Increasing analytical separation of polycyclic aromatic hydrocarbon from crude oil using GC-TIMS-TOF

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Goal

►Increase the analytical power of mass spectrometry with complementary gas-phase separations: Gas Chromatography coupled to Trapped Ion Mobility Spectrometry.

Significance

►The characterization of crude oils to their molecular level is extremely challenging due to the large number components and their structural diversity.

►The knowledge of the crude oil composition is an important component during the refining process and is directly related to its commercial value.

►There is a need for high-throughput analytical tools capable of molecular characterization for crude oils.

►In addition to the molecular formula, we focus on the determination of structural motifs in order to assign 3D structures in complex mixtures, with minimal sample preparation and short processing timescales.

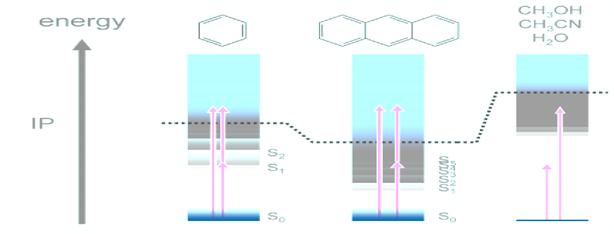


Figure 1. Scheme of the multi photon ionization process utilized for the analysis of polyaromatic hydrocarbons (PAHs) during GC-APLI-TIMS-MS.

Research Methodology

GC-APLI-TIMS-TOF Analysis

A Scion 436 gas chromatography (equipped with Agilent HP-5MS-UI column) was coupled to a commercial timsTOF instrument (Bruker Daltonics). Molecules eluting the GC were introduced into an atmospheric pressure laser ionization source (APLI), followed by TIMS-MS analysis in positive ion mode. A series of PAH and dPAH standards were used for method development. The PAH fraction (SARA) of three common crude oil was studied.

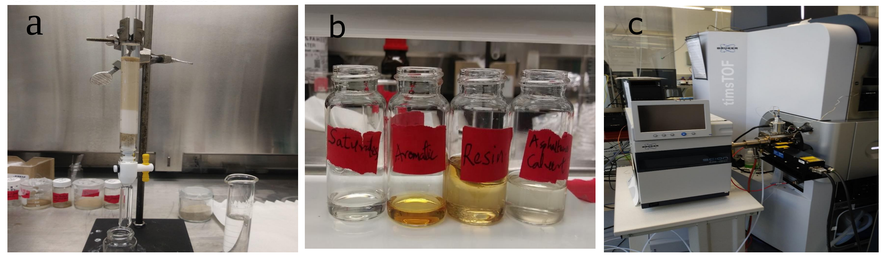


Figure 2. Typical SARA column (a) and fractionation products (b). Illustration of the GC-APLI-timsTOF instrument utilized in this study

Results

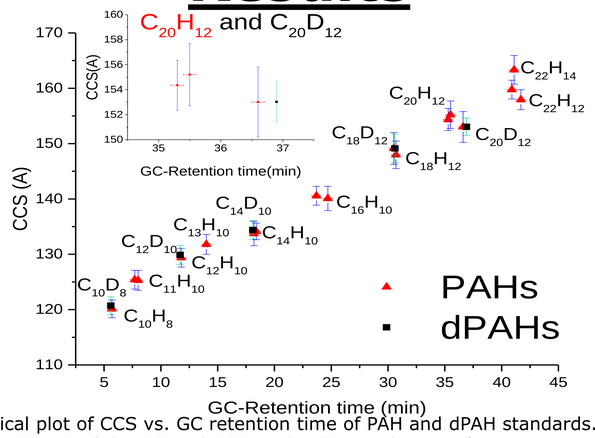


Figure 3: Typical plot of CCS vs. GC retention time of PAH and dPAH standards. The bar represents the FWHM of the GC and CCS peaks. Notice the complementary separations between GC and TIMS for $C_{20}H_{12}$ and $C_{20}D_{12}$ isomers (inset)

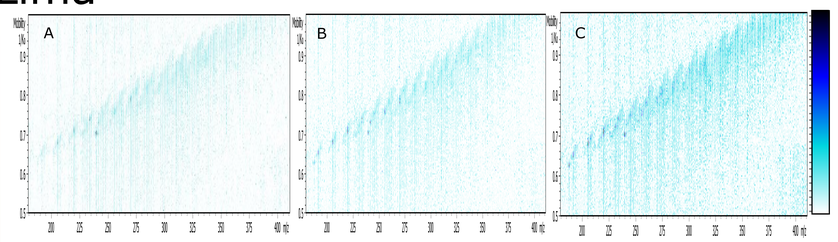


Figure 4: Typical 2D-IMS-MS contour plot of the PAH SARA fractions of three common crude oil samples analyzed by GC-APLI-TIMS-MS: (A) light oil (B) medium oil (C) heavy oils

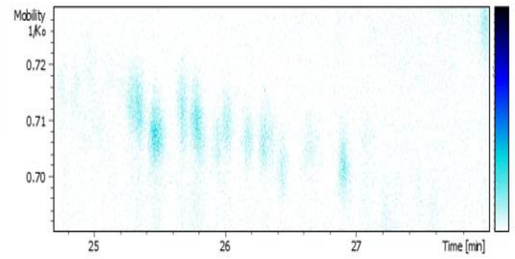


Figure 5: Typical 2D-IMS-MS contour plot at 220 m/z from the PAH SARA fraction of a light oil. Notice the complexity at the level of nominal mass and the orthogonality between GC and TIMS in the separations.

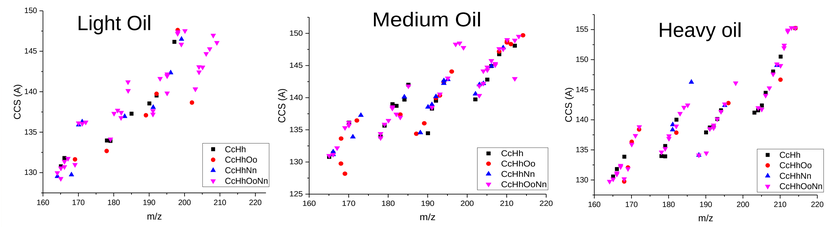


Figure 6: Typical plot of CCS vs. m/z of the PAH SARA fraction of three common crude oils. The plot shows the prevalence of $C_cH_hO_oN_n$ class in the 160 – 215 m/z range.

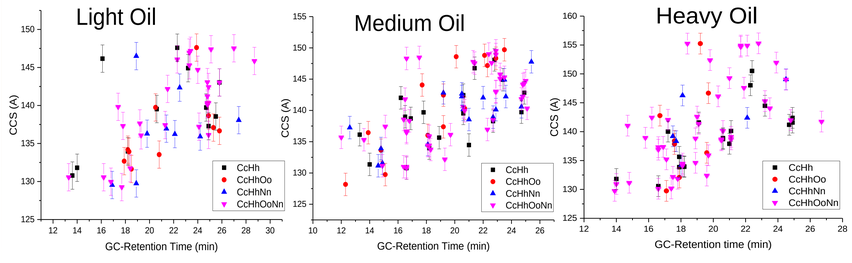
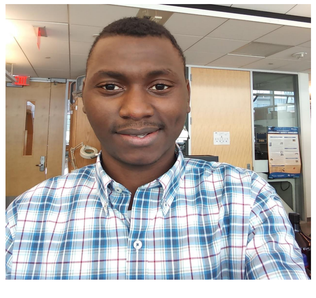


Figure 7: Typical plot of CCS vs. GC retention time of the PAH SARA fraction of three common crude oils (m/z range 160 – 215). The bar represents the FWHM of the GC and CCS peaks. Notice the isomeric complexity



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