

Isomeric species detection of base oil hydrocarbons by photo ionization GC×GC-HRTOF-MS

Anupam Giri¹, Marion Courtiade², Amandine Racaud², Jean-François Focant¹

¹University of Liège, Department of Chemistry, Organic & Biological Analytical Chemistry Group, Allée du 6 aout, B6c, B-4000 Liège (Sart Tilman), Belgium

²Total Marketing Services, Centre de Recherche de Solaize, Chemin du Canal - BP 22, 69360 Solaize, France

Abstract

Comprehensive structural elucidation of hydrocarbon classes and functional biomarkers in petroleum products are always in high demand. Base oil, the major component of lubricant, determines many of the critical performance properties. Thus, detailed understanding of chemical compositions of the base oil is required.

The sheer number of compounds in a base oil sample quickly exceeds the available peak capacity of single-column techniques. Consequently the use of multidimensional separation techniques will almost invariably be required. Despite the superior separation afforded by GC×GC, the identification of individual compounds in complex base oil remains challenging when majority of compounds in a chemical class displays similar skeleton-spectra at conventional (70 eV) ionization energies.

In this study, application of photo-ionization (PI) coupled with GC×GC-HRTOF-MS was evaluated for authentic standard mix called century mix along with several groups of base oil samples. To have clear understanding of molecular ionization and fragmentation, vertical ionization energies as well as orbital energy distributions were additionally calculated. This soft-ionization technology was shown to enhance analyte speciation by providing supplementary data on both molecular ions and structurally significant fragments in the low-energy (10.5 eV) mass spectra. The enhanced sensitivity and selectivity stemming from the dramatic reduction in fragmentation at low energies also greatly increases the number of compounds identified permitting robust statistical comparisons essential for successful chemical fingerprinting of base oils. In addition, applicability and added benefits of PI for different functional groups of VOCs including esters, alcohols, and phthalates etc other than hydrocarbons were evaluated and will be discussed.