Direct Analysis of Thin-Layer Chromatography Separations of Petroleum Samples by Laser Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry Imaging

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Results and Discussion

We present an analytical method for direct analysis of thin-layer chromatography (TLC) separations of petroleum samples by laser desorption ionization (LDI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) imaging. LDI of TLC plates selectively ionizes condensed aromatic hydrocarbons and facilitates two-dimensional imaging of TLC-separated petroleum compounds. Molecular-level characterization available only with ultrahigh-resolution FT-ICR MS provides elemental composition assignment and surpasses conventional TLC readout-based flame ionization detection. Resolution and assignment of migrated molecules targeted by LDI combined with FT-ICR MS provides elemental composition assignment and, therefore, chemical information, i.e., heteroatom class, aromaticity (double bond equivalents), and carbon number. Here, three petroleum samples (a field deposit, a crude oil, and a tar ball) were TLC-separated by their solubility in *n*-heptane and imaged by LDI FT-ICR MS.

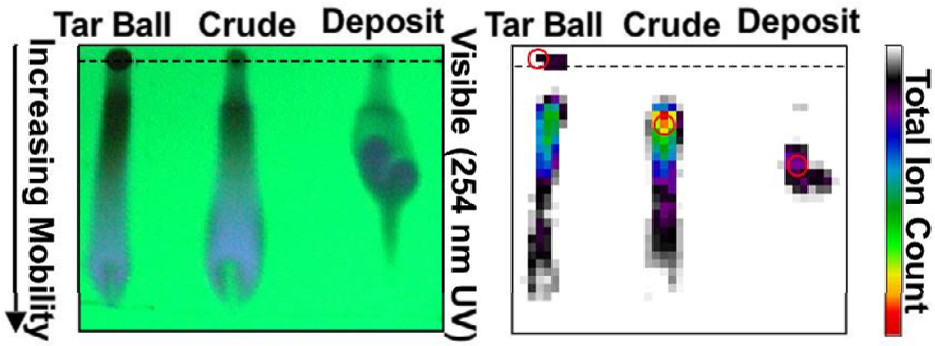

Figure 1. Images of TLC separations for a petroleum deposit, light crude oil, and tar ball. (right) Total ion count from LDI FT-ICR MS (left) Visible fluorescence (254 nm UV light). The dotted line indicates the chromatographic origin. Isoabundance-contoured plots of DBE versus carbon number for the hydrocarbon class of the pixels circled in red (see text). Figure 1 shows total ion count (TIC) for all mass spectral peaks in each pixel (right) and a fluorescence image of the developed TLC plate (left; 254 nm UV illumination). The TIC image reproduces spatial features of the TLC plate development, such as the area of high ion abundance at the center of the deposit separation (aromatic fraction) and the tar ball asphaltene fraction that does not move from the origin. The structure observed for the deposit separation is likely due to two sample aliquots that were spotted at the origin before separation. No asphaltenes were detected for the light crude oil or the field deposit. For all samples, the TIC signal decreases for the saturate fraction, because less aromatic molecules in the saturate fraction do not absorb the 355 nm laser light as well and, thus, are less efficiently desorbed and ionized.

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References

[1] Smith, D.F. *et al*., Energy Fuels, **28**, 6248-6288 (2014)