Solid-Phase Extraction Fractionation to Extend the Characterization of Naphthenic Acids in Crude Oil by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Results and Discussion

Naphthenic (NAP) acids have been previously characterized by negative electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), both directly and from acid extracts. Here, we show that collective characterization of NAP acids with negative-ion ESI, both with and without prior extraction, results in a loss of signal from high mass acids because of ion suppression by low mass acids. We have developed an extraction to simultaneously isolate and fractionate NAP acids into distinct molecular weight ranges, thereby grouping acids into fractions with similar ionization efficiency. A NAP acid fraction was isolated (all acids isolated collectively in one fraction) and compared to NAP acid isolation by molecular weight. Characterization of acid molecular weight fractions extended the observed upper mass limit from ~850 Da for the collectively isolated acids to ~1450 Da for the acids isolated by molecular weight range, thereby approximately doubling the observed mass range for NAP acids. Plots of double bond equivalents (DBE = number of rings plus double bonds to carbon) versus carbon number span both higher carbon number and higher DBE values than are accessed by collective acid characterization. The high mass resolving power and mass accuracy of FT-ICR MS are essential for identification and resolution of acidic species across a wide mass range.

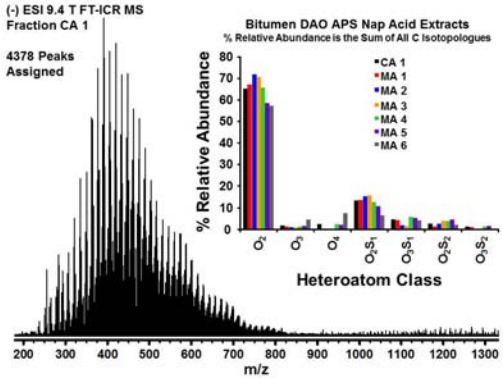

Figure 1. Negative ESI FT-ICR mass spectrum of the collectively isolated acid fraction for APS extraction. (Inset) Heteroatom class distribution for APS and MAPS fractions. Percent relative abundances are calculated for the sum of all detected carbon isotopologues. A bitumen sample was deasphalted with n-heptane and loaded onto a preconditioned APS SPE cartridge in dichloromethane (DCM). The noncarboxylic acid species were eluted in two steps with DCM and DCM/MeOH (50:50, v/v). NAP acids were then eluted with a mixture of DCM/MeOH/FA (50:50:5, v/v/v). All carboxylic acids are thereby collectively isolated from the crude oil in one chromatographic fraction (CA 1). The CA 1 acid fraction was evaporated under dry nitrogen, redissolved in toluene, and electrosprayed in TOL/MeOH (50:50, v/v) with ~0.2% NH4OH to aid in deprotonation. The resulting mass spectrum (Figure 1) shows a distribution centered at ~425 Da and extending up to ~850 Da, in good agreement with previously reported Canadian bitumen (−) ESI mass spectra. The (−) ESI-derived heteroatom class distribution is also shown in Figure 1.

Acknowledgements

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References

[1] Rowland, S.M. *et al*., Energy Fuels, **28**, 5043-5048 (2014)