsible for environmental contamination events.

In the past, such complex samples were analysed by chemical fractionation followed by one-dimensional gas chromatography with mass spectrometry (GC–MS). However, fractionation is a time-consuming, labour-intensive process, which uses large volumes of solvents and can be prone to error.

Two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC–TOF MS) is now used routinely in the oil industry to combat this problem. The coupling of two columns of different selectivity provides

enhanced separation of complex mixtures, allowing all chemical classes to be monitored in a single analytical run.

Despite the superior separation afforded by GC×GC, the identification of individual compounds in complex samples remains challenging when multiple compounds in a chemical class have similar spectra at conventional (70 eV) ionisation energies. Branched alkanes are a prime example, with weak molecular ions that further complicate the process. Spectral similarity can be addressed by the use of soft ionisation to reduce the degree of ion fragmentation, but this approach has been cumbersome to implement until now.

In this Application Note, we show how the problem of compound identification in petrochemical samples can be resolved without recourse to the time-consuming analysis of multiple standards. We achieve this by the application of Select-eV, a revolutionary MS source technology that enhances compound identification by enabling efficient electron ionisation at much lower (softer) energies without compromising sensitivity. We also show how Select-eV complements the other fundamental advantages of Markes' BenchTOF time-of-flight mass spectrometers for the GC×GC identification of hydrocarbons.

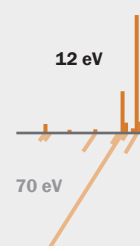


Select-eV

Markes' flagship BenchTOF-Select™ instrument features Select-eV® ion-source technology as standard.

Select-eV breaks new ground by allowing ionisation energies to be reduced on a sliding scale from 70 eV to 10 eV, without impacting sensitivity, simply by changing a parameter in the method.

This low-energy (*i.e.* 'soft') electron ionisation reduces analyte fragmentation, which benefits a wide range of GC and GC×GC analyses by enhancing selectivity, sensitivity, and aiding structural elucidation – all while avoiding the inconvenience of reagent gases, ion source pressurisation, or changes in hardware setup typically associated with other soft ionisation techniques for GC–MS.



[†] Formerly ALMSCO Application Note 024.

Background to BenchTOF instruments

Markes' BenchTOF™ time-of-flight mass spectrometers are designed specifically for gas chromatography. They are particularly appropriate for the GC×GC analysis of complex samples, such as petrochemicals, because they offer exceptional sensitivity, spectral quality and speed:

- **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.
- **Spectral quality:** The 'reference-quality' spectra produced by BenchTOF instruments 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.

Experimental

GC×GC separations were conducted using a conventional apolar–polar column set, using a 100 mg/mL dilution of crude oil in dichloromethane.

GC:

Instrument:	Agilent 7890A
Injector:	Split/splitless injector
Liner:	4.0 mm i.d. liner, 1 µL injection
Carrier gas:	He, constant flow at 1.0 mL/min
Mode:	Split, 100:1
Temperature:	280 °C
Septum purge:	On, 3 mL/min

2D column set:

1st dimension:	DB-5, 28 m × 0.25 mm × 0.25 µm
2nd dimension:	SGE BPX50, 3.3 m × 0.1 mm × 0.1 µm
Modulation loop:	As for 2nd dimension
Column set:	Equivalent pneumatic impedance to 41.5 m × 0.18 mm (calculated from K factor look-up charts for 1st- and 2nd-dimension columns used)

Temperature programme:

Main oven:	50 °C (1.0 min), 4.0 °C/min to 325 °C (10 min)
Secondary oven:	75 °C (1.0 min), 4.2 °C/min to 340 °C (hold time matched to total run time)
Hot jet:	150 °C (1.0 min), 4.0 °C/min to 400 °C (hold time matched to total run time)
Cold jet:	Dewar fill: high, 50%; low, 40%
Modulation period:	6 s, hot-jet pulse 350 ms
Total run time:	79.75 min

TOF MS:

Instrument:	BenchTOF-Select (Markes International)
Filament voltage:	2.2 V
Ion source:	250 °C
Transfer line:	325 °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)
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Results and discussion

Enhanced selectivity with Select-eV

The GC×GC–TOF MS contour plots shown in Figure 1 provide a comparison of the analysis of crude oil at 70 eV and 14 eV. The results show an improvement in selectivity at low-energy ionisation, particularly within the aliphatic region, due to dramatically reduced fragmentation of these compounds within the ion source.

The enhanced selectivity provided by Select-eV low-energy ionisation allowed the automated detection of over 1000 additional 'blobs' in the 14 eV GC×GC contour plot, compared to the same sample run at 70 eV. This extra information provides more robust statistical comparisons for chemical fingerprinting of whole oils – an advantage that is extremely important in environmental forensic investigations, where spilled oils need to be matched to potential sources.

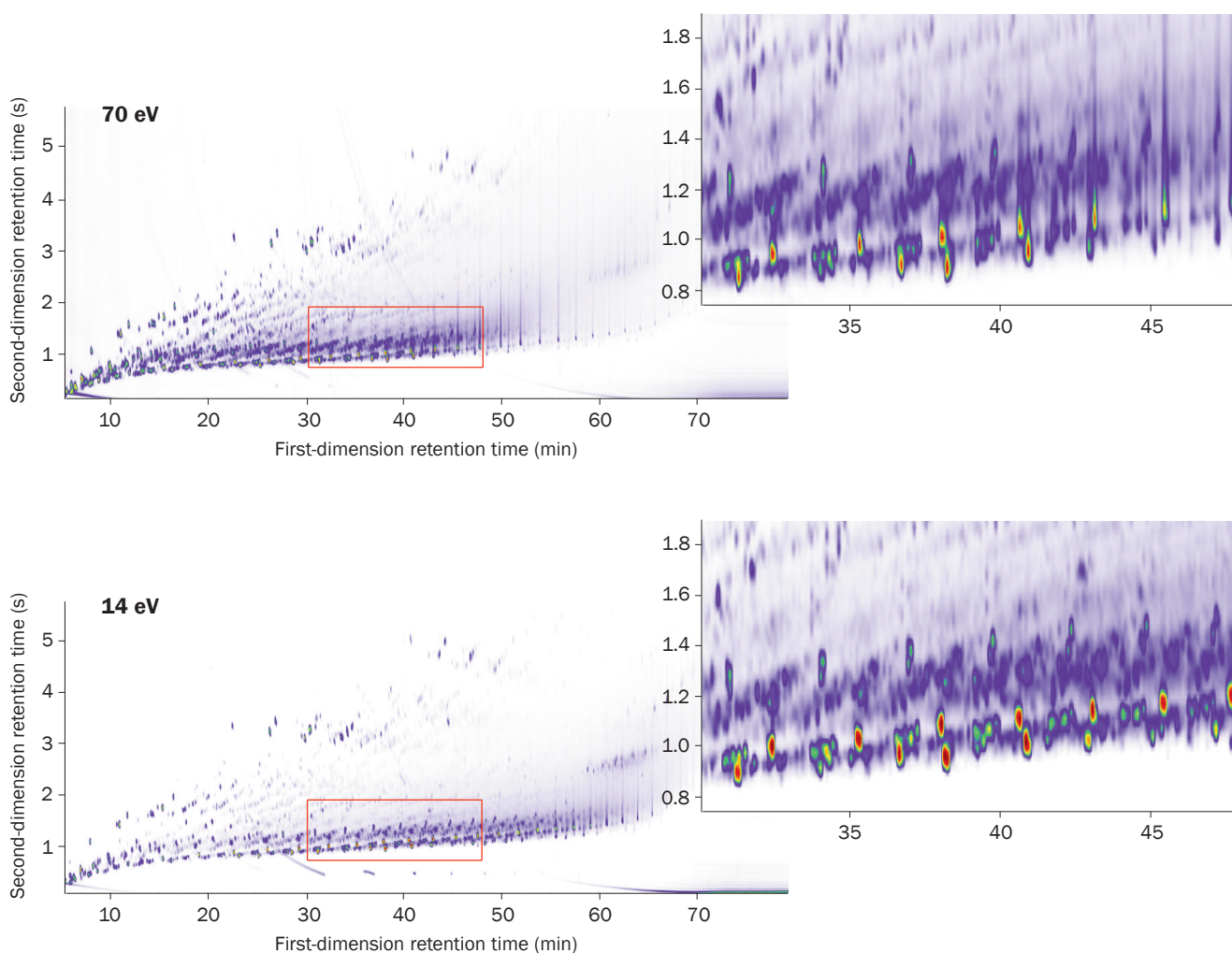


Figure 1: Comparison of GC×GC–TOF MS contour plots of a crude oil analysed at 70 eV (top) and 14 eV (bottom), with expansions highlighting the improved chromatographic resolution for hydrocarbons at low ionisation energies.

Enhancement of structurally-significant fragment ions

Figure 2 demonstrates how the reduced fragmentation resulting from soft ionisation with Select-eV can improve the differentiation of isomeric species, by increasing confidence in compound identification. In effect, the spectrum at 14 eV provides both additional information and independent corroboration of compound identification using the reference-quality 70 eV spectrum. This is particularly useful in the field

of forensics, where rigorous, defensible results are essential. The enhancement of molecular ion and structurally-significant fragments at low energies can also aid structural elucidation of compounds that are not present in commercial libraries.

Note that the low-energy spectra generated using Select-eV are repeatable, and that searchable libraries can be readily developed at any ionisation energy of interest.

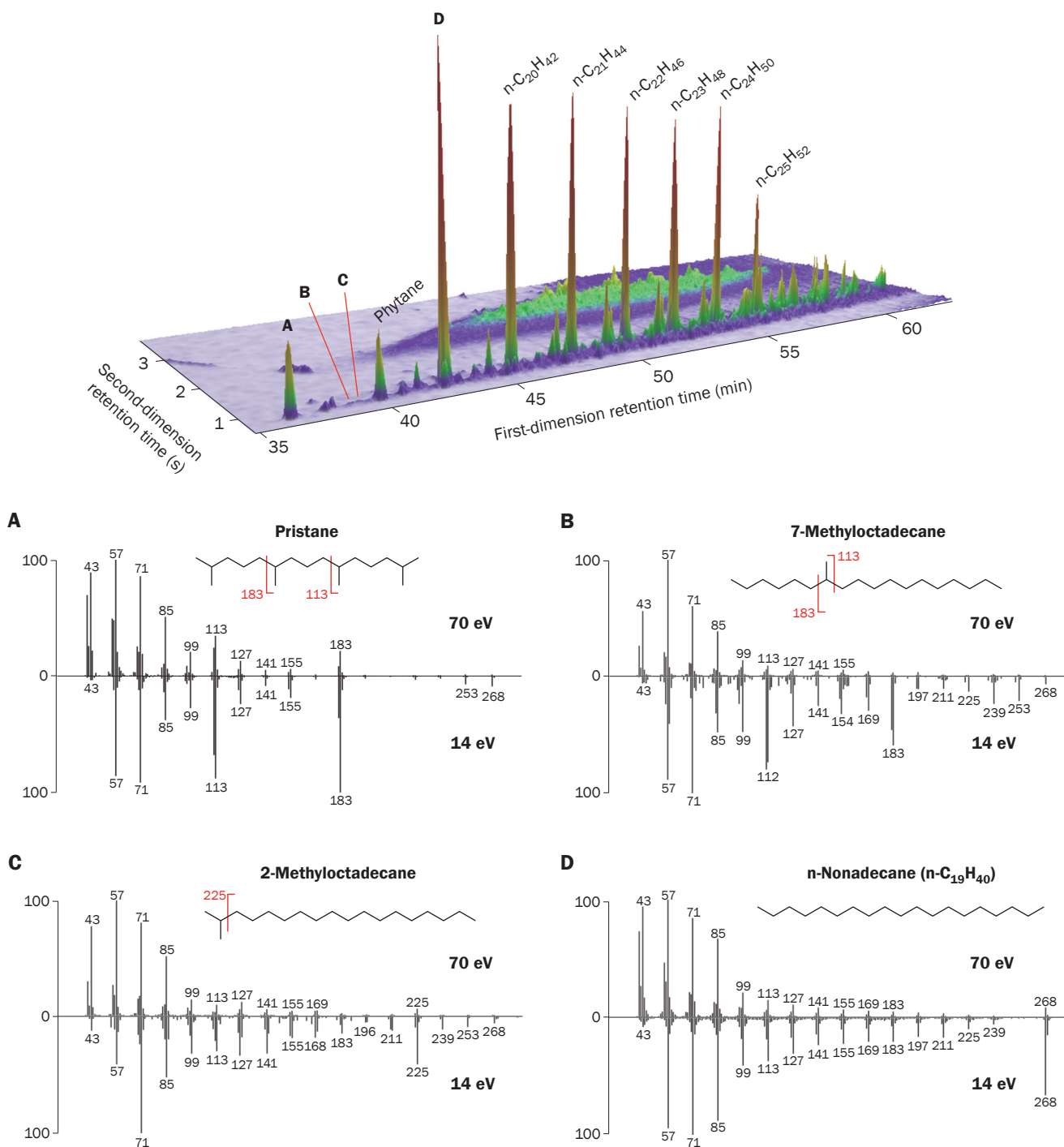


Figure 2: Top: GCxGC-TOF MS contour plot of a crude oil, showing overlaid EICs (m/z 268 + 282 + 296 + 310 + 324 + 338 + 352), analysed using Select-eV with an ionisation energy of 14 eV. The panels for each of the four labelled peaks **A-D** show the significant differences in fragmentation between 70 eV and 14 eV, and that it is much easier to discriminate between these compounds using the low-energy spectra.

Identification of biomarkers

Select-eV technology can also aid the identification of crude oil biomarkers. These are breakdown products of the biomolecules in the original oil-producing organisms, and are known as 'chemical fossils' because of their resistance to degradation.

Figure 3 compares the 70 eV and 14 eV mass spectra for two sterane-type biomarkers in the crude oil. In both cases, the mass spectra at low energies have dramatically reduced fragmentation, as well as enhanced molecular ion signals, resulting in improved signal-to-noise values and lowered limits of detection. However, unlike other soft ionisation techniques that produce a sole molecular ion, Select-eV retains significant fragments that can aid structural elucidation.

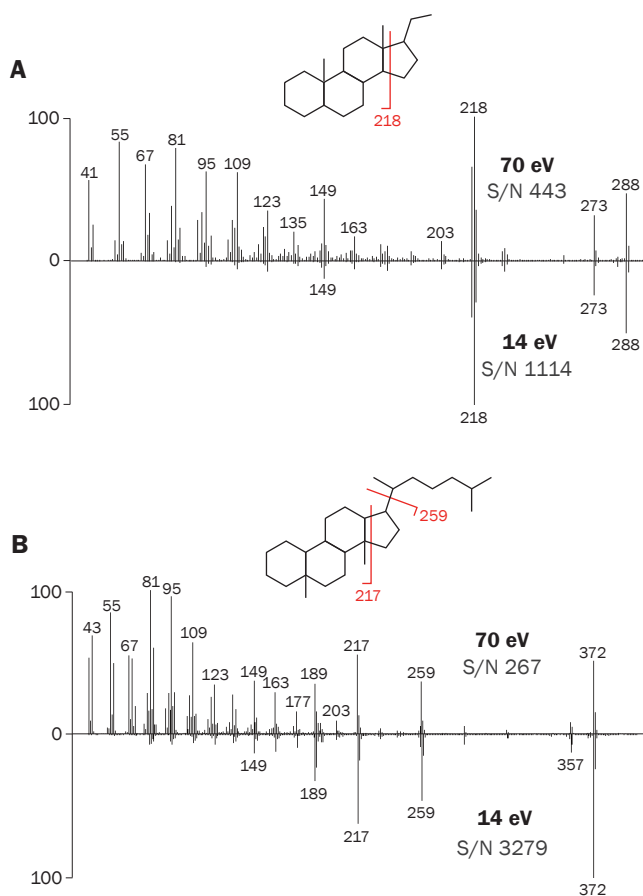


Figure 3: Mass spectral comparisons for two sterane-type biomarkers at 70 eV and 14 eV. In each case, signal-to-noise ratios are given for the molecular ion.

Conclusion

In this Application Note, we have shown that GC×GC-TOF MS provides the sensitivity and chromatographic resolving power necessary to deliver highly structured, data-rich chromatograms, alongside the 'classical' library-searchable spectra that provide a high degree of confidence in analyte identification.

Furthermore, Select-eV has been shown to provide improved sample characterisation for these complex crude oils, by reducing fragmentation and increasing molecular ion response, with no inherent loss in sensitivity. Select-eV also enhances productivity, by providing lower (softer) ionisation energies at the push of a button, minimising the instrument downtime often associated with source-switching in other soft ionisation techniques.

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.