Silver Cationization for Rapid Speciation of Sulfur-Containing Species in Crude Oils by Positive Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

Lobodin, V.V.; Juyal, P. (Nalco); McKenna, A.M. (NHMFL, Chemistry); Rodgers, R.P.; Marshall, A.G. (NHMFL, FSU, Chemistry)

Results and Discussion

Silver cationization constitutes a complementary approach for analysis of petroleum components with positive-ion electrospray ionization (ESI) mass spectrometry and accesses species that lack a basic nitrogen atom and, hence, are not observed by conventional positive ESI. Four samples of different origin [Canadian bitumen, Canadian bitumen heavy vacuum gas oil (HVGO; 475–500 °C) and South American and Middle East heavy crude oils, all high in sulfur content] were used to study silver cationization by (+) ESI. Cationization with Ag+ is essentially instantaneous and accesses hydrocarbons and nonpolar sulfur-containing heteroatom classes (e.g., S_s and S_sO_o), providing an attractive alternative to time-consuming derivatization by S-methylation to ionize sulfur-containing species. For each sample, we compare Ag+ cationization (+) ESI to conventional (+) ESI with formic acid to promote ion formation. Other ionization methods, such as chemical ionization (CI), field desorption (FD), matrix-assisted laser desorption ionization (MALDI) chemical ionization, field desorption ionization, and MALDI, are low in throughput and/or involve thermal processes that may degrade substrate molecules from non-volatile high-boiling petroleum components. Mix-and-spray Ag+ cationization with avoids tedious separation and time-consuming derivatization and results in the rapid speciation of sulfur-containing compounds in petroleum and its fractions without the need for thermal desorption.

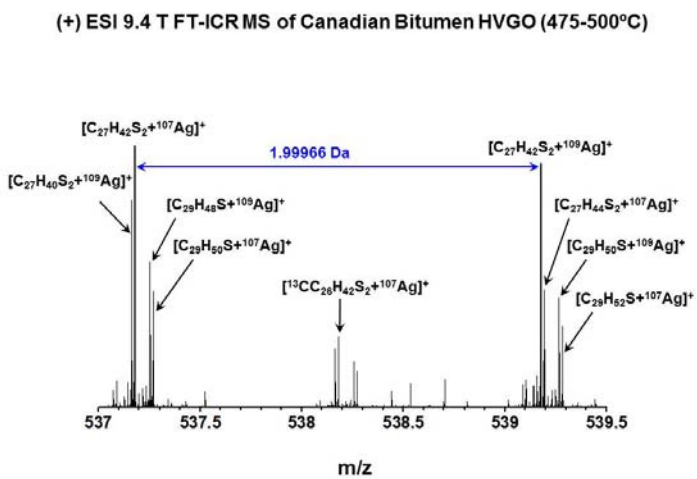

Figure 1. Mass scale-expanded segment (537–539.5 Da) of the (+) ESI FT-ICR mass spectrum of Canadian bitumen HVGO (475–500 °C) with silver trifluoromethanesulfonate (CF_3SO_3Ag, AgOTf). The doublets corresponding to [M + ^{107}Ag]+ and [M + ^{109}Ag]+ ions are fully resolved for every silver-cationized elemental composition throughout the mass spectrum. Moreover, the distinctive isotope distribution because of the presence of silver isotopes enables further verification of elemental composition assignments. Thus, for example, although the possible mass difference of 0.074 mDa (H_5 ^{107}Ag versus C_4S_2) that requires ultrahigh resolving power (m/Δm50% > 6 800 000 at 500 Da) cannot be resolved in the broadband FT-ICR mass spectrum, detection of the corresponding H_5^{109}Ag isotopomer provides additional evidence for the correct molecular formula assignment, because the presence of the ^{109}Ag isotopic peak confirms that the (H_5 ^{107}Ag versus C_4S_2) peak derives from ^{107}Ag and not C_4S_2.

Acknowledgements

This work was supported by the National Science Foundation (NSF) Division of Materials Research through DMR-1157490, NSF Division of Chemistry through Rapid Grant CHE-1049753, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, the Florida State University Future Fuels Institute, and the State of Florida.

References

[1] Lobodin, V.V. *et al*., Energy Fuels, **28**, 447-452 (2014)