



Technical Note # TN-34

Rapid Analysis of Complex Mixtures Using the solariX-CM, FTMS Platform

Abstract

The solariX-CM FTMS represents the ultimate MS solution for addressing complex mixtures that are not easily amenable to chromatographic separation techniques. These application areas include, but are not limited to, petroleomics (e.g. crude oil analysis), environmental analysis (e.g. humic acid analysis in river waters), and metabolomics. The resolving power required for dealing with the inherent and extreme complexity of these applications is typically greater than 400,000. Mass accuracies in the sub-ppm range are also essential to help ensure reliable molecular formulae assignments. The solariX-CM routinely delivers ultimate selectivity and specificity with “benchtop” ease-of-use.

Introduction

Mass spectrometry, in combination with chromatographic separation methods, has been widely used to address the challenges associated with complex mixtures. However, the development and optimization of chromatographic separation methods for complex mixtures can be laborious and increases the overall analysis time. Moreover, some compound classes and mixtures are simply not amenable to standard separation techniques such as high pressure liquid chromatography (HPLC) or capillary

electrophoresis (CE). The unparalleled resolving power of the solariX-CM Fourier transform mass spectrometer (FTMS) reduces the demands on chromatographic separation methods thereby making complex mixture analysis much more efficient.

The classification of the components in crude oil including the speciation of heteroatomic compounds like sulfur or nitrogen compounds with specific double bond equivalents are necessary for crude oil analysis on the molecular level. Leveraging the resolution and mass accuracy of the FTMS, the elemental composition of individual compounds of crude oil has been analyzed [1] – [5].

Since the compound classes in oil represent a range of polarity and gas-phase basicity it is essential to analyze each sample under both positive and negative modes and with different atmospheric pressure ionization (API) techniques. An advantage of the solariX is quick change-over (in less than 5 minutes!) between API sources, such as electrospray (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photo ionization (APPI).

Complex, rich datasets are quickly analyzed using Composer™ from Sierra Analytics. Composer is a comprehensive software package that is specific to petroleomics data. It quickly and accurately provides classification and DBE

information through a range of data representations that include Kendrick mapping and Van Krevelen plots.

Experimental

Analyses were carried out using a solariX-CM 12T (Bruker Daltonics, Billerica, MA, USA) which was operated in positive or negative ion mode. Infusion experiments were also conducted with Bruker's ESI and APPI interfaces. Solutions of the crude oil were prepared by mixing 50 μL of crude oil with 950 μL dichloromethane. This was further

diluted 1:100 with a solution of 50% MeOH/50% toluene. This sample was infused at a flow rate of 120 $\mu\text{L}/\text{h}$ for ESI and @ 6 ml/h for APPI, respectively.

Facilitated by Composer (Sierra Analytics, Modesto, CA, USA), data was internally calibrated using identified and known series of compound classes: ESI positive (N series), ESI negative (O_2 series), APPI positive (CH series). All other data analysis was carried out using Composer.

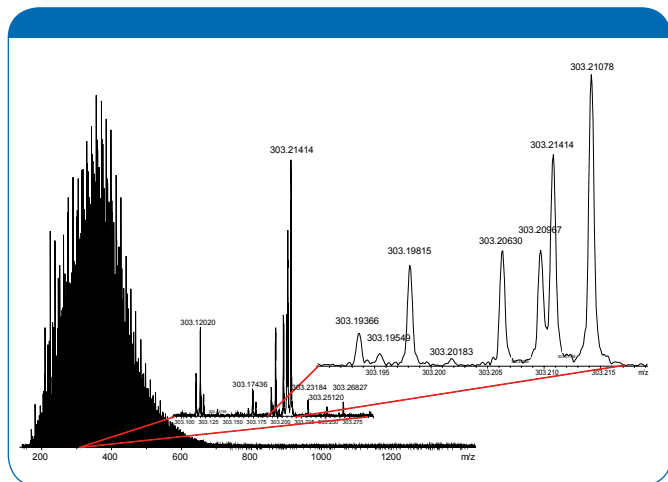
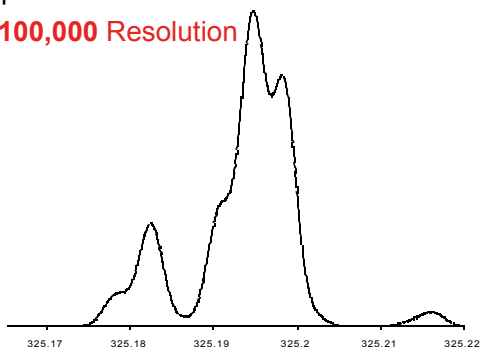


Figure 1: Broad band spectrum of a crude oil measured by APPI in positive ion mode. Insets illustrate the extreme high resolving power ($> 550,000$) of the solariX-CM.

Figure 2: Comparison of a broadband spectrum of a crude oil sample from solariX-CM with lower resolution spectra.

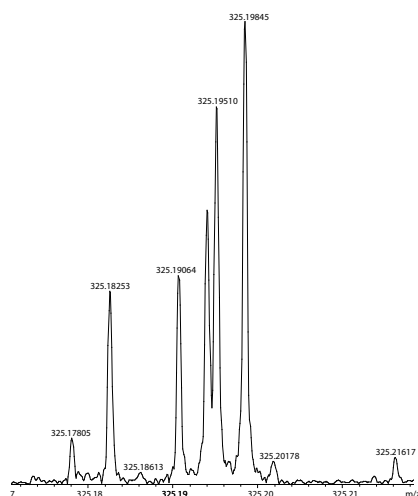
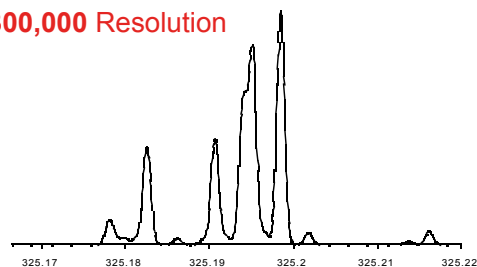
Spectrum with

100,000 Resolution



Spectrum with

300,000 Resolution



Broad band spectrum
Resolution 550,000

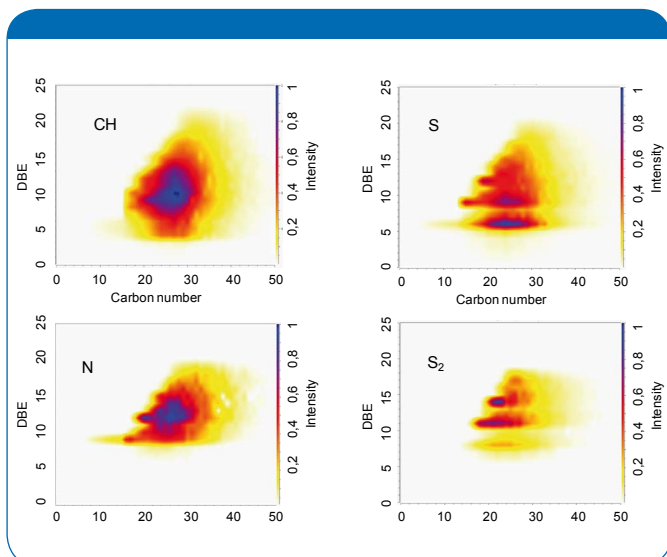
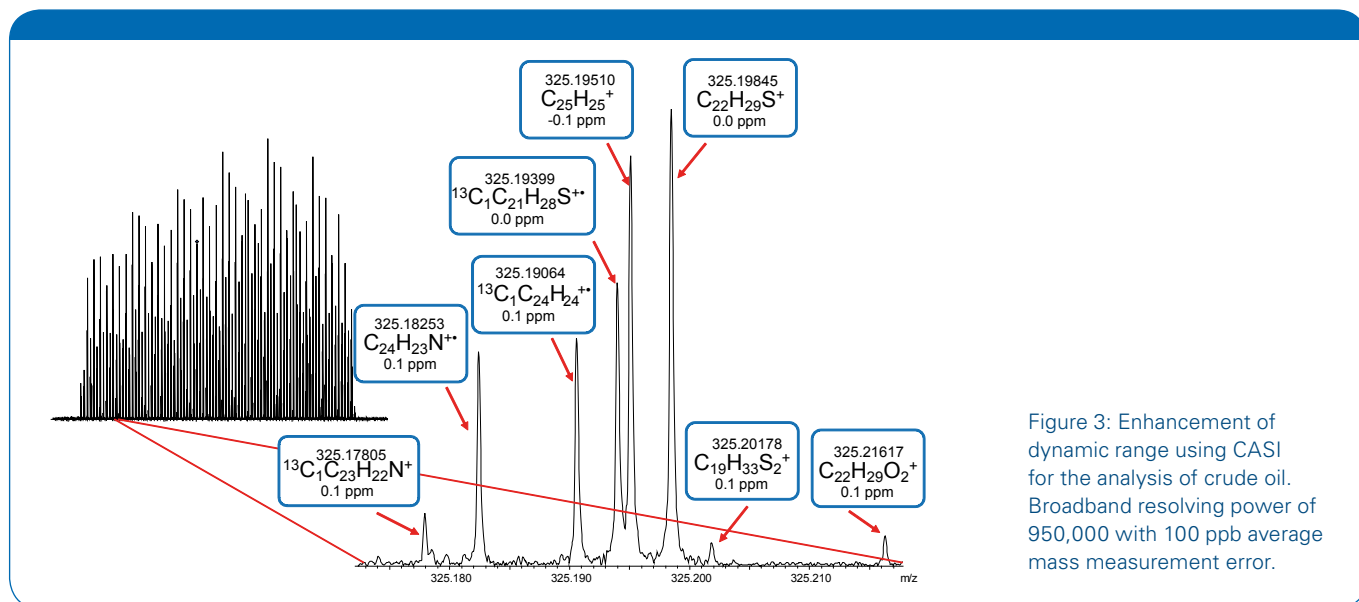


Figure 4: DBE vs. carbon number plots for different compound classes of crude oil (APPI Positive, radical ions), average error for all assigned compounds is 85 ppb

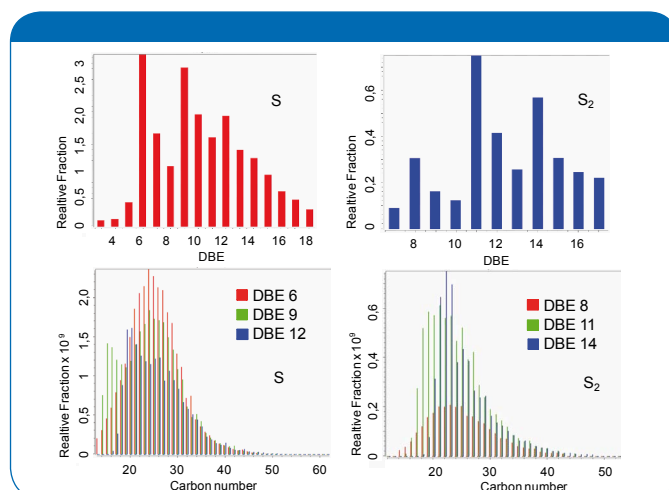


Figure 5: Distribution of different DBE for different compound classes. For compound class [S] DBE 6, 9 and 12 are preferred, whereas compound class [S₂] shows a preference of DBE 8, 11 and 14. The lower graphs show the distribution of these DBEs in relation to the carbon number, respectively.

Results

Perhaps the most challenging and complex samples to analyze by mass spectrometry are crude oils. Therefore, the analysis of these samples requires extreme resolving powers to discern each elemental component within a dense matrix. Figure 1 illustrates this complexity with a broad band spectrum of a crude oil measured by APPI in positive ion mode. The two expanded insets show the richness of the data with thousands of detected peaks. As shown in Figure 2, true FTMS performance is required for these analyses as other types of mass spectrometers are inadequate at resolving the elemental components present. In these cases, information is lost and mass

accuracy is compromised by the myriad of unresolved, overlapping peaks.

The unique geometry of the solariX-CM can be used to further augment and enhance both resolution and dynamic range. Using a mode known as Continuous Accumulation of Selected Ions (CASI™), ions of a specific m/z region are filtered, thereby filling the charge capacity with the region of interest without overloading the detection cell.

Assignment of molecular formulae is automatically performed using Bruker's DataAnalysis™ software, as shown in Figure 3.

Composer is used to comprehensively analyze the data from oil samples. Loading peak lists into Composer is straightforward and facile. From the main user interface one can easily generate different plots ranging from DBE vs. carbon number, Kendrick- and van Krevelen-plots. For example, Figure 4 displays DBE vs. carbon number-plots for different compound classes. Another example of the output from the data analysis is shown in Figure 5.

To illustrate the contrast and influence of ionization mode for these samples, Figure 6 shows spectra of a gas oil sample that was ionized with ESI and APPI in positive mode.

The DBE plots in Figure 6 show different distributions, demonstrating the need for different ionization sources to achieve complete analysis of the heteroatom fraction of crude oil samples.

The combination of the powerful solariX-CM FTMS system with the rapid and comprehensive data mining software Composer is the ultimate solution for analyzing complex mixtures that are not easily amenable to separation methods.

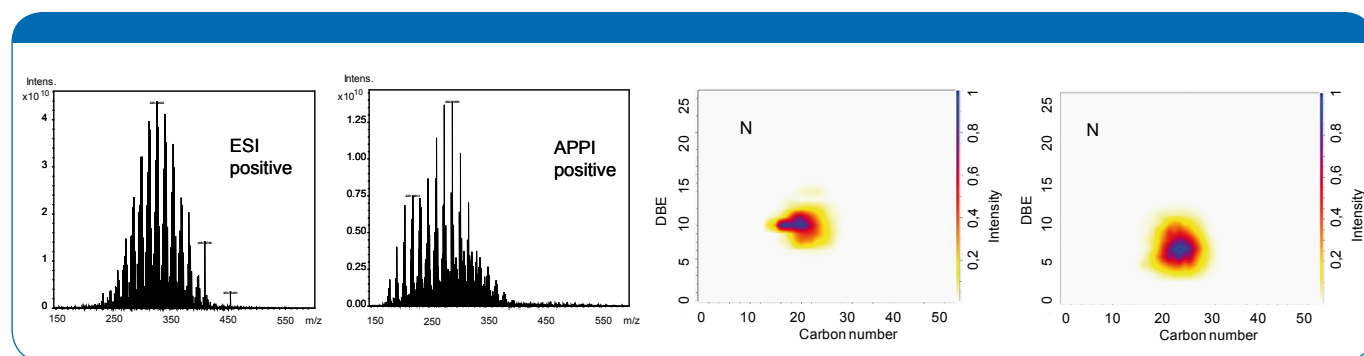


Figure 6: ESI (left) vs. APPI (right): spectra of gas oil with positive ionization, and DBE vs. carbon number plots for protonated compound class [N] (ESI, left) and radical compound class [N] (APPI, right).

References

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- [5] Matthias Witt, Jens Fuchser and Boris P. Koch, *Fragmentation Studies of Fulvic Acids Using Collision Induced Dissociation Fourier Transform Ion Cyclotron Resonance Mass Spectrometry*, *Anal. Chem.*, 2009, 81 (7), pp 2688–2694.

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Instrumentation & Software

solariX-FTMS

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