Characterization of Nickel Porphyrins in Heavy Crude Oil by Positive-Ion Electrospray Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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In this study, nickel porphyrins were separated using a novel pretreatment method. Metal-free porphyrins were then characterized through methanesulfonic acid (MSA) demetallization via positive-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The results show that the pretreatment was effective in improving the extraction yield as well as in releasing a number of compounds that were associated with polycyclic aromatic hydrocarbons and heteroatomic compounds. Five types of metal-free porphyrins were identified in the purified fractions using their accurate molecular weights. Deoxophylleoerythroetioporphyrin (DPEP) was the predominant porphyrin, with its carbon number ranging from C_{27} to C_{52} and its center of mass located on C_{32}. This finding reveals the evolutionary stage of Liaohe heavy crude oil. In addition, various sulfur class species were identified after MSA demetallization, particularly the S_1 class species, which was not directly detected via ESI FT-ICR MS, The double bond equivalents (DBE) values of the S_1 class species range from 1 to 15. The most abundant S_1 class species had a DBE of 4, indicating the presence of low-aromaticity S_1 species such as cyclic-ring sulfides. Therefore, a new pretreatment method for the identification of polycyclic aromatic sulfur heterocycles via ESI FT-ICR MS was developed.