

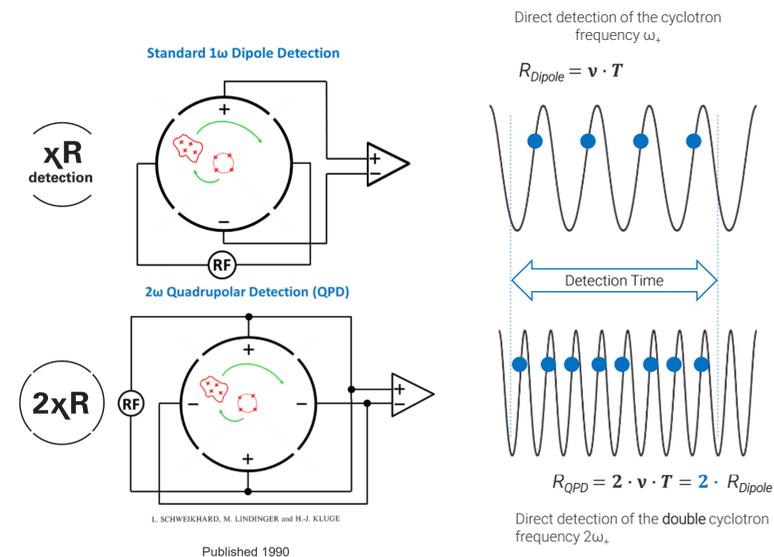
Direct Analysis of Petroleum and Biofuels with FT-ICR MS and Direct Ionization Probe APPI

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Introduction

Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) provides ultra-high resolution to enable comprehensive molecular characterization of complex petroleum samples. Complex mixtures such as pyrolysis oils and asphaltenes are not soluble in typical solvents effective mass spectral analysis and require lengthy sample preparation. A direct ionization approach allows for a rapid screen to quickly collect preliminary data and test multiple samples without laborious preparation. This sample introduction approach enables a variety of materials to be directly introduced into the mass spectrometer, including solids and insoluble liquids. As the desire to develop and characterize renewable fuels (e.g., pyrolysis oils) continues to grow, novel sample preparation and analysis techniques are needed, due to inherent solubility challenges associated with these materials.

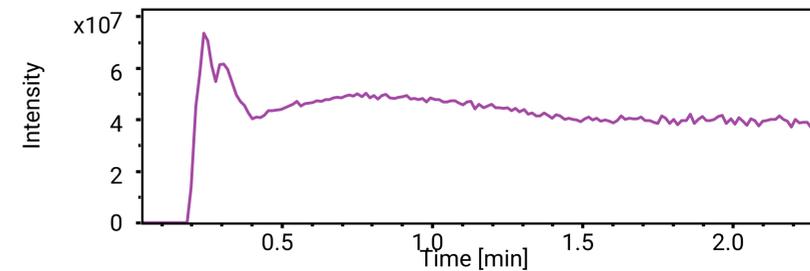


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Methods

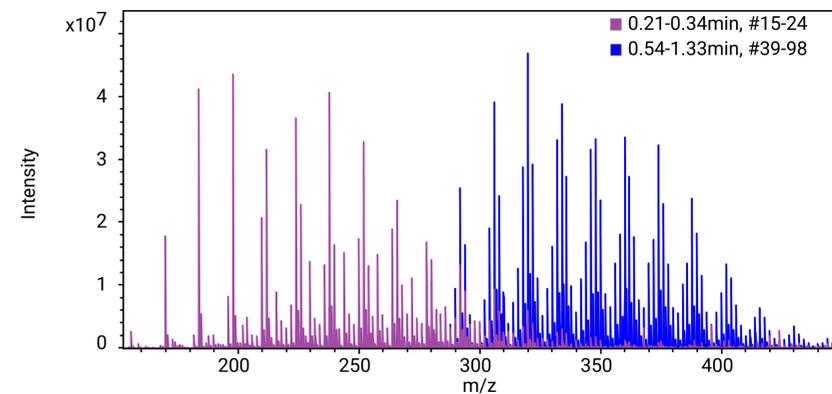
A Bruker scimaX FT-ICR with a 7 Tesla cryogen-free magnet was employed for mass spectral analysis. NIST SRM 2722 heavy-sweet crude oil samples were analyzed alongside a pyrolysis oil from woody biomass. An atmospheric pressure photoionization (APPI) source was used with and without a direct ionization probe (DIP) attachment for direct sample introduction. Sample was placed directly onto a glass capillary and inserted into the vaporizer of the APPI source. Toluene was optionally added to the nitrogen flow entering the instrument as a dopant to facilitate ionization. Various ICR conditions were tested to optimize sample introduction, including transients from 0.5 to 4 seconds.

Time Profile

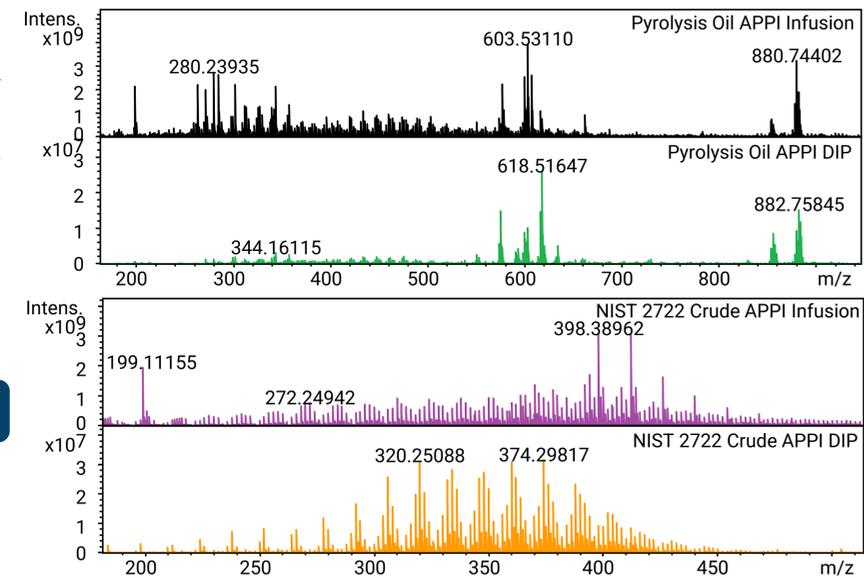


Above: There is an initial spike in signal upon insertion of the capillary coming from the more volatile lower masses.

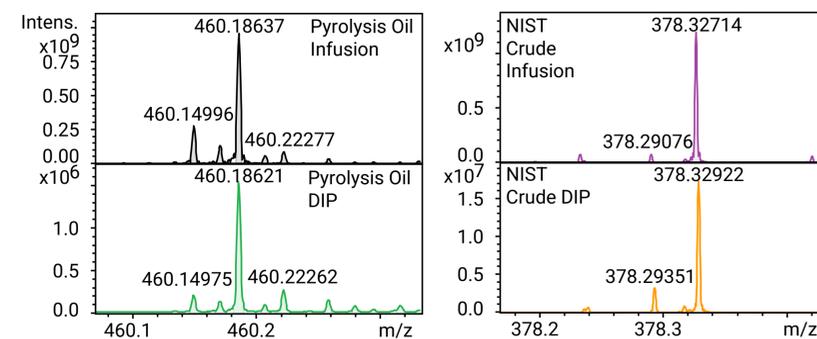
Below: Differences in spectra from the initial insertion of the capillary (purple) and the rest of the run (blue) are shown. There is a significant low mass bias in the initial peak.



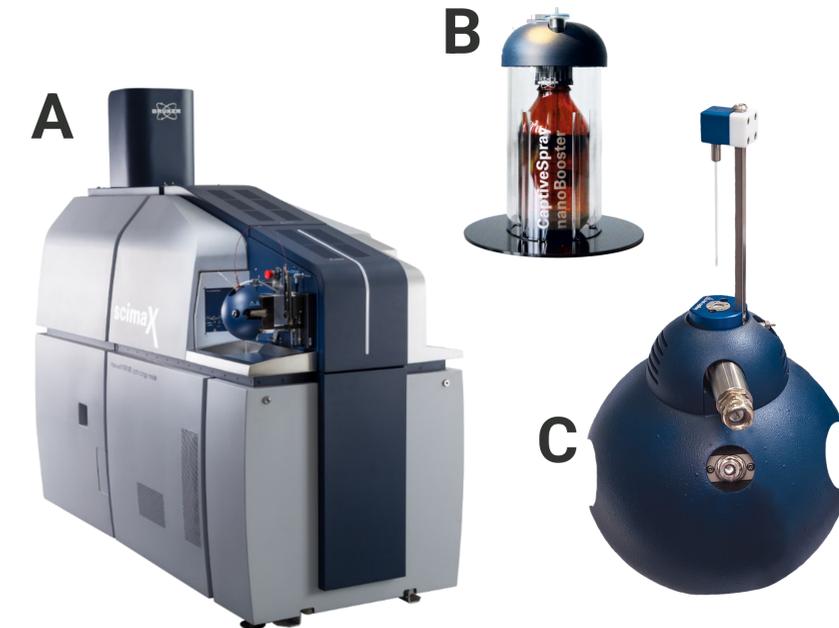
Result Spectra



Mass spectral results demonstrate effective ionization with the DIP, with ion counts comparable to traditional (direct infusion) APPI. Differences in spectra above are due to the summation process of infusion. For a standard crude sample, toluene dopant was not needed, because the presence of aromatic hydrocarbons allowed for effective direct ionization. Dopant was used for pyrolysis oil analysis and was shown to improve ionization versus direct ionization. Extremely low masses of material were required for analysis, and no carryover was observed. Resolving power and peak shape with the DIP were consistent with data collected with direct infusion APPI.



Instrumentation



A: Bruker scimaX FT-ICR mass spectrometer with 7T magnet
B: nanoBooster used to provide toluene vapor for APPI source
C: Direct Probe attachment for direct sample analysis

Conclusions

- Direct ionization is an effective way to quickly analyze volatile materials without the need for sample preparation
- Toluene vapor introduction offers a consistent source of dopant in the gas phase, especially important for mixtures that are insoluble in toluene