

Progress Towards Online LC-MS Analysis of Naphthenic Acids

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INTRODUCTION:

Naphthenic (NAP) acids are abundant, oxygen-containing compounds in crude oils. NAP acids are of great interest to the petroleum industry because they can cause problems on both the upstream (oil recovery and transportation) and downstream (upgrading and refining) sides of the production chain. A complete characterization of the NAP acids in a sample can provide useful information to potentially mitigate these complications; however, ionization biases make the comprehensive characterization of both low and high molecular weight NAP acids challenging. Using current ionization methods, lower molecular weight acids (easily ionized) will interfere with the detection of the higher molecular weight acids (poorly ionized). This study aims to establish an efficient method to develop a comprehensive profile of NAP acids in oils.

A complete profile of NAP acids was determined for Doba (DBA), a blend of three oils from the Republic of Chad with high acid content and naphthenates. To aid in the construction of the NAP acid characterization, the Modified Aminopropyl Silica (MAPS) (Figure 1) separation was performed to isolate acid fractions that vary in hydrophobicity, and thus molecular weight. To combat ionization suppression of the high molecular weight NAP acids, this method separates the low molecular weight acids from the high molecular weight acids. Analysis by direct infusion of the sample and its fractions was performed by Fourier Transform Ion Cyclotron Resonance (FT-ICR MS), and analysis of the combined, traditionally-isolated acids was performed by High Performance Liquid Chromatography Mass Spectrometry (HPLC-MS) as a comparison. Both methods provide additional information about the chemical composition of the acidic species present in the sample.

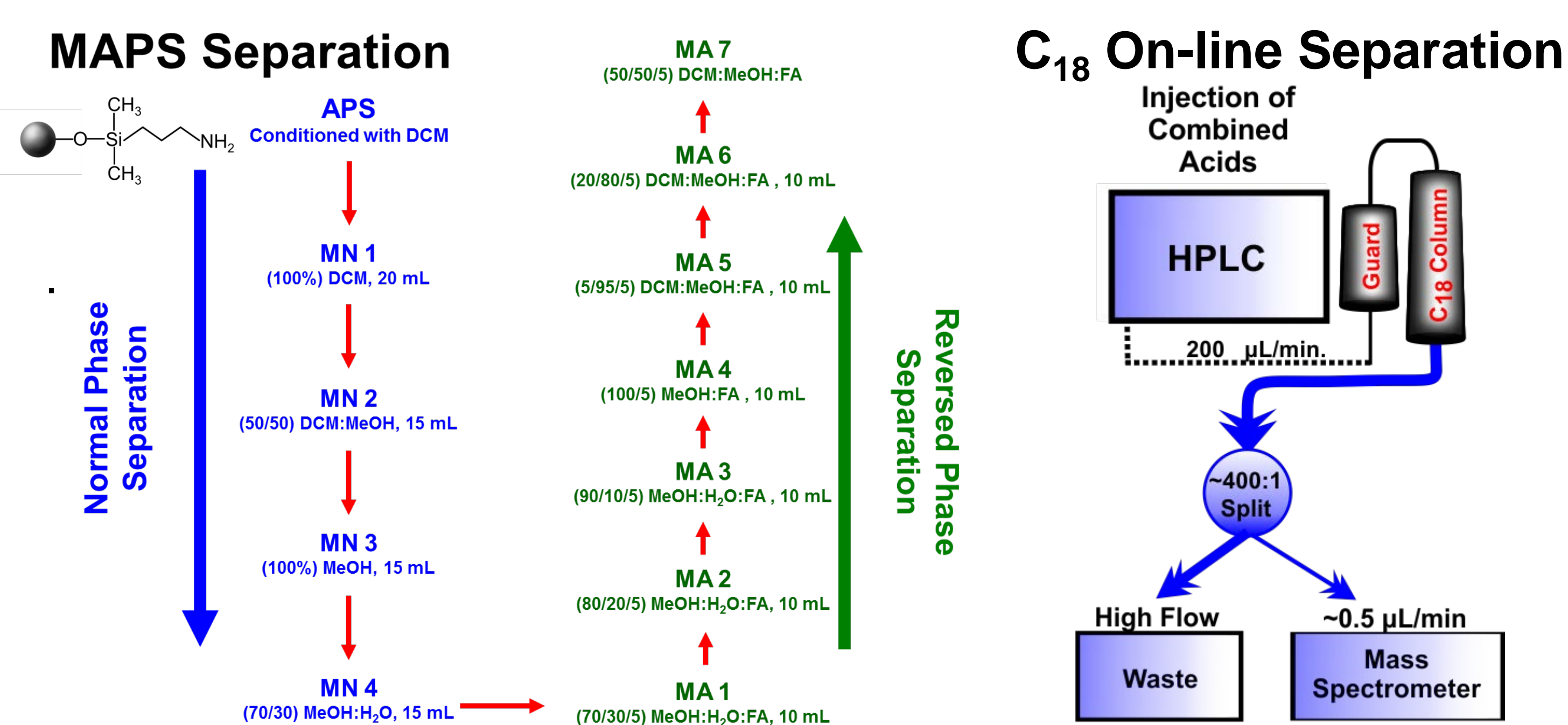


Figure 1. Left: Modified APS (MAPS) fractionation schematic. Right: On-line separation schematic

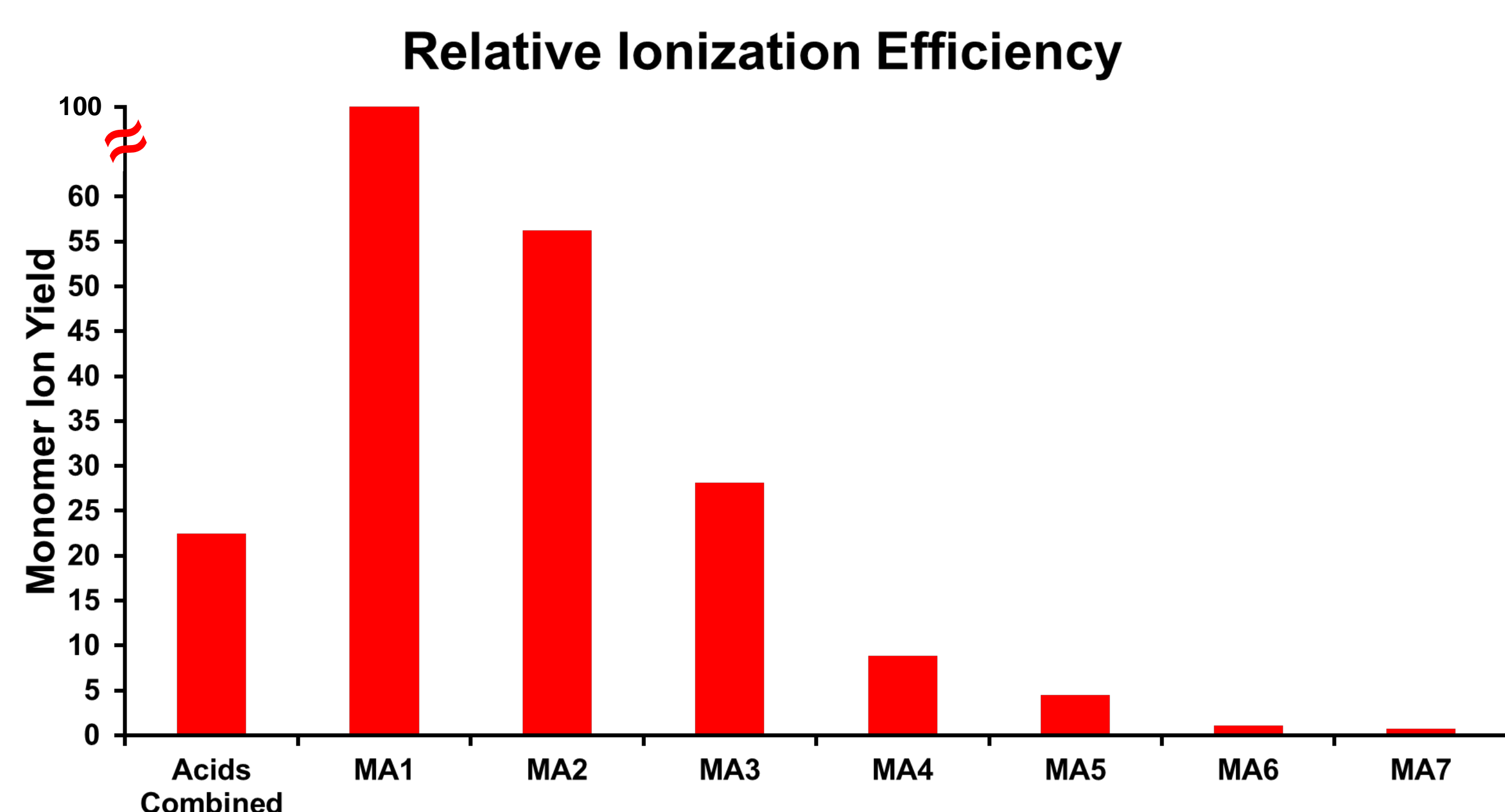


Figure 2. Shows the relative ionization efficiencies for the traditionally isolated acids and the corresponding MAPS fractions. Monomer Ion Yield was calculated from the inverse of the accumulation time used to collect the (-) ESI FT-ICR spectra and normalized to the fraction that ionized most efficiently.

Separations help overcome ionization biases to improve characterization of complex mixtures.

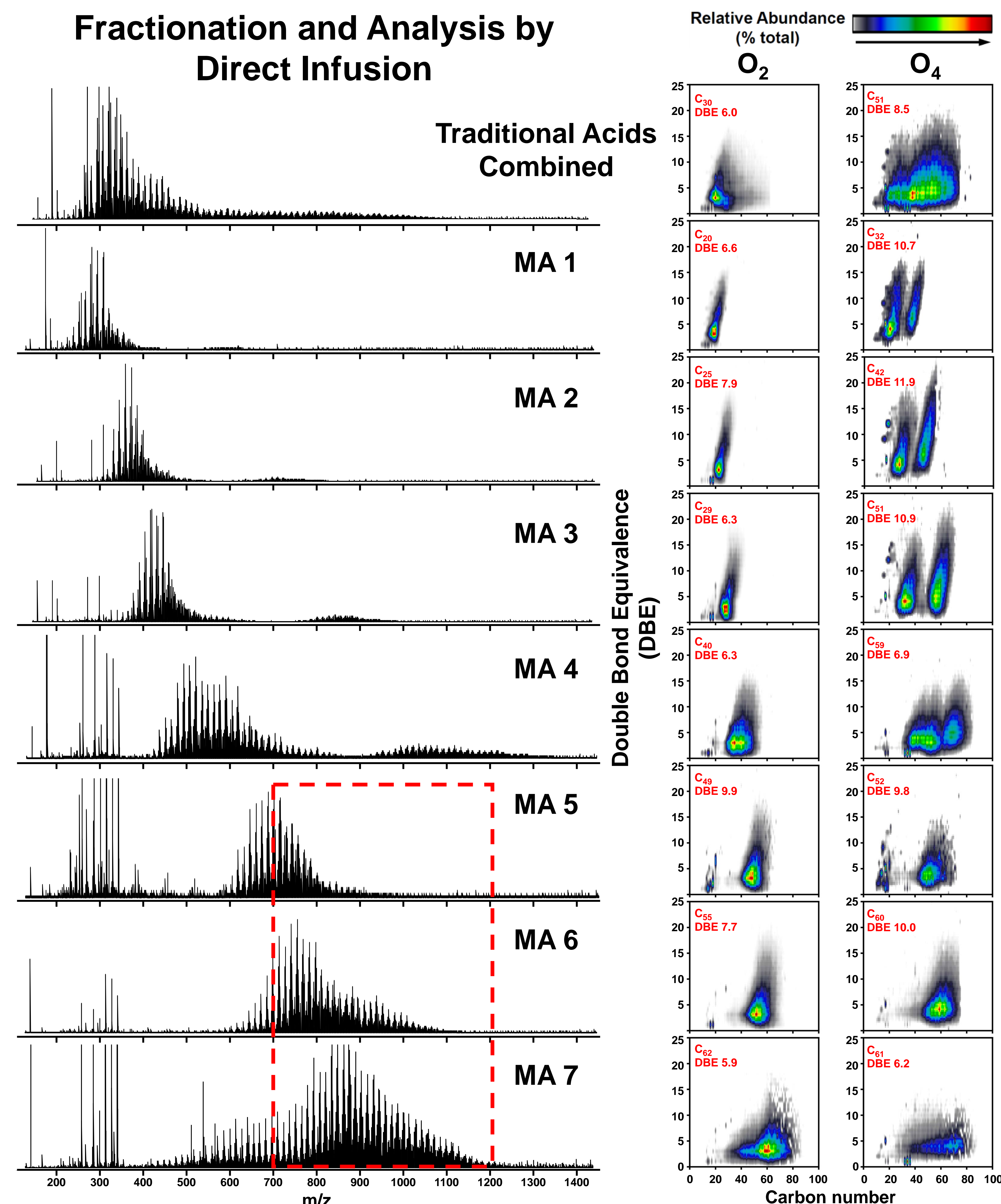


Figure 3. Left: Negative electrospray 9.4 T FT-ICR MS broadband mass spectra for the traditionally isolated acids (top) and its corresponding MAPS fractions. Right: Isoabundance color contour plots for the O_2 (left) and O_4 (right) heteroatom classes derived from the broadband mass spectra of the combined acids and MAPS fractions shown on the left. The red box highlights the high molecular weight acids that were only identified post-fractionation.

Analysis of Traditional Acids Combined with On-line Detection

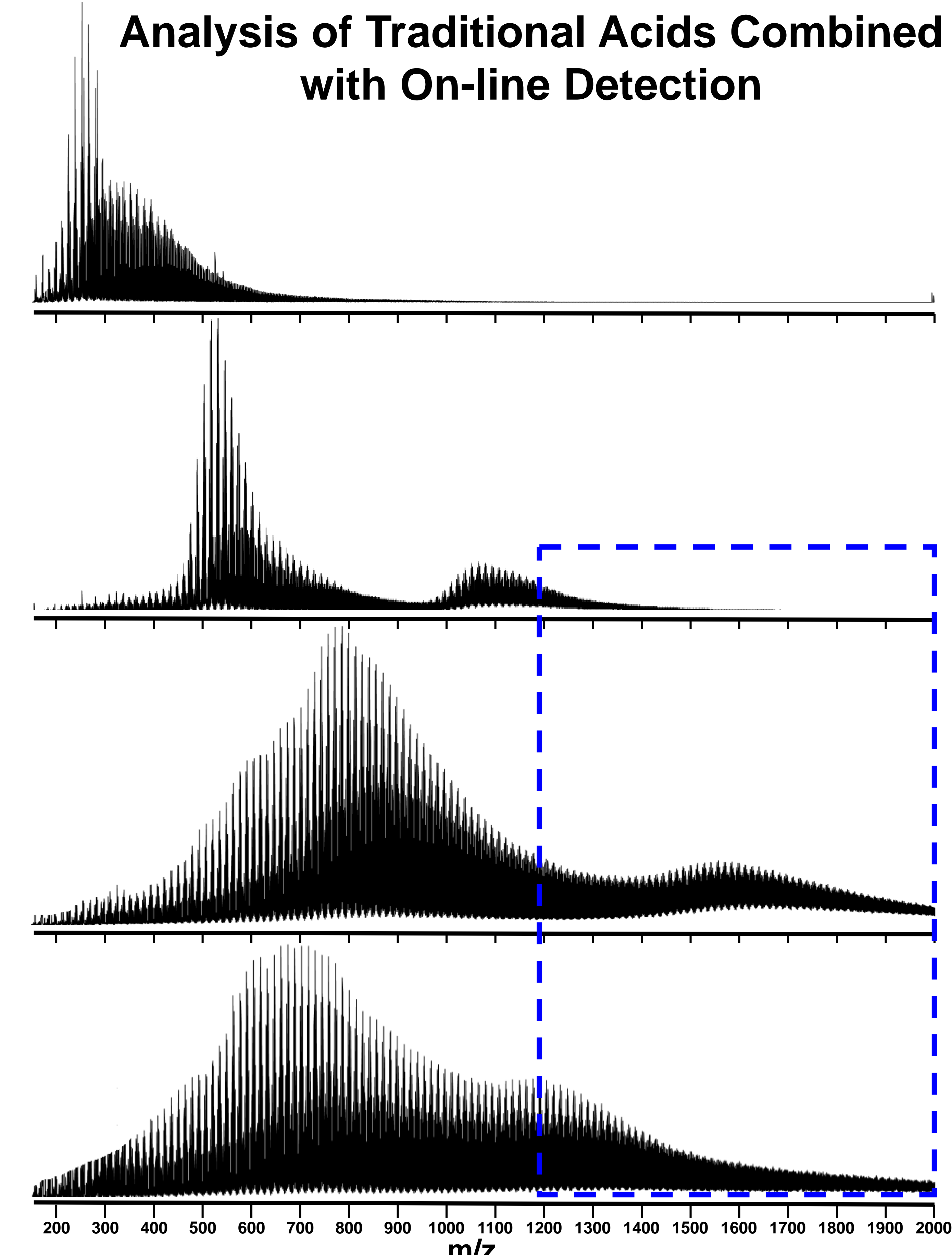


Figure 5. Broadband mass spectra from four discrete elution periods during the on-line separation of the traditional (combined) acids using a C18 stationary phase. The blue box highlights the high molecular weight acids only observed with on-line detection.

CONCLUSIONS:

This study highlights the advantages of chromatographic separations to improve compositional coverage of complex matrices. The MAPS method separates traditional acids by hydrophobicity to yield seven fractions (MA 1-7). The monomer ion yields of the fractions reveal a clear trend in differences in ionization efficiency. Figure 2 shows that the smallest, most hydrophilic acids in MA 1 ionize ~100x more efficiently than the later-eluting, more hydrophobic acids. Compared to traditionally isolated acids, analysis of the fractions by direct infusion expanded compositional coverage to reveal species previously not observed. As shown in Figure 3, the O_2 heteroatom class in the combined acids has a distribution that extends from ~ C_5 to C_{60} with the most abundant hotspot centered at C_{30} . Fractionation revealed that as molecular weight increases the average carbon number increases while the abundance-weighted average DBE decreases. In the highest molecular fraction (MA7) acidic species with more than 80 carbon atoms were revealed. These species were present in the combined acids, but their ionization was suppressed to the point that they were not observed. Complicated fractionation methods do have their limitations. More fractions extend the compositional coverage of a sample, but at the cost of decreased throughput. Additionally, the process of fraction collection and the evaporation of large volumes of solvent can up concentrate chemical contaminants, which can limit the ability to characterize fractions with extremely low ionization efficiencies. On-line detection eliminates these steps, which can improve compositional coverage and at the same time increase sample throughput. Figure 5 demonstrates the extended coverage that can be achieved by on-line detection and reveals acidic species extending out to m/z 2000, whereas the largest species observed by direct infusion have a molecular weight of only m/z ~1200.

ACKNOWLEDGEMENTS:

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