A Modern IMS-MS Petroleomics Workflow for Users of Thermo Scientific™ Trap-Based Mass Spectrometers

Petroleum samples are inherently complex mixtures containing thousands of molecules that range in structure from linear alkanes to compact asphaltenes. However, within this diverse molecular soup one can find multiple series of relatively similar compound classes or types that may vary by just the heteroatom present (-O, -S, -N), alkyl chain length, or degree of branching. Crude oil analysis by mass spectrometry (MS) results in extremely information rich data, where species are observed at each nominal mass. Components may only differ in mass by less than 10 mDa, necessitating the utilization of high resolution mass analyzers for these applications. Although ultrahigh mass resolution can aid in the characterization of these samples, it still cannot address the presence of true isobaric species, a commonly encountered challenge within the petroleomics community. Distinguishing several structural isomers comprising a single peak in the mass spectrum can sometimes be accomplished through fragmentation or upfront separation techniques. However, confident structural assignments still prove to be difficult due to the overall sample complexity. To circumvent the limitations of even high resolution mass spectrometers, an additional dimension of analysis with the ability to effectively separate ions based upon their unique gas phase structure greatly increases overall peak capacity. Ion mobility spectrometry (IMS), a well established technique for separating ions by shape, has proven to be a valuable tool when coupled with MS for the analysis of oil based samples. Comprehensive IMS-MS multidimensional separations lead to spectral deconvolution and a significantly improved analytical performance. Ions with similar structure pertaining to the same molecular class, will occupy a different space (trend band) on two dimensional IMS-MS plots than ions from another molecular class. These observed average trend lines (**Fig 1**) can then be used to readily distinguish different classes of compounds that may be present from one another, information that is ultimately essential for characterization and identification.
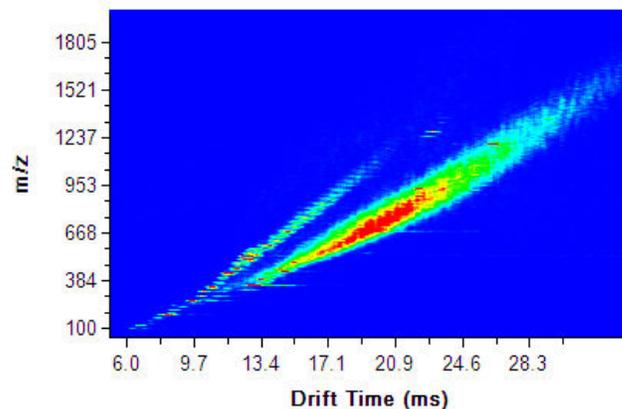

Fig. 1 Mobility-mass correlation curve of crude oil intermediate vacuum resid obtained from major petroleum company.

The MA3100 is a compact, fully functional ion mobility spectrometer able to interface with all Thermo Scientific™ mass spectrometers. Two-dimensional plots are generated by sequentially stepping the delay time (t_{del}) between the opening of the first (entrance of drift tube) and second (exit of drift tube) ion gates up through the longest drift time (t_d) of interest (**Fig 2**). By doing so (with trap-based instrumentation), a full mass spectrum is recorded for each mobility window across the IMS period, thus achieving comprehensive mobility-mass correlation.
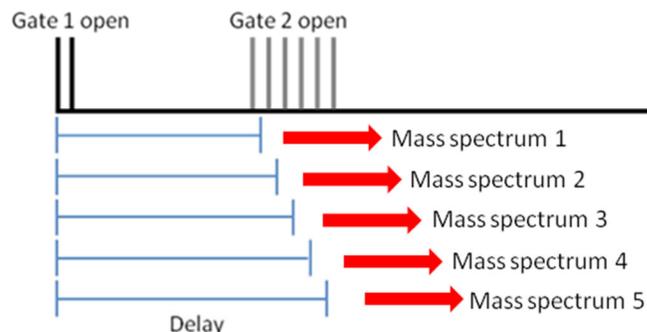

Fig. 2 Mass spectra from a series of variable gate delay pulses are combined during scan mode operation to create 2D t_d vs. *m/z* data sets.

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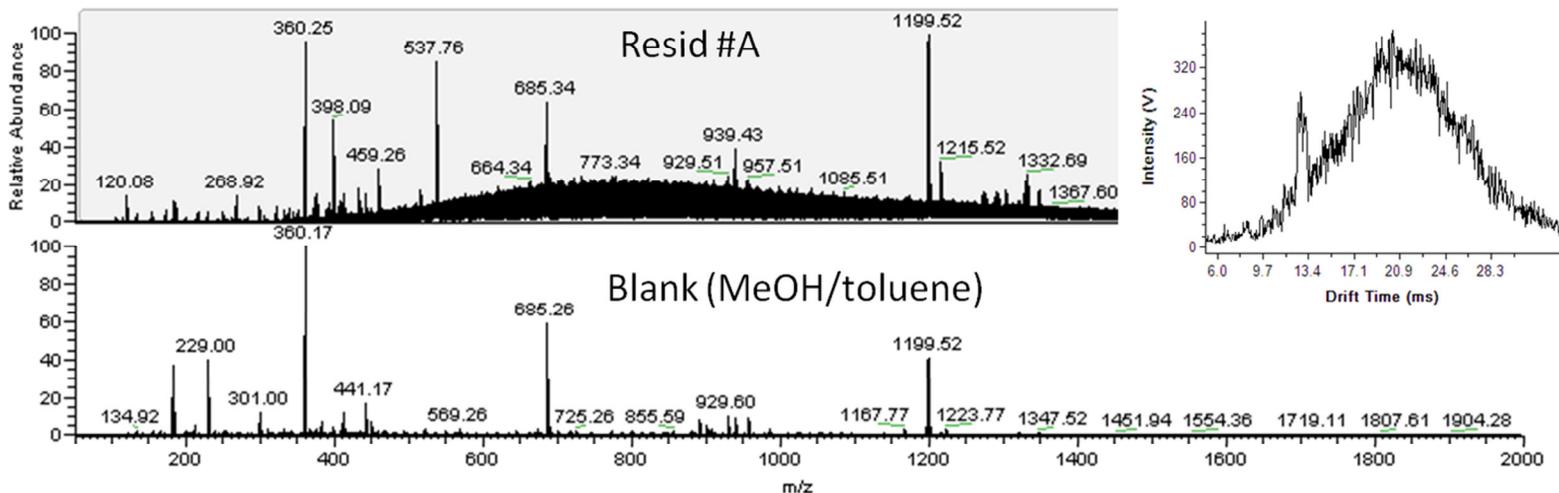**Innovation for Excellence in Detection Technology**

Fig. 3 Average mass spectra from vacuum resid with no IMS separation and summed over all mobilities.

Efficient IMS separation clearly indicates the presence of two distinct series of hydrocarbon compounds (**Fig 1**), likely indicating incomplete fractionization in the refining process for this sample. However, without an additional post-ionization separation mechanism (IMS) prior to mass analysis, the detection of low level ions and the determination of species from different molecular classes is lost in the collective chemical signal/noise (**Fig 3**). Resolution of these component classes is achieved on a timescale of milliseconds without time intensive prefractionization protocols that potentially require hours of work prior to analysis. Coupled with the unique power of visIon Trap's control and acquisition software, a user can generate an extracted ion mobility or mass spectrum (**Fig 4**) by selecting a targeted region on the two-dimensional plot.   This effectively removes contributions due to unwanted matrix/background ions and coexisting constituents of contrasting chemical classes.

An inherent advantage to this approach is the ability to specifically fill both linear ion trap and orbitrap mass spectrometers with a desired analyte. Separation by mobility with subsequent selection by the second ion gate preferentially allows a trap analyzer to collect a narrow band of ions contained within each step during scan mode operation.
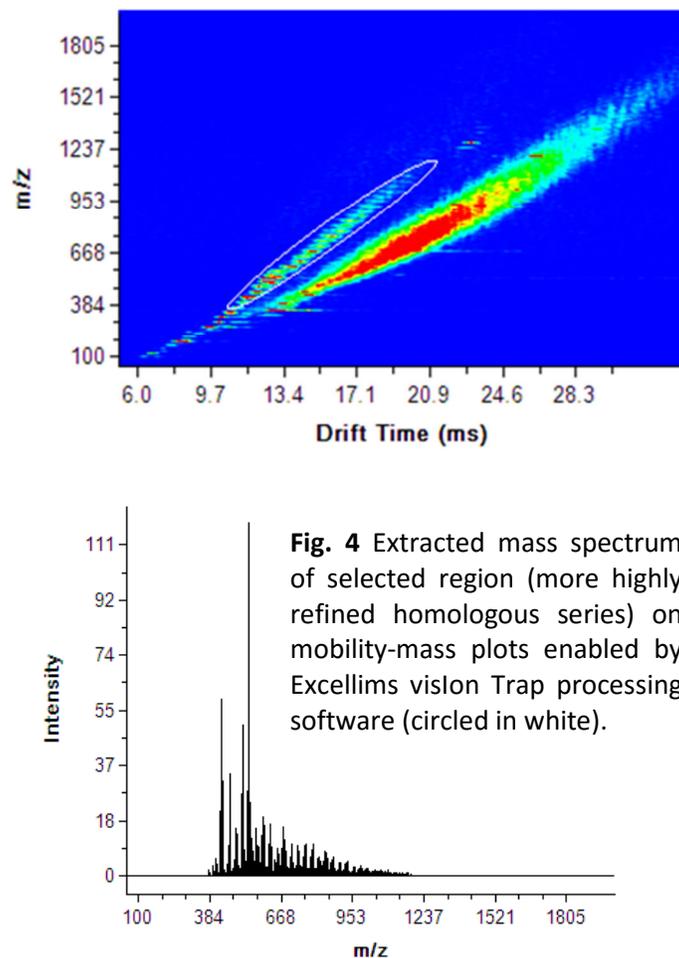

Fig. 4 Extracted mass spectrum of selected region (more highly refined homologous series) on mobility-mass plots enabled by Excellims visIon Trap processing software (circled in white).

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As a result, mobility separation prevents indiscriminate introduction and possible trap saturation of analytically unrelated or untargeted species, including strongly ionizing background material(s). Functioning in this case as a dynamically adjusted selective ion filter, the entire ion injection period during the MS scan function is spent accumulating ions contained within the mobility window for that t_{del}.

Fig. 5 IMS-MS separation of background (A), diesel fuel (B), and kerosene (C) ions with (yellow band) and without selective mobility transmission.

A clear improvement is achieved for the detection of low-abundance kerosene ions (**Fig 5**) that were previously only a very small percentage of the total unfiltered ion population (kerosene + diesel). Ion injection is exclusively defined by the specific mobility window highlighted in yellow. Application of a similar IMS-MS workflow would also be quite valuable for lighter, more highly refined fuels since electrospray (ESI) mass spectra of consumer grade gasoline have been shown to be dominated by the preferential ionization of N class components such as alkyl pyradines. However, when present, additives frequently exhibit higher ionization efficiencies, thereby reducing the available number of these specific principle component ions for detection. The dramatic increase in sensitivity afforded by our device extends the functionality of these mass analyzers in a data independent manner, where *a priori* knowledge of the sample and the *m/z* of trace level ions present are not required. Space charge limitations from excess ions will also be reduced, facilitating a wider dynamic range for MS/MS analysis of these low-abundance or "masked" components.
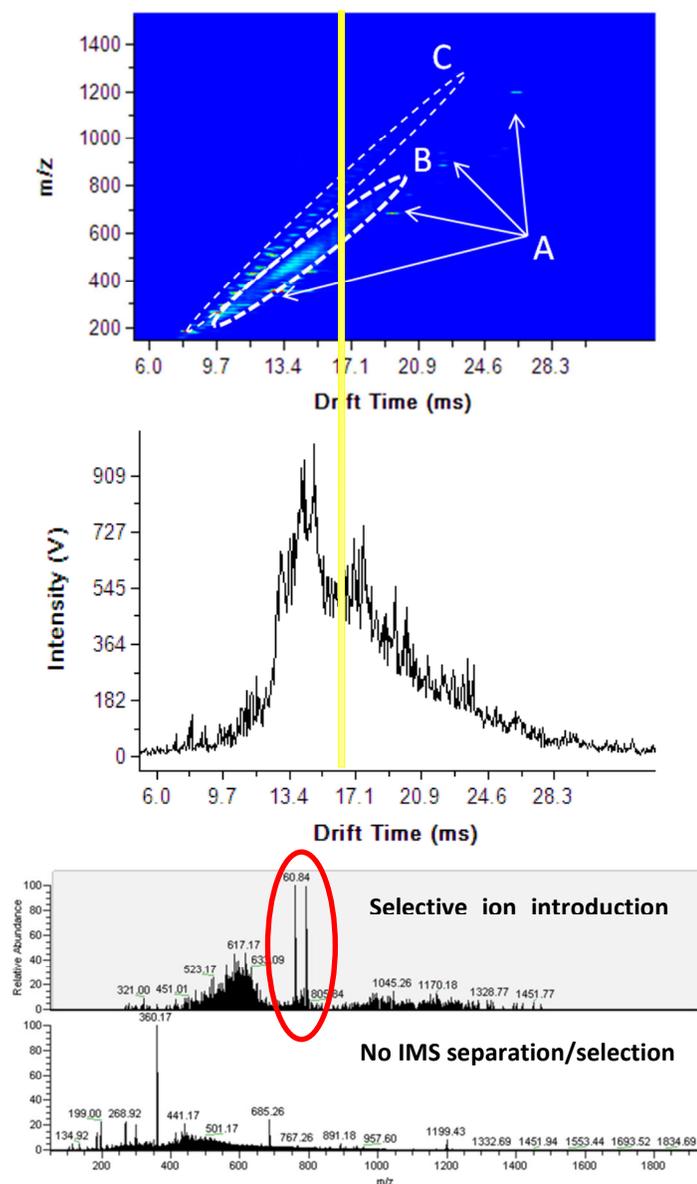
In addition to the selectivity that the MA3100 offers for MS analysis, such mobility-mass correlation plots can serve as a rapid tool to assess the collective gestalt of the sample. As a detailed overall chemical signature is generated, the analyst now has information that can be used to determine if the sample may contain additives, solvents, supplements, impurities, or contaminants that manifest as additional trend bands. This data is unattainable solely by MS analysis alone, as these samples are highly diverse mixtures and subtle variations may go undetected in the mass spectrum due to the degree of chemical complexity. Often these observed differences are of use for quality control purposes, traceability, typification, and potential correlation for the type and geographical origin of the crude oil from which the sample was produced. When spiking common road use diesel fuel with a commercially available fuel treatment such as

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Diesel Formula STA-BIL® Fuel Stabilizer (**Fig 6**), extra species are observed within and around the main band (denoted by white circles). Although the additive ions exhibit rather low intensities, their deviation from the diesel band on the correlation curve easily distinguishes the spiked sample (Diesel + Stabil) from the unadulterated original fuel (Diesel). The strength of IMS is further showcased when truly isomeric constituent species are present (**Fig 7**), potentially arising from diesel treated with winterization additives from the supplier. When coupled with the MA3100, Thermo Scientific[TM] mass spectrometers can become *efficient* and more robust instruments for routine analytical work conducted at refineries wishing to determine the quality of petroleum products before they are distributed.
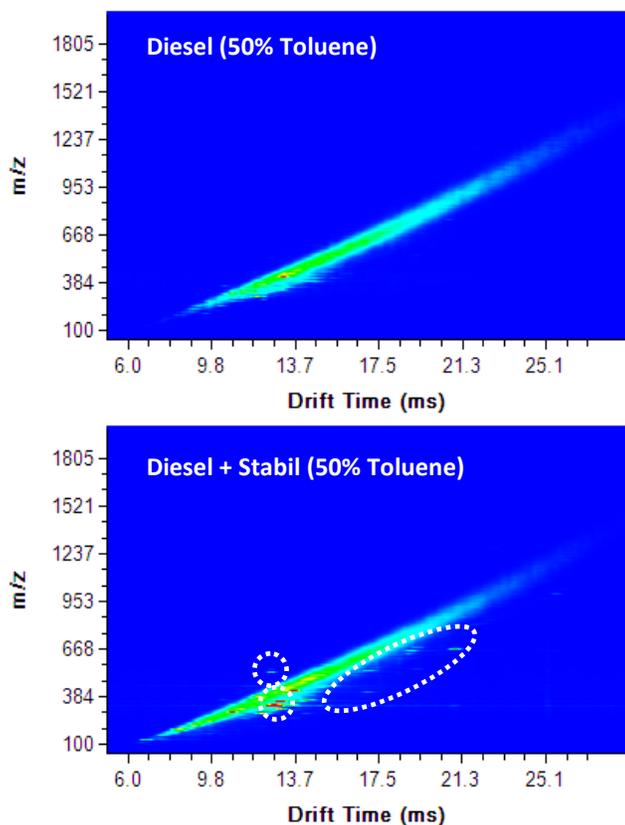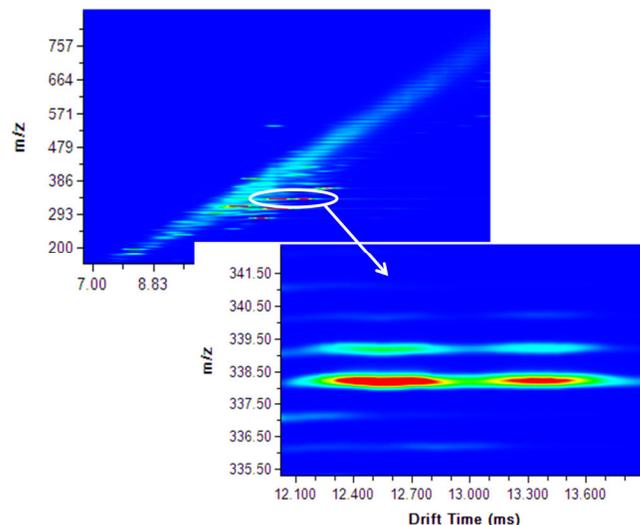

Fig. 7 Diesel fuel sample with abundant main constituent isomeric ions at *m/z* 338.3, transparent to MS.

MA3100 Benefits for Petroleum Analysis

1. Orthogonal post-ionization separation technique based upon ion size/shape now available to current users of Thermo Scientific[TM] mass spectrometers.
2. Operation in scan mode allows flexible user control of parameters to generate and optimize mobility-mass correlation plots. The ion signal for a particular *m/z* is spread over a continuous, featherlike distribution of drift times.
3. Evaluation of correlation plots leads to rapid qualitative identification of distinct molecular classes present within the sample.
4. Excellims visIon Trap software analysis suite captures extracted mass spectrum of selected mobility region to remove background and dissimilar chemical series.
5. Significantly improved sensitivity and analytical performance of low abundant ions governed by targeted mobility-based accumulation.
6. IMS-MS plots function as a better chemical fingerprint than MS alone, easily distinguishing slight component variations.

Fig. 6 Common road diesel with and without fuel treatment stabilizer additive.

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