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Raman Spectroscopy

Olefins

Application Note

Olefins are unsaturated hydrocarbons containing only hydrogen and carbon that contain one or more pairs of carbon atoms linked by a double bond. Cyclic olefins (closed-ring) have ring-shaped structures with double bonds, while in acyclic (aliphatic) olefins, double bonds are located between carbon atoms forming an open-chain structure. Olefins can be classified as monoolefins, diolefins, triolefins, where the number of double bonds per molecule is one, two, three, respectively, or some other number.

Acyclic monoolefins have the formula C_nH_{2n} and are formed in large quantities through industrial processing. Linear alpha olefins (LAOs) are produced through polymerization (oligomerization) and olefin metathesis. In olefin oligomerization, long chain compounds are produced by combining lower molecular weight monoolefins (ethylene). Olefin metathesis involves the exchange of chemical substituents with subsequent reformation of carbon double bonds.

LAOs produced via oligomerization and olefin metathesis are used as starting materials for plastics (polyethylene), detergents, adhesives, and other products. Higher molecular weight olefins (propylene and butylene) are the basis for an extensive petrochemicals industry.

Propylene, a key building block, is central to the production of polypropylene, one of the most versatile plastics used in automotive parts, consumer goods, and textiles because of its durability and resistance to various chemicals. Beyond polypropylene, propylene is also crucial for manufacturing other significant chemicals such as propylene oxide, acrylonitrile, and isopropanol, highlighting its versatility and essential role in modern manufacturing processes. Butylene (or butene), on the other hand, encompasses a group of isomeric compounds that are equally important in the synthesis of polymers, particularly polybutene, and as intermediates in the production of butadiene, an essential component of synthetic rubber, as well as other chemicals like methyl ethyl ketone (MEK). Butylene is also utilized in the alkylation process to produce high-octane gasoline components.

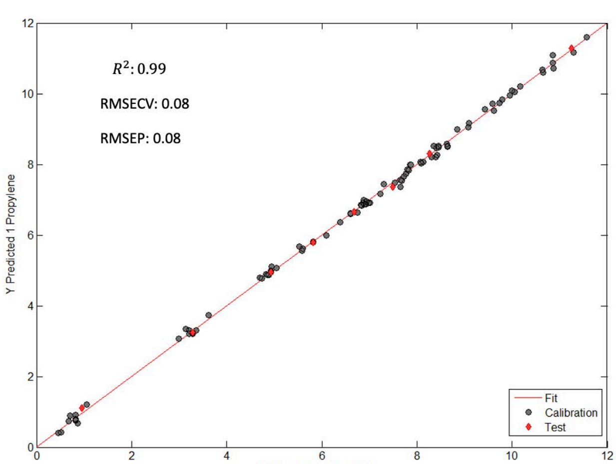

Figure 1: Predicted vs Measured Propylene. Measurement performed via GC analysis.

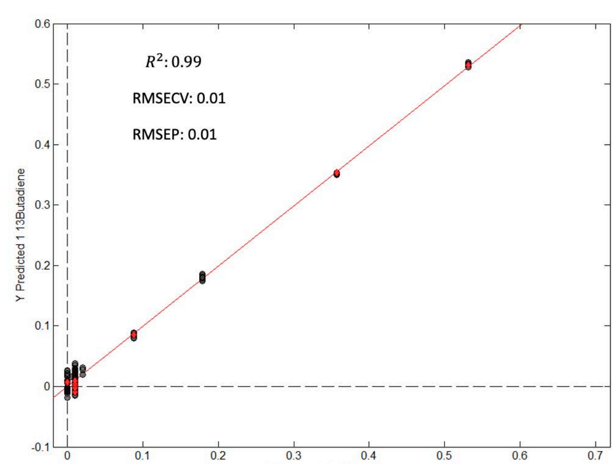

Figure 2: Predicted vs Measured Butadiene. Measurement performed via GC analysis.

Alpha olefins are manufactured by two main routes: oligomerization of ethylene and dehydration of alcohols.

- C4 - C8 are used as comonomers in production of polyethylene.
- C10 - C14 are used in making surfactants for aqueous detergent formulations.
- C16 - C18 are used as hydrophobes in oil-soluble surfactants and as lubricating fluids.
- C16 - C18 are used as synthetic drilling fluid base for high value, primarily off-shore, synthetic drilling fluids.

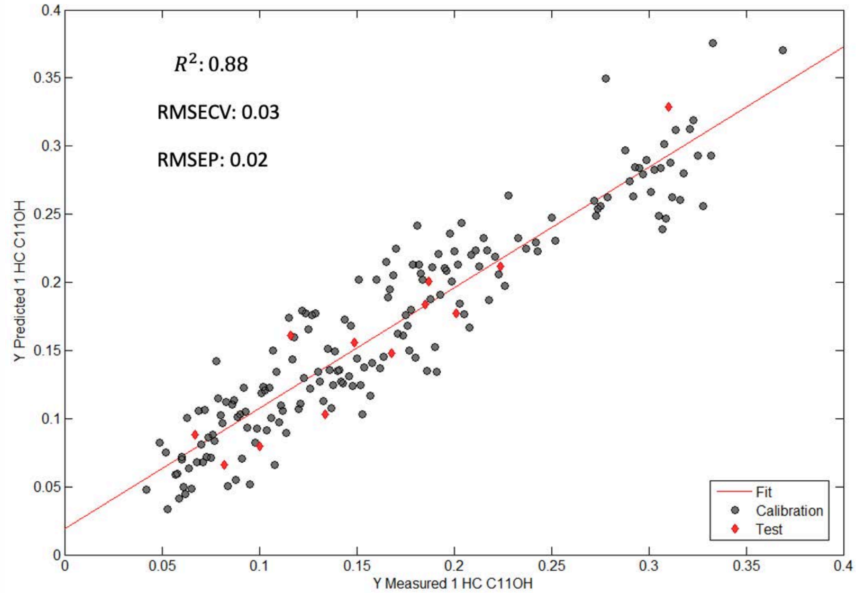

Figure 3: Predicted vs Measured C11 OH. Measurement performed via GC analysis.

Acyclic diolefins have the formula C_nH_{2n-2}, contain two double bonds, and undergo reactions like the monoolefins. The best-known dienes are butadiene and isoprene. Olefins, paraffins, and aromatics are the key components in gasoline, while paraffins, aromatics, and naphthenes are the key components in diesel. Olefins tend to increase reactivity of gasoline fuel while improving fuel octane number and affect engine combustion and emission characteristics. Olefins are an important component of gasoline and an important property with respect to the development of reformulated gasolines using regulatory models. Higher olefin content in fuel increases 1,3-butadiene emissions which are photoreactive and tend to contribute to photochemical smog. Despite the benefits associated with olefins in fuel formulations, their potential to foster photochemical smog necessitates strict regulation of their levels in gasoline.

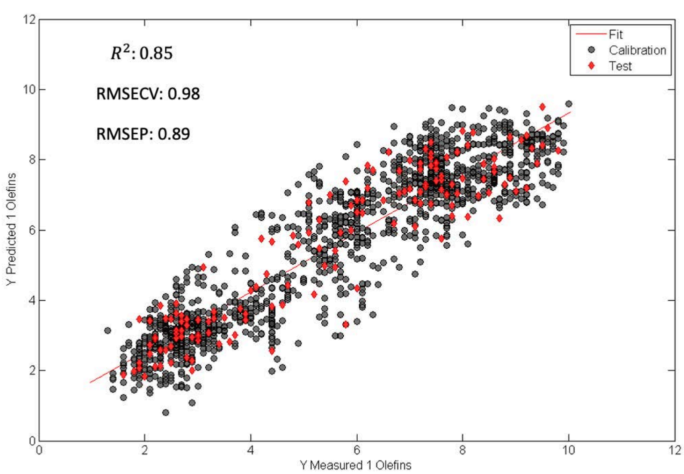

Figure 4.1: Predicted vs Measured Olefins in Gasoline.

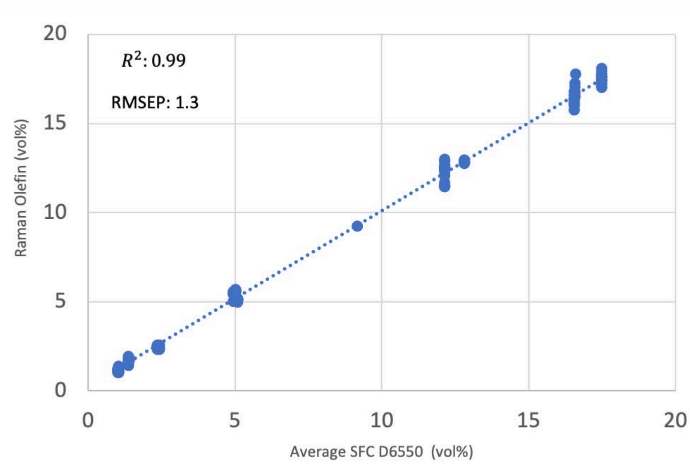

Figure 4.2: Calculated vs Measured Olefins in Gasoline using 14 different ASTM Interlaboratory Round Robin gasoline results. Measurements performed via SFC ASTM D6550, repeatability (r) 0.65 vol% and reproducibility (R) 2.5 vol%.

This creates the need for rapid monitoring of olefin levels in petroleum products. Traditional analytical methods for determining olefin content face challenges, including lengthy analysis times, extensive solvent use and disposal requirements, the need for high-purity gases, and limited applicability for on-the-go process monitoring. In this context, Process Raman spectroscopy emerges as a strong solution, offering an ideal approach for the real-time determination of olefin content in refined streams. HORIBA Process Instruments is also developing an ASTM method for directly determining olefin concentrations (vol%) in gasoline and voting on this method will be during Q2 of 2024.

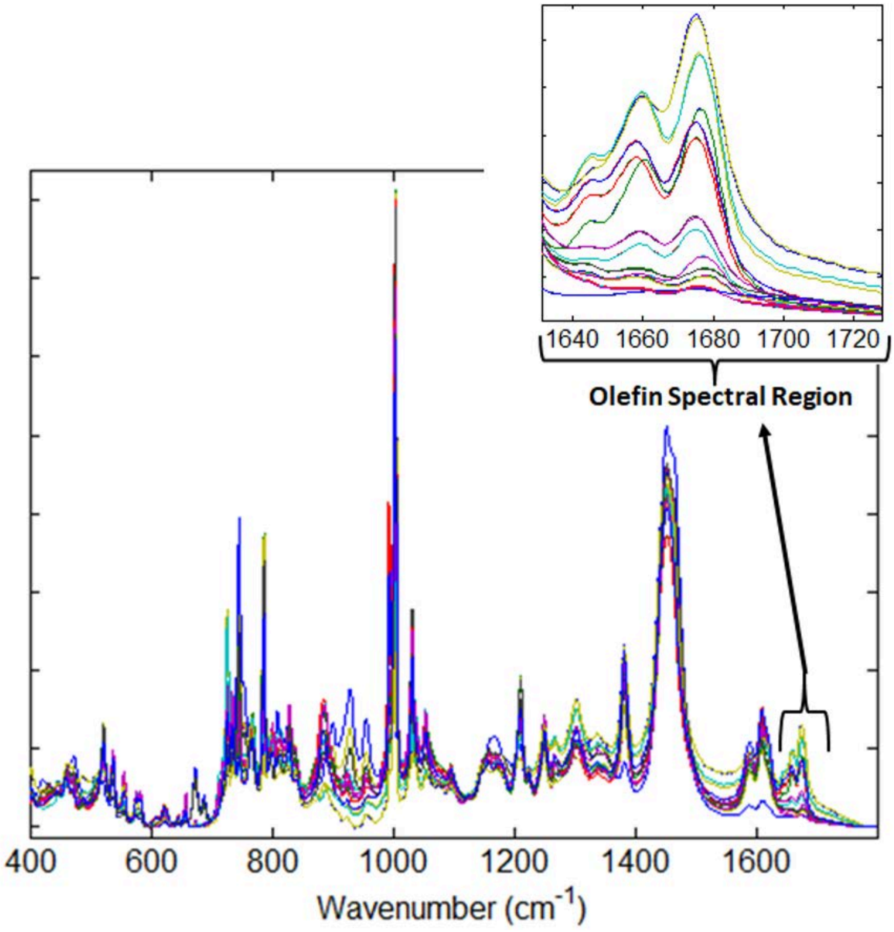

Figure 5: Raman spectra of gasolines with different olefin concentrations.

HORIBA's Process Instruments brand is specifically designed to detect to below 100ppm, with some compounds in the single digit ppm range. A diode laser is optimized for fiber optics illumination and collection via a flow cell with a sapphire window. Collected radiation is returned to the monochromator with a fiber optics slit which is mated to a diffraction grating and 4-stage cooled CCD camera for detection. The HORIBA Process Instruments design is fast with minimum energy loss to maximize detection.

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