Ultrahigh Resolution Mass Spectrometry: Determining the Molecular Composition of Petroleum

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Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) has been at the forefront of petroleum analysis for more than a decade. Not to be confused with Fourier transform infrared (FTIR) spectroscopy, FTICR MS represents the state-of-the-art for mass spectrometry. The performance characteristics and flexibility of the instrumentation have made the technique extremely well-suited to the analysis of complex mixtures, such as petroleum and environmental samples.

Introduction to FTICR MS

First described in 1974 by Comisarow and Marshall,[1] the underlying principle is that ions are trapped by appropriate electric and magnetic fields,[2-4] orbiting within a "cell." The cell is typically a cylinder of a few centimetres in diameter, consisting of six electrodes: two, circular end plates (trapping electrodes) and four electrodes spanning the length of the cylinder (two detection electrodes and two excitation electrodes). The cell is located within a magnetic field, most commonly positioned within the bore of a superconducting magnet.

Figure 1: 12 T solariX FTICR mass spectrometer located in the Ion Cyclotron Resonance Laboratory (University of Warwick, Coventry, UK).

Due to the Lorentz force, the ions orbit within the cell. In order to make the motion suitable for detection, these orbits must be increased in radius by applying a radio frequency (rf) potential to the two excitation electrodes. The ions induce sinusoidal image currents as they pass the detection electrodes of the cell during their orbits. The image currents induced by ions of different mass-to-charge ratios (m/z) are detected at the same time and lead to a complex time domain data set. By using a Fourier transform, the frequencies of the various orbits can be determined. As shown by Equations (1) and (2), an ion orbits with a cyclotron frequency that is inversely proportional to its m/z; lower mass ions therefore have a higher frequency than higher mass ions with the same number of charges. Thus, by measuring the image currents for the different ions, using a Fourier transform to determine the associated frequencies, and then converting between frequency and m/z, a mass spectrum (signal intensity vs. m/z) can be produced.[4]

$$f = \frac{qB}{2\pi m} \tag{1}$$

where f is the cyclotron frequency in hertz (Hz), q is the charge on the ion in coulombs (C), B is the magnetic flux density in tesla (T), and m is the mass of the ion in kilograms (kg). Note that m/z can be determined by converting the mass from units of kg to daltons (Da) and through the relationship shown in Equation (2):

$$q = ze \tag{2}$$

where z is the integer number of charges (number of electrons gained or lost) on the ion and e is the charge of an electron (in coulombs, C). For petroleum components, ions are typically singly-charged and so the m/z value is equivalent to the mass (in Da).

FTICR MS instruments are primarily known for their unrivalled performance characteristics: ultrahigh resolving power and mass accuracy. Resolving power is a measure of the width of the peaks within the mass spectrum. Narrower peaks (higher resolving power value) are superior because it means that more peaks can be resolved within a narrow m/z region. A larger number of components within a complex mixture can therefore be observed and the result is there is reduction in the probabilities of peaks overlapping, information being lost, and misassignments of elemental compositions (where each composition is provided by a molecular formula; dibenzothiophene has a composition of $C_{12}H_8S$, for example). Resolving power is determined by Equation (3):

$$\frac{m}{\Delta m} \tag{3}$$

where m is the m/z of the centre of the peak and Δm is the width of the peak at half its height, full width half maximum (FWHM).

To provide examples, modern time-of-flight (TOF) mass spectrometers are capable of a resolving power of approximately 10,000 – 50,000 (FWHM), while FTICR mass spectrometers are capable of one or two orders of magnitude higher (hundreds of thousands or millions; in other words, peaks that are ten or a hundred times narrower).

Mass accuracy is a figure of merit associated with the confidence in an assignment of an elemental composition to a particular peak. Once the user has assigned a composition to a peak in the mass spectrum, the theoretical m/z and the observed m/z can be compared using Equation (4) to determine the mass error in parts per million (ppm):

$$\frac{mass_{observed} - mass_{theoretical}}{mass_{theoretical}} \times 1,000,000 \tag{4}$$

Lower mass errors (lower number of ppm) indicate higher confidence in the assignments being correct. For comparison, data from TOF instruments may typically have mass errors of 2-5 ppm associated with the assignments of elemental compositions, while data from FTICR MS instruments will typically be sub-ppm (e.g. parts per billion [ppb] to tenths of ppm). Smaller errors associated with an m/z measurement result in fewer potential candidates for the elemental composition, increasing confidence in the assignments made during data analysis.

The combination of ultrahigh resolving power and mass accuracy makes FTICR MS extremely well-suited to the analysis of complex mixtures. When compared to lower performance varieties of instrumentation, a greater number of components can be resolved and the m/z values can be measured with greater accuracy. This leads to more detailed profiles of molecular composition for complex mixtures. A natural area of research for FTICR MS, therefore, is the analysis of petroleum.

Petroleum Analysis Using FTICR MS

Petroleum can contain tens of thousands of organic components, where each component includes carbon and hydrogen, but may also contain heteroatoms, such as nitrogen, oxygen, or sulfur. The molecular characterisation of petroleum using mass spectrometry, in particular ultrahigh resolution mass spectrometry, has been termed "petroleomics." Once a mass spectrum has been acquired, for the purposes of data analysis, the masses of the ions can be converted from IUPAC masses (where the mass scale for the periodic table is normalised to ^{12}C) to the Kendrick mass scale, which is normalised to CH_2 instead.[5-7] The IUPAC mass for each ion can be converted to the Kendrick mass scale using Equation (5):

$$Kendrick\ mass = IUPAC\ mass \times \frac{CH_2\ value\ on\ Kendrick\ scale}{CH_2\ value\ on\ IUPAC\ scale}$$

$$Kendrick\ mass = IUPAC\ mass \times \frac{14.00000}{14.01565} \quad\quad (5)$$

After the calculation of the exact Kendrick mass for an ion using Equation (5), the nominal Kendrick mass can be produced by rounding this value to the nearest integer. The difference between the exact and nominal Kendrick masses, as shown in Equation (6), is used to determine the Kendrick mass defect (KMD).

$$Kendrick\ mass\ defect = Nominal\ Kendrick\ mass - Exact\ Kendrick\ mass \quad (6)$$

The reason for using the Kendrick mass defect relates to patterns that can be found within the complex molecular composition of petroleum. Homologous series (same heteroatom content, same number of rings and double bonds, but differing alkyl chain lengths) have the same KMD. By plotting KMD vs. nominal Kendrick mass, data points lie along horizontal lines. These horizontal lines indicate homologous series, where adjacent data points differ in composition only by the addition of CH_2.

Once homologous series are known, the elemental composition for only one data point needs to be determined; other compositions within the series can be produced through the simple addition/subtraction of CH_2, instead of determining the elemental composition for every data point individually. This process significantly reduces the challenges posed by the data analysis.

Following the acquisition of a mass spectrum of a petroleum sample, the data can be analysed and a breakdown can be produced using a variety of visualisation approaches.[8]. Assignments can be categorised using three criteria. The first of these is the compound class, which simply describes the heteroatom content of an organic molecule. A molecule belonging to the "HC" class contains only carbon and hydrogen, while a molecule belonging to the "S_1" (or simply "S") class would contain carbon, hydrogen, and one sulfur atom, and so on. The second criterion is the double bond equivalents (DBE), which is a measurement of rings and double bonds within the carbon frame of the molecule. The third criterion is the carbon number, which is simply the number of carbon atoms in the molecule, providing an indication of the size and degree of alkylation. Using these three categories, it is common, for example, to produce plots of DBE vs. carbon number for individual compound classes as a means to generate a visual profile for part of the sample composition.

Exposure of Crude Oil to Light

One example of an application of FTICR MS to the study of petroleum is an investigation of the exposure of crude oil to light. Whether through human activity or through natural seepage, crude oil will get into the environment. Once released, there are various processes which will change the molecular composition of crude oil, including evaporation, biodegradation, photodegradation, and more. In a recent study, photodegradation was specifically targeted so that a single process could be monitored under controlled, laboratory conditions.[9]

One crude oil sample was exposed to ultraviolet (UV) light and another was exposed to light produced from a SoLux lamp, which has a similar output to the solar emission profile. The two samples were characterised using FTICR MS after approximately five and a half weeks of exposure and the profiles were compared to that of a control sample. By determining the changes in composition, the effects of exposure different light sources were monitored.

As seen in Figure 2, there were subtle differences between the overall appearance of the mass spectra for the three samples, but the significant changes to the molecular compositions would only be highlighted following data analysis. Figure 3 shows an example of the importance of ultrahigh resolving power; as a side investigation into the effects of sample preparation, a sample was prepared in toluene only and in a mixture of propan-2-ol and toluene. The addition of propan-2-ol aided the protonation (and, therefore, observation) of nitrogen-containing compounds. Without ultrahigh resolving power, such subtle differences between mass spectra could not be readily studied.
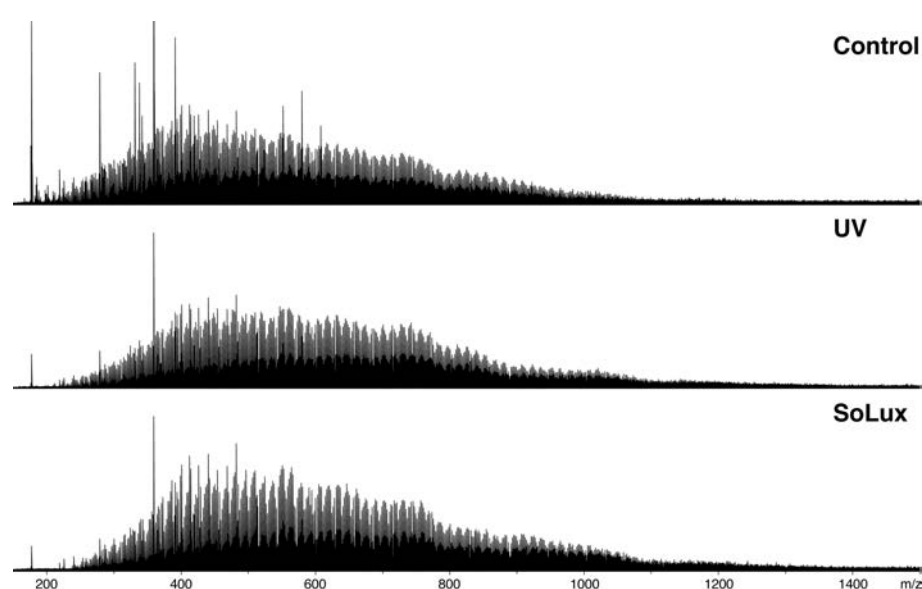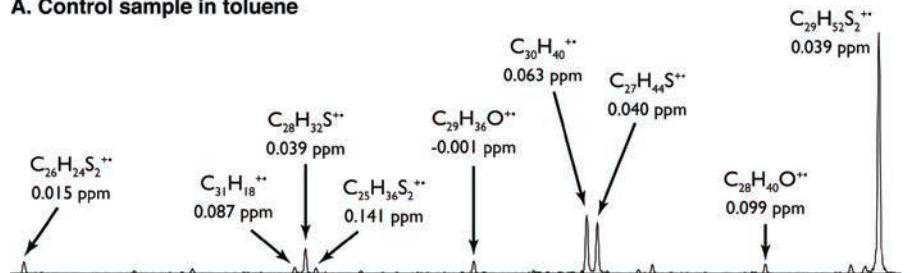

Figure 2: Mass spectra of the control sample and crude oils exposed to a UV lamp and a SoLux lamp after five and a half weeks. Reprinted with permission from Analytical Chemistry, 2014, 86 (1), pp 527–534. Copyright 2013 American Chemical Society.
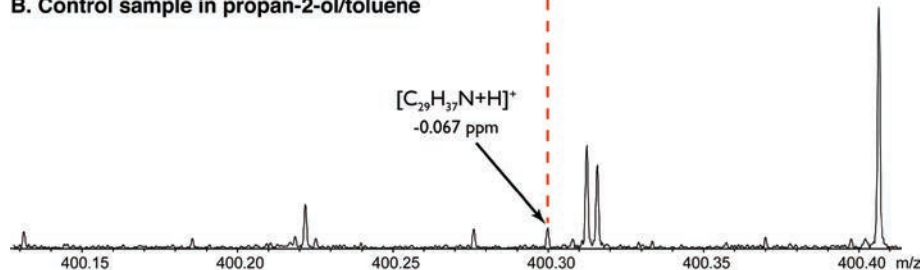

Figure 3: Enlarged regions (approximately m/z 400.13 – 400.45) of mass spectra produced using samples prepared in different solvents. The ultrahigh resolving power affords the ability to determine small differences in profile. Here, it was found that the addition of a co-solvent aided the observation of protonated nitrogen-containing species. Reprinted with permission from Analytical Chemistry, 2014, 86 (1), pp 527–534. Copyright 2013 American Chemical Society.

Once mass spectra had been obtained and an elemental composition had been assigned to each of the thousands of components, the data could be represented using different formats. Figure 4 provides an overview of the molecular compositions of the three samples, plotting the relative contributions from each of the compound classes. Note that the label "[H]" indicates that the associated ions were observed in a protonated form, while classes listed without this label indicate the species were observed as radical ions. A comparison of the samples reveals that nitrogen (only)-containing and sulfur (only)-containing components were reduced in their relative contributions following exposure to light, while various oxygen-containing components increased. It can therefore be seen that heteroatom-containing components preferentially underwent oxidation.
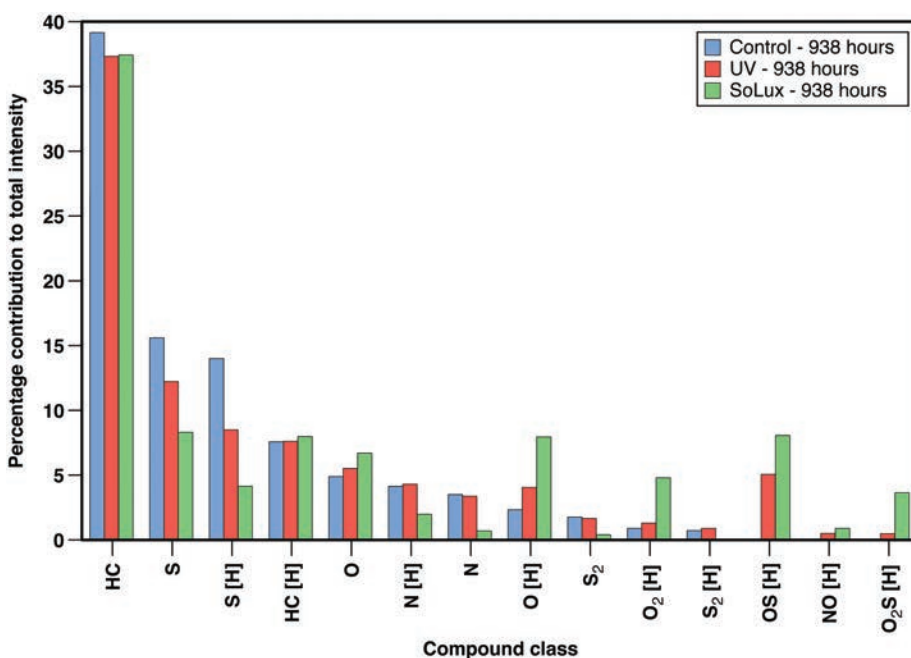

Figure 4: Bar chart showing the relative contributions from different compound classes for the three samples. Exposure to light was observed to result in photooxidation, where heteroatom-containing components preferentially underwent oxidation. Reprinted with permission from Analytical Chemistry, 2014, 86 (1), pp 527–534. Copyright 2013 American Chemical Society.

The data can also be examined in more detail. The different components providing the total contribution from a chosen compound class can be represented as DBE vs. carbon number, as shown in Figure 5. Here, the radical ions associated with the S_1 class are shown for the three samples. Each data point represents a single elemental composition. From Figure 4, it was clear that the S_1 class was amongst the compound classes that were most reduced after exposure to light; from Figure 5, however, it can be seen that not all components of the S_1 class photooxidised equally and that the lower DBE species preferentially reacted. Note the "magic numbers" for the DBE range, which are consistent with the abundance of thiophene-based structures. Although information about the carbon number range is not retained, it can be convenient to plot the contributions as a function of compound class and DBE within a single plot, as shown in Figure 6. The contributions from protonated ions and radical ions are shown for the three samples. While there was relatively little change in the contribution from the radical ions, with the exception of a reduction of lower DBE components, significant changes were observed for the contributions from protonated ions. In particular, the protonated S_1 class, which represented the predominant protonated species, was notably reduced and the components at lower DBE were most significantly affected.
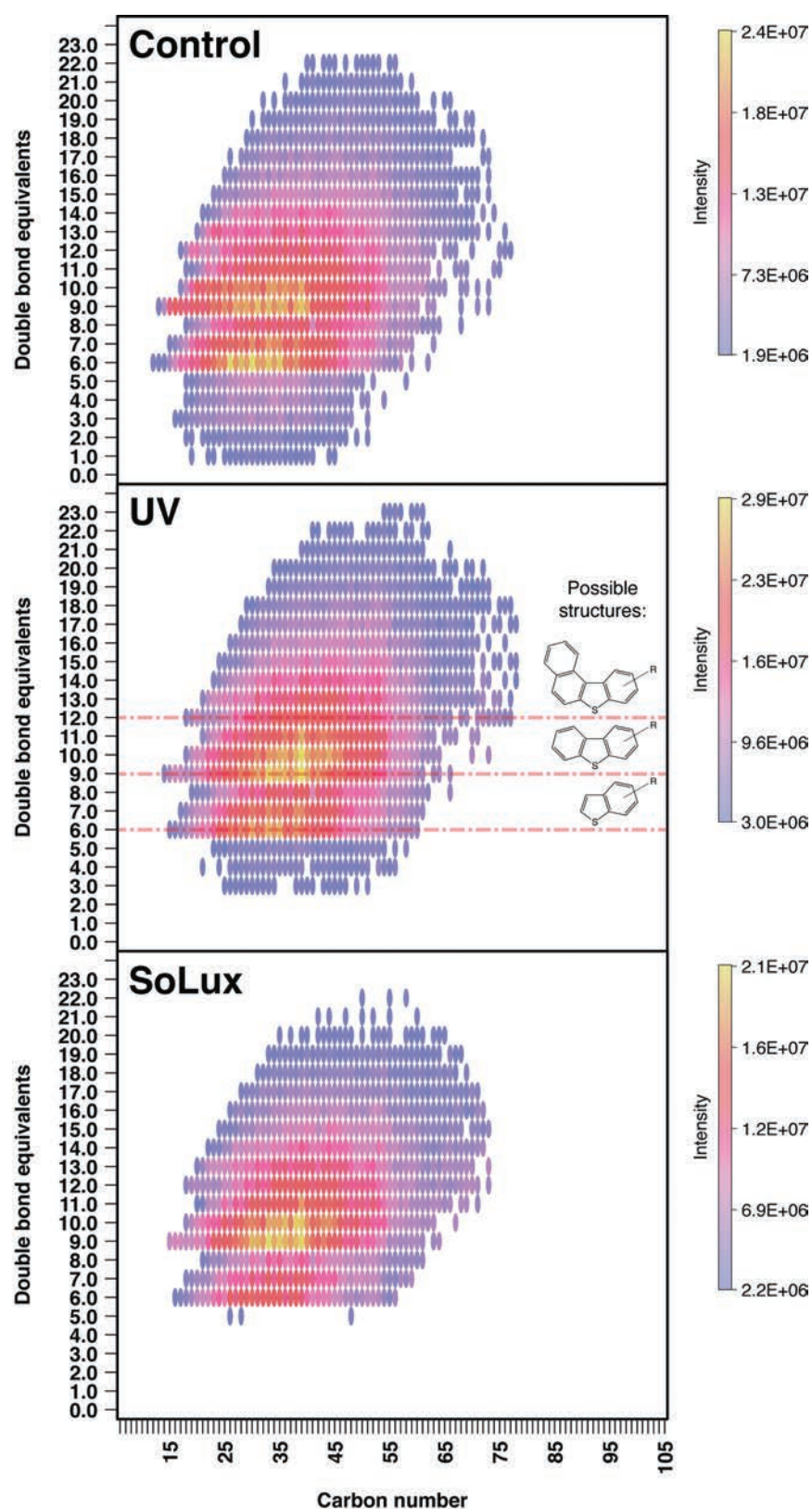
Figure 5: Plots of DBE vs. carbon number for the radical ions associated with the S_1 class (i.e. $[C_cH_hS_1]^{\bullet\bullet}$) for the three samples. Reprinted with permission from Analytical Chemistry, 2014, 86 (1), pp 527–534. Copyright 2013 American Chemical Society.
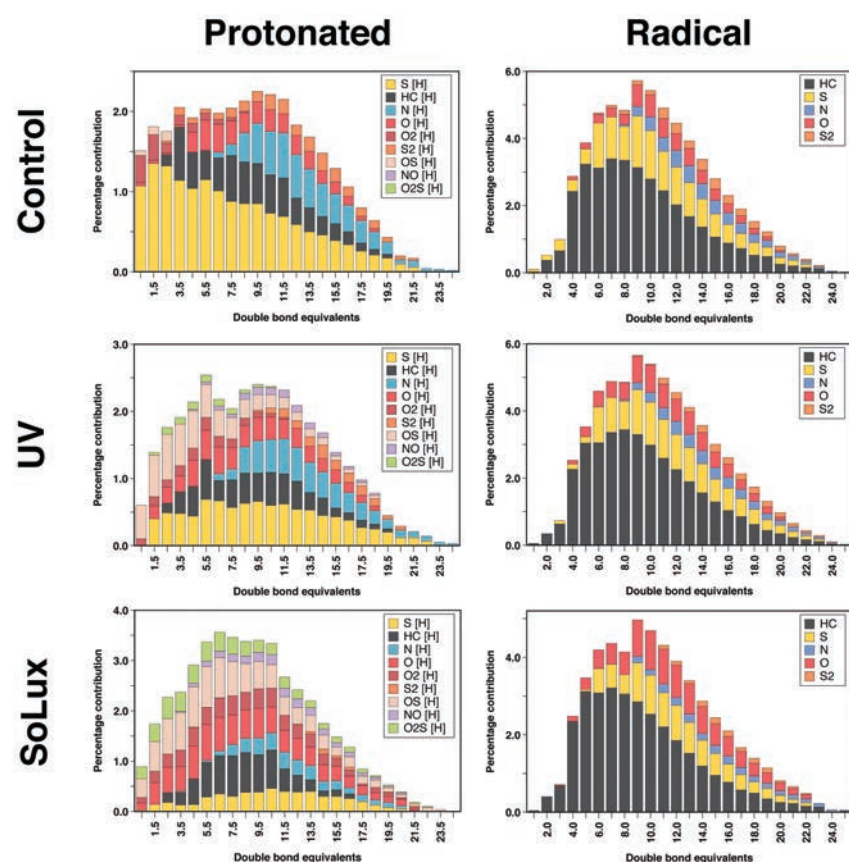

Figure 6: Bar charts of contributions as a function of compound class (both as protonated ions and as radical ions) and DBE. Reprinted with permission from Analytical Chemistry, 2014, 86 (1), pp 527–534. Copyright 2013 American Chemical Society.

This example study represented a controlled investigation of the effects of photodegradation of crude oil, as one process which can affect its molecular composition in the environment. It was determined that photooxidation was primary reaction pathway, that heteroatom-containing components were most significantly affected, and that there was a more pronounced effect for lower DBE components. Additionally, the photooxidation resulted in potential increases in acidity and solubility in water, with the associated consequences for petroleum entering aquatic environments.[9] The ability to monitor changes in the molecular composition of a highly complex sample, with the resulting impact of improved understanding of petroleum and the environment, was made possible through the performance of a high field FTICR mass spectrometer. For more than a decade, FTICR MS has been playing a leading role in the furthering of understanding of complex mixtures such as petroleum, and this looks set to continue in the coming years.

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Dr. Mark P. Barrow is a Senior Research Fellow at the University of Warwick in the United Kingdom. Since 2000, his research has primarily focused upon the study of petroleum-related complex mixtures using high field Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Dr. Barrow's work involves the development of analytical methods and also applications using real world samples, entailing collaborations with the petroleum industry and Environment Canada, amongst others. He serves as a reviewer for approximately twenty journals and for various British, American, and Canadian funding bodies, as well as being a member of the Royal Society of Chemistry (RSC), the British Mass Spectrometry Society (BMSS), the American Society for Mass Spectrometry (ASMS), and the Energy Institute (EI).

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