Atmospheric Pressure Laser-Induced Acoustic Desorption Chemical Ionization Mass Spectrometry for Analysis of Saturated Hydrocarbons

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Results and Discussion

We present atmospheric pressure laser-induced acoustic desorption chemical ionization (AP/LIAD-CI) with O_2 carrier/reagent gas as a powerful new approach for the analysis of saturated hydrocarbon mixtures. Non-thermal sample vaporization with subsequent chemical ionization generates abundant ion signals for straight-chain, branched, and cycloalkanes with minimal or no fragmentation. $[M-H]^+$ is the dominant species for straight-chain and branched alkanes. For cycloalkanes, $M^{+\bullet}$ species dominate the mass spectrum at lower capillary temperature (<100 °C) and $[M-H]^+$ at higher temperature (> 200 °C). The mass spectrum for a straight-chain alkane mixture (C_{21}-C_{40}) shows comparable ionization efficiency for all components (see **Figure 1**). Coupling of the technique to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) for the analysis of complex hydrocarbon mixtures provides unparalleled mass resolution and accuracy to facilitate unambiguous elemental composition assignments: e.g., 1,754 peaks (rms error = 175 ppb) corresponding to a paraffin series (C_{12}-C_{49}, double bond equivalents, DBE = 0) and higher DBE series corresponding to cycloparaffins containing 1 to 8 rings. Isoabundance-contoured plots of DBE vs. carbon number highlight steranes (DBE = 4) of carbon number C_{27} to C_{30} and hopanes of C_{29} to C_{35} (DBE = 5), with sterane-to-hopane ratio in good agreement with field ionization (FI) mass spectrometry analysis, but performed at atmospheric pressure. The overall speciation of nonpolar, aliphatic hydrocarbon base oil species offers a promising diagnostic probe to characterize crude oil and its products.[1]

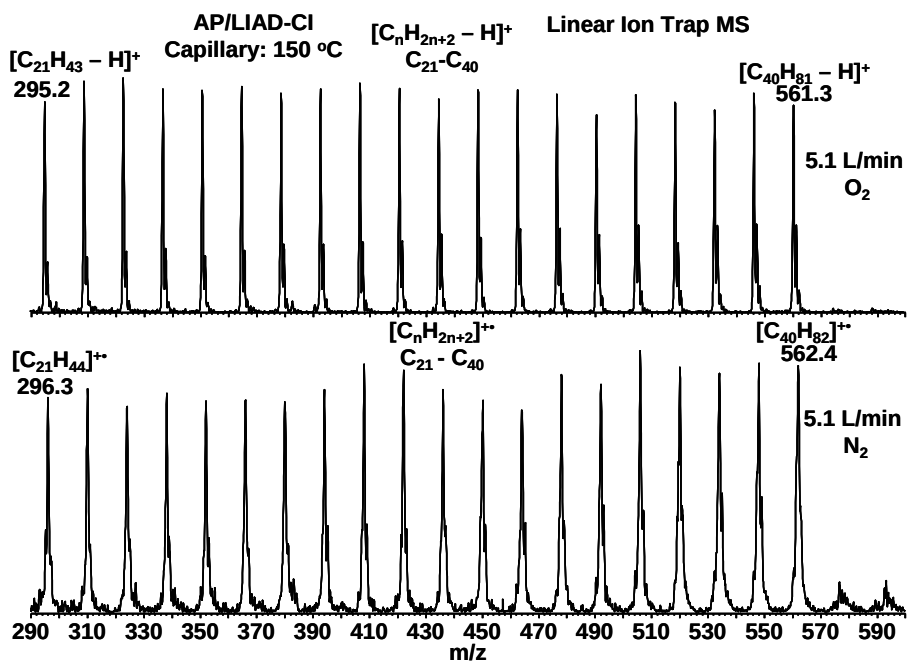

Figure 1. AP/LIAD-CI linear ion trap mass spectra for a mixture (40 µg/mL each) of straight-chain alkanes (C_{21}-C_{40}) for O_2 (top) or N_2 (bottom) carrier/reagent gas.

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References

[1] Nyadong, L., *et al.*, Anal. Chem., **84**, 7131-7137 (2012).