

SELECTIVE IONISATION AND AFFORDABLE HIGH RESOLUTION MASS SPECTROMETRY IS REVOLUTIONISING MOLECULAR CHARACTERISATION IN THE PETROLEUM AND PETROCHEMICAL INDUSTRIES

Since its early days High Resolution Mass Spectrometry (HRMS) has been a key technique for the molecular characterisation of the complex mixtures experienced in the petroleum based industries and in recent years the power and application of the technique has increased dramatically.



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In 2005 Marshall and Rogers (1)(2) wrote "Ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometry has recently revealed that petroleum crude oil contains heteroatom-containing (N,O,S) organic components having more than 20 000 distinct elemental compositions. It is therefore now possible to contemplate the ultimate characterisation of all of the chemical constituents of petroleum, along with their interactions and reactivity, a concept we denote as "Petroleomics".

Selective resolution of the components of interest is the key to successfully analysing complex sample matrices by any technique and in mass spectrometry this can be achieved by a combination of the resolution of the mass analyser with selective ionisation which targets only the compound classes of interest. In addition, the components of interest can be resolved from matrix interferences by coupling with pre-separation techniques such as chromatography or ion mobility spectrometry.

In Rodgers and McKenna's (3) review of Petroleum Analysis in 2011 more than half the text discussed advances in mass spectrometry with the remainder covering all other analytical techniques. This dominance was attributed to developments in a range of atmospheric pressure ionisation techniques combined with the resolving power of Fourier Transform Ion Cyclotron Resonance Mass Spectrometers (FT-ICR-MS). FT-ICR-MS is still the gold standard for high resolution mass spectrometry but the instrumentation is expensive, requires significant laboratory space and has large cryo-cooled superconducting magnets. FT-ICR-MS also requires a high degree of operator experience and as such is generally only found in universities or large corporate research facilities. However, in recent years significant advances have been made in "bench-top" HRMS technology through the introduction of Time of Flight and Orbitrap™ type instruments (4) which have proved to be affordable, robust and easy to operate and as a result they have revolutionised the potential for routine application of HRMS in petro industry laboratories.

Why is the Mass Spectrometer Resolving Power So Important?

The mass spectrum shown in Figure 1(a) was acquired from a crude oil sample using electrospray ionisation (ESI) with FT-ICR-MS and comprises ~8000 peaks over a m/z range of circa 800. An expanded area from this spectrum covering a range of circa 0.15 in Figure 1(b) shows a number of components and illustrates why high resolution is critical to the detailed analysis of complex mixtures such as crude oil.

In addition to achieving individual compound resolution, HRMS systems capable of acquiring high resolution with high mass accuracy make it possible to determine elemental compositions from the exact mass data of the detected ions. This is illustrated for several of the peaks in Figure 1(b) with molecular formulae derived from the accurate mass for components containing different combinations of nitrogen, oxygen and sulphur.

Another benefit of HRMS for petroleum analysis is the ability to easily identify homologous series and the presence of double bonds. For a saturated hydrocarbon homologous series, a unit spacing of m/z 14.0157 is observed for the addition of each CH₂

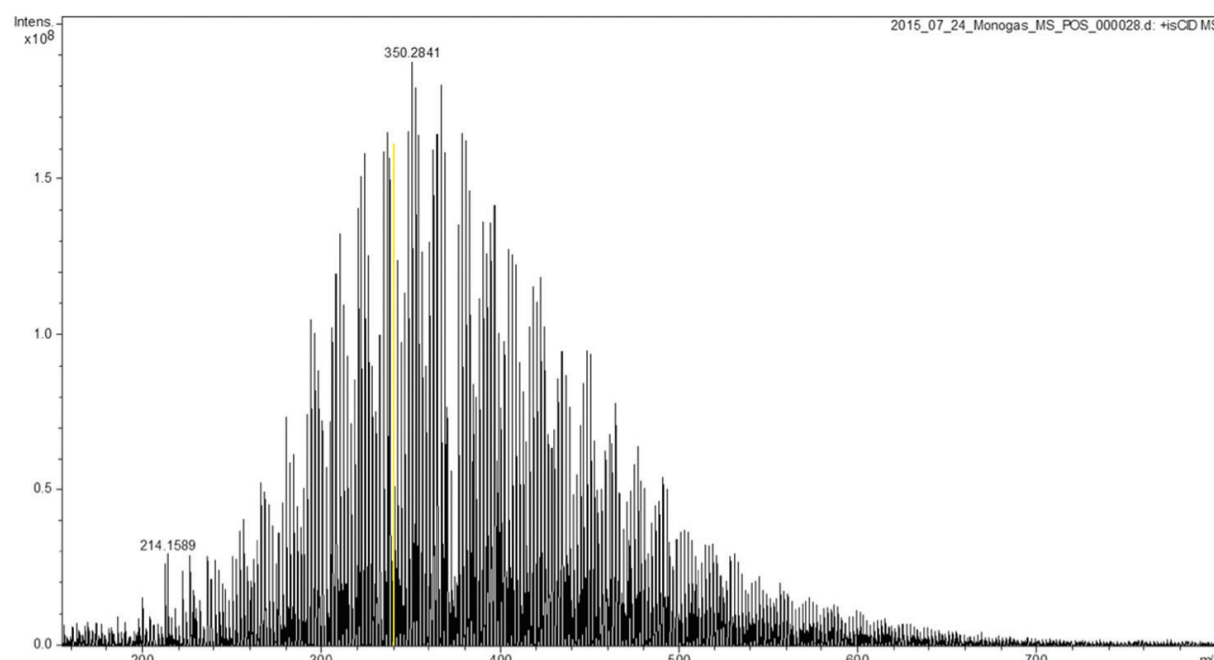


Figure 1(a): Mass Spectrum containing circa 8000 peaks obtained from a crude oil sample by ESI-FT-ICR-MS (Courtesy Prof J G Langley, Southampton University, UK)

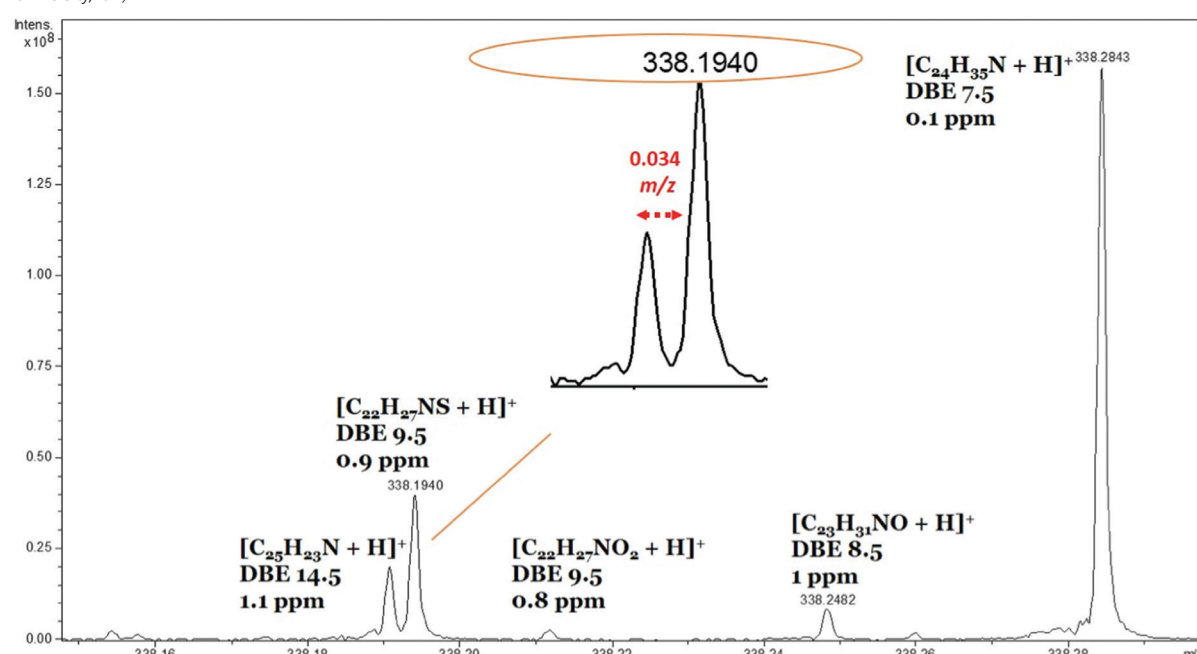


Figure 1(b): Expanded FT-ICR Mass Spectrum from Fig 1(a) showing resolution of components differing by 0.034 m/z (Courtesy Prof J G Langley, Southampton University, UK)

unit and a spacing of m/z 2.0157 in the spectrum is equivalent to the mass of 2 hydrogen atoms. Thus, the addition of -CH₂ increases the mass by m/z 14.0157 unit and the addition of ring or double bond lowers the mass by m/z 2.0157 units. These parameters can then be used to calculate the double bond equivalent (DBE) which can be directly correlated to the degree of

unsaturation and aromaticity of the molecular classes.

High mass resolution data analysis is also simplified by converting the data to the Kendrick mass scale (2) where the mass of a methylene CH₂ is set to 14.0000 instead of 14.01565 Daltons. This rescaling of the data aids in the identification of homologous series according to alkylation, number of heteroatoms, and the

DBE. Kendrick normalisation gives series that appear as horizontal rows in a plot of DBE versus Kendrick mass thus facilitating visualisation of complex data sets. The data can also be plotted as a 3D heat-map to indicate the relative intensity of the mass spectral peaks. From the Kendrick plot, the species with peaks in the mass spectrum can be sorted into compound classes by the number of nitrogen, oxygen and sulphur heteroatoms. Example Kendrick plots for only two of the many compound classes in a crude oil are shown in Figure 2.

Exploiting the Power of Different Ionisation Techniques

In recent years a range of ambient ionisation techniques have been developed for use with mass spectrometry which have significantly increased the routine applicability of HRMS in the petroleum industry (1)(2)(3)(5) and there are currently >80 different techniques listed in Wikipedia as ambient ionisation techniques. Many of these have specific attributes which can be valuable tools for the petro industry analyst. For example, techniques such as desorption electrospray ionisation (DESI) and direct analysis in real time (DART) can be employed for the direct analysis of molecules present on surfaces which can be particularly useful for the analysis of deposits and stains on samples such as pipes and engine components. The application of DESI for the quantitative analysis of lubricant additives (6) on surfaces and also the analysis of corrosion inhibitors (7) on metal surfaces has been reported by De Costa et al.

Petroleomics aims to fully characterise all of the chemical constituents of petroleum samples including crude oil. However, it soon became clear that no single ionisation technique would ionise all of the species in a crude oil. For example, ESI is most efficient for polar molecules but not for hydrocarbons so the ~8000 peaks shown for crude oil in Fig 1(a) will result from heteroatom components which typically may account for only circa 10% of the species in the crude. However other ionisation techniques such as field ionisation (FI), field desorption (FD) and atmospheric pressure photo-ionisation (APPI) can be applied to access many of the remaining 90% of components in a crude. Marshall and Rodgers reported that an APPI mass spectrum of a crude typically contains circa 5 times as many peaks as an ESI mass spectrum of the same sample (2).

Although the lack of a universal ion source may be an issue for Petroleomics it is a major benefit for many application areas which require the characterisation of specific chemical classes of compounds present in complex mixtures. By selecting an ionisation technique with high sensitivity and selectivity for the chemical class of interest and combining it with HRMS to give detailed molecular characterisation we have a powerful tool applicable to many areas of the petroleum and petrochemical industries.

The Analysis of Hetero species in Petroleum Based Samples

As discussed, electrospray ionisation is especially efficient in generating gas phase ions from hetero atom species without ionising the hydrocarbon matrix and this can be a powerful tool for the petroleum industry chemist whose day to day work requires the detailed characterisation of a wide range of hetero containing components. For example, differentiated products, such as fuels and lubricants, which claim enhanced performance in the field, are now a major revenue generator for many companies. Product differentiation is usually achieved using functionalised additive molecules such as detergents, dispersants antioxidants etc. which are often present at only trace levels in the final product. ESI coupled with HRMS has provided new possibilities in the analysis of such samples allowing the characterisation and identification of active species at the molecular level. The techniques can be applied through product research and development to develop structure property relationships and identify the key molecular species which are contributing to enhanced performance. They can also be applied through the manufacturing and supply chain to study feedstock variations, product stability and degradation and in customer support to identify field issues such as cross contamination and adulteration.

In recent years the drive towards sustainability and environmental protection has seen a dramatic increase in the development of biofuels and bio lubricants. These are usually derived from plant oils or synthetic esters manufactured from sustainable feedstocks and as such usually contain oxygen. The plant derived feedstock

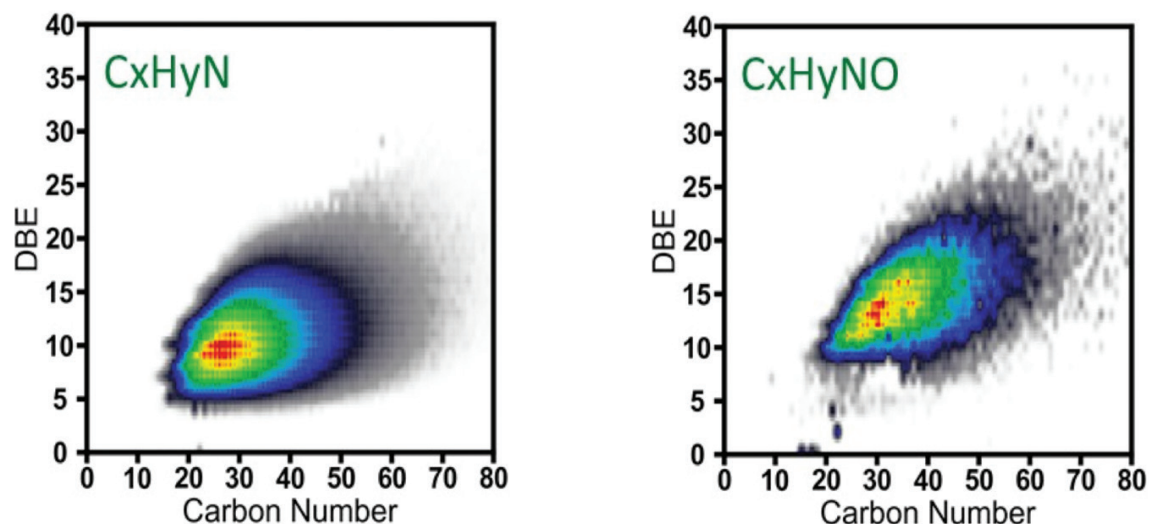


Figure 2: Example Kendrick plot heat maps for 2 compound class distributions from a crude oil sample using ESI-HRMS (Courtesy Dr C Wicking, BP Pangbourne UK)

composition can vary due to many external factors such as the location and weather and therefore it can be difficult to maintain final product consistency at the molecular level. Also, many of these products are blended with conventional hydrocarbons for field use and ESI in combination with HRMS is the ideal tool to characterise and identify bio derived molecules of interest in blends. For example, in biodiesel production trace levels of sterol glucosides may be present which can accelerate precipitation problems and cause filter blocking issues and the sensitivity and selectivity of ESI-HRMS is ideal for detecting and quantifying such components in blended fuels.

Soft Ionisation for Hydrocarbons

For hydrocarbon only molecules, and especially saturated hydrocarbons, most ionisation techniques produce extensive fragmentation but field ionisation and field desorption ionisation techniques have been successfully applied to produce molecular ions with minimal fragmentation for hydrocarbon type analysis. The 4th generation Jeol Accutof GCx instrument can be equipped with a range of ionisation options including electron ionisation (EI), chemical ionisation (CI), field ionisation (FI), desorption electron ionisation (DEI), desorption chemical ionisation (DCI), and field desorption (FD) ionisation using specialised direct sample inlet probes. The TOF-MS has a mass resolution >10,000 (FWHM) with a mass accuracy: <1.5mDa or 4 ppm (RMS) and a mass range: m/z 4 to 6,000.

The optional EI/FI/FD combination ion source is a single ion source that supports sample analysis using 3 different ionisation techniques. An ionisation mode is selected by replacing the probe which can be changed while keeping the ion source in high vacuum thus minimising system downtime for an ionisation mode switch.

In addition, up to 50 spectra/sec can be collected which means the instrument is ideally suited for use with both 1D and Comprehensive 2D GC using the EI/FI/FD combination ion source to further expand the application area of the technique for complex petrochemical samples. The FI mass spectrum of hydrocarbon molecular ions from a crude oil sample shown in Figure 3 was obtained by accumulating the data from an entire GC run. The FI and FD modes of the instrument are particularly useful in generating Kendrick Mass Defect Plots for hydrocarbon group type analysis as in the characterisation of fuels and lubricant base oils. Jeol have produced a comprehensive applications book (8) which highlights many areas where the different ionisation techniques can be applied to provide unique information.

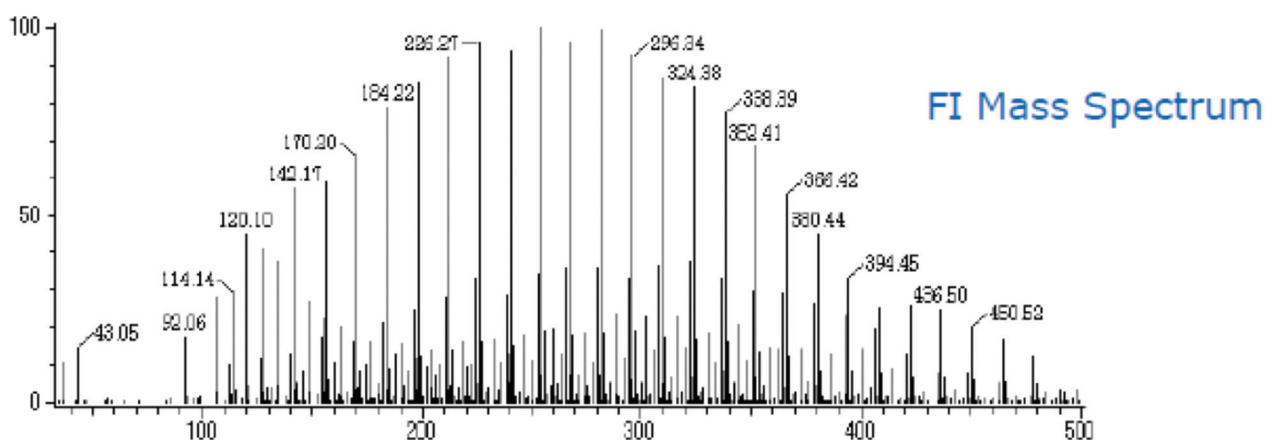


Figure 3: Mass spectrum obtained with FI from a crude oil sample showing the hydrocarbon species detected as molecular ions. (Courtesy Joel UK Ltd)

In Conclusion

Recent developments in lower cost, robust HRMS instrumentation combined with the plethora of ionisation techniques have provided a huge opportunity for the petroleum industry to generate comprehensive chemical characterisation of complex mixtures at the molecular level. The data generated can be used to develop new structure property relationships which in turn can lead to enhanced product performance. By selecting an ionisation technique with high sensitivity and selectivity for the chemical class of interest relative to that for the sample matrix and combining it with HRMS to give detailed molecular characterisation we have a powerful tool applicable to many areas of the petroleum and petrochemical industries.

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