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}.

INTRODUCTION

The spectrometric analysis of olefins in gasoline has inherent relevance due to concern by regulatory bodies to limit contribution by olefins to formation of ozone and smog, their reactivity as a class being particularly high as measured on the "k_{OH} reactivity scale" (1). Though the Fluorescent Indicator Adsorption (FIA) method (2) has been a mainstay of refinery laboratories for over five decades, its interlaboratory reproducibility is poor, as is its accuracy at low olefin levels (3). More recently, the supercritical fluid chromatography (SFC) method (4) has gained currency not only because of its improved performance, but also because it permits the laboratory analysis to be automated.

Perhaps the main motivation to develop spectrometric methods for measuring olefins in gasoline is that the established methods are not amenable to online implementation. Though properties like octane and RVP have principal importance for blending economics, the ready availability of information about other properties also has benefit. The possibilities to generate spectroscopy-based multivariate correlations for gasoline properties are well known, examples including research and motor octane numbers (RON and MON), distillation yield temperatures, benzene, and total aromatics. Such correlations may be applied to provide real-time, online property predictions and also to improve sample throughput in the laboratory. In both contexts, the ability to also quantify olefins reliably would be beneficial. However, olefins in gasoline are regulated, and as with many other properties, refiners are constrained to base their certification of gasoline quality on industry-standard test methods. Thus, the FIA and SFC methods cannot be replaced outright by NIR and Raman spectrometry because in general, property predictions by these techniques are referenced to primary test method results (PTMRs) generated by ASTM test methods.

TRADITIONAL APPROACHES TO QUANTITATIVE SPECTROMETRY

Two traditional approaches to measuring olefins in gasoline by Raman spectrometry are currently under consideration in ASTM working groups. Summarized below, they are examples of what can be described as "hard" and "soft" spectrometry due to their use, respectively, of a particular standard and simple linear regression or of multivariate correlation.

1. **Classic "hard" spectrometry:** based on a) creating a linear calibration curve relating the intensity of a spectral response for a standard olefin (with responses around 1645 cm^{-1} to 1675 cm^{-1}) to the concentration (w/w) of an olefin standard; then b) measuring the intensity of the olefin band in an unknown gasoline sample and interpolating the olefin concentration (5).

2. **Classic "soft" spectrometry:** based on a) collection of spectra and PTMRs for a population of gasoline samples spanning an appropriate range of composition variations including percent olefin; b) applying standard methods to create a multivariate correlation using a wide frequency range in the sample spectra (a "full-spectrum" correlation); then c) predicting olefin content by applying that correlation to spectra of unknown gasoline samples (6).

The authors of both methods recognized that to replace the established methods with a Raman-based approach, refiners would require sanction in the form of an approved ASTM

method. The intent of the Method 1 authors seems to be, admirably, to build an analytical structure upon first-principles so that the method stands on its own as an ASTM primary test method (PTM). But a limitation of the method is that it relies on operations that obviate the possibility for online implementation, namely, the dilution of sample and inclusion in the sample solution of an internal standard. (Another potential limitation for those who nevertheless might wish to implement the method is that it is covered by a patent (7).)

By contrast, Method 2 seeks to achieve the goal of adoption by refiners through a method carefully aligned with other established ASTM methods and practices, notably ASTM D6550-15 Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography and E1655 Practices for Infrared Multivariate Quantitative Analysis, the latter governing the generation of spectrometric correlations. Importantly, Method 2 also supports *in situ* analysis of sample as-is, making it amenable to concurrent implementation with other Raman-based multivariate property correlations, whether in the lab or online.

THINKING HARD ABOUT HARD AND SOFT CORRELATIONS

Methods 1 and 2 merit consideration by dint of their procedural detail and a nominal basis in established methodologies. However, they are not obviously undergirded by some important considerations related to the fundamental chemistry and spectroscopy of olefin molecules. The second paper in this series examines the issue in terms of the "information supply chain" that prompts a key question (8):

> To what extent does the chemistry that determines the property of interest
> in gasoline express itself directly and distinctly in the spectrum of the
> sample(s) being analyzed?

When spectral expression of the chemistry is direct and distinct, property correlations are "hard," whereas direct/indistinct yields correlations that are "soft." Correlations also may be obtained without direct causation (the chemistry responsible for the property of interest expresses itself *neither directly nor distinctly*), excluding the notion that multivariate correlations differ simply in extent to which they are inferential (some are more inferential than others). A more accurate formulation might be as follows:

- Hard correlations *measure*
- Soft correlations *infer directly*
- Correlations Without Direct Causation (CWoDC) *infer indirectly*

Practitioners who apply multivariate calibration techniques to the spectrometric analysis of motor fuel properties will readily acknowledge that decreased analytical robustness generally attends the hard/soft/CWoDC progression (9).

The question now is whether olefins in gasoline can be measured by means of correlations that are hard or soft, or by CWoDC? The quest to develop a method grounded solidly in first principles brings to light issues that are broadly relevant and often overlooked when seeking to leverage molecular spectroscopy for motor fuel property analysis. Specifically, Methods 1 and 2

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collide with these principles, exposing both the assumptions upon which they are based and suggesting a third approach that coherently integrates spectroscopy, chemistry, and chemometrics.

A Note on Terminology. The terms alkene and olefin are often used interchangeably. In organic chemistry, alkene is understood to refer specifically to a functional group characterized by a carbon-carbon double bond, although in common usage the term alkene also can refer to an entire molecule containing an alkene group. For reasons historical, the refining industry and regulators predominantly use the term olefin. Though definitions are not strict, an olefin can be defined as a hydrocarbon *molecule* that *contains* one or more alkene groups. Further, an olefin molecule might be regarded as comprising only alkene and other hydrocarbon functional groups, but no heteroatoms like O, S, or N. Understood this way, it would not be appropriate to talk about an olefin group, but instead to use the terms "olefin functionality," "olefinic functionality," "olefinic carbon-carbon double bond," "olefinic equivalents," etc. Because this paper concerns motor fuel, it mainly applies such terminology, exceptions including the terms monoolefins and diolefins, which convey the number of alkene groups in an olefin molecule. Alkene, alkenyl, and related terms are used when technical precision is required.

PROBLEM DEFINITION: CHEMICAL REALITIES

Three questions provide the starting point for evaluating possibilities to apply molecular spectroscopy for analysis of olefins in gasoline. Though they might at first seem trivial, they and Table I point to deeper issues.

    Q1: What units of concentration are available for expressing olefin concentration?
    Q2: What concentration units does the industry use?
             (In what units do the standard analytical methods report olefin concentration?)
    Q3: In what concentration units do molecular spectroscopy techniques measure
             olefins in gasoline?

Before examining the implications of Table I for analysis of olefins by spectrometry, it should be noted that Appendix X1 of ASTM D6550-15 (the SFC method) reconciles its mass-basis results with the volume-basis results of ASTM D1319 (the FIA method) by means of a simple factor:

Volume% (D1319) = 0.857 x Mass% (D6550)   (1)

The three significant figures suggest a precision in the relationship between Volume% (D1319) and Mass% (D6550) that belies the notoriously poor reproducibility of the D1319 FIA method. Also, by definition, the factor 0.857 is the ratio between the average in-solution density of olefins and the average density of gasoline. If 66 °API (0.717 g/mL) is taken as a typical density value for gasoline, then the average in-solution density of olefins in gasoline calculates to be 0.836 g/mL. Supposing that density values like those in Table II are typical of pure olefins (not surprisingly, they are similar to densities of gasoline), a high value like 0.836 g/mL for the in-solution density of olefins cannot be explained in terms of non-ideal behavior of hydrocarbon solutions. Rather, the 0.857 correction factor suggests that the FIA method overestimates olefin content by about 20% versus the more accurate SFC method. Nevertheless, regulations on olefins in gasoline express limits as volume %, necessitating a convenient conversion.

TABLE I. UNITS FOR EXPRESSING AND MEASURING OLEFIN CONCENTRATION.

UNITS	DEFINITION	ANALYTICAL METHOD
Volume Fraction	Total volume of all olefin compounds in a given volume of sample (mL/mL or volume %)	Fluorescent Indicator Adsorption (FIA) ASTM D1319-15 (1)
Weight Fraction	Total mass of all olefin compounds in a given mass of sample (g/g or mass %)	Supercritical Fluid Chromatography (SFC) ASTM D6550-15 (3)
Normality	Equivalents of C=C per unit volume of sample (eq/L)	All molecular spectroscopy techniques applied in the spectrometric analysis of gasoline (IR, NIR, Raman, and NMR).
NOTES • This table cites the two ASTM Standard Test Methods used for routine analysis of olefins in gasoline. ASTM D6623-01, "Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by High Resolution Gas Chromatography", which also determines olefins on a mass basis, is not used routinely. • Molality is a fourth concentration unit. ASTM D1159 may be used to quantify olefins in petroleum distillates as g bromine that reacts with 100 g of sample. Given that each C=C group reacts with one mole of bromine (Br_2), the bromine number effectively is an expression of molality. This method is not generally applied to gasoline. • Calibrations created to make volume- and mass-percent measurements of whole compounds by molecular spectrometry techniques actually measure eq/mL and rely on nominally ideal solution behavior across the concentration range of interest, e.g. Wt%/Vol% ≈ constant. Refer to Appendix A for a full discussion.		

SPECTROMETRIC TECHNIQUES MEASURE FUNCTIONAL GROUPS

Table II and the discussion in Appendix A define an even more fundamental problem confronting any attempt to quantify olefins spectrometrically: the molecular spectroscopy techniques IR, NIR, Raman, and NMR cannot measure compounds in a complex mixture like gasoline. Figure 1 and Table I help illustrate that these molecular spectrometry techniques can inventory the amounts of functional groups in the mixture but cannot to assign those functional groups to specific compounds or even classes of compounds in a complex mixture like gasoline.

Figure 1 shows that the type, number, and relative position of substituents on the carbon-carbon double bond may generate great diversity in olefin structure. With the additional possibility to join adjacent R-groups to form cyclic structures, the number of hydrocarbons containing five to eight carbons exceeds 200. Appendix C provides a partial accounting of possible structural $C_5 - C_8$ isomers.
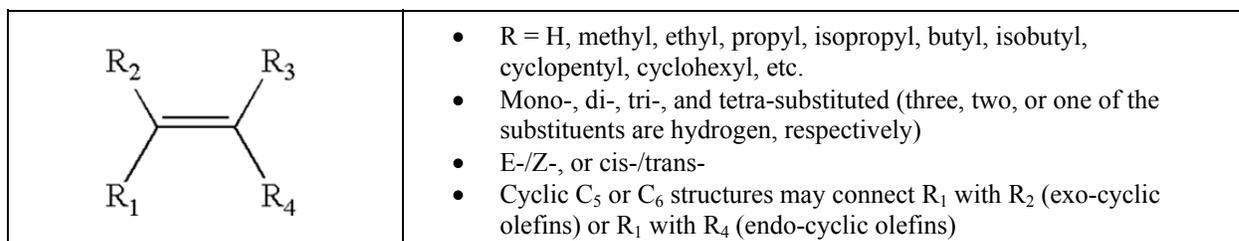

R_2 R_3 / R_1 R_4 (olefin structure)	• R = H, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, cyclopentyl, cyclohexyl, etc. • Mono-, di-, tri-, and tetra-substituted (three, two, or one of the substituents are hydrogen, respectively) • E-/Z-, or cis-/trans- • Cyclic C_5 or C_6 structures may connect R_1 with R_2 (exo-cyclic olefins) or R_1 with R_4 (endo-cyclic olefins)

FIGURE 1. DIVERSITY IN THE STRUCTURE OF OLEFINS.

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TABLE II. CHEMICAL AND PHYSICAL PROPERTIES OF SIX RELATED OLEFINS.

COMPOUND	MOLECULAR FORMULA	MOLECULAR WEIGHT. (g/mol)	DENSITY (g / mL)	OLEFIN CONC. (meq / g)	OLEFIN CONC. (meq / mL)
trans-hex-3-ene	C_6H_{12}	84.16	0.6727 [a]	11.88	7.99
trans-hept-3-ene	C_7H_{14}	98.19	0.6938 [a]	10.18	7.07
trans-oct-4-ene	C_8H_{16}	112.21	0.7099 [b]	8.91	6.33
trans-6-methyl-hept-3-ene	C_8H_{16}	112.21	0.709 [b]	8.9	6.3
trans-2-methyl-oct-4-ene	C_9H_{18}	126.23	0.730 [c]	7.9	5.8
trans-2,7-dimethyl-oct-4-ene	$C_{10}H_{20}$	140.27	0.741 [d]	7.1	5.3

[a] Reference (10)
[b] Reference (11)
[c] Density value not available. That given is from the preceding reference for *trans*-2-methyl-oct-1-ene and is expected to be representative of that for *trans*-2-methyl-oct-4-ene.
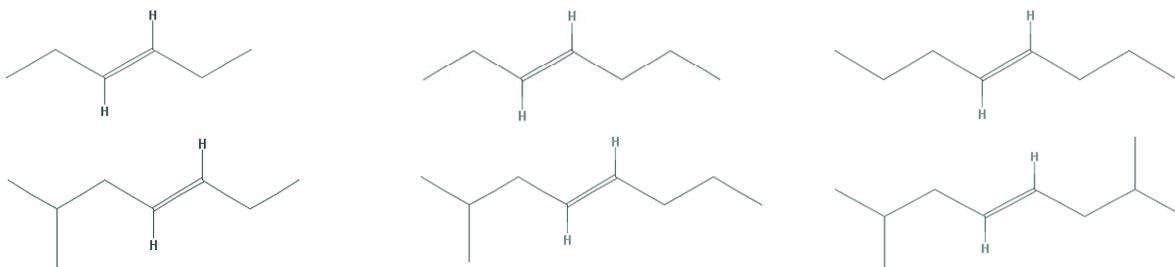
FIGURE 2. MOLULAR STRUCTURES OF COMPOUNDS IN TABLE II.

In considering a small subset of possible olefins in gasoline, Table II and Figure 2 elucidate why the diversity of possible structures limits options for spectrometric analysis of olefins. Shown are all possible pairs of ethyl, propyl, and isobutyl substituents that can be arranged in the *trans* configuration. All except the two C_8 compounds have different formula weights and densities. Consequently, concentrations of olefinic C=C in the pure compound, expressed in terms of equivalents (as meq/g or meq/mL), are different: the same mass or volume of each compound will have a different number of olefin equivalents (C=C groups). Each is 100% olefin but the concentration of C=C functional group equivalents varies with carbon number.

Note also that at the center of all compounds in Figure 2 is the same butylene structure, -CH₂CH=CHCH₂-. Thus, they have the same number of alkenyl hydrogens (C=C-H, also referred to as vinylic hydrogens) and also the same number of hydrogens attached to alpha carbons. Suppose now that solutions containing all six compounds are prepared in toluene such that none of their concentrations correlated with the concentrations of C=C or the three different

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substituents. This thought experiment is an extension of a study presented previously involving an even simpler set of compounds (12). It showed conclusively that, for mixtures comprising compounds assembled from even a limited number of functional groups (to yield different compounds that differ in structure, molecular weight, and physical properties), the spectroscopy underdetermines the chemistry, i.e. the degrees of freedom in the chemical composition exceed those for the spectral data set. That means that molecular spectroscopy techniques (IR, NIR, Raman, or high-field proton NMR) can quantify the total concentrations of functional groups in a complex mixture but not the concentrations of individual compounds.

In gasoline, the situation is exacerbated because many substituents attached to the C=C bond (ethyl, propyl, isopropyl, butyl, isobutyl, etc.) also may be contained in paraffins and naphthenes. If the underdetermination of sample chemistry by molecular spectroscopy undermines spectrometric analysis for simple mixtures containing just a few functional groups, then the situation is no less impossible in gasoline where the permutations are innumerable.

RAMAN SPECTROSCOPY OF OLEFINS IN GASOLINE

The spectral behavior of olefins will now be examined by Raman spectroscopy to the exclusion of NMR and NIR for the simple reason that Raman permits direct observation of the carbon-carbon double bond while the latter do not. Low field ^{1}H NMR ($\leq$ 100 MHz) that might be used for routine analysis in refinery laboratories "sees" olefin-ness expressed only indirectly via vinylic protons attached to it or alpha protons on adjacent carbons. Problematic in that regard is the fact that a carbon-carbon double bond or an alpha carbon may bear three, two, one, or zero hydrogens. The situation in NIR spectroscopy is analogous: overtones of fundamental C-H stretching modes dominate generally, but NIR overtones also may contain information from the IR fingerprint region. Regardless, the information is "mixed," meaning that olefin-ness expresses itself variably as a function of the number of vinylic C-H groups. These facts prevent the direct quantification of olefin content in gasoline by NMR and NIR.

THE CENTRAL QUESTION ABOUT RAMAN SCATTERING BY OLEFINS

Given that Raman responses of carbon-carbon double bonds are direct and relatively strong, a basic question arises about them:

> Does Raman scattering *per olefinic equivalent* vary in terms of position, intensity, and bandshape as a function of structural variations presented in Figure 1?

(Note that this study is limited to consideration of monoolefins. However, answers to the question above likely are equally valid for diolefins whose C=C bonds are not conjugated but almost certainly are not valid for compounds in which they are.)

The objective of the present study is to test two hypotheses that bear on the possibility to successfully apply Raman spectroscopy to measure olefins in gasoline. Each is stated in turn and discussed, the results of experiments presented, and conclusions offered.

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HYPOTHESIS 1

Partial molar volumes and absolute Raman scattering cross-sections for functional groups in a solute and its solvent are constant across a broad range of concentrations.

Discussion. Raman scattering cross-section is the Raman counterpart to molar absorptivity in the Beer-Lambert law. (Refer to Appendix A for a detailed discussion.) Suppose a solute and a solvent contain distinct functional groups whose Raman scattering cross-sections are independent of solute concentration. Then the ratio of scattering intensities plotted against the solute:solvent mole ratio will yield a linear function across a wide range of solute concentrations. Positive results would provide strong experimental validation for Eq. (A-7) (see Appendix A).

Experimental. Solutions of butylnitrile (C_4CN) in cyclohexane (cC_6) were prepared covering a concentration range of 5% to 25% (w/w), corresponding to a C_4CN:cC_6 mole ratio 0.04 to 0.35. Samples were prepared gravimetrically by weighing the amounts of C_4CN and cC_6 injected into sealed vials through perforable septa. Sample spectra were measured with a Tornado Spectral Systems HyperFlux PRO Plus Raman spectrometer by means of an optical probe placed in contact with the vial wall to avoid error due to evaporative loss of components that would attend the opening of sample vials for spectral acquisition by direct insertion of the optical probe.

Results. Figure 3 shows overlaid spectra that are the averages of duplicate C_4CN/cC_6 solutions while Figure 4 provides an expanded view of the averaged spectra showing the peaks used to measure cC_6 and C_4CN. Both figures exhibit the decrease in the intensity of the cC_6 band at 1165 cm^{-1} due to dilution by C_4CN and the concomitant increase of the nitrile band at 2250 cm^{-1}. Figure 5 plots relative intensity versus relative concentration in accordance with Eq. (A-7).

Conclusion. The highly linear response of data plotted in Figure 5 provides strong evidence that the theory and assumptions underlying Eq. (A-7) are valid. Specifically, it suggests that the absolute Raman scattering cross-sections for butylnitrile and cyclohexane do not vary. Or, if they do, the relative magnitudes of those changes are coincidently the same. The same thinking applies to partial molar volumes of the two compounds.

HYPOTHESIS 2

Partial molar volumes and Raman scattering cross-sections of two solutes are constant. In particular, relative volumes occupied by the C=C group in olefin molecules and their absolute Raman scattering intensities are relatively uniform across a range of molecular structures.

Discussion. The idea here is to use butylnitrile (C_4CN) as an internal standard in solutions with known olefins where cyclohexane (cC_6) is the solvent. Knowing the weight fractions for the three components in the solution permits Hypothesis 2 to be tested as provided by the application of Eq. (A-7).
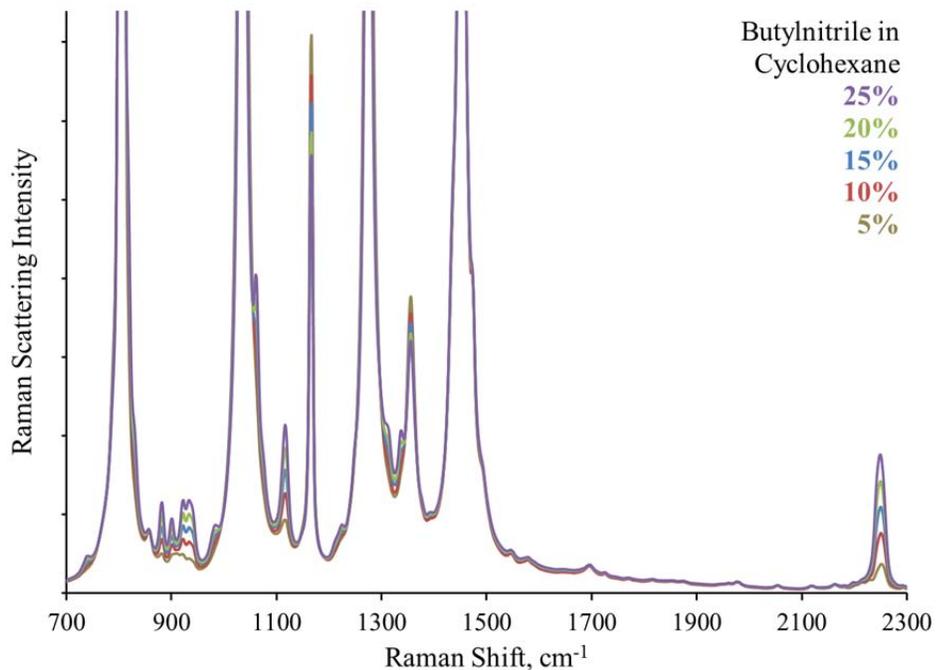
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FIGURE 3. RAMAN SPECTRA OF SOLUTIONS OF BUTYLNITRILE IN CYCLOHEXANE.
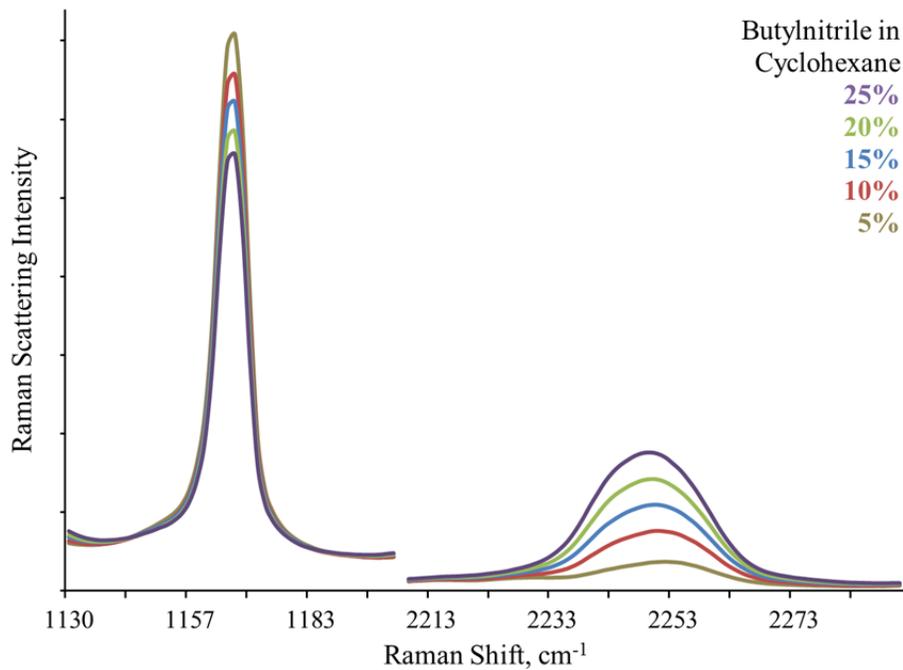
FIGURE 4. BANDS AT 1166 cm^{-1} AND 2250 cm^{-1} USED TO MEASURE cC$_6$ AND C$_4$CN, RESPECTIVELY.

The figure contains a plot with the y-axis labeled "Rel. Band Intensity, Butylnitrile/Cyclohexane" and the x-axis labeled "Butylnitrile/Cyclohexane Mole Ratio", with the following equation shown within:

$$\frac{I_{C_4CN}}{I_{cC_6}} = \left[\frac{K'_{C_4CN}}{K'_{cC_6}}\right] \cdot \left[\frac{C_{C_4CN}}{C_{cC_6}}\right] \qquad Eq.\ (A\text{-}7)$$
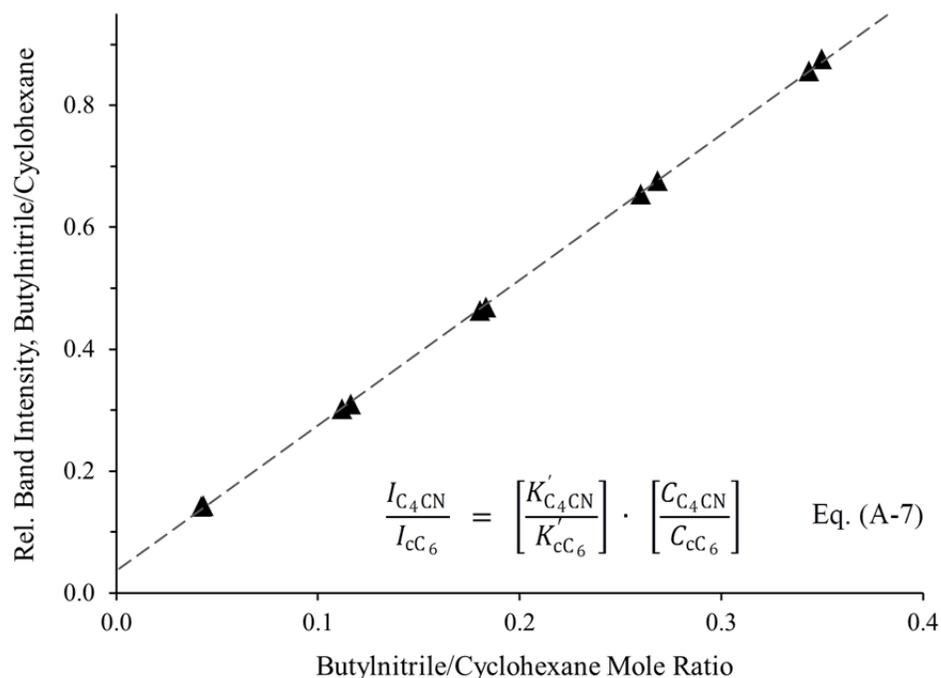
FIGURE 5. PLOT OF RELATIVE BAND INTENSITY VERSUS RELATIVE CONCENTRATION FOR SOLUTIONS OF BUTYLNITRILE IN CYCLOHEXANE.

Experimental. The high cost for small quantities of olefin compounds studied precluded preparation of solutions with a wide range of olefin concentrations, as was done with C_4CN in the preceding experiment. Instead, only solutions containing 10% octenes and 10% C_4CN in cC_6 were prepared.

Results: Figure 6. This figure concerns only the positions and shapes of the bands for the seven octenes studied. (Intensities were not concentration-normalized). The significance is self-evident: band frequencies increase with the progression from terminal to *cis*-disubstituted to *trans*-disubstituted olefins; and the C=C band for *cis*- and *trans*-oct-2-ene compounds that bear a methyl group is shifted by +4 cm^{-1} relative to other *cis*- or *trans*- isomers. No effort was made to measure the bandwidths, but cursory visual evaluation suggests they are similar for the seven compounds examined, those for oct-1-ene and the oct-2-enes appearing to be slightly narrower.

Results: Figure 7. Data points identified by "X" are the same as those plotted in Figure 5. The rest of the data points are from the experiment designed to test Hypothesis 2. Data points for the second set of $C_4CN/cC6$ values fall squarely on the line defined by the first set, confirming experimental repeatability. The other data from the second set are well-clustered: the $C=C/cC_6$ data group tightly while the $C=C/C_4CN$ data points are somewhat more diffuse. The latter represent values that would have been obtained by simply dividing values for the $C=C/cC_6$ data points by values for the corresponding C_4CN/cC_6 (2) data points. The scatter among the $C=C/C_4CN$ points may be no greater on a relative basis than it is for the $C=C/cC_6$ and C_4CN/cC_6 (2) data points, or if it is, the cause may be due simply to conventional error propagation.
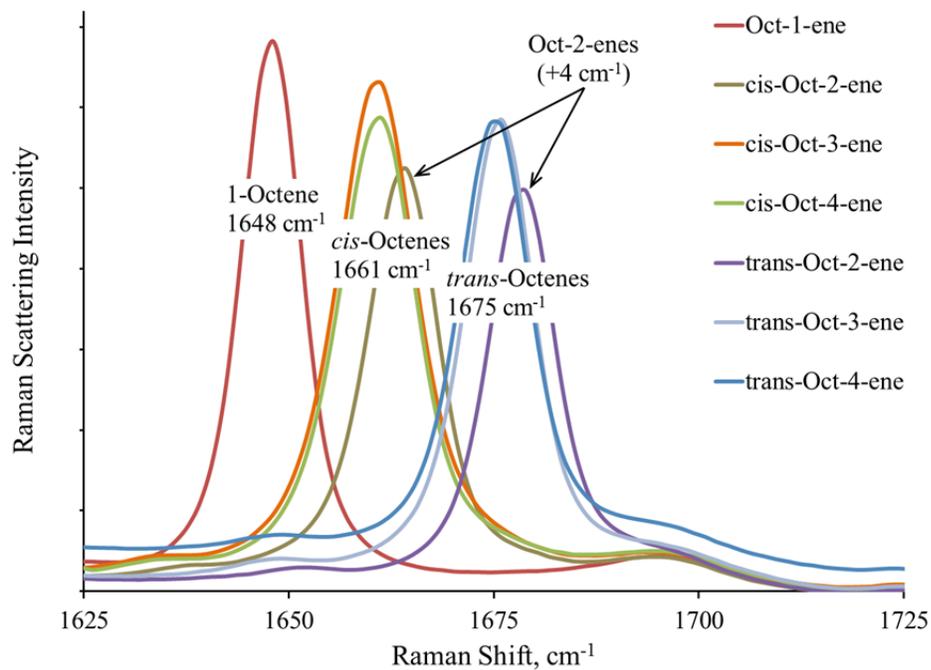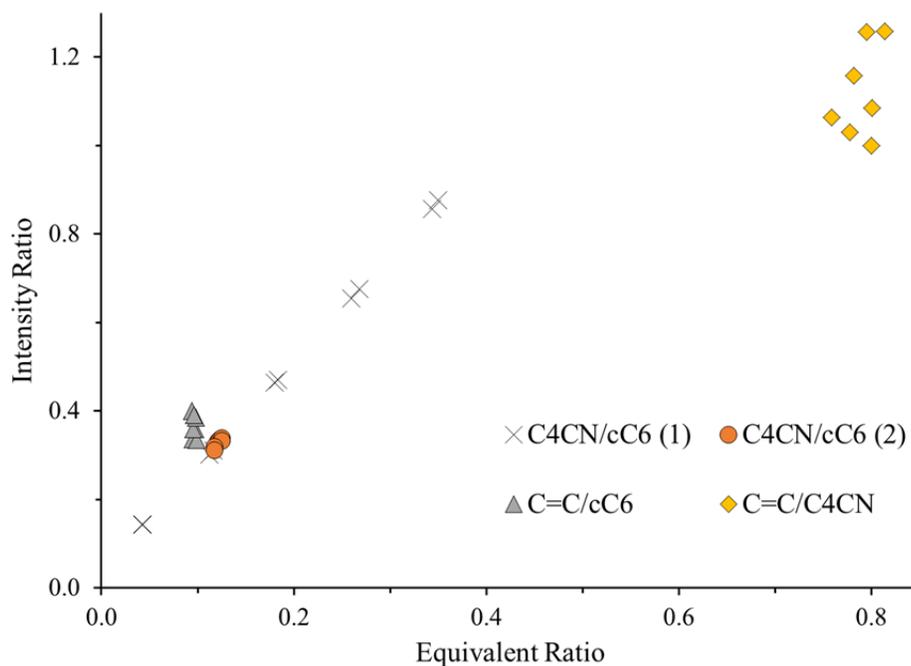
FIGURE 6. OLEFIN BANDS FOR STRAIGHT-CHAIN OCTENES.

FIGURE 7. PLOT OF RELATIVE BAND INTENSITY VERSUS RELATIVE CONCENTRATION FOR SOLUTIONS OF C_8 OLEFINS AND BUTYLNITRILE IN CYCLOHEXANE.
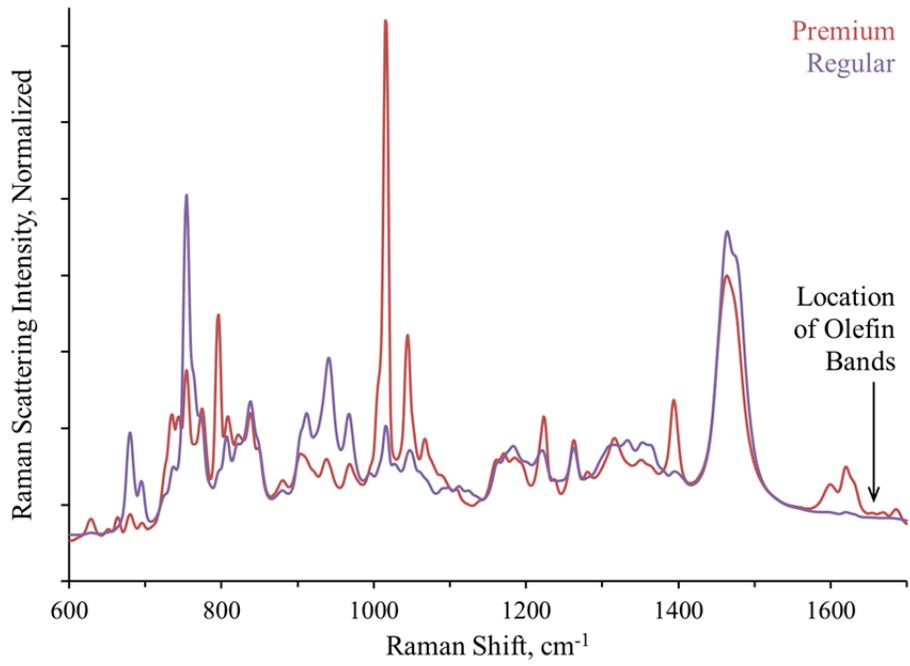
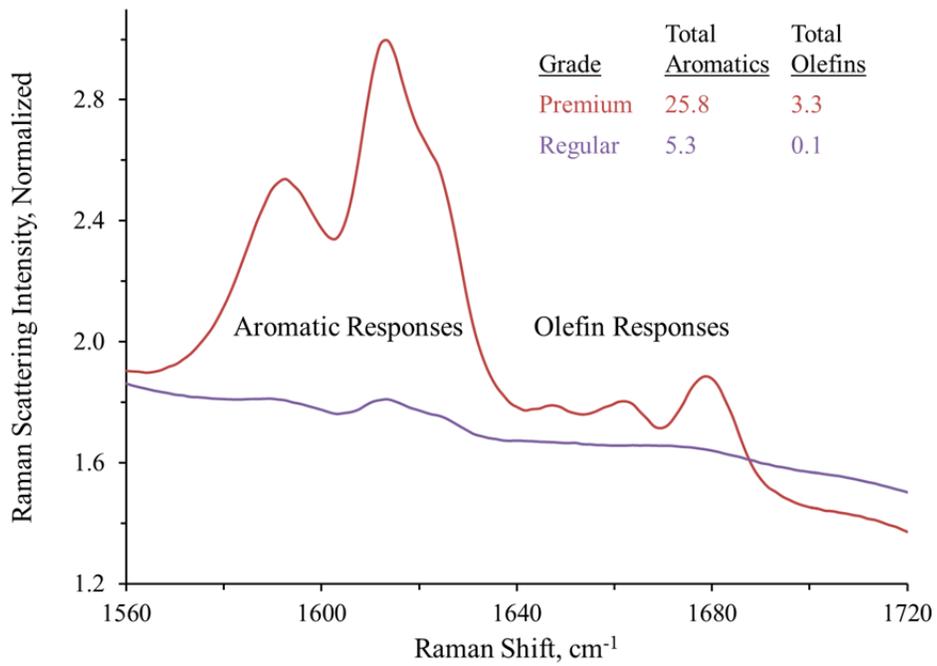**FIGURE 8. OVERLAID SPECTRA OF REGULAR AND PREMIUM GASOLINE SAMPLES.**

FIGURE 9. OVERLAID SPECTRA OF REGULAR AND PREMIUM GASOLINE SAMPLES: EXPANDED VIEW.

Conclusions. Responses of the limited set of olefins considered in this study appear to behave in accordance with Eq. (A-7), just as did the more rigorous investigation of responses for butyl-nitrile in cyclohexane (Hypothesis 1). Furthermore, the groupings of data points in Figure 7 indicate that the magnitudes of Raman scattering cross-sections for double bonds are similar in olefins of similar structure, as suggested by Eq. (A-8).

FURTHER OBSERVATIONS AND FUTURE WORK

Figure 8 presents overlaid spectra of regular (RBOB) and premium (PBOB) gasoline samples supplied by a refiner. The spectrum for premium gasoline exhibits much stronger responses around 1050 cm^{-1} and 1625 cm^{-1}, which are characteristic of higher aromatics content. Figure 9 expands the region around 1600 cm^{-1} to 1700 cm^{-1} to reveal that the premium gasoline also has the highest concentration of olefins.

Particularly intriguing is the hint of a trio of bands in Figure 9 whose positions coincide with the groupings evident in Figure 6. Appearance of this pattern in other gasoline samples would suggest the possibility to apply Raman spectrometry to not merely quantify total olefins, but also provide information about olefin type. Definitive confirmation could be obtained by simply spiking gasoline samples with pure olefins possessing appropriate structural variations.

Referring to Figure 6, the peak on the left is due to a terminal olefin whereas the two sets of peaks to the right are for "internal" olefins. (In terminal olefins, which are alk-1-enes, the carbon-carbon double bond bears geminal hydrogens whereas it does not in internal olefins.) These are referred to, respectively, as OLE1 and OLE2 in connection with environmental models that take into account reactivities of different classes of volatile organic compounds (VOCs) (13). (Refer to Appendix C for further discussion.)

The olefins used in the exploration of Hypothesis 2 admittedly represent a limited subset of the wide range of potential structural variations depicted in Figure 1, Table II, and Appendix C. Consequently, results are suggestive but do not support generalizations. For example, no conclusion can be made about the peak position for 2-alkyl-1-enes (i.e. alk-1-enes that bear an alkyl substituent in the second position) or cyclic compounds such as methylenecyclopentane or methylenecyclohexane in which the olefinic functionality is exocyclic: is it also centered at about 1648 cm^{-1}? A similar question arises in regard to tri- or tetra-substituted olefins.

With respect to Hypothesis 1, this study represents a modest but important effort to test theory through experiment, the linear plot in Figure 5 providing strong evidence for the validity of Eqs. (A-6) and (A-7). This gives credence to the reasoning underlying their derivation and also to the methodology based on them, which is proposed in Appendix B.

ACKNOWLEDGEMENT

REFERENCES

1.   Derwent, R.G., Jenkin, M.E., Pilling, M.J., "Reactivity Scales as Comparative Tools for Chemical Mechanisms: SAPRC vs MCM", Air Quality and Industrial Pollution Division of the United Kingdom Department for Environment, Food and Rural Affairs, March, 2009.

2.   ASTM D1319-15, "Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption", ASTM International, West Conshohocken, PA, 2015.

3.   Lubeck, Axel J., Cook, Robert D., "Bromine Number Should Replace FIA in Gasoline Olefins Analysis", Oil & Gas Journal, 90, 52, December, 1994, p. 86.

4.   ASTM D6550-15, "Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography", ASTM International, West Conshohocken, PA, 2015.

5.   ASTM WK34260, "New Test Method for Determination of Olefins in Gasoline by Raman Spectroscopy", Developed by Committee D02, Subcommittee D02.04.0F.

6.   ASTM WK49499, "New Test Method for Standard Test Method for Determination of Total Olefins in Gasoline by Raman Spectroscopy", Developed by Committee D02, Subcommittee D02.04.0F.

7.   Uibel, Rory H., Benner, Robert E., Jacobsen, Eric R., Smith, Lee M., "Methods for Determining Olefin Concentrations in Olefin-Containing Fuels", Patent No. 7,973,926 B1, Process Instruments, Inc. (Assignee), Salt Lake City, UT, July, 2011.

8.   Trygstad, Marcus, Pell, Randy, Roberto, Michel, "Motor Fuel Property Prediction by Inferential Spectrometry 2: Overcoming Limitations", AD.15.04.02 in Proceedings of the ISA 60th Analysis Division Symposium, Galveston, Texas, April 26 – 30, 2015.

9.   Ibid.

10.   Steele, W.V., Chirico, R.D., "Thermodynamic Properties of Alkenes (Mono-Olefins Larger Than C_4)", J. Phys. Chem. Ref. Data, 22, 2, March, 1993, p. 377.

11.   "Physical Constants of Hydrocarbons C_1 to C_{10}", ASTM Special Technical Publication No. 109A, ASTM International, West Conshohocken, PA, July, 1963, pp. 14-20.

12.   Trygstad, Marcus, Horgen, Dana, "Motor Fuel Property Prediction by Inferential Spectrometry: Understanding Conditions and Limitations", AD.14.10.03 in Proceedings of the ISA 59th Analysis Division Symposium, Baton Rouge, Louisiana, May 4 – 8, 2014.

13.   Carter, William, "Development of the SAPRC-07 Chemical Mechanism and Updated Ozone Reactivity Scales", Contract No. 03-318, California Air Resources Board, Riverside, California, August, 2007.

APPENDIX A

COUNTING FUNCTIONAL GROUPS VERSUS COUNTING MOLECULES

The organic chemist appreciates intuitively that quantitative IR, NIR, NMR, and Raman spectroscopy only provides information about the abundances of functional groups. In spectra of *pure* compounds, the relative abundances of functional groups are fixed uniquely, which is why the integration of protons in ^{1}H NMR spectra of pure compounds is valuable for structural elucidation. But that uniqueness is lost for gasoline, and spectra obtained by molecular spectroscopy comprise responses due to the relative abundances of the various chemical functionalities comprising all compounds in the mixture. By way of contrast, chromatography physically resolves and detects molecules or groups of molecules in a mixture on the basis of their boiling points and their differential affinity for the stationary phase. In short, chromatography can count molecules while IR, NIR, NMR, and Raman spectroscopy techniques can only count functional groups.

More particularly, the application of molecular spectrometry to liquid hydrocarbon samples fundamentally provides concentration information only in terms of functional group equivalents. Presently, elaboration on this matter in full is not possible, and the reader is referred to the paper by Trygstad and Horgen (2014) for a fuller treatment (12). But the following sequence of points elucidates the central limitation of molecular spectroscopy techniques applied for basically every quantitative problem in the analysis of motor fuels by molecular spectrometry:

a) Motor fuels comprise mixtures of many hundreds of, or even a thousand or more, different compounds that have in common many of the same basic functional groups, e.g. ethyl, n-propyl, isopropyl, n-butyl, isobutyl, *tert*-butyl, etc. in gasoline;

b) These functional groups are substituents in individual compounds comprising the major classes of compounds, e.g. paraffins, olefins, naphthenes, and aromatics;

c) Molecular spectroscopy techniques can measure responses arising directly from the functionality that differentiates these classes from each other, e.g. carbon-carbon double bonds, cyclic structures, and aromatic structures; and/or they may detect the local effect that these structures have on small groups of atoms proximate to them;

d) However, because proximity effects may have limited "reach," a given functionality removed by one or more carbons from the differentiating structures may have similar spectral responses;

e) This severely limits or prevents altogether molecular spectroscopy techniques from providing information about entire molecules in motor fuel mixtures.

Equivalents per unit volume (eq/L). In accordance with the Beer-Lambert law (Eq. A-1), intensities for near- and mid-IR spectral responses of liquid hydrocarbon samples are expressed as absorbance, which is unitless.

$$A = \varepsilon \cdot \ell \cdot c \tag{A-1}$$

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where ε = absorptivity *at some particular wavelength λ*, expressed in the units
$\qquad$ (molarity $\cdot$ cm)$^{-1}$ or M^{-1}cm^{-1}

$\qquad\ell$ = pathlength, cm

$\qquad$c = concentration, molarity (M)

Note that the Beer-Lambert law is explicitly volumetric, the absorptivity coefficient and concentration being expressed in terms of molarity (M). In the application of mid- and near-IR spectroscopy to measure the concentration of a particular compound, it is understood that what is being measured is not an entire molecule, but a functional group whose relationship to the molecule of interest is fixed. For example, when using the hydroxyl band to measure ethanol in gasoline, it serves as a proxy for the entire ethanol molecule because the ratio between hydroxyl equivalents and moles of ethanol is constant. Therefore, rewriting the Beer-Lambert law as shown in Eq. (A-2) is appropriate for molecular spectroscopy techniques, and it is understood that Eqs. (A-1) and (A-2) are equal when the ratio [equivalents of a given functional group in a given molecule]/[moles of a given molecule] has a fixed value.

$$A = \varepsilon' \cdot \ell \cdot c' \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\text{(A-2)}$$

where ε' = absorptivity of some functional group at some particular wavelength λ, expressed in
$\qquad$ the units, 1/(normality $\cdot$ cm) or N^{-1}cm^{-1}

$\qquad\ell$ = pathlength, cm

$\qquad$c′ = concentration, equivalents/L (N)

Though perhaps self-evident in relation to transmission spectroscopy, this principle has a less obvious analog in Eq. (A-3), which describes the intensity of Raman scattering (Adolfson, *et al.*, 1977).

$$I_R = I_0 \cdot (d\sigma/d\Omega) \cdot \ell \cdot d\Omega \cdot N \cdot \eta \qquad\qquad\qquad\qquad\qquad\qquad\text{(A-3)}$$

where I_R $\qquad$ = Raman scattering intensity

$\qquad I_0$ $\qquad$ = laser power delivered to the sample

$\qquad (d\sigma/d\Omega)$ = Raman differential scattering cross section of the mode (functional group)

$\qquad \ell$ $\qquad\quad$ = length of the laser beam over which scattered light is collected

$\qquad d\Omega$ $\qquad$ = solid angle over which light is collected

$\qquad$N $\qquad\quad$ = number density of molecules/functional groups in the initial scattering state

$\qquad \eta$ $\qquad\quad$ = a temperature-dependent factor determined by the investigated molecule; the
$\qquad\qquad\qquad$ spectral width; and the resolution and efficiency of the collection and detection system

Integration over the solid angle Ω subtended by the Raman probe optics and assumption of angular uniformity of the scattering cross section yields Eq. (A-4), which shows that the Raman scattering intensity *at some particular Raman shift frequency* is directly proportional to the volume of sample impinged by the laser beam (as determined by the pathlength ℓ and the cross-sectional area of the excitation laser beam) and also to the number density N of scattering molecules (or of scattering functional groups in molecules).

$$I_R = I_0 \cdot \sigma \cdot \Omega \cdot \ell \cdot N \cdot \eta = I_0 \cdot K \cdot V \cdot C \cdot \eta \qquad \text{(A-4)}$$

where N = number density of molecules (functional groups) in the initial scattering state, proportional to concentration, C

   σ = scattering cross section, cm^2 per molecule (or functional group)

   Ω = solid angle visible to the Raman probe collection optics

   C = concentration of molecules (functional groups) in the initial scattering state, proportional to N, equivalents per mL

   K = proportionality constant which includes the solid angle Ω of collection, the scattering cross section σ, the scaling factor between N and C, and the reciprocal of the cross-sectional area of the excitation laser beam

   V = net volume of the region interrogated by the laser and visible to the probe collection optics, approximated by the pathlength ℓ times the cross-sectional area of the laser beam

For a material whose composition is nominally constant and which is sampled under nominally isothermal conditions, and when the optical configuration of the spectrometer system (including the sampling probe) is fixed, then η, σ, K, and V are also fixed, permitting them to be combined into a single constant K′ as shown in Eq. (A-5).

$$I_R = I_0 \cdot K \cdot V \cdot C \cdot \eta = I_0 \cdot K' \cdot C \qquad \text{(A-5)}$$

Thus, the intensity of Raman scattering recorded by the spectrometer is proportional to laser intensity and the concentration of the analyte in the volume corresponding to that which yields the measured Raman signal.

Now Eq. (A-5) can be rewritten as Eq. (A-6) to explicitly denote that the measured Raman scattering intensity for the ith functional group in a mixture of compounds such as gasoline is a function of a) the equivalents of that functional group per unit volume and b) its scattering cross section, the latter being embedded in the constant K_i'. Notice how Eq. (A-6) compares directly to the Beer-Lambert law, Eq. (A-2).

$$I_i = I_0 \cdot K_i' \cdot C_i \qquad \text{(A-6)}$$

Given that the values K_i' for two different functional groups are constant, then their ratio is also constant. (It will be understood that I_i and K_i' apply for particular Raman shift frequencies, which are different for two different functional groups.) In experiments described in this paper, spectra were measured for mixtures containing known amounts of butylnitrile (C_4CN) and cyclohexane (cC_6). The intensities of bands for the two compounds were measured and then their ratios plotted against the corresponding mole ratios (Figures 5 and 7). The nearly perfect linear function has the form of Eq. (A-7) and provides strong evidence for its validity.

$$\frac{I_{C_4CN}}{I_{cC_6}} = \frac{I_0 \cdot K'_{C_4CN} \cdot C_{C_4CN}}{I_0 \cdot K'_{cC_6} \cdot C_{cC_6}} = \left[\frac{K'_{C_4CN}}{K'_{cC_6}}\right] \cdot \left[\frac{C_{C_4CN}}{C_{cC_6}}\right] \qquad \text{(A-7)}$$

Finally, consider that if the Raman scattering cross-sections of all olefins in a mixture are approximately equal, then the ratio $[K'_{C_4CN}]/[K'_{cC_6}]$ also would be approximately constant. Accordingly, the ratio of relative scattering intensity to relative concentration (e.g. for C=C versus C₄CN) also would be approximately constant, as expressed in Eq. (A-8):

$$\frac{I_{C=C}/I_{C_4CN}}{C_{C=C}/C_{C_4CN}} \;=\; \frac{K'_{C=C}}{K'_{C_4CN}} \;\approx constant \tag{A-8}$$

REFERENCES

Adolfson, W. F., Schlecht, R. G., Morton, J. B. "Raman Scattering Cross Section and Density Measurements in UF₆", <u>Applied Physics A</u>, Springer Berlin Heidelberg, 14, 1, September, 1977, pp. 49-51.

Pelletier, Michael J., "Introduction to Applied Raman Spectroscopy", <u>Analytical Applications of Raman Spectroscopy</u>, Pelletier, Michael J. (editor), Blackwell Science Ltd., Osney Mead, Oxford, U.K., 1999, p. 11. Note that the expression for Raman scattering intensity given in this reference compares directly with Eqs. (A-4), (A-5), and (A-6):

$$I_R = I_L \cdot \sigma \cdot K \cdot P \cdot C \tag{A-9}$$

where I_R = measured Raman intensity, photons per second
I_L = laser intensity, photons per second
σ = absolute Raman cross-section, cm^2 per molecule
K = measurement parameters
P = sample path, cm
C = concentration, in molecules per cm^3

APPENDIX B

METHOD FOR MEASURING OLEFINS IN GASOLINE

In NIR transmission spectroscopy the pathlength is fixed. While it can in principle be measured and factored into the Beer-Lambert equation, Eq. (A-1), this is seldom done. In part, the reason is that doing so adds a layer of calibration and validation that must be managed, e.g. when cells are disassembled for maintenance. Some possibility also exists that small errors in determining values for pathlength, or failure to calibrate pathlength when required, will undermine analytical reliability. But the main reason is that pathlength calibration is not necessary. Rather, the issue of variable or indeterminate pathlength can be addressed mathematically through methodologies known generally as spectral normalization which remove scalar variations. Normalization by closure is one category of normalization. It includes so-called area normalization, which is particularly simple and often very effective (Martens and Næs, 1989).

Whether based on algorithms simple or complex, spectral normalization overcomes limitations associated with pathlength calibration: it requires no physical intervention by analyzer technicians, can be performed automatically in the course of spectral analysis, and is very precise. In Raman spectroscopy, most or all of the parameters included in K_i' are unknowable but nevertheless are constant for a spectrometer system with a fixed configuration. I_0 is also unknowable. But more important, it is not absolutely constant and can produce significant variations in total spectral intensity across a population of samples. Yet, this variation can be eliminated by applying the same spectral normalization techniques used in NIR spectrometry. In the derivations that follow, area normalization is used for ease of illustration. However, the principles apply equally when other normalization techniques are used.

1. Raman scattering intensity for the ith functional group. This is the net intensity of a peak or group of peaks in the Raman spectrum of a sample, which is due to Raman scattering by some particular functional group of interest. The expression for this value is derived in Appendix A and given by Eq. (A-6).

$$I_i = I_0 \cdot K_i' \cdot C_i \tag{A-6}$$

where C_i has units of functional group equivalents per unit volume, i.e. eq/mL.

2. Total integrated value for all spectral responses. This value represents total area of the sample spectrum, obtained by summing all spectral responses across the entire sample spectrum.

$$\Sigma I_j = I_0 \cdot \Sigma(K_j' \cdot C_j) \tag{B-1}$$

where I_j are the values for all individual data points contained in a sample spectrum. These are due to all Raman-active functional groups j in all compounds in the sample mixture, which express themselves across the sample spectrum and also include the ith functional group that is the subject of analysis.

3. Normalized scattering intensity for the ith functional group. As shown in Eq. (B-2), division of I_i from Eq. (A-6) by ΣI_i from Eq. (B-1) cancels out I_0 and yields the normalized intensity I_i':

$$\frac{I_i}{\Sigma I_j} = I_i' = \frac{I_0 \cdot K_i' C_i}{I_0 \cdot \Sigma(K_j' C_j)} = \frac{K_i'}{\Sigma(K_j' C_j)} \cdot C_i \tag{B-2}$$

Rearranging Eq. (B-2) yields an expression for C_i as a function of I_i':

$$C_i = \left[\frac{K_i'}{\Sigma(K_j' C_j)}\right]^{-1} \cdot I_i' \approx K_i'' \cdot I_i' \tag{B-3}$$

This expression assumes that the bracketed ratio, and in particular the summation $\Sigma(K_j' C_j)$, is approximately constant. This approximation does not hold in the limit, but is nominally valid when the sample comprises a mixture of hydrocarbon compounds whose identities and proportions vary within relatively narrow ranges. Thus, it is expected to hold for a given grade of gasoline produced from blending components whose composition and blend ratios do not vary wildly.

4. Relating C_i to weight fraction olefin in gasoline, X_i. When the ith functional group is the olefinic carbon-carbon double bond, C=C, contained in a sample of gasoline, Eq. (B-3) must be related to olefin values obtained by the Primary Test Method (PTM). For purposes of this discussion, the PTM Results (PTMRs) will be regarded as those obtained by ASTM D6550-15 rather than ASTM D1319-15. The latter is the Fluorescent Indicator Adsorption FIA) method, which is generally understood to be far less precise than the former, a method based on supercritical fluid chromatography (SFC). Given that Eq. (B-3) and ASTM D6550-15 express olefin concentration in terms of eq/mL and weight fraction, respectively, additional factors are required to relate C_i to the output obtained by SFC in Eq. (B-4).

$$C_i = \frac{X_{Olefin} \cdot d_{Gasoline}}{GEW_{Olefin}} = \frac{X_{SFC} \cdot d_{Gasoline}}{GEW_{Olefin}} \tag{B-4}$$

where X_{Olefin} = weight fraction total olefins in a gasoline sample, (g olefin)/(g gasoline)
$\quad\quad\ X_{SFC}$ = the weight fraction of olefins in gasoline, X_{olefin}, determined by ASTM D6550-15
$\quad\quad\ d_{Gasoline}$ = density of the gasoline sample, (g gasoline)/(mL gasoline)
$\quad\quad\ GEW_{Olefin}$ = average gram equivalent weight for olefins in a gasoline sample, (g olefin)/(eq C=C)

Eqs. (B-3) and (B-4) reveal an important difference between methods that quantify olefins in gasoline in terms of a) equivalents per unit volume and b) weight-percent. It can be reconciled by first setting Eq. (B-4) equal to Eq. (B-3) to obtain Eq. (B-5); and then dividing both sides of Eq. (B-5) by K_i'' and $d_{Gasoline}$, giving an expression of the density-normalized value for I_i' as a function of X_{SFC}:

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$$K''_{Olefin} \cdot I'_{Olefin} = \frac{X_{SFC} \cdot d_{Gasoline}}{GEW_{Olefin}} \tag{B-5}$$

$$\frac{I'_{Olefin}}{d_{Gasoline}} = \frac{X_{SFC}}{GEW_{Olefin} \cdot K''_i} = K'''_{Olefin} \cdot X_{SFC} \tag{B-6}$$

5. Spectrometric calibration based on X_{SFC}. In accordance with Eq. (B-6), obtain a correlation for X_{SFC} based on a population of samples for which the values $\left(I'_{Olefin}\right)_m$, $(d_{Gasoline})_m$, and $(X_{SFC})_m$ have been determined for each sample m. The following describes a general procedure for creating such a correlation:

a) Collect over time a population of gasoline samples of a given grade, whose composition spans a relevant range of process conditions and total olefin concentration. As they become available, measure and record the spectrum of each as well as $(d_{Gasoline})_m$ and $(X_{SFC})_m$ by means of established ASTM methods.

b) Apply an appropriate spectral normalization technique, e.g. area normalization, to the spectra collected in the preceding step to obtain intensity-normalized spectra.

c) Generate a multivariate correlation (a calibration) for $d_{Gasoline}$ using normalized spectra from the preceding step and their corresponding density values. (N.B. Multivariate correlations for density have notoriously high precision. Certainly, this owes in part to the high precision of density measurements. But it also provides credence to the assertion in Appendix A that, at the core, spectrometric methods only measure equivalents/unit volume, i.e. correlations are obtained in terms of equiv/mL versus g/mL.)

d) Generate density-normalized spectra by dividing each spectrum from Step b) by the corresponding density value $(d_{Gasoline})_m$.

e) Measure the net intensity of olefin responses between about 1625 cm^{-1} and 1725 cm^{-1} by the application of appropriate methods, which may include the step of first obtaining the first derivative spectrum. This value is the density-normalized intensity value in Eq. (B-6), $\left(I'_{Olefin}/d_{Gasoline}\right)_m$.

f) Create a correlation for olefins in accordance with Eq. (B-6) using values obtained in Step 5.e) for $\left(I'_{Olefin}/d_{Gasoline}\right)_m$ and the corresponding reference values $(X_{SFC})_m$ from Step 5.a).

6. Determination of $X_{olefins}$ in "unknown" gasoline samples. Now, the correlation obtained in the preceding step can be applied to obtain measurements of spectrometry-based values for weight fraction olefins in gasoline, $X_{Olefins}$.

a) Measure the spectrum of the unknown sample and normalize by the method applied in 5.b).

b) Apply the calibration generated in 5.c) to predict $d_{Gasoline}$ for the sample.

c) Generate the density-normalized spectrum of the unknown sample by dividing the spectrum from 6.a) by the value $d_{gasoline}$ predicted in 6.b).

d) Measure the net intensity of olefin responses by the same approach applied in 5.e). This value is $I'_{Olefin}/d_{Gasoline}$ for the unknown sample.

e) Apply the correlation generated in 5.f) to predict $X_{Olefins}$.

NOTES

- This procedure produces an explicitly "hard" correlation based on Eq. (B-6). An algorithm such as partial least squares (PLS) may be used to generate a multivariate correlation using spectra generated in Step d) and the reference values $(X_{SFC})_m$. Provided the same spectral region defined in Step e) is employed, the resulting PLS correlation will also be "hard," not inferential.

- The foregoing method assumes that $\overline{GEW}_{Olefin}$ in Eqs. (B-4) to (B-6) is constant. However, because $\overline{GEW}_{Olefin}$ may vary over time, spectrometry-based values $X_{Olefins}$ should be compared periodically with values X_{SFC} measured by the primary method. A statistically-derived scalar correction value, a, (a slope adjustment) can then be applied as shown in Eq. (B-7).

$$\frac{I'_{Olefin}}{d_{Gasoline}} = \frac{X_{SFC}}{\overline{GEW}_{Olefin} \cdot K''_i} = a \cdot K'''_{Olefin} \cdot X_{SFC} \tag{B-7}$$

- The term $\left(a \cdot K'''_{Olefin}\right)$ in the preceding equation is constant when the Raman spectrometer, sampling configuration, the method of spectral preprocessing, and the method for determining the intensity of olefin responses in sample spectra are defined and applied invariantly. Accordingly, the method described above should lend to formalization as a solid, first-principles method for consideration in an industry forum such as ASTM. Note also that results obtained by the method, $X_{Olefins}$, correspond directly to X_{SFC}. This presents the possibility to apply the same conversion defined in Appendix X1 of ASTM D6550-15, Eq. (1), that relates X_{SFC} to Volume% as measured by ASTM D1319:

Volume% (D1319) $= 0.857$ x Mass% (D6550) $= 0.857 \cdot X_{Olefins}$ (B-8)

where $X_{Olefins}$ is the weight-basis value for olefins in gasoline determined in Step 6.e) above.

REFERENCES

Martens, Harald, Næs, Tormod, "Pretreatment and Linearization", Multivariate Calibration, John Wiley & Sons, New York, New York, 1989, pp. 337-341.

APPENDIX C

PARTIAL INVENTORY OF STRUCTURAL ISOMERS FOR C5 – C8 OLEFINS

General information about all olefins with five to eight carbon atoms is presented in Table C-I while Table C-II lists all structural isomers of open-chain monoolefins with five to seven carbons. In Table C-II, the number in the column immediately to the right of the isomer name indicates how many hydrogen atoms are bonded directly to the carbon-carbon double bond (C-H per C=C). The variability in this number serves to emphasize the problem of applying ^{1}H NMR and NIR spectroscopy to measure olefin content in gasoline in terms of alkenyl C-H functionality.

The second column to the right of the isomer name indicates if the isomer is an OLE1 (primary or terminal) or OLE2 (internal, typically disubstituted), where the terms OLE1 and OLE2 are among the many abbreviations used by the California Statewide Air Pollution Research Center (SAPRC) to denote classes of compounds with environmental implications. Of particular importance as regards the persistence and fate of organic pollutants (volatile organic compounds, VOCs) in the atmosphere is the k_{OH} scale. The k_{OH} values for olefins are generally the highest among VOCs, and between OLE1 and OLE2, the latter are generally the most reactive, having values on the k_{OH} reactivity scale (1) above the 70,000 $\text{ppm}^{-1} \cdot \text{min}^{-1}$ threshold that divides these two classes of olefins (13). Interestingly, about 60% of both the acyclic isomers ($C_5 – C_7$ only) and the cyclic isomers ($C_5 – C_8$) are the more reactive OLE2 variety.

TABLE C-I. NUMBERS OF ACYCLIC AND CYCLIC STRUCTURAL ISOMERS AND STEREOISOMERS OF OLEFINS WITH FIVE TO EIGHT CARBONS.

TOTAL NO. CARBON ATOMS	ACYCLIC COMPOUNDS[†]	CYCLIC COMPOUNDS[‡]
5	6	1
6	17	5
7	36	16
8	93	38
OLE1	23[*]	14
OLE2	36[*]	46

[*] $C_5 – C_7$ only
[†] Totals count the *cis-* and *trans-* isomers as separate compounds
[‡] Includes isomers with 5-, 6-, and 7-membered rings

TABLE C-II. ACYCLIC STRUCTURAL ISOMERS OF C_5 – C_7 OLEFINS

COMPOUND	C-H per C=C	TYPE	Compound	C-H per C=C	TYPE
C_5 Olefins			**C_7 Olefins** (cont.)		
cyclopentene	2	OLE2	3-methylhex-3-ene*	1	OLE2
pent-1-tene	3	OLE1	2,3-dimethylpent-1-ene	2	OLE1
trans-pent-2-ene	2	OLE2	2-methylhex-2-ene	1	OLE2
pent-2-ene	2	OLE2	3-methylhex-2-ene*	1	OLE2
cyclopentene	2	OLE2	4-methylhex-2-ene*	2	OLE2
2-methylbut-1-ene	2	OLE1	5-methylhex-2-ene*	2	OLE2
3-methylbut-1-ene	3	OLE1	2-methylhex-3-ene*	2	OLE2
2-methylbut-2-ene	1	OLE2	3-methylhex-3-ene*	1	OLE2
C_6 Olefins			2,3-dimethylpent-1-ene	2	OLE1
hex-1-ene	3	OLE1	2,4-dimethyl-pent-1-ene	2	OLE1
hex-2-ene*	2	OLE2	3,3-dimethyl-pent-1-ene	3	OLE1
trans-hex-2-ene	2	OLE2	3,4-dimethyl-pent-1-ene	3	OLE1
hex-3-ene*	2	OLE2	4,4-dimethyl-pent-1-ene	3	OLE1
trans-hex-3-ene	2	OLE2	2-ethylpent-1-ene	2	OLE1
2-methylpent-1-ene	2	OLE1	3-ethylpent-1-ene	2	OLE1
3-methylpent-1-ene	3	OLE1	2,3-dimethylpent-2-ene	0	OLE2
4-methylpent-1-ene	3	OLE1	2,4-dimethyl-pent-2-ene	1	OLE2
2-methylpent-2-ene	1	OLE2	3,4-dimethylpent-2-ene*	2	OLE2
3-methylpent-2-ene*	1	OLE2	4,4-dimethylpent-2-ene*	2	OLE2
2-ethylbut-1-ene	2	OLE1	3-ethylpent-2-ene	1	OLE2
3,3-dimethylbut-1-ene	3	OLE1	3-methyl-2-ethylbut-1-ene	2	OLE1
2,3-dimethylbut-2-ene	0	OLE2	2,3,3-trimethylbut-1-ene	2	OLE1
C_7 Olefins			2,4-dimethyl-pent-1-ene	2	OLE1
cycloheptene	2	OLE2	3,3-dimethyl-pent-1-ene	3	OLE1
hept-1-ene	3	OLE1	3,4-dimethyl-pent-1-ene	3	OLE1
hept-2-ene*	2	OLE2	4,4-dimethyl-pent-1-ene	3	OLE1
hept-3-ene*	2	OLE2	2-ethylpent-1-ene	2	OLE1
2-methylhex-1-ene	2	OLE1	3-ethylpent-1-ene	2	OLE1
3-methylhex-1-ene	3	OLE1	2,3-dimethylpent-2-ene	0	OLE2
4-methylhex-1-ene	3	OLE1	2,4-dimethyl-pent-2-ene	1	OLE2
5-methylhex-1-ene	3	OLE1	3,4-dimethylpent-2-ene*	2	OLE2
2-methylhex-2-ene	1	OLE2	4,4-dimethylpent-2-ene*	2	OLE2
3-methylhex-2-ene*	1	OLE2	3-ethylpent-2-ene	1	OLE2
4-methylhex-2-ene*	2	OLE2	3-methyl-2-ethylbut-1-ene	2	OLE1
5-methylhex-2-ene*	2	OLE2	2,3,3-trimethylbut-1-ene	2	OLE1
2-methylhex-3-ene*	2	OLE2			

* *cis/trans* stereoisomers exist for these compounds.