Transmission Geometry Laser Desorption Atmospheric Pressure Photochemical Ionization Mass Spectrometry for Analysis of Complex Organic Mixtures

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Results and Discussion

We present laser desorption atmospheric pressure photochemical ionization mass spectrometry (LD/ APPCI MS) for rapid throughput analysis of complex organic mixtures, without the need for matrix, electric discharge, secondary electrospray, or solvents/vaporizers. Analytes dried on a microscope slide are vaporized in transmission geometry by a laser beam aligned with the atmospheric pressure inlet of the mass spectrometer. The laser beam initiates a cascade of reactions in the region between the glass slide and MS inlet, leading to generation of reagent ions for chemical ionization of vaporized analyte. Positive analyte ions are generated predominantly by proton transfer, charge exchange, and hydride abstraction, whereas negative ions are generated by electron capture or proton transfer reactions, enabling simultaneous analysis of saturated, unsaturated, and heteroatom-containing hydrocarbons. The absence of matrix interference renders LD/APPCI MS particularly useful for analysis of small molecules (<2000 Da) such as those present in petroleum crude oil and petroleum deposits. [M + H]+ and M+• dominate the positive-ion mass spectra for olefins and polyaromatic hydrocarbons, whereas saturated hydrocarbons are observed mainly as [M−H]+ and/or M+•. Heteroatom containing hydrocarbons are observed predominantly as [M + H]+. [M− H]− and M−• are the dominant negative ions observed for analytes of lower gas-phase basicity or higher electron affinity than O_2. The source was coupled with a 9.4 T Fourier transform ion cyclotron resonance mass spectrometer (FTICR MS) to resolve and identify thousands of peaks from Athabasca bitumen heavy vacuum gas oil distillates (400−425 and 500−538 °C), enabling simultaneous characterization of their polar and nonpolar composition. We also applied LD/APPCI FTICR MS for rapid analysis of sodium and calcium naphthenate deposits with little to no sample pretreatment to provide mass spectral fingerprints that enable reliable compositional characterization.

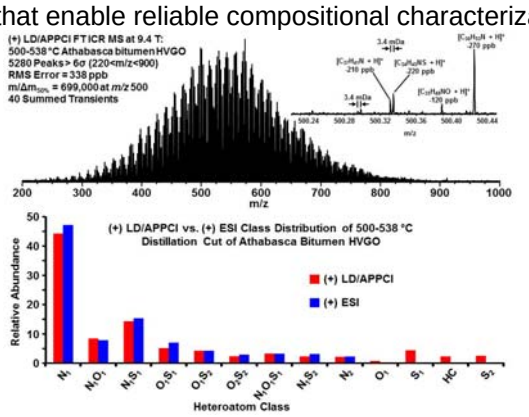

Figure 1. Top: broad-band positive-ion LD/APPCI 9.4 T FTICR mass spectrum of a 500−538 °C distillation cut from Athabasca bitumen heavy vacuum gas oil (HVGO), and that shows a mass-scale-expanded segment spanning a 0.25 Da range. The mass resolution is more than sufficient to distinguish between peaks differing by only 3.4 mDa in mass (corresponding to a difference in elemental composition of C_3 versus SH_4, top, inset), for confident elemental composition assignments. Bottom: corresponding heteroatom class distribution for the 500−538 °C distillate by LD/APPCI and ESI 9.4 T FTICR MS. Compounds containing one nitrogen atom (N_1) were the most abundant with both ionization techniques, followed by N_1S_1 and N_1O_1 classes. The relative abundance of the N_1 class is slightly higher by ESI, which efficiently ionizes the basic pyridinic nitrogen-containing species. All of the polar classes generally show similar ionization efficiency by both LD/APPCI and ESI; however, the nonpolar classes such as HC (hydrocarbon), S_1, and S_2 are observed only by LD/APPCI, consistent with the model compound data, but requiring minimal sample preparation, with the desorption/ ionization of samples occurring in one step, simplifying the experiment to provide rapid throughput.

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References

[1] Nyadong, L. *et al*., Anal. Chem., **86**, 11151-11158 (2014)