Application note

Enhancing real-time monitoring and quality control of refined fuels with the Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer

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Summary

Raman spectroscopy has evolved from a specialized technique into a premier analytical method for real-time monitoring and quality control in the oil and gas industry. For all the oil and gas industry segments - including upstream, midstream, downstream, and petrochemicals- Raman spectroscopy has emerged as a key in-line process monitoring solution with three key advantages: non-destructive direct measurements, rapid analysis, and a compact instrument footprint without the need for hardware calibration. These features make it particularly suitable for downstream oil and gas operations, where real-time monitoring and stringent fuel quality control are critical.

This study highlights the application of the Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer in measuring refined fuel properties. Nearly 300 samples of gasoline, diesel, and jet fuel were examined, correlating key properties such as API gravity, Reid vapor pressure, cetane index, flash point, and more with the collected spectra. The data underwent chemometric processing to develop predictive models, which were implemented using the RunSpex™ software for efficient real-time analysis.

The results demonstrate the process Raman system's high accuracy and reliability in measuring important refined fuel properties. The system's rapid analysis capability and compact design make it ideal for dynamic industrial environments, such as pipeline monitoring, truck filling operations, and distillations. Additionally, the system's ATEX Zone 0 certification ensures safe operation in hazardous locations.

Overall, the MarqMetrix All-In-One Process Raman Analyzer proves to be a robust and efficient solution for real-time monitoring and quality control in the refined fuels industry, offering a viable alternative to traditional instrumentation like gas chromatographs and knock engines. Its versatility in accurately analyzing multiple fuel types underscores its value in maintaining fuel quality and operational efficiency across various industrial settings.

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Introduction

Raman spectroscopy, once considered a specialized technique for the monitoring of pipelines and industrial processes, has undergone significant advancements over the past decade. These technological improvements have transformed process Raman spectroscopy into a premier analytical method, widely recognized for its ability to deliver three distinct advantages: non-destructive direct measurements, rapid analysis, and a compact instrument footprint. These features make it an ideal choice for real-time monitoring and quality control in various industrial applications.

One key benefit of process Raman spectroscopy is its non-destructive nature, allowing direct measurements without compromising sample integrity. This is crucial in the oil and gas industry, where maintaining the original state of the sample is essential. This is typically achieved through high-performance and robust optics design – typically in the form of a probe or a flow cell - that allows measurement at extreme temperature and pressure conditions.

Another advantage is its rapid analysis capability. Unlike traditional methods that require lengthy preparation and analysis times, process Raman spectroscopy delivers results in seconds, enabling real-time monitoring and decision-making. This speed is vital in dynamic environments in oil and gas industry for maintaining production efficiency and product quality. Furthermore, the rapid speed of analysis provided by process Raman spectroscopy makes it an ideal choice for various applications. For instance, in pipeline monitoring, the ability to quickly and accurately assess fuel properties can significantly enhance operational efficiency and safety. Similarly, in truck filling operations, the swift analysis ensures that fuel quality is consistently maintained, reducing the risk of contamination and ensuring compliance with regulatory standards.

Additionally, the compact footprint of modern Raman spectroscopy instruments makes them easy to integrate into existing process lines and control systems. Their portability allows for in-site analysis, reducing the need for sample transportation and minimizing downtime. Moreover, the safety of process Raman spectroscopy can be further enhanced with ATEX Zone 0 certifications. These certifications ensure that the instruments can safely operate in hazardous locations, such as areas with flammable gases or dust. This capability is particularly important in industries like refineries, where safety is a top priority.

Refined fuels, including gasoline, jet fuel, and diesel, are critical commodities, serving as the lifeblood of transportation and industry. The quality of these fuels is determined by several ASTM-defined testing methods in the refineries, such as API gravity, Reid vapor pressure (RVP), cetane index, and flash point. These parameters are essential for ensuring that the fuels meet regulatory standards and perform reliably in their intended applications.

This application note outlines the testing performed using a Thermo Scientific MarqMetrix All-In-One Process Raman Analyzer to measure various refined fuel properties through process Raman spectroscopy. The MarqMetrix All-In-One Process Raman Analyzer leverages the advantages of Raman spectroscopy to provide accurate and reliable measurements of fuel quality parameters. By integrating this advanced analytical technique, industries can achieve better control over their processes, enhance product quality, and ensure compliance with regulatory standards.

Experimental

Nearly 300 refined fuel samples were analyzed using a MarqMetrix All-In-One Process Raman Analyzer. No hardware calibration was performed on the process Raman system prior to analyzing the sample, as the system comes factory calibrated and requires no in-field calibration after installation. The analyzed samples were categorized by their fuel type and correlated with key testing properties such as API gravity, RVP, cetane index, and flash point. The collected spectra and correlated properties underwent chemometric processing to develop predictive models. In all cases PLS regression was used to build predictive models. These models were subsequently deployed using the RunSpex ™ software integrated into the MarqMetrix All-In-One Process Raman Analyzer to enable efficient and accurate real-time analysis of fuel properties.

In addition to the samples collected for model building and assessment, a series of ten diesel repeatability standards were collected. These samples were excluded from the model building to retain independence of the resulting measurement. Using this data, the standard deviation and repeatability coefficient were determined for each of the diesel models.

Results and Discussion

Fuel Properties

The models developed using the MarqMetrix All-In-One Process Raman Analyzer demonstrate excellent accuracy across all refined fuel analyses. Table 1 indicates the fuel properties analyzed, the number of samples in the method, the linearity coefficient of the calibration dataset (R^2), and the accuracy (RMSECV) of each method.

The gasoline analyses show outstanding accuracy for RON (Research Octane Number) and MON (Motor Octane Number), with an R^2 of 0.99. This indicates a potentially viable supplement or a replacement for traditional refined fuel instrumentation, such as knock engines.

RON and MON are crucial parameters for evaluating gasoline performance. RON reflects fuel performance under city driving conditions, while MON indicates performance under highway driving conditions. The value displayed at the pump, known as the Anti-Knock Index (AKI), is the average of RON and MON values. Therefore, accurate determination of these values is not only essential for optimal engine performance but also has significant financial implications. Inaccurate measurements can lead to regulatory issues or unnecessary octane giveaways.

Typical lab analysis for RON and MON can take several hours using a calibrated knock engine. Figure 1 and Figure 2 illustrate the calibration model for the RON and MON using the process Raman system. The rapid analysis time and high degree of correlation enable real-time determination of RON and MON values.

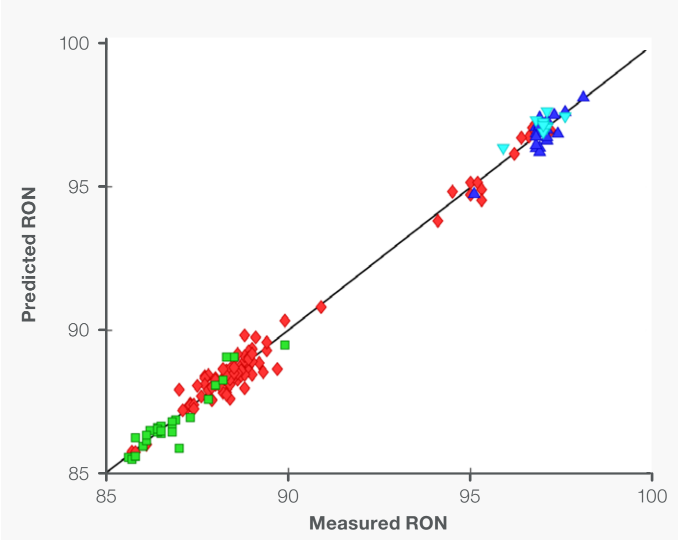

Figure 1. Predictions of RON for Gasoline.

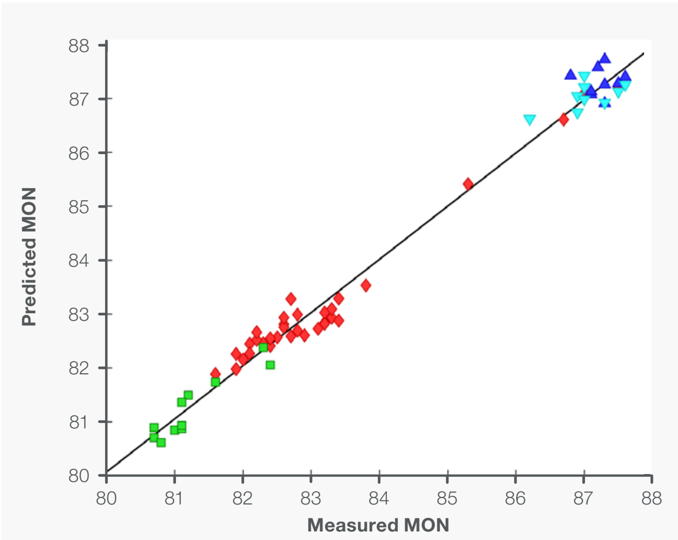

Figure 2. Prediction of MON for Gasoline.

Fuel Type	Property	Number of Samples	R^2	Model Accuracy (RMSECV)	ASTM Method
Gasoline/Petrol	API (°API)	152	0.999	0.24	D4052
	Benzene (Vol. %)	40	0.969	0.047	D3606
	RON (O.N.)	144	0.992	0.35	D2699
	MON (O.N.)	62	0.987	0.28	D2700
	RVP (psi)	173	0.980	0.2	D323
Diesel	API (°API)	76	0.994	0.1	D4052
	Cetane (°C)	17	0.917	0.41	D613
	Flash (°F)	76	0.982	1.7	D93
	T10	12	0.936	2.9	D86
	T50	12	0.948	1.7	D86
	T90	12	0.790	2.2	D86
Jet Fuel	API (°API)	34	0.939	0.1	D4052
	Cetane (°C)	15	0.900	0.3	D613
	Flash (°F)	51	0.718	1.0	D93
	T50	15	0.957	1.3	D86

Table 1. Properties and Model Accuracies.

The analysis of diesel and jet fuel samples followed a similar trend to that of gasoline, demonstrating excellent accuracy in key quality parameters such as API gravity, cetane index, and flash point. Although the number of diesel and jet fuel samples available for analysis was considerably limited, the results were still highly reliable and consistent.

The cetane index is one of the key properties for diesel and jet fuel, as it is a key indicator of fuel quality and combustion performance. There are multiple methods for determining the cetane index of diesel, ranging from 30 minutes to multiple hours, and may involve the use of a cetane engine. On the other hand, the Raman analyzer used in this study provided results within a few minutes and with an excellent linearity coefficient (R^2 >0.90). Figure 3 shows the calibration dataset for the cetane index method for diesel fuel.

The American Petroleum Institute (API) gravity is one of the most important measurements for all fuel types, as it plays a key role in identifying and quantifying fuels. API gravity varies by fuel type, making it an excellent indicator for distinguishing different fuels, especially during transmix events in pipelines.

Figure 4 demonstrates the correlation between the analysis from the process Raman system and the ASTM test method for determining the API gravity of jet fuel. The strong correlation observed for jet fuel, as well as for diesel and gasoline products, highlights the ability of the Raman system in measuring API gravity in real-time. This real-time monitoring is essential for managing multiproduct pipelines and detecting transmix events efficiently without requiring sample collection, improving performance and safety. The ability to accurately and efficiently analyze multiple types of refined fuels ensures robust quality control and operational efficiency across various applications.

Repeatability

For the repeatability standards, the standard deviation and repeatability coefficient were calculated. Table 2 indicates these parameters for key diesel properties. These values represent the precision of the repeated measurements made by the process Raman system. For each of the properties, the Raman system demonstrates excellent repeatability in measurements, further signifying its ability to supplement or replace traditional fuel analysis instruments such as gas chromatography (GC).

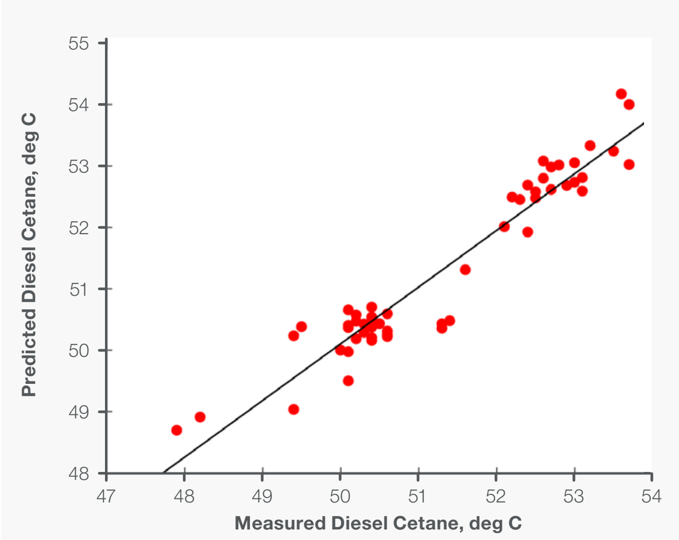

Figure 3. Prediction of Cetane for Diesel.

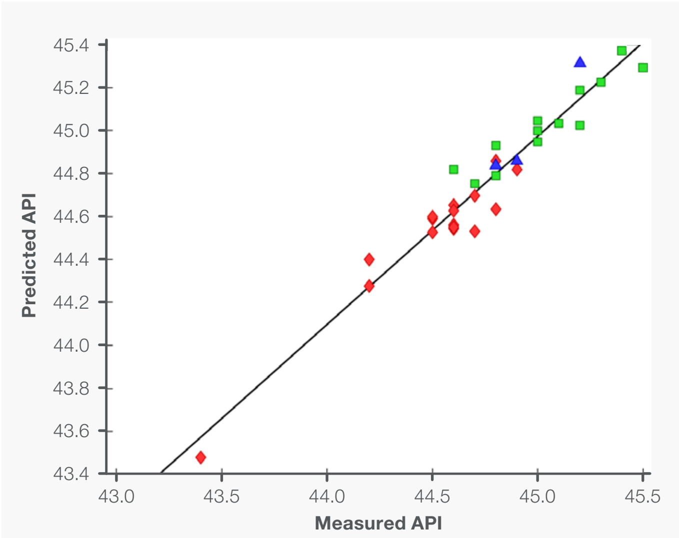

Figure 4. Prediction of API for Jet Fuel.

Property	Mean Value	Standard Deviation	Repeatability Coefficient (95%)
API (°API)	35.90	0.007	0.02
Cetane (C)	52.67	0.005	0.01
Flash (°F)	144.8	0.16	0.43
T10 (°F)	205.3	0.13	0.36
T50 (°F)	519.3	5.23	14.5
T90 (°F)	633.6	0.47	1.32

Table 2. Repeatability Data for Diesel Samples.

Conclusion

The MarqMetrix All-In-One Process Raman Analyzer demonstrates the capability to perform non-destructive direct measurements of refined fuel properties with high specificity and rapid turnaround.

The results indicate that Raman spectroscopy can serve as a complementary or alternative technique to conventional methods, such as gas chromatographs (GCs) or knock engines. The rapid analysis capability makes it ideal for applications such as pipeline monitoring and truck filling operations, ensuring consistent fuel quality and compliance with regulatory standards. The ability to characterize multiple fuel types with a single platform supports its application in monitoring blended streams, detecting transmix events, and ensuring compliance with established fuel specifications.

Overall, these findings suggest that Raman spectroscopy offers a robust and efficient solution for continuous monitoring and quality control in refined fuels processes.