

# Analysis of complex petrochemicals by GCxGC-TOFMS with variable-energy electron ionisation

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## Introduction

Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry (GCxGC-TOF MS) offers greatly enhanced peak capacity, through the coupling of two columns of different selectivity, as well as highly sensitive detection and definitive mass spectral identification of trace-level analytes, making it the ideal choice for the analysis of complex petrochemicals.

Despite this increased separation capacity, the identification of individual compounds in complex samples may be further complicated due to weak molecular ions or when similar mass spectral characteristics are evident across entire chemical classes.

Select-eV<sup>®</sup> is a new innovation in ion source technology that aims to solve this problem by the ability to switch between hard and soft electron ionisation with no inherent loss in sensitivity. The use of soft electron ionisation enhances the intensity of molecular and structurally-significant fragment ions, magnifying differences between isomeric spectra and, by consuming less instrumental dynamic range, a wider concentration range of analytes can be supported in any single analysis.

This poster provides an introduction to Select-eV, as applied to GCxGC-TOF MS analyses of complex crude oils.

## Theory

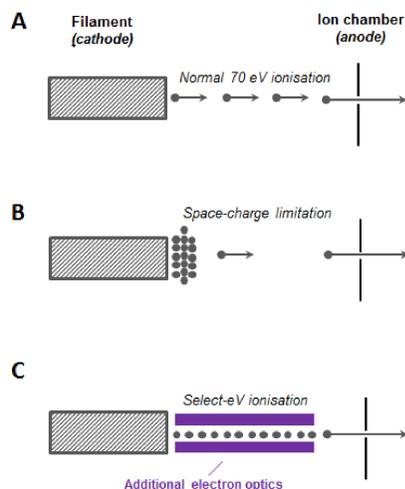
In GC-MS analyses, a potential difference (or electron energy) of, conventionally 70 eV, exists between the ion chamber (anode) and the e-gun (cathode). In this electrical configuration, thermionic electrons are easily accelerated away from the surface of the filament and directed through an aperture in the ion chamber wall for normal electron ionisation (Figure 1A).

In a properly constructed ion source, small variations in the electron energy, impart very small differences to the ionisation efficiency and thus the ion flux, available for gating into the mass analyser, resulting in reliable and repeatable mass spectral results.

However, at lower ionisation energies, electron emission from the filament becomes space-charge limited. Electrons are not efficiently directed into the ion chamber, due to the lower potential difference between the anode and cathode, resulting in electron clustering around the filament, which further shields the potential difference (Figure 1B).

Until now, the space-charge limitation has hindered the use of low ionisation energies in conventional EI GC-MS due to the resulting catastrophic loss in sensitivity. In the Select-eV ion source, depicted in Figure 1C, an additional electrostatic element is placed between the e-gun and the ion chamber. In this configuration, electrons emitted from the filament are channelled efficiently into the ion chamber at the defined electron energy.

Therefore, the signal is improved by reducing coulombic effects and increasing the number of electrons produced by the filament. This improves instrument sensitivity at low ionisation energies and allows soft ionisation in an e-gun arrangement.



**Figure 1:** Illustration of thermal emissions in electron ionisation. A: Conventional 70 eV ionisation. B: The space-charge limitation in conventional (EI) GC-MS systems at low ionisation energy. C: How the Select-eV ion source overcomes this problem.

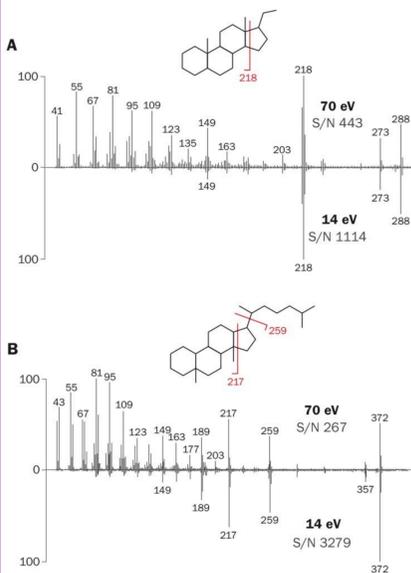
## Experimental

The Select-eV e-gun has been integrated into the BenchTOF-Select<sup>™</sup> time-of-flight mass spectrometer, allowing generation of electrons over a wide, tuneable range of energies (10–70 eV). The electron beam is focused into an ionisation chamber that also acts as an efficient extraction chamber for the TOF instrument, maximising ion transmission rates into the mass analyser. This arrangement proved to be extremely sensitive.

A GCxGC gas chromatograph was used in combination with the BenchTOF-Select for the following case study on the analysis of crude oil.

A “normal phase” column set was used, consisting of a DB-5 (28 m × 0.25 mm × 0.25 μm) in the 1<sup>st</sup> dimension and SGE BPX50 (3.3 m × 0.1 mm × 0.1 μm) in the 2<sup>nd</sup> dimension. For full experimental details, please see Application Note 524.

## Results



**Figure 2:** 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.

Select-eV technology was applied for 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.

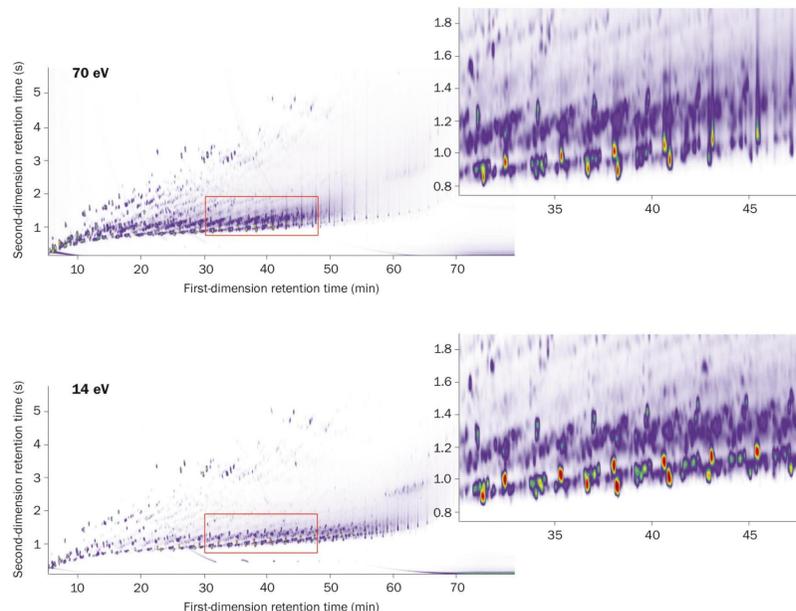
Figure 2 compares the 70 eV and 14 eV mass spectra for two sterane-type biomarkers in the crude oil. In both cases, the mass spectra at low energies have dramatically reduced fragmentation, as well as enhanced molecular ion signals, resulting in improved signal-to-noise values and lowered limits of detection. However, unlike other soft ionisation techniques that produce a sole molecular ion, Select-eV retains significant fragments that can aid structural elucidation.

In contrast to chemical ionisation, electron ionisation can be applied to almost every vaporised substance. Therefore, the ability to generate a low-energy electron beam makes this a universal soft ionisation technique. Furthermore, Select-eV does not require source-switching, reagent gases or source pressurisation. The ionisation energy is simply entered as a method parameter within the accompanying TOF-DS<sup>™</sup> software package, allowing a fully automated sequence of samples to be analysed at various ionisation energies.

## Enhanced selectivity

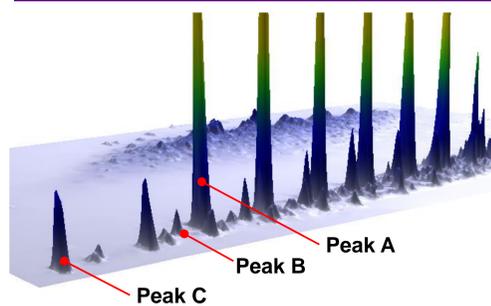
The GCxGC-TOF MS contour plots shown in Figure 3 provide a comparison of the analysis of crude oil at 70 eV and 14 eV. The results show an improvement in selectivity at low-energy ionisation, particularly within the aliphatic region, due to dramatically reduced fragmentation of these compounds within 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 GCxGC 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.

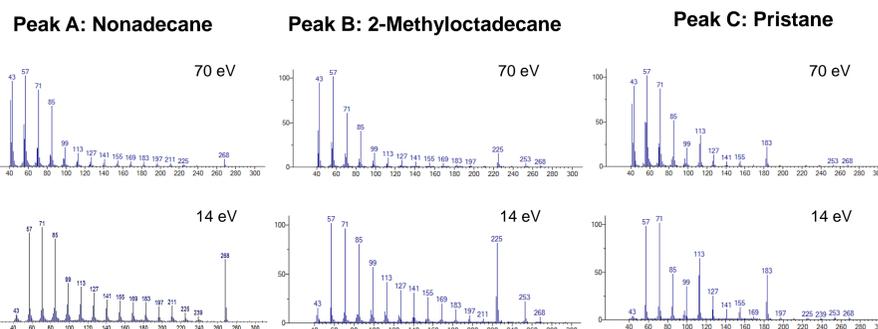


**Figure 3:** Comparison of GCxGC-TOF MS contour plots of a crude oil analysed at 70 eV (top) and 14 eV (bottom), with expansions highlighting the improved chromatographic resolution for hydrocarbons at low ionisation energies.

## Differentiation of isomers



**Figure 4:** Section of a GCxGC-TOF MS chromatogram for crude oil, with increased orthogonality in the spectra of isomers demonstrated by the 14 eV spectral comparisons.



The presence of only structurally-significant fragments in Select-eV mass spectra leads to a reduced demand on dynamic range and an increase in peak capacity for GCxGC-TOF MS. Furthermore, the ability to provide enhanced molecular ions whilst retaining structurally-significant fragment ions allows for greater orthogonality between the mass spectra of isomeric compounds, thus simplifying compound identification. Figure 4 shows an example of this increased orthogonality for the identification of hydrocarbons in a crude oil.

The preservation of some fragmentation also allows increased confidence in deconvolution as well as quantitation. The enhanced signal for heavier, more structurally-significant ions provides increased probability of finding a unique quantitative ion.

These results indicate that the BenchTOF-Select can provide an additional level of sample information with no disruption to analytical workflow.

## Conclusion

In this work, we have shown that GCxGC-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.

By suppressing the fragmentation at low ionisation energies, matrix interferences are greatly reduced. Furthermore, carrier gases and/or residual background gases are not ionised, due to their higher ionisation potentials. Therefore, the signal-to-noise ratios for target substances are dramatically improved, allowing lower limits of detection to be achieved.