NEGATIVE-ION ESI FT-ICR MS CHARACTERIZATION OF LACUSTRINE SHALE EXTRACTS AND SHALE OIL MOBILITY

Peng Liu [1,2], Maowen Li [1,2], Qigui Jiang[1,2], Zhiming Li[1,2], Tingting Cao[1,2]

1. Sinopec Petroleum Exploration & Production Research Institute, 100083, China
2. State Key Laboratory of Shale Oil and Gas Enrichment Mechanisms and Effective Development, China

Hydrocarbon liquids in shale systems occur in different modes, either free or absorbed onto solid rock matrix. Without artificial intervention, only free hydrocarbon liquids could be a potential contributor to shale oil production, as the absorbed hydrocarbon liquids have stronger interactions with the surrounding mineral or kerogen. Because the NSO-containing polar compounds in the organic matrix of many shale oil systems play a critical role in reservoir wettability and oil mobility, it is important to develop a sound knowledge of the class type distribution of these compounds in hydrocarbon fluids generated within the shales of different source facies at different maturity levels. Therefore, choosing an appropriate stepwise organic solvent extract methods was useful to get the different polarity hydrocarbon fluids. It is in this context that we report here the results of NSO-containing compound distributions in series of step extraction, as revealed by negative-ion electrospray Fourier Transform Ion Cyclotron Mass Spectrometry (ESI FT-ICR MS).

Samples used in this study came from a vertical wells (Liye 1 well) drilled by Sinopec in the Jiyang Depression, Bohai Bay Basin. Over 240 m of lacustrine shales were cored continuously from the lower Es3 and upper Es4 sections of the Oligocene-Eocene Shahejie Formation. On the basis of detailed Rock Eval/TOC and over a large sample collection, 5 organic-rich shale samples were stepwise extracted. In the first step, the small shale blocks were extracted by dichloromethane/methanol (87:13, v/v) for 24h to get the first extract. In the second step, the extracted shale blocks were further extracted by methanol / acetone / chloroform (23:30:47/ V:V:V) for another 24h to get the second extract. Then the first extracts and second extract were sent to ESI FT-ICR MS and GC-FID analysis, prior to FT-ICR MS analysis using a 12-Tasla Bruker FT-ICR MS in negative-ion ESI mode. Solvent extracts were diluted to a concentration of 0.1mg/mL in the mixture of methanol and toluene (V:V/1:1) and then subjected to ESI analyses. The FT-ICR mass spectrometer was operated at 200-800 Da mass range, with homologous series of acidic compounds (O_2 classes) being used as internal calibrants. Spectral interpretation was performed with COMPOSER 1.0.6 (Sierra Analytics, Inc.) software using an automated peak picking algorithm for rapid and reliable selection. Elemental formulas were calculated from the calibrated peak list and assigned based on m/z values of the radical molecular ions within a 0.5 ppm error range. Normal conditions for petroleum data ($C_cH_hN_nO_oS_s$, c unlimited, h unlimited, $0 \leqslant n \leqslant 5$, $0 \leqslant o \leqslant 5$, $0 \leqslant s \leqslant 4$) were used for these calculations.

Fig. 1 shows the qualitative heteroatom class distribution for neutral nitrogen and acidic compounds derived from Negative-ion ESI FT-ICR mass spectra of step extracts of lacustrine shales from Liye1 well. Compound classes identified from the first step extracts include N_1, N_1O_1, N_1O_2, N_2, N_2O_1, and $O_{x(x=1-5)}$ class species, with the N_1 is the highest relative abundance species, followed by O_2, O_3 and N_1O_1. Compound classes identified from the second step extracts contains more complex heteroatom composition than these in first extracts, which include N_1, $N_1O_{x(1-7)}$, N_1S_1, N_2, N_2O_1, and $O_{x(x=2-7)}$, O_4S_1 and O_5S_1 class species, with the O_2 is the highest relative abundance species, followed by and O_3, O_4. Whereas N_1 class species only has low relative abundance. The results showed that the multi oxygen containing compounds have much stronger interactions with the surrounding mineral or kerogen than the nitrogen containing compounds.

The first and second step extracts were also subjected to GC-FID analysis. The result showed that the first extract contains more low molecular weight hydrocarbons with n-C_{17} alkane dominance, whereas the second extract displays a n-C_{23} alkane maxima. The average molecular weights of these polar NSO-containing class species in the first and second step extracts are similar for the samples studied. As polar compounds are difficult to move, the mobile fractions may contain more hydrocarbon species. Comparison of the variations in the ESI data with Rock Eval/TOC and GC-FID data has provided us with useful clues on geochemical processes at and close to mineral-kerogen-hydrocarbon interfaces, which may be used to unravel key controls on how hydrocarbon fluids are microscopically stored in shale oil reservoirs.
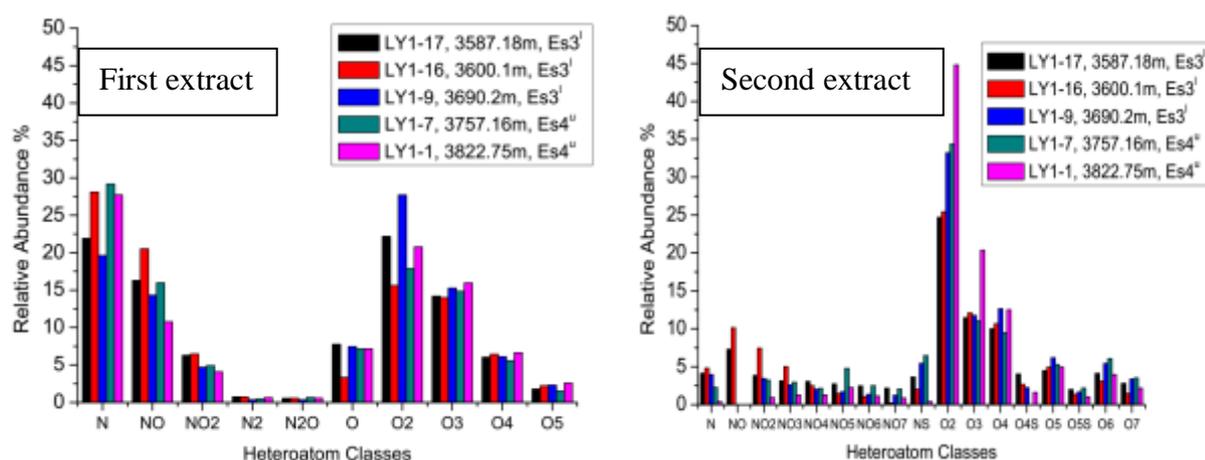

Fig. 1 Qualitative heteroatom class distributions for neutral nitrogen and acidic compounds derived from Negative-ion ESI FT-ICR mass spectra of stepwise extracts of lacustrine shales from Bohai Basin.