THE NEED FOR MODERN CHROMATOGRAPHY MASS-SPECTROMETRY FOR THE ANALYSIS OF SUSTAINABLE FUELS AND OILS

This presentation explores the need for chromatography and mass spectrometry for the analysis of modern fuels and oils. The article will address why we need hyphenated techniques and particularly why an updated modern approach to analysis is required. Some of the reasons expressed are related to changes in fuel and fuel stocks, improved selectivity of separation and inherent sensitivity of modern technology to detect low-level materials, the need to understand materials at molecular level and finally to explore the sustainability of fuels and their analysis. There is an inherent challenge in taking standard methods that use old technology and converting them into new methods by utilising different chromatography and mass spectrometry approaches. A simple example could be the HPLC method from the 80s which today would most likely be a UHPLC method: quicker, more sensitive and using significantly less organic solvent; the latter is an important factor when we consider the sustainability of our analytical laboratories.

There are still times when you should question whether you need chromatography and the petroleomics community has shown that you can answer many questions purely by using ultra-high-resolution mass spectrometry. But - and it's a big but - you can only access information about isomers through the addition of a separation science step, typically chromatography, but with today's technology, chromatography and ion mobility can be used.

The question of which type of chromatography and which type of mass spectrometry requires some deep thought and understanding of the materials in hand. There is often the need to use multiple hyphenated solutions, for example, GC-MS and LC-MS and also low and high resolution mass spectrometry.

The complexity of some of the materials used Is so great that one-dimensional (1D) chromatography does not provide sufficient separation power, hence the need for two-dimensional (2D) chromatography solutions. To give an accessible example of 1D and 2D data, consider taking a photograph of a city at ground level and compare that with a photograph taken from the same point by a drone 200 metres above. The second picture reveals many more features and details that you cannot see in the first picture, in essence, that's what 2D chromatography gives us. The power of two-dimensional chromatography can be seen in the examples below. In the 2D data set the more intense the colour the greater the intensity of the peaks. The second separation along the Y axis was achieved using a different phase column. Under each spot in the 2D trace we have a mass spectrum and so can identify each component within the samples.

Example 1 shows the separation of biodiesel components within a commercial diesel sample. The red dots of the long-chain hydrocarbons within the diesel fuel next to those along the same trend line are isomers of those hydrocarbons. Highlighted at the middle and top of that trace are different biodiesel components, in this case, fatty acid methyl esters (FAMEs), C18:1, C18:2 and C18:3, where C18 identifies the number of carbon atoms in the original fatty acid and the number after the colon identifies the number of double bonds within that carbon chain. Inserted in the top right-hand corner is the 3D plot of those peaks where you can see differences in intensity where once again red denotes the highest intensity species present.
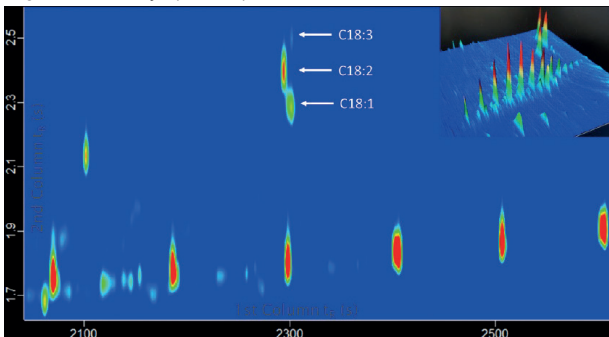
Example 2 is a scenario where three different aviation turbine fuels have been analysed, firstly by 1D GC-MS and secondly by 2D GC-MS. The 1D data shows a great similarity between the three different fuels, whereas the 2D data immediately shows the similarities and differences between the fuels. For example, interrogation of these data shows the presence of aromatic species in BF1 that are absent from JTF.
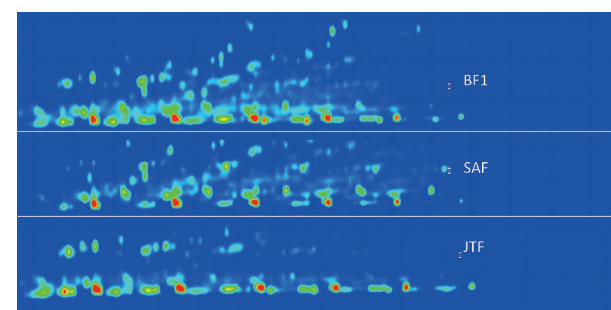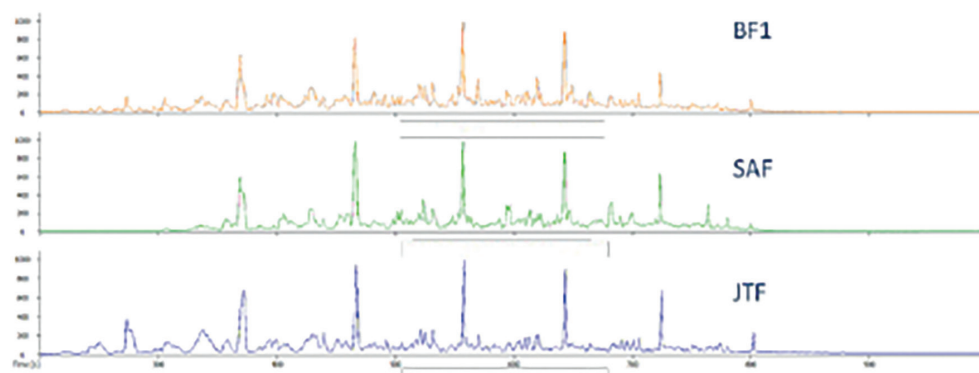
In both examples the information density of the 2D data is much higher compared to the 1D data sets and the improved separation also improves confidence in the assignment of the individual species present.

Another feature of modern hyphenated solutions is the different soft ionisation techniques available to allow for forensic examination of different materials, be they polymerics or large molecule additives that are not accessible by GC-MS and the availability of robust supercritical fluid chromatography (SFC) mass spectrometry solutions. SFC uses supercritical CO_2 as a mobile phase, this is hexane-like in properties and so allows for the injection of gasoline or diesel, or aviation turbine fuel directly into the eluent stream. It also offers great selectivity of separation and fast analysis. For example, we have a 2-minute SFC method

for looking at biodiesel (1) within aviation turbine fuel that compares with an approximate one-hour runtime for the equivalent GC-MS analysis. Another example of the use of SFC-MS is in the identification of the fiscal marker Accutrace S10 which is used in low-duty fuels. Not only is the SFC method 15 times faster than the GC-MS method, but there are other benefits of using the SFC-MS route. The molecule itself showed an unusual and unexpected propensity to ionise under electrospray ionisation conditions, this specificity of ionisation technique means that the fuel matrix diesel matrix, in this case, is basically invisible to that ionisation technique. Furthermore, because this is an atmospheric pressure ionisation source, this does not get dirty from the fuel matrix in the same way as an electron ionisation source does, therefore routine maintenance and cleaning of the ion source is not required.

Detection and Quantitation of ACCUTRACE S10, a New Fiscal Marker Used in Low-Duty Fuels, Using a Novel Ultrahigh-Performance Supercritical Fluid Chromatography−Mass Spectrometry Approach

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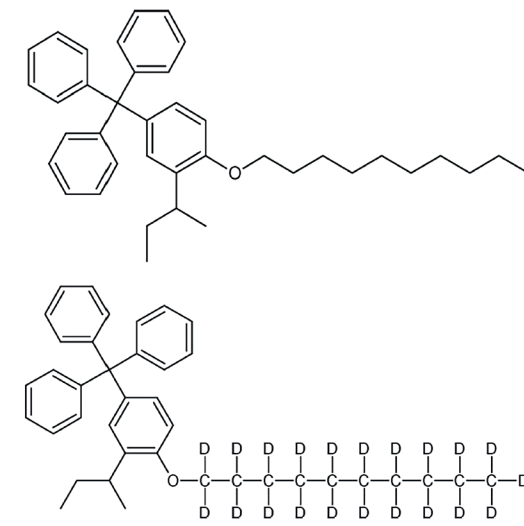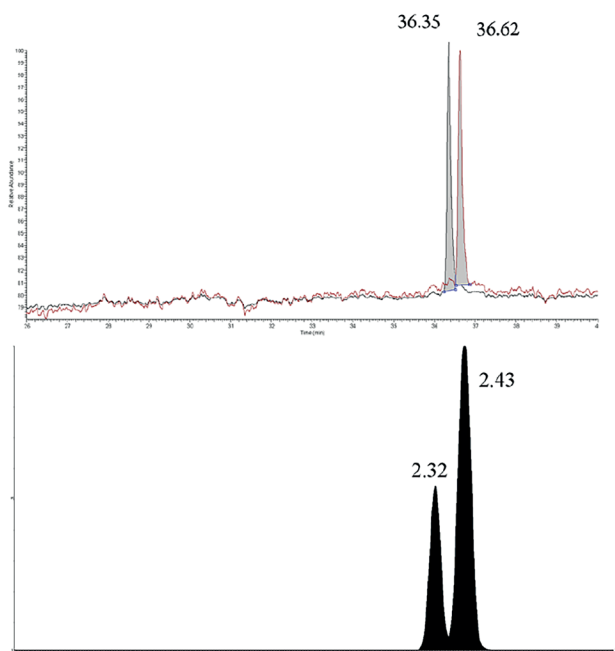
My concluding remarks are that we definitely need chromatography and mass spectrometry because of the different materials we now work with, the complexity of the materials and the different requirements demanded by the industry. There are challenges ahead in providing sustainable solutions and the updating of historic methods to deliver this alongside the ever-changing fuels and fuel delivery systems. Fortunately, we have different and robust hyphenated solutions to answer these questions.

Professor John Langley (orcid.org/0000-0002-8323-7235) is an internationally recognised leader in chromatography - mass spectrometry (MS) with >35 years' experience, and has led and managed the chromatography-MS facility at Southampton Chemistry since 1988.

John has 120 publications and has delivered innovative approaches to MS and chromatography-MS, e.g., the first academic open access MS instrumentation in 1995, open access LC-MS, GC-MS and then SFC-MS in 2014.

He is a Fellow of the Royal Society of Chemistry (RSC), Chartered Chemist, Chartered Scientist, Member of RSC Analytical Division Council (2014-20), Chair of the RSC Separation Science Group (2009-) and Past President of the International Mass Spectrometry Foundation (2018-22). He is the only person to have been Chair of the BMSS and the RSC Separation Science Group, and was presented with the British Mass Spectrometry Society medal in 2021.

He is director of the SW Regional GCxGC-HRMS facility, and the equivalent SW Regional LCxLC-IMS-HRMS facility.

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