

HART

May 2001

World Refining

A Chemical Week Associates Publication





Analysis of Fuel Properties by Mid-Infrared Spectroscopy

DR. MICHAEL C. CROUDACE, Product Manager, PetroSpec/Petroleum Analyzer Co.

Spectroscopic analysis uses light of varying wavelengths to differentiate and quantify the individual chemicals in fuel. Many chemicals and chemical classes found in fuel have unique structures that absorb specific wavelengths of light in the mid-infrared (mid-IR) and near-IR spectral regions. For example, aromatics are found in the IR region between 600 and 900 wavenumbers; saturates between 4000 and 4400 and 2600 and 3100 wavenumbers; oxygenates between 900 and 1250 wavenumbers; and cetane improver at 1635 wavenumber.

Specific chemical absorbances are separated enough from other component absorbances in the fuel that a spectroscopic separation of these chemicals is possible. This spectroscopic separation allows for the characterization and quantification of the chemicals or chemical classes.

Figure 1 compares two gasolines produced at one refinery. Gasoline is used as an example because the types of aromatics typically found in gasolines are well established. Between 600 and 900 wavelengths, the aromatics become evident. In this range, one can easily see the individual chemicals (such as benzene at 667 cm^{-1} , toluene at 690 cm^{-1} and the xylenes at 740 cm^{-1}) present in the fuels.

The aromatic chemistry differences between the two fuels is most easily seen in the lower graph. This trace shows

results when the spectrum of fuel one is subtracted from fuel two. Each individual aromatic compound is readily recognized and quantified, even when very small concentration changes exist.

Mid-IR analysis is very effective for this fuel because much more spectroscopic information is available in the mid-infrared range. Many of the absorbance peaks in the graph represent a single gaso-

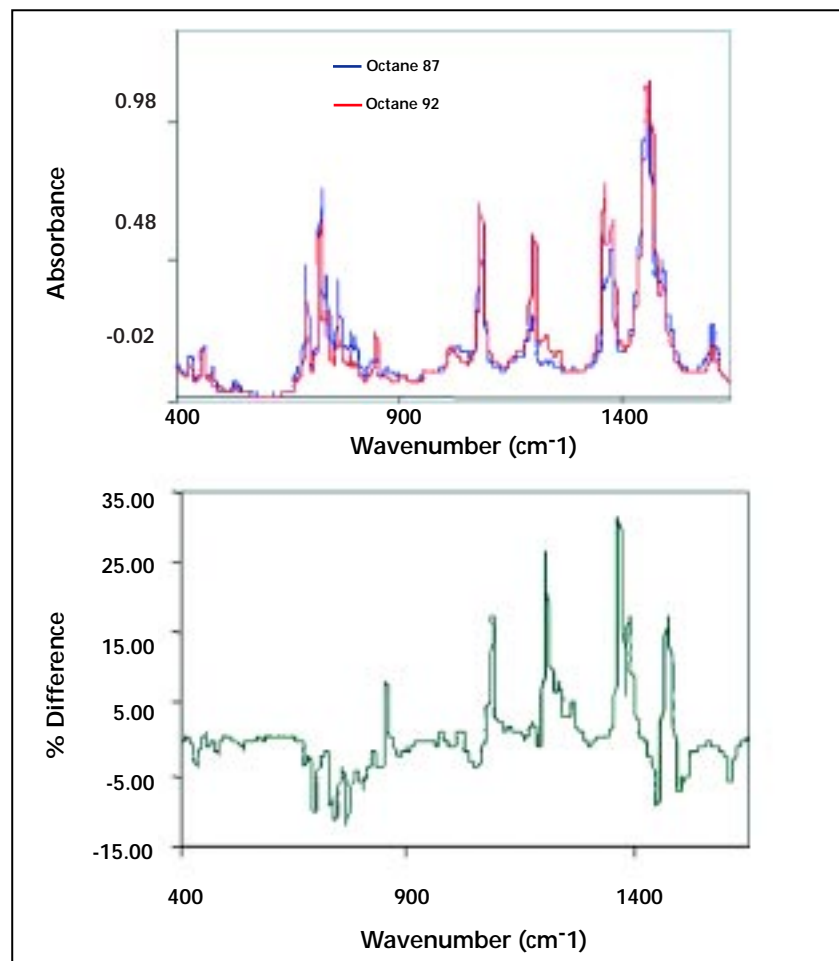


Figure 1. Gasoline aromatics as identified by mid-IR spectroscopy.

Table 1. Cetane Number of Specific Chemical Compounds

Type of Hydrocarbon	Cetane Number
n-Cetane	100
Heptamethylnonane	15
Iso-octane	0
Naphthlene	0

line component or functional group. The magnitude of absorbance differences is large and easily measured, even with numerous components blended into the fuels. The mid-IR gasoline analyzer used here can measure individual oxygenates as well as total oxygen and benzene, olefins and saturates, and calculate characteristics such as octane, T₅₀ and T₉₀. Diesel fuel analysis utilizing the same technology provides cetane number, cetane index, cetane improver (2EHN), total aromatics, polynuclear aromatics (PNA) and density measurements.

This method of spectroscopic separation and quantification proves extremely accurate. For analysis of chemicals like benzene, an established standard ASTM procedure (D6277) based on this technique provides greater accuracy than any other standard gas chromatographic method. Further, it offers the added advantages of fast, non-destructive analysis using very little sample. For these reasons, it is ideally suited for process control.

Spectroscopy and Diesel Fuel

For many years, refiners have applied the same types of IR analysis to diesel fuel, but with less success. Although IR analysis has been able to pinpoint many physical properties that are directly related to the chemical composition of a fuel, it has nonetheless been difficult to calculate diesel's cetane number and cetane index. (Reminder: Cetane number is a measurement of a fuel's ability to spontaneously combust when pressure is applied in a single-cylinder test engine.)

Cetane number and cetane index are directly related to the quantity and type of hydrocarbon in a mixture. This measurement is directly correlated to the degree of straight-chain, saturated hydrocarbon and cetane improver in the test fuel. As can be seen in Table 1,

the long, straight-chain hydrocarbons produce high cetane numbers.

Branched, short-chain-length or aromatic hydrocarbons produce low cetane numbers. By quantifying these chemical differences, it is possible to correlate to the physical properties of the fuel.

Once the fuel composition has been assessed, a refiner can employ complex mathematical algorithms to determine cetane number, density and cetane index. Critical to producing an accurate correlative analysis such as this is the production of an accurate calibration set. But the cetane number test method is notorious for inaccuracies.

In an effort to minimize the errors inherent in cetane number, Shell Oil's Thornton Laboratories and Ethyl Corp. developed a cetane number calibration set. These data points are made up solely of diesel samples that have been multi-rated on the best cetane engines available. Shell Research provided a European calibration set in which each of the diesel samples included a minimum of three independent ratings. Many were rated 17 times. Results were the average of the multiple tests. Ethyl's calibration set included over 600 samples with varying amounts of cetane improver from all over the United States.

Correlating IR Analysis With Traditional Cetane Tests

The partners in this project then used the PetroSpec CETANE 2000 to correlate the physical test data with spectroscopic analysis data. The PetroSpec CETANE 2000 is a robust machine with extensive composition models that allow it to measure diesel fuel blends worldwide, based on a multi-rated calibration matrix collected over the past four years by PetroSpec and its industry partners.

Table 2 shows the machine's correlations to the ASTM method. As can be seen, the results are well within the ASTM reproducibility of each method.

A mini-round robin for cetane number was performed via mid-IR analysis in the U.S. using diesel fuels from around the country. The analysis

was performed on a CETANE 2000 instrument and utilized the standard cetane calibration. The results were compared to average cetane number results produced from the ASTM national exchange group. These national exchange group results are the average of multi-test results on the best test engines in the U.S. Results are shown in Figure 2.

Benefits for Refiners, Full Distribution Chain

Well established in the U.S., PetroSpec's mid-IR analyzers are increasingly being utilized by refiners and distributors around the world to ensure product quality, reduce giveaway and monitor improver blending. These instruments are fully automated and pre-calibrated to quickly, easily and conveniently provide important product insight throughout the production and distribution network via accurate yet low-cost means.

The uses of the mid-IR analyzers are varied. A refinery in Spain uses a GS1000 on-line analyzer to monitor and control the amount of benzene and aromatics content produced by two reformers. This allows the refiner to meet European 2001 benzene and aromatic standards without adding new processing equipment (as well as replacing an expensive online GC). A French refinery uses a GS1000 online analyzer to monitor benzene, aromatics and octane in final gasoline blends to meet these same European environmental standards. Thus the refinery has been able to delay for several years a round of refinery upgrades to meet fuels specifications. Additional application examples include a U.S. refinery that monitors octane and olefin content to meet U.S. EPA standards, allowing it to introduce low-cost cracked stocks into its final fuels blends; a refinery on the U.S. West Coast that monitors naphthalene in its final jet fuel blends; and an Alaskan refinery that uses an at-line GS1000 to monitor its reformers.

The speed of the systems is one of their major attractions to refiners and terminals operators. In less than three minutes, the instruments predict all properties simultaneously using an international calibration set. They also feature an accuracy-enhancing, temper-

Table 2. Cetane 2000 Mid-IR Analysis vs. Correlated ASTM Method

Measurement	ASTM Method	ASTM Reproducibility	Standard Error of Validation
Total Aromatics	D 5186	1.5 @ 20 Wt.%	1.3 Wt.%
Polynuclear Aromatics	D 5186	5.6 @ 10 Wt.%	0.6 Wt.%
Cetane Number	D 613	2.9	1.3
Cetane Index	D 4737	—	1.2
Cetane Improver	—	—	30 ppm

Source: PetroSpec

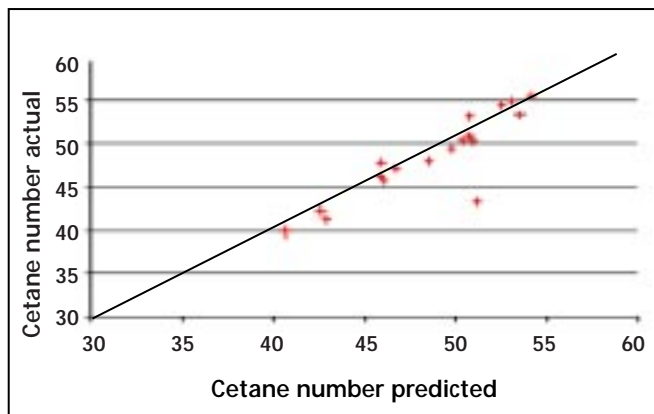


Figure 2. Cetane number (predicted vs. actual) using national exchange samples.

ature-controlled optical bench, which eliminates temperature fluctuations and effects on measurement results generally seen in field use. The optical bench is a dual-beam design so that a reference spectrum is taken each time an analysis is run. This eliminates any drift in the instrumentation, increasing the result's stability over time and also eliminating need for messy, costly and potentially hazardous calibration that could come from actual fuel samples in order to achieve a baseline.

Regulators also are aware of the benefits of IR spectroscopy for testing compliance with fuels standards. For the past two years, the Thai government has utilized the GS1000 to aggressively monitor gasoline products throughout Thailand, checking primarily for adulterations. The success of this program has generated interest in developing a similar program using the CETANE 2000 to monitor diesel products, and the government agency in charge is swiftly moving in that direction. As with the Thai government, Malaysia's largest gasoline producer has instituted its own mobile monitoring program. Six agents currently blanket the country, using the GS1000 to ensure the quality of their product at the pumps.

While the European regulation of petroleum products for environmental

pollutants has been set, official test methods for determining compliance are still being debated. In 1998, the CEN TC19 Committee was established to examine the methods used to evaluate the new specifications for fuels. Interested in eliminating the D1319 FIA method because it is time consuming and has poor reproducibility, this committee is currently reviewing PetroSpec's mid-IR method as a possible replacement. In addition, a second committee was created to evaluate a systematic method for analyzing fuels in the field to show that they meet specification before they travel downstream. This committee is evaluating PetroSpec's portable mid-IR gasoline analyzer (GS1000) and portable mid-IR cetane analyzer (CETANE 2000) as field standards. Today, French, Greek and Italian customs agencies already use mid-IR instruments in their fuel evaluation programs.

Flexibility is built into the calibration of the IR analyzers to enable use of the systems by industry's fuel-quality testers and government compliance officers around the world. Each mid-IR analyzer includes a standard calibration set that encompasses most fuels that would be encountered almost anywhere. Fuels or blending streams introduced into the instrument that are not included in the standard calibration set are detected by outlier detection mathematics. The instrument's calibration is updateable by the user, making it capable of handling specific fuel blends or special fuel compositions not included in the

worldwide calibration set. A major refinery in Singapore utilizes calibration update methods to achieve remarkable results. Working in conjunction with PetroSpec and Abel Scientific (PetroSpec's Singapore agent), the lab technician in charge of the instrument has built an extensive calibration set and thus has been able to realize reproducibility within 0.3 Research Octane Numbers during a recent survey. Six GS1000 instruments are now in use in China.

Support services from PetroSpec add an additional layer of utility to the systems. In South America, PetroSpec and its distributor, Pensalab, have developed a mobile laboratory that verifies fuel quality directly at fuels stations. This provides expedient support to resellers, unions and customers. In the automotive industry, companies such as Mercedes Benz, Audi, Fiat, General Motors and Volkswagen quickly check the quality of fuels running in their engines via mid-IR analysis. ●

The Author



Michael C. Croudace, Ph.D., is product manager and one of three founders of PetroSpec (a division of PAC Petroleum Analyzer Company L.P.). He received his Ph.D. in Organic Chemistry from the University of California at Davis in 1982.

A fuels chemist with experience in fuel and lubricant design and combustion chemistry, Croudace worked at the Unocal Corp. from 1981 to 1992 before joining the team of scientists that developed and introduced the first PetroSpec portable fuel analyzer in 1992.

Dr. Croudace has been granted more than 25 U.S. patents and has authored seven publications.