Comparison of Green River Formation shale oils by Fourier transform ion cyclotron resonance mass spectrometry

Jang Mi Jin[1], Sunghwan Kim[1], Justin Birdwell[2], Michael Lewan[2]

[1]*Kyungpook National University, Department of Chemistry, Republic of Korea,* [2]*U.S. Geological Survey, USA*

Differences in retort oil composition depend both on the source rock and the pyrolysis method applied. Traditional characterization tools, such as gas chromatography (GC), provide information on the hydrocarbon component of retort oil but not on the more polar, heteroatom-containing (NSO) compounds. Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) is an ultrahigh resolution technique that can provide molecular level information on retort oil polar constituents and can be used with different ionization methods to examine specific chemical fractions. In this study, oils generated by Fischer Assay (FA), the In Situ Simulator (ISS) and hydrous pyrolysis (HP) were characterized by FT-ICR MS. Mass spectra were obtained using both positive-mode electrospray ionization (ESI+), which selectively ionizes basic compounds, and atmospheric pressure photoionization (APPI), which more efficiently ionizes aromatic compounds. Source rocks were collected from sites within the Eocene Green River Formation, specifically Piceance and Uinta Basin Mahogany zone oil shale and a Garden Gulch Member oil shale from the Piceance Basin. The goal of this work was to determine how the distribution of heteroatom-bearing compounds in retort oils differs based on source rock origin and the pyrolysis method. ESI+ results showed that the most abundant polar compounds were those containing one nitrogen atom (N1) followed by those with both a nitrogen and oxygen atom (N1O1). The APPI results showed that N1 and N2 class compounds were present in all samples. The FA and HP oils had higher average molecular weights and more double-bond equivalents (a measure of aromaticity) than those generated by the ISS across all compound classes. HP-generated oils contained the greatest diversity of compounds in terms of heteroatom distribution and aromaticity for all shale samples. The Garden Gulch shale produced oils with higher aromaticity regardless of the pyrolysis method applied. The detailed characterization of polar compounds provided by FT-ICR MS could help shale oil producers to better understand the nature of problematic components in their liquid product, facilitating the selection of treatment methods for use prior to refining.