Status on WK49499

Standard Test Method for Total Olefins in Gasoline by Raman Spectroscopy

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Key Aspects of the Proposed Method (Revised)

•Open method that is not subject to licensing and/or exclusive to a Raman instrument vendor

•Develop robust calibrations that are not dependent on the user having their own calibration samples as part of the method

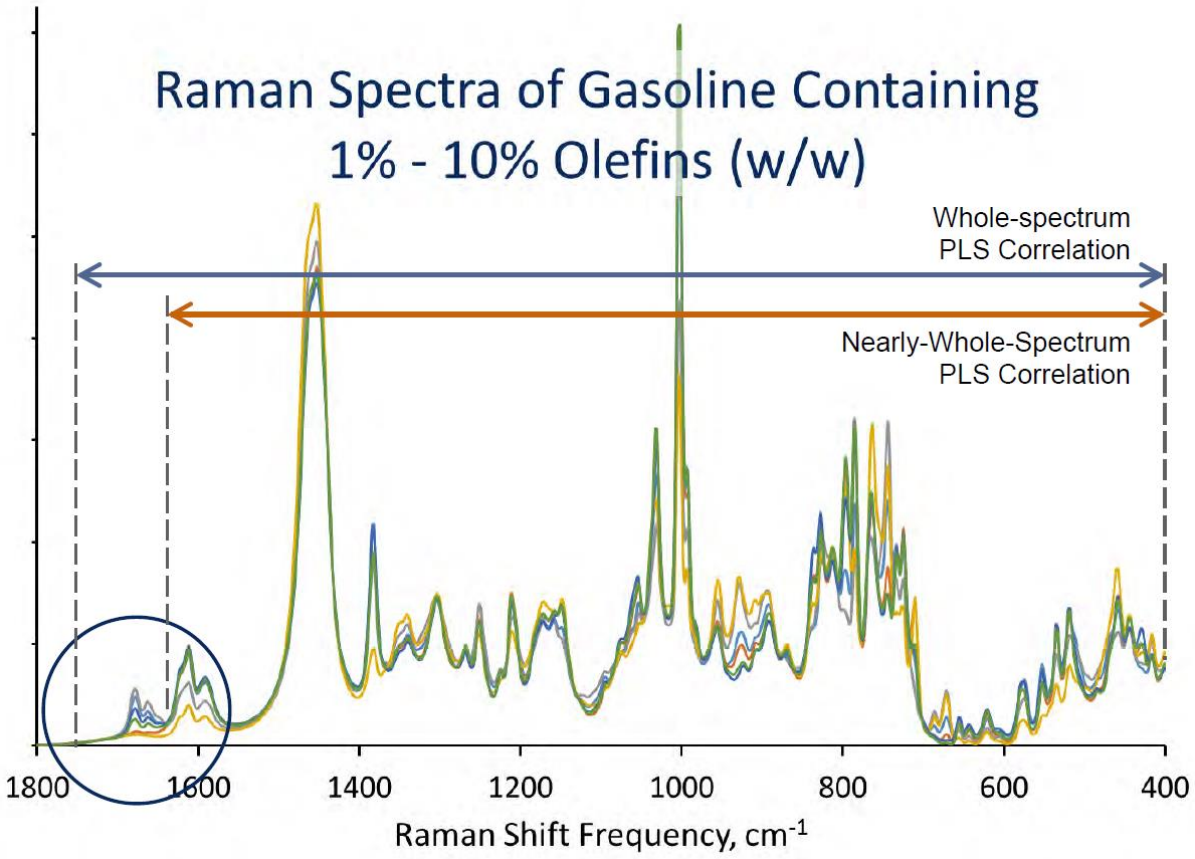
~~•Similar approach that was successfully applied within D02.04.0F that lead to ASTM publication of two methods for gasoline analysis~~

- ~~•ASTM 6277- Benzene quantification via mid-IR spectroscopy~~
- ~~•ASTM 5845- Oxygenates in gasoline via mid-IR spectroscopy~~

•Leverage recent advances in quantitative Raman spectroscopy that have been applied to pharmaceutical, forensics, and product quality applications:

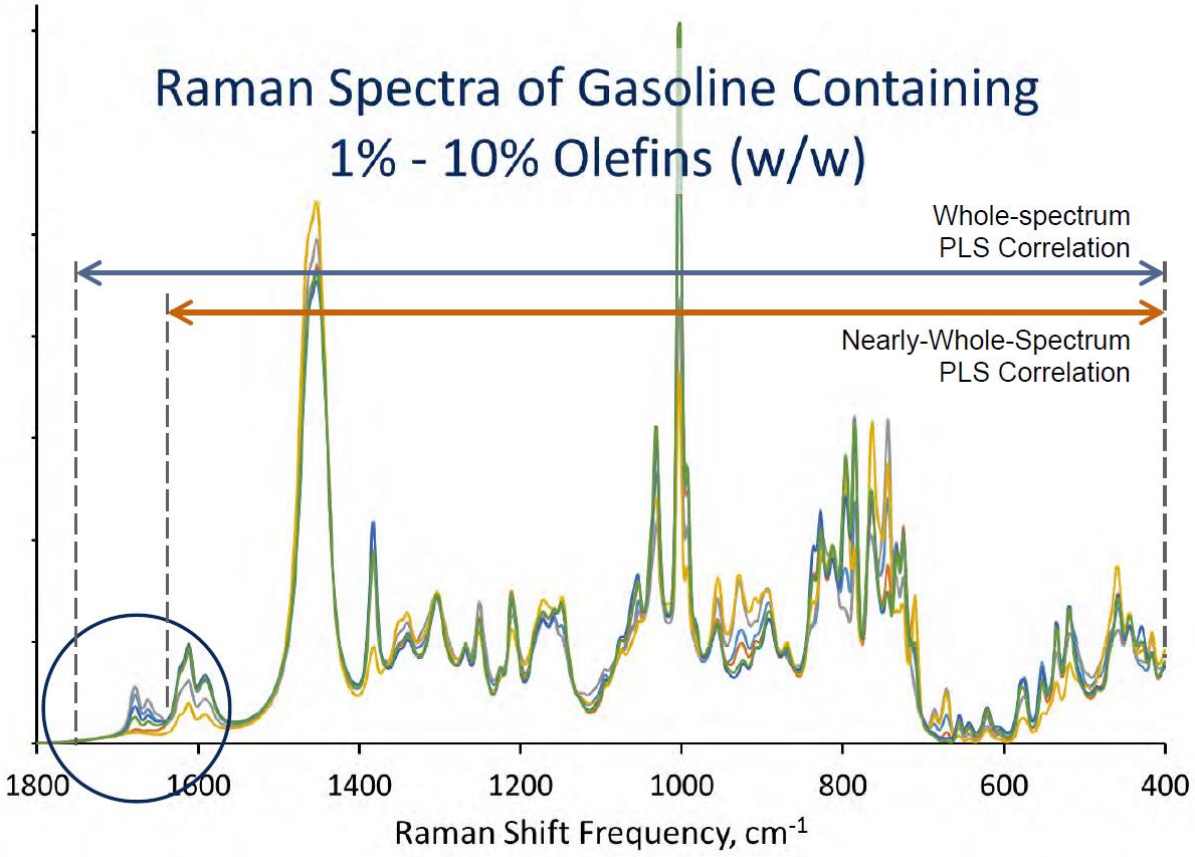
- ~~•Algorithims to build, append, and transfer spectroscopic calibrations~~
- •Methods and standards to normalize spectral intensities

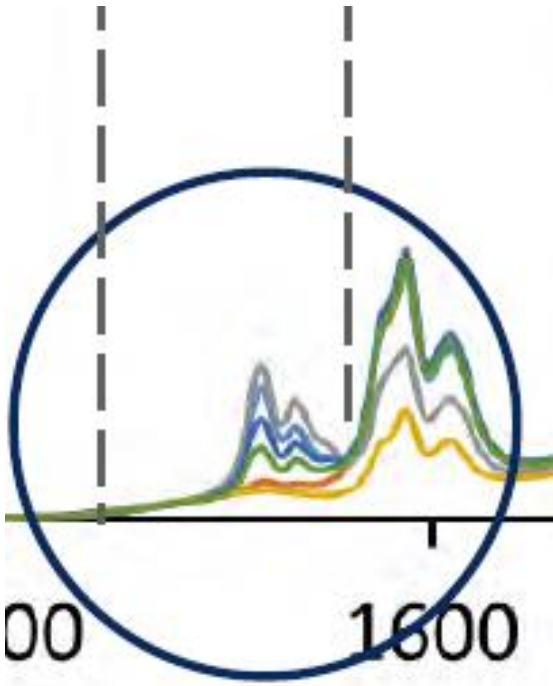
Raman Spectra of Gasoline Blend Stocks



- Raman spectra for olefins has very good separation against other common blend stocks
- Advances in Raman core technology (hardware and software) enables measurement with very high SNR, repeatability, and reproducibility

What is Raman Actually Measuring for Olefins?





- "Olefins" are organic molecules with C=C bond (mono-olefins)
- The peaks ~ +1650 cm-1 derive from C=C vibrational energy and provide no information about the rest of the molecule.
- Chemometric PLS methods to use the rest of the spectrum will only produce a weak and tenuous calibration that will need constant oversight (e.g. octane, distillation)

MOTOR FUEL PROPERTY PREDICTION BY INFERENTIAL SPECTROMETRY 3. HARD AND SOFT REALITIES OF MEASURING OLEFINS IN GASOLINE

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KEY WORDS

OLEFINS, ALKENES, GASOLINE, SPECTROSCOPY, SPECTROMETRY, RAMAN, NIR, NMR, FIA, SFC, ASTM D1319, ASTM D6550, OCTENE, MOLECULAR STRUCTURES, BEER'S LAW, BEER-LAMBERT LAW, RAMAN SCATTERING INTENSITY, RAMAN SCATTERING CROSS-SECTION

ABSTRACT

This study is the third in a series whose aim is to "put chemistry back into chemometrics" where multivariable methods of spectral analysis are applied in an effort to quantify motor fuel properties. Determining the weight- or volume-percent olefins in motor fuels by FTIR or Raman spectrometry is conceptually straightforward but practically problematic. Actually, it is not possible. Some will insist that it is, citing the indisputable fact that olefinic functionality expresses itself directly and distinctly in FTIR and Raman spectra of gasoline. However, that fact hints at the very issue: those techniques measure the olefin equivalents per unit volume of gasoline but cannot differentiate entire molecules. Thus, because of the complexity of the mixture, no molecular spectroscopy technique (IR, NIR, Raman, or even high-resolution NMR) can provide complete information about the size of substituents attached to carbon-carbon double bonds of olefins in gasoline. That limitation notwithstanding, this study identifies a first-principles approach to quantifying percent olefins in gasoline based on Raman spectrometry. The starting point is to understand how the number, relative positions, and types of substituents on a carbon-carbon double bond affect the intensity, location, and shape of the band associated with its stretching mode, which appears around 1645 cm^{-1} – 1675 cm^{-1}.

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http://www.pembrokeinstruments.com/olefins-1.pdf

http://www.pembrokeinstruments.com/olefins-2.pdf

- Directly quantifies olefins in terms of mole eq./ml
- Does not need spectral library (cal trans not needed)
- Uses internal reference standard (acetonitrile) to capture ratioed spectra
- Guidance for conversion to wt% and vol% through known values of gasoline density and average gram eq. weight
- Should be 100% robust against wide range of olefin molecular profiles

WK49499 Going Forward and Next Critical Actions

- Revise method to exclusively test for mole eq/ml with guidance to convert to vol% and wt % total olefins
- Design validation set for R&D study that tests method against wide range in olefin molecular profile
- Present results at next D02 meeting