

DETAILED CRUDE OIL ANALYSIS: GC_xGC, FIELD IONIZATION MASS SPECTROMETRY AND FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY JOIN FORCES

Kevin Van Geem (1), Hendrik Muller (2), Nadrah Alawani (2)

1) Technologiepark 918, 9052 Zwijnaarde, Belgium

2) Saudi Aramco, Ctr Res & Dev, Dhahran 31311, Saudi Arabia

Process development, comparison of processes, and selection of feedstocks all require in-depth characterization of heteroatom (particularly sulfur) containing and poly-aromatic containing compounds, in feed and product streams [1-3]. However, a quantitative characterization at the molecular level is only available for light fractions, difficult for higher boiling cuts, and not available for non-boiling fractions [4]. Gas chromatography (GC) and comprehensive GC (GC_xGC) have been used to provide quantitative information on low- and mid-boiling fractions [5], but are inherently limited by analyte boiling point to a maximum of 400 °C to 500 °C [6-8]. Additionally, the complexity of hydrocarbon mixtures increases rapidly with the boiling point, thereby making a complete separation and identification of all components by chromatographic means difficult. Hence, alternative characterization methods have been implemented for amending GC_xGC to obtain information concerning the heavier, non-volatile fraction of samples. The highest resolving power in MS has been achieved by Fourier-transform ion cyclotron resonance (FT-ICR) MS, here up to 1000000 FWHM are achievable. However, limitations of FT-ICR MS are that it cannot differentiate between, molecules which have exactly the same molecular formula but different structures. Another interesting technique is Field ionization mass spectrometry (FIMS), a “soft”ionization technique in which a relatively small quantity of internal energy is supplied to the molecule, so that molecular ions are produced for most molecular species. Thus, field ionization affords substantially reduced fragmentation and much higher molecular ion intensities compared with electron impact ionization. This feature makes assignment of peaks to compound types straightforward. It allows one to perform quantitation based on the intensity of molecular ions only and obviates the need for complex matrix inversion routines. It also opens up the possibility of analyzing complex multicomponent hydrocarbon mixtures without prior LC separation by utilizing gas chromatography with FIMS (GC-FIMS). [9]

In this work, we assessed FT-ICR MS with different ionization modes for a quantitative characterization of sulfur and aromatic compounds. The focus of this study lies on vacuum gas oil (VGO) samples because these can be partially quantitatively speciated using GC_xGC and GC-FIMS, therefore, used as a reference. The desired comprehensive quantitative analysis of aromatic and sulfur species by FT-ICR MS carries a potential of being readily extended to higher boiling fractions, where quantitative speciation is not available today. To allow a quantitative comparison between FT-ICRMS, GC_xGC and GC-FIMS results for VGO samples, FT-ICR MS parameters were optimized and data obtained by both techniques were standardized. Response factors were established for two ionization modes: atmospheric pressure photo ionization (APPI) and electrospray after selective derivatization of sulfur compounds (MeESI). Comparison with GC_xGC and GC-FIMS results showed good agreement (deviation in the order of 10%).

References

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