Maximizing knowledge from a single drop using ultra-high resolution mass spectrometry

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Summary

Fluid properties and oil stability and performance depend on the molecular composition of the petroleum. Moreover, oil properties are controlled by the interaction of the multitude of hydrocarbon and polar non-hydrocarbon components in oils, not just the components themselves, similar to the interaction of genes that is biology, rather than genomes themselves.

New technological developments, namely Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR-MS) allows us for the first time to make an almost comprehensive analysis of all oil or bitumen components with their functional groups. In this study it will be shown that we are able to predict physical properties, such as the Total Acid Number (TAN), by molecular compositional proxies using a Bruker 12T FT-ICR-MS. Naphthenic acids (NA) or naphthenates as their salt form and related compounds are the most important components in tackling production fluid issues. They are key players for flow assurance, plugging, corrosion and stable emulsions problems. Apart of compound systematics of NA in reservoirs, examples of different geochemical applications of FTMS to source facies predictions of severe biodegraded heavy oils and oilsands will be shown.

Introduction

For over forty years petroleum geochemist's main molecular tool for exploration and production issues was based on gas chromatography – mass spectrometry (GC-MS) technology. Many useful molecular proxies based on hydrocarbon distributions were developed for conventional oil fields. However, most of recent oil recoveries and predicted future recoveries are highly biodegraded which results in heavy oil and oil sands bitumen. Biodegradation alters petroleum with hydrocarbons being preferentially degraded by microorganisms in the reservoir. This also affects and alters all geochemical hydrocarbon proxies developed in the past. The new technology allows us instead of only a few hundred hydrocarbon compounds (GC-MS) to analyze tens of thousands of polar compounds which are mostly more resistant to biodegradation and therefore especially suitable as geochemical proxies for heavy oil and bitumen.

Furthermore, in comparison to conventional oil which commonly contain less than 10% nitrogen, sulfur and or oxygen (NSO) containing compounds or condensates [NSO content < 1%], heavy oils and bitumen contain a high amount of NSO components [e.g. Athabasca bitumen NSO content > 50%]. These high concentrations of multiple high polarity constituents cause many problems during production and transportation/pipelining and during refining. Being able to identify the problem causing moieties in petroleum will help to solve many problems such as flow assurance, corrosion, the origin of stable emulsions, well plugging and many more.

Method

This technology (12T FT-ICR-MS) is an ultra-high resolution mass spectrometer. Figure 1 illustrates the extremely high resolving power of the 12 Tesla magnet allows. Where low resolution mass spectrometry such as GC-MS produces only one peak the 12 T magnet resolves over 50 peaks (compounds) in a 0.4 Dalton range.

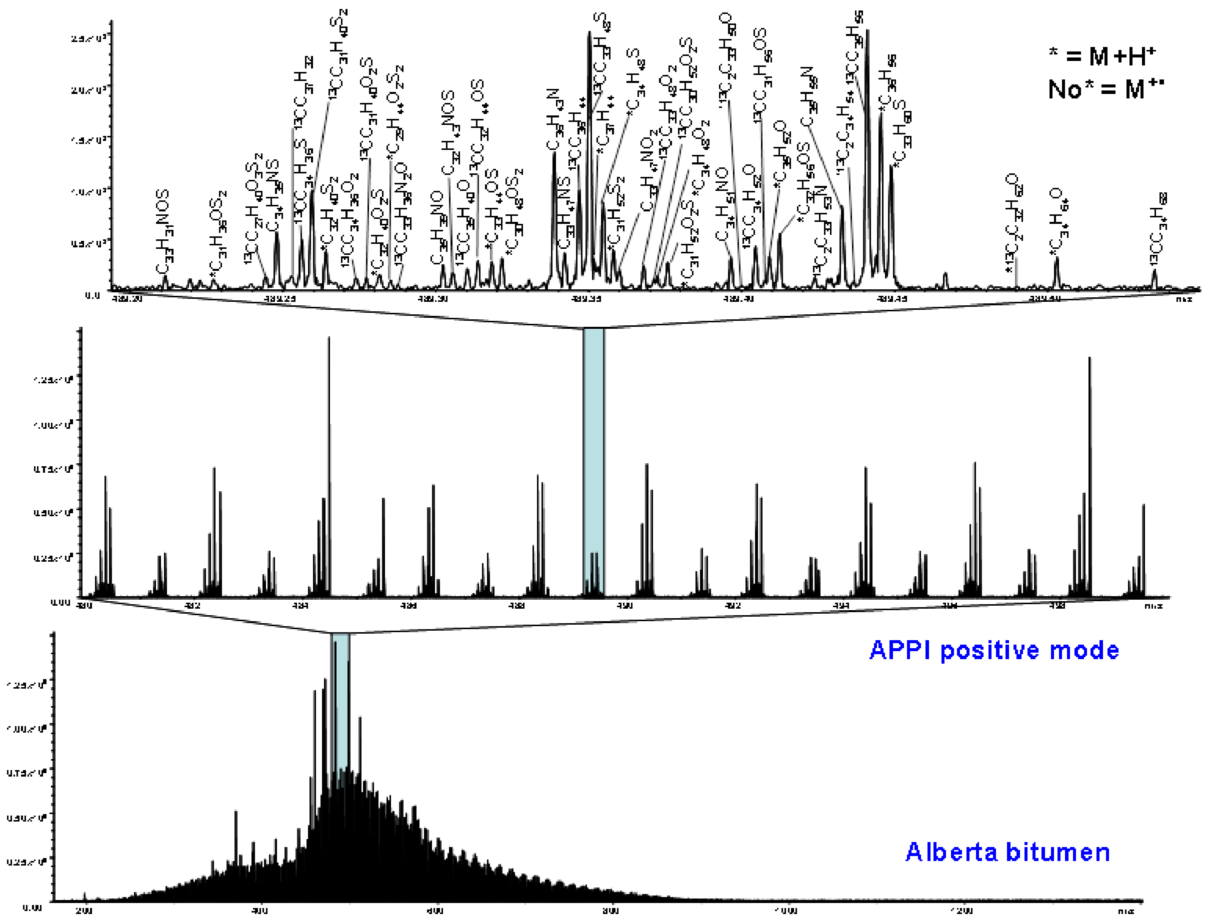

Figure 1: Ultra-high resolution mass spectra of an Alberta bitumen with zoomed-in spectra.

Examples

To demonstrate the possibility that molecular composition can predict fluid properties the following example is shown; for instance a correlation between molecular fluid properties and traditional oilfield measurements shown in Figure 2. The graph shows the extremely good correlation between measured Total Acid Number (TAN) by conventional titration technique and a molecular parameter developed from the molecular composition of an oil. Even over a broad range of acidity a good correlation was achieved if the oil is from the same source.

A common gradient of increasing concentration of the production issues creating naphthenic acids is shown in Figure 3. A strong increase of these unwanted oil components are especially typical observed at the oil water transition zone in an oil reservoir.

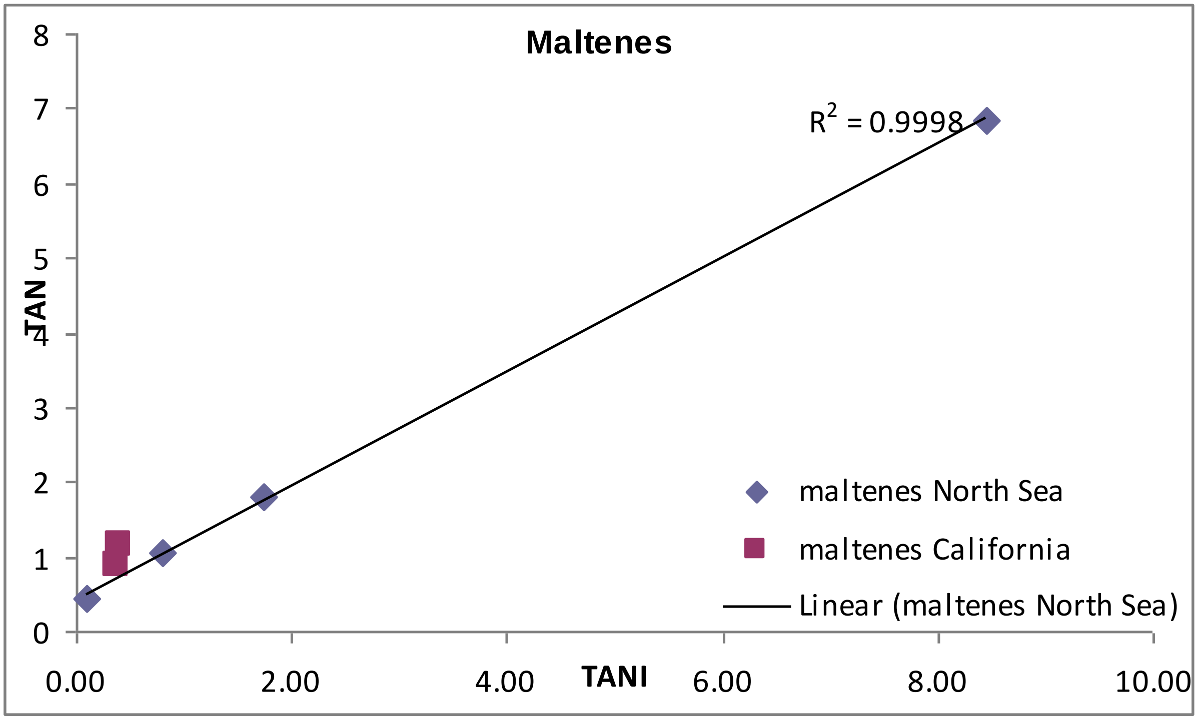

Figure 2: Measured Total Acid Number (TAN) by conventional titration technique versus molecular compositional acidity index (TANI).

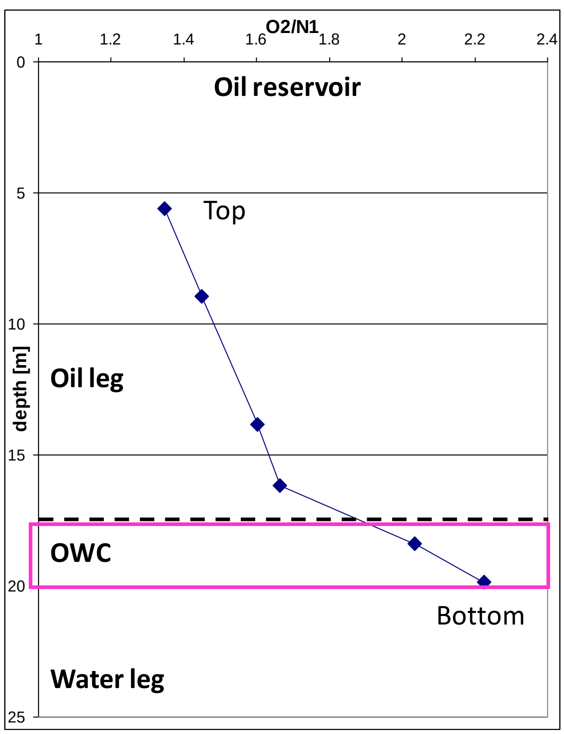

Figure 3: Strong increase in production issues creating NA (O2 class) especially in the transition zone within an oil reservoir

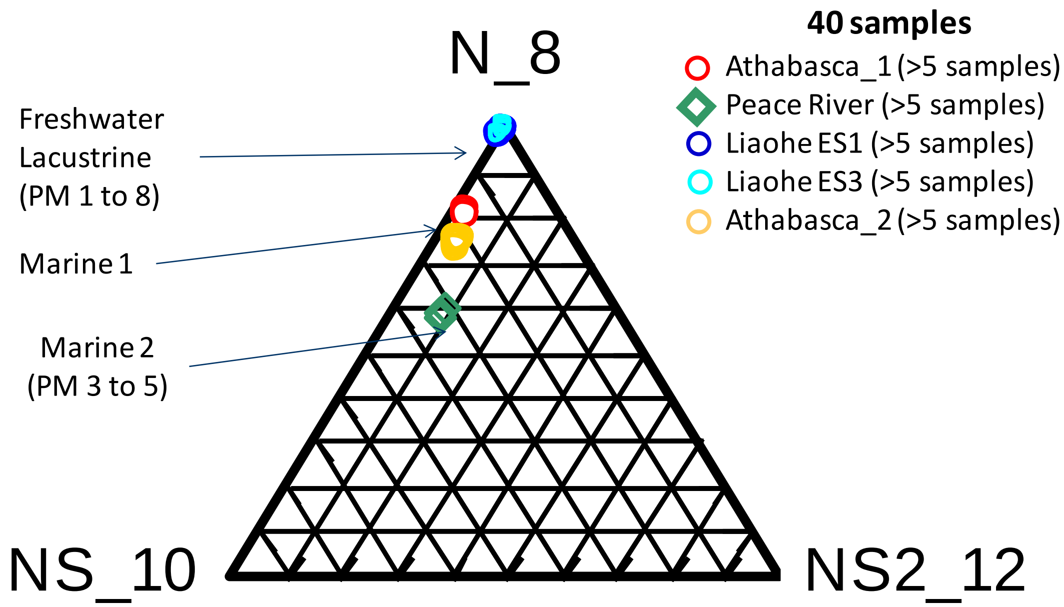

Figure 4: Degradation resistant source markers evident within cognate compound groups. N_8 means nitrogen compound class containing 1 nitrogen atom and having 8 double bond equivalents (DBE); NS_10 means N1S1 class with DBE 10; NS2_12 means N1S2 class with DBE 12.

Another example is shown in Figure 4 which demonstrates an application of degradation resistant oil source markers. Even though the samples analyzed are differently affected by biodegradation (covering a range on the Peters & Moldowan biodegradation scale of 1 to 8; Peters and Moldowan, 1993) the same sourced oils plot close together in the triangular graph yet samples from different sources can clearly be differentiated. Even two different marine sourced oil families are separated in this graph. Thus FTMS brings the benefit of high resolution source facies typing even in much degraded oils such as the oil sands.

Conclusions

Fourier Transform Ion Cyclotron Resonance Mass Spectrometry is a powerful novel, ultra-high resolution mass spectrometric tool for petroleum geochemistry. The comprehensive molecular analysis now available will help to:

1. develop new geochemical proxies where necessary to replace conventional through biodegradation altered hydrocarbon parameters for exploration and production issues
2. identify problem creating fluid components and their locations in reservoirs. Many production, pipelining and refining issues such as corrosion, plugging, flow assurance, stable emulsions and many more will be better solved by knowing the problem making moieties in an oil or bitumen.

Acknowledgements

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