# Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry for the Investigation of Large Polycyclic Aromatic Sulfur Heterocycles in Petroleum Products

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Sulfur is the third most common element in petroleum but is particularly noxious on combustion. The sulfur oxides formed react with moisture to give strong acids, known as acid rain which is a strong environmental pollutant. Sulfur is nowadays removed in the refineries, most commonly in a hydrodesulfurization (HDS) step with metal catalysts and a high hydrogen pressure at elevated temperatures. While working fine for lower-boiling fractions such as the gasoline and diesel boiling ranges, the HDS is less efficient for the less volatile fractions. This project was initiated to study the molecular features that lead to resistance to HDS among polycyclic aromatic sulfur heterocycles (PASH) in vacuum gas oils and vacuum residues.

The volatility is too low for gas chromatographic analysis and therefore liquid chromatographic methods have to be used despite their low resolving power. These are mainly used to cut a few fractions that are separated based on well-defined separation principles. The aromatic fraction is isolated from other classes of compounds through column chromatography on silica/alumina and then the aromatic compounds are separated into two fractions on a Pd(II) containing column. For high-boiling petroleum fractions, PASHs will be found in both fractions. Studies on the retention of PASHs on this column show that non-cata condensed thiophenes are eluted in the first fraction.

The sulfur-containing compounds have to be preionized before mass spectrometric analysis since the electron spray ionization mode is not particularly efficient for aromatic compounds. This is done by methylating the sulfur atom so that methylthiophenium ions are formed.

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) is a very sensitive mass spectrometric technique of high resolving power. When applied to the PASHs of a vacuum residue (b.p. > 466 °C) a mass range of ca 350 – 800 Da was found with signals at each m/z value. Two to four exact masses were found for each nominal mass. Because of the high resolving power, a chemical composition can be assigned to most signals. Based on the composition, the double bond equivalent (DBE), which is the sum of the number of double bonds and rings in the molecule, can be calculated. If all compounds of a given DBE are plotted vs. the molecular mass, a series of lines of homologues will result. Thus benzothiophenes with up to 47 aliphatic side-chain carbon atoms were found and dibenzothiophenes with up to 42 carbon atoms. HDS treatment simplified the pattern.

Vacuum gas oils of different boiling ranges have also been investigated and will be demonstrated to contain not only a larger number of alkyl carbons at higher boiling point but also a change to more complex parent aromatic structures. Liquid chromatographic techniques can further reduce the complexity of such samples and thus yield more information on the sulfur compounds present.