ANALYSIS OF COMPLEX MIXTURES OF HETEROATOM HYDROCARBONS USING TIMS-MS

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Introduction

Tens of thousands of chemically distinct organic compositions with concentrations ranging over more than four orders of magnitude are commonly observed in crude oil samples. In turn, crude oil derived applications typically necessitate a method for rapidly and accurately identifying these complex heteroatom mixtures (e.g., non-covalent multimers and distributions of heteroatoms, rings, and double bonds). Common practice limits the description of these complex mixtures to the identification and quantification of a limited number of *a priori* selected compounds. Over the last decades, more detailed characterizations of crude oil's elemental composition, carbon number, and double bond equivalents (ring structures and carbon double bonds), have been measured using ultra-high-resolution and accurate mass measurements using Fourier transform ion cyclotron resonance, FTICR-MS.[1-3] On the other hand, the use of post-ionization, gas-phase separation prior to mass analysis (e.g., Ion mobility/mass spectrometry, IMS-MS) has shown a unique capability for separating chemical classes as well as identifying conformational and structural motifs. That is, ions are separated as they drift in a bath gas under the influence of an external electric field; thus, separation is based on the ion-neutral collision cross section on a millisecond time scale. This has resulted in increased utilization of IMS for a wide variety of applications, including the analysis of crude oils.[4-6] This is partially driven by the continual development of new types of IMS analyzers (e.g., periodic focusing DC ion guide, segmented quadrupole drift cell, multistage IMS, field asymmetric IMS and transient wave ion guide). A common pursuit has been to improve both the mobility separation and ion transmission. The recent introduction of the Trapped Ion Mobility Spectrometer (TIMS), and its coupling to mass spectrometry (TIMS-MS), represents a paradigm shift in the way an IMS-MS separation and structural identification are performed.[7, 8] In the present work, we describe the use of a TIMS-MS analyzer to achieve higher analytical separation and unambiguous structural characterization of individual components from crude oil samples.

Experimental

Sample preparation. Hydrocarbon NIST standard reference materials with increasing complexity were used in this study (e.g., diesel and a crude oil light sour). Samples were diluted in toluene and analyzed as received.

Characterization Methods. In the example presented here, ions were generated by atmospheric pressure photoionization (APPI) using an ion source based on the Apollo II design (Bruker Daltonics Inc., MA). A TIMS analyzer was incorporated into the ion funnel region of a commercial micrOTOF-Q™, quadrupole orthogonal time-of-flight mass spectrometer (Bruker Daltonics Inc., MA). Accordingly, a quadrupolar funnel optic was used and the capillary coupling the APPI spray chamber to the first pumping stage was orthogonal to the axis of the TIMS analyzer. Details on the TIMS schematics can be found elsewhere.[7, 8] Briefly, a TIMS funnel is comprised of three main regions: the entrance funnel, the mobility analyzer section, and the exit funnel. Each funnel electrode is divided into four electrically insulated segments, which are used to create a dipolar field in the entrance and exit section to focus the ions downstream and a quadrupolar field in the separation region to radially confine the ions during the ion trapping and analysis. The concept behind TIMS is the use of an electric field to hold ions stationary against a moving gas, so that the drift force is compensated by the electric field and ion packages are separated based on their size-to-charge ratio. This concept follows the idea of a parallel flow ion mobility analyzer, with the main difference that ions are also confined radially to guarantee higher ion transmission and sensitivity.

Once ions elute from the mobility separation section, they pass through the exit funnel and on towards the QTOF mass analyzer. As the voltage on the mobility analyzer section is being ramped, the oTOF analyzer is used to acquire a series of mass spectra, typically one mass spectrum every 0.2 ms. Each mass spectrum corresponds to a given elution voltage in the voltage ramp and therefore to a specific ion mobility. After emptying the separation section, a new cycle starts. The results of several successive TIMS analyses may be summed in order to produce a statistically meaningful 2-D TIMS-MS spectrum.

Results and Discussion

The integration of a TIMS analyzer with MS analyzer creates a powerful analytical tool due to the complementary size-to-charge and mass-to-charge separation in a single experiment. In particular, TIMS analysis has the unique advantage that IMS separations are not based on time as traditional drift tubes (e.g., drift time) – but on elution voltage. Thus, TIMS-MS has added flexibility over conventional IMS in that the speed and range over which the voltage (mobility) is scanned can be readily adjusted according to the requirements of the application – i.e., speed vs. range vs. resolution. To better illustrate this concept, **Figure 1** contains typical APPI-MS spectra of a diesel and a crude oil (light sour) sample. Notice that in the case of the diesel sample, the molecular components are distributed over small m/z ranges (e.g., $100<m/z<600$). However, in the case of crude oils, heavier components are observed and the mass distribution shifts to larger m/z (e.g., $100<m/z<900$).

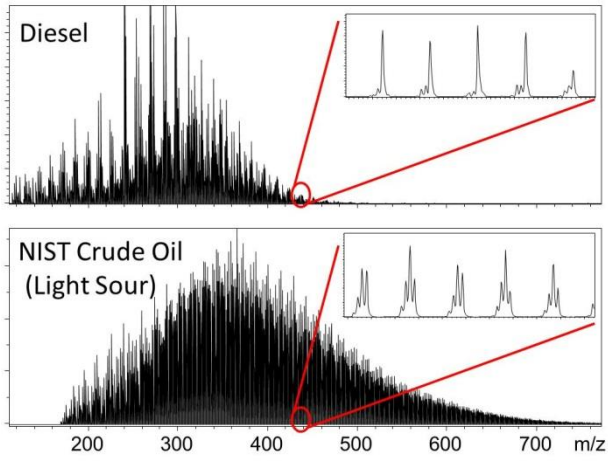

Figure 1. APPI-MS spectra of a diesel and a NIST crude oil (light sour) sample obtained using a micro-q-ToF instrument (typical MS resolution ~10k). Notice the increase in complexity at the level of nominal mass in the insets.

When the same analysis is performed using TIMS-MS, ions are initially separated in the mobility domain and mass spectra are collected per ramp step.[7, 8] This concept is illustrated in **Figure 2** with a 2D-TIMS-MS plot of a diesel and a crude oil (light sour) sample. Inspection of the 2D-TIMS-MS of the diesel sample (Figure 2, top) permits the observation of the C_mH_n series, where parallel trend lines correspond to the increase of the number of carbon atoms (e.g., C_m -> C_{m+1}). In the case of the crude oil sample, the contribution of other heteroatom families (e.g., C_mH_nX series, where X = N_1, S_1, O_1, etc.) can be observed by the increase of the number species observed per nominal mass.

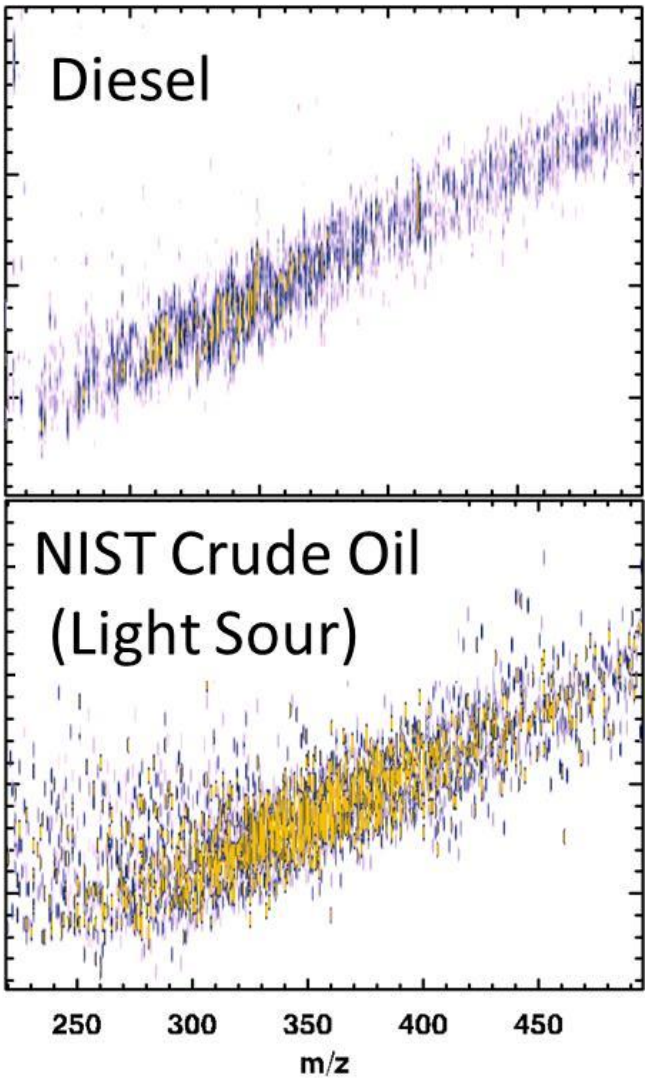

Figure 2. 2D-TIMS-MS plots of APPI-MS spectra of a diesel and a crude oil (light sour) sample obtained using a TIMS-micro-q-ToF instrument (typical IMS resolution ~60-120). Notice the increase in peak separation in the mobility domain.

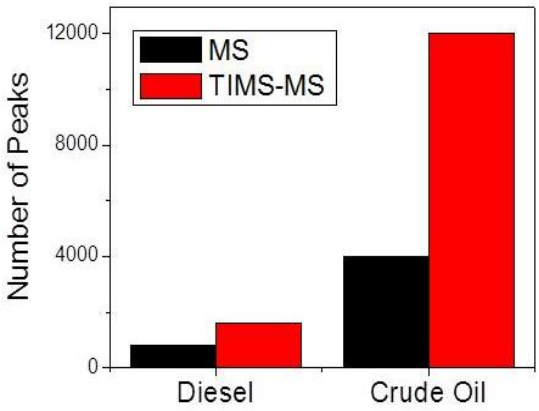

Figure 3. Number of peaks detected in the diesel and crude oil samples. Notice the near 3 fold increase in the number of peaks observed using TIMS-MS relative to MS analysis.

Closer inspection of the 2D TIMS-MS plots show that a number of components are separated in the IM domain within a single nominal mass. The TIMS separation observed in **Figure 2** is based on the inherent differences in ion gas-phase structure of the different heteroatom hydrocarbons. That is, more compact, branched, or condensed structures will be trapped at lower trapping potential values, while ions of the same molecular class but different masses will be separated in the m/z dimension. The advantage in molecular ion identification by size/shape speciation using TIMS-MS is illustrated in **Figure 3**. Notice that a near 3 fold increase in ion peak detection is observed by activating the TIMS analyzer in the front end.

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