Application note

Accelerating the analysis of refined fuel properties using a novel solid state Raman analyzer

Introduction

Refinery laboratories must analyze hundreds of samples per day. In a medium size refinery, this can be 250 samples per day and in a large refinery, the number can be as high as 500 per day. The current analytical tools conventionally used are gas chromatographs, simulated distillation, flash & freeze point devices, densitometers, vapor pressure testers, test engines for RON & MON and many others.

Solid state Raman spectroscopy can measure multiple properties of gasoline, jet and diesel fuels accurately, precisely and rapidly in a matter of seconds. In this paper, we will describe the methodology for collecting high quality Raman spectroscopy spectra and the strategy for turning the spectral data into actionable information to inform critical decision-making processes.

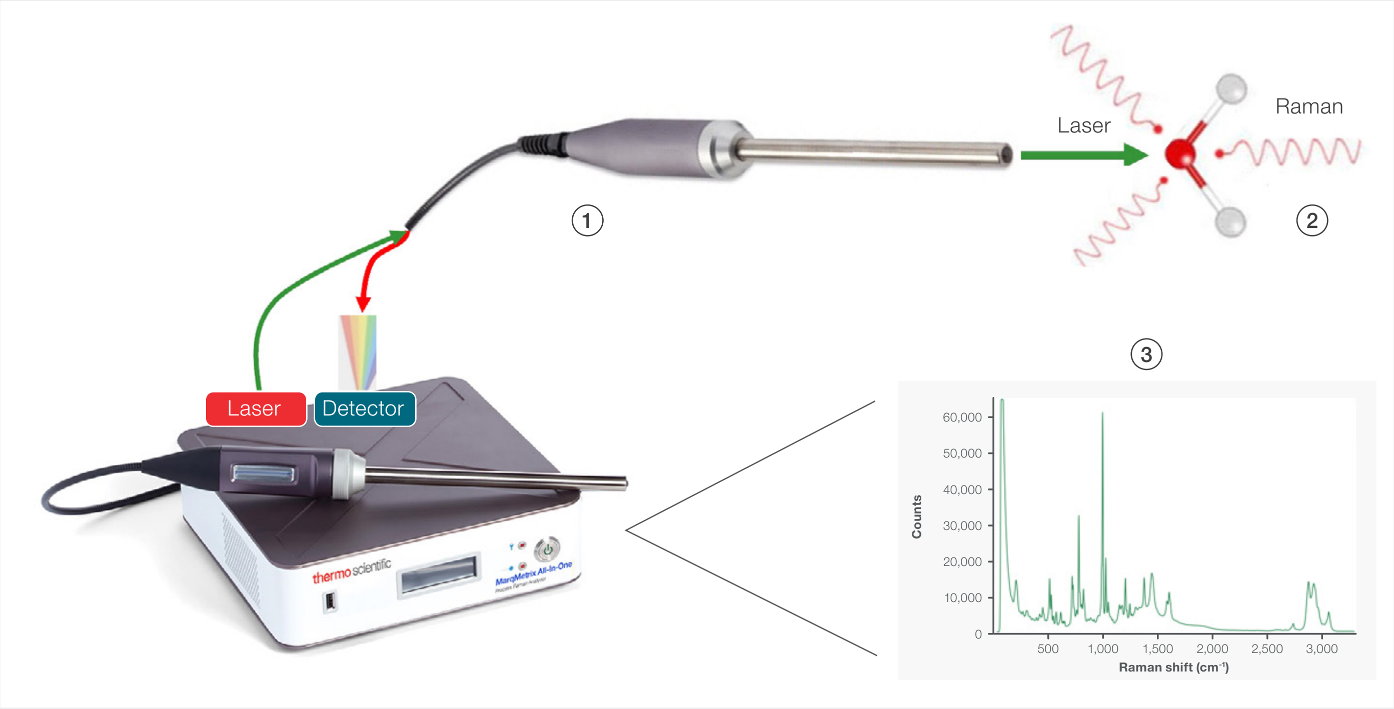
Analysis of multiple fuel types including gasoline, jet, and diesel as well as component streams such as reformate, isomerate, and alkylate will be described as well as modeling strategies to ensure a simplified approach for laboratory workflow for technicians and operators.

What is Raman spectroscopy

Raman spectroscopy is a laser-based optical analysis technique used to measure composition through the vibrational properties of molecules. Samples are collected using a 785nm excitation laser and a contact probe that produces a unique spectral fingerprint that identifies the chemical composition and molecular structure of a hydrocarbon. The distribution of the spectral peaks describes the molecule’s composition, while the signal intensity correlates linearly with concentration.

Since its discovery in the 1920s, Raman spectroscopy has revolutionized process analysis with its non-destructive mode of operation and capability to measure sample composition. However, the broader adoption of this technique is the result of advancements in the stability and portability of solid-state Raman spectroscopy systems and technological improvements in lasers, optics, and detectors that have made the technique faster and more accessible.

Raman spectroscopy overview



[1] Laser light directed at sample. [2] Small portion of scattered light, Raman effect, returns through collection fiber to the detector.
[3] System displays the Raman spectrum of the sample which is unique for every molecule (molecular fingerprint).

Methodology

Measurement collection

A Raman spectroscopy instrument measures using a vial holder that analyzes samples in 20mL scintillation vials. Spectra are collected using 250ms integration times.

After spectral collection, the chemometrics software automatically preprocesses, performs a discriminate analysis to identify the type of sample, and then applies PLS regression models for that type of sample.

Vial holder accessory for laboratory measurement.

Analysis

The analysis results are then sent in readable format to a Laboratory Information Management System (LIMS). The operator workflow is extremely simple and designed to reduce bottlenecks. The operator will place the sample in the vial holder, input the unique ID, and press the acquisition button on the software. The entire process takes approximately 15 seconds.

Using this approach, the Raman spectroscopy instrument can analyze close to 500 samples in an 8-hour shift or 1500 samples in a 24-hour period. Sample volume is also greatly reduced (20mL) compared to the quart size container normally used, resulting in reduced sample footprint and easier to retain storage. Sample handling is also minimized by using the non-contact probe to analyze the fluid through the vial.

Experiment conditions

A total of 127 refined fuel samples were processed using the Thermo Scientific™ MarqMetrix™ All-In-One Process Raman Analyzer. The sample makeup included 87 gasoline, 20 diesel, and 20 jet fuel samples.

The acquisition parameters were optimized for signal intensity and signal to noise ratio. All samples were measured in a Thermo Fisher Scientific vial holder.

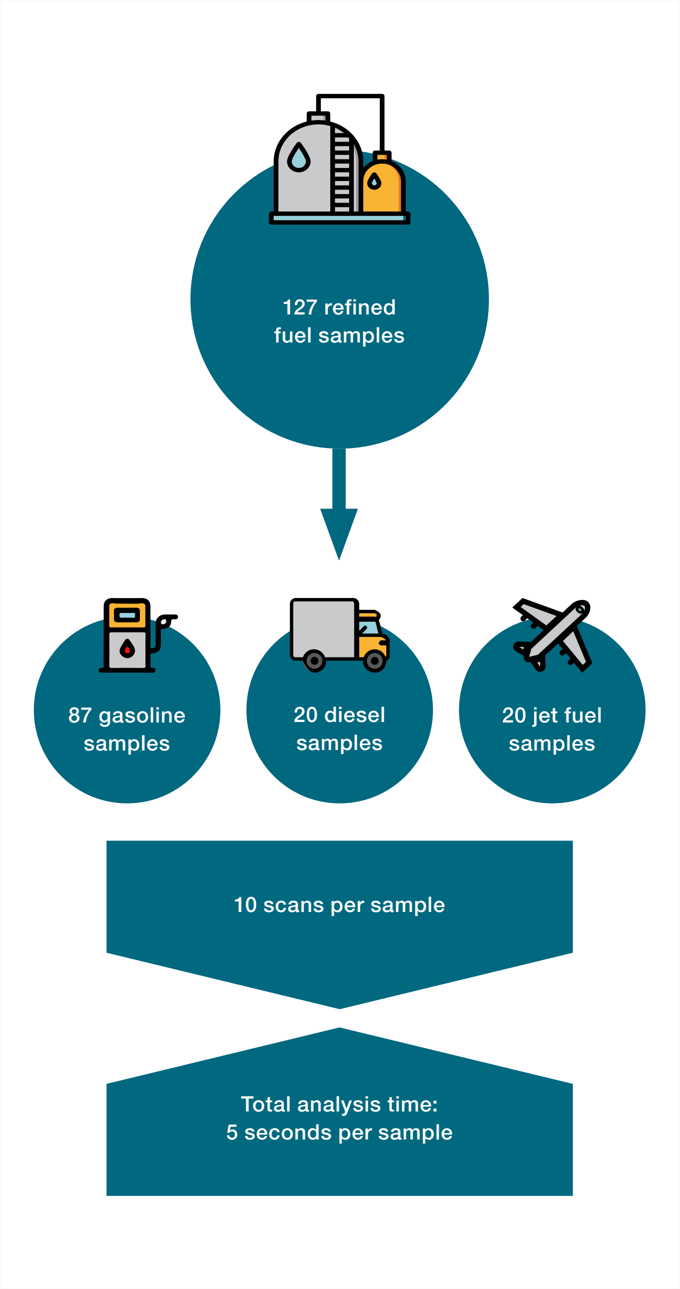
The spectra collected were averages of 10 scans, with each scan being a 250ms acquisition at 450mW. All spectra were dark subtracted. Total analysis time per sample was 5 seconds.

The generated spectra were processed using SOLO (Eigenvector). Models were built using either Partial Least Squares (PLS) or Partial Least Squares Discriminant Analysis (PLSDA). Cross validation was used to optimized model calibration.

For the gasoline models, a holdout set was retained to determine model accuracy. Model accuracy for the diesel and jet models was determined using the cross-validation results. The reference data used to build the model was collected using the relevant ASTM method.

Products	ASTM method	Output
Gasoline	D2699	RON
Gasoline	D2700	MON
Gasoline	D5191	Vapor pressure
Gasoline	D5188	V/L ratio
Diesel	D0093	Flash point
Diesel	D0976	Cetane number
Diesel	D2500	Cloud point
Jet	D2386	Freeze point
Jet	D0093	Flash point
All	D0086	Distillation boiling points
All	D4052	API gravity

Experiment at-a-glance



127 refined fuel samples

87 gasoline samples

20 diesel samples

20 jet fuel samples

10 scans per sample

Total analysis time:
5 seconds per sample

Results and discussion

Two paths of investigations were pursued: classification of fuel type and quantification of various fuel properties.

Fuel type classification

PLSDA was applied to a dataset of all the fuel spectra. The spectra were preprocessed using EMS and mean centering. Figure 1A shows the mean EMSC spectra of each fuel type, with clear differences observed between the different fuel types. The resulting PLSDA model was able to easily differentiate between the fuel types. Figure 1B shows the PLS scores plot from the PLSDA model.

The success of the PLSDA model opens the door to a multitude of applications and workflow enhancements. Real-time application of the classification model can be used for transmix applications to monitor the transition between products, thereby reducing the transmix waste while increasing safety and profitability. The classification model could also be used in analytical laboratories to increase throughput.

The model is the first stage in a modeling pipeline that would automatically switch the models being used and the results reported based upon the type of fuel being analyzed.

MarqMetrix All-In-One Process Raman Analyzer with a Thermo Scientific™ MarqMetrix™ Proximal Probe Sampling Optic and vial holder accessory for laboratory measurement.

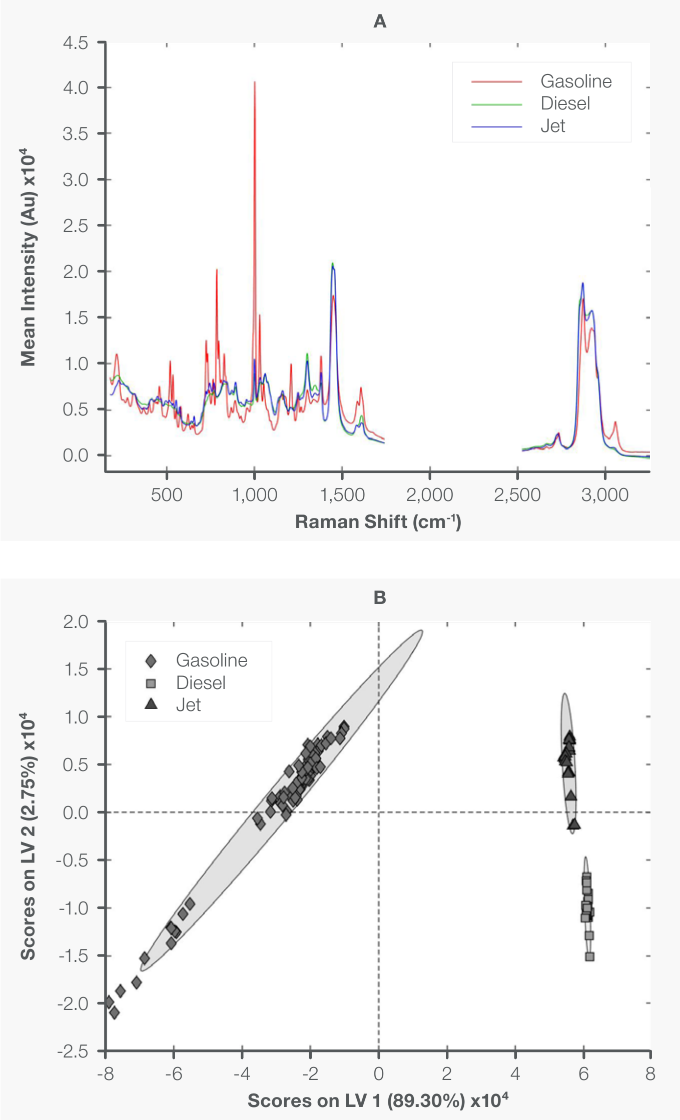


Figure 1. Mean preprocessed Raman spectra of each fuel type (A) and PLSDA classification model (B).

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Results and discussion

Gasoline fuel properties

A total of 87 samples were used to build models to predict six fuel properties for gasoline. Table 1 outlines the properties modeled and the resulting model accuracy.

Property	Accuracy
API (°API)	0.26
Benzene (Vol. %)	0.026
RON (O.N.)	0.27
MON (O.N.)	0.30
V/ L ratio	1.82
RVP (psi)	0.22

Table 1. Gasoline fuel properties and model accuracies.

Figure 2 shows the models that resulted for API (A), Benzene (B), RON (C), and MON (D).

The excellent model performance, especially for the prediction of RON and MON, demonstrates the potential of Raman and chemometrics as supplements, if not viable alternative for costly Knock engines and other challenging laboratory methods. The rapid speed at which the spectra are collected and results calculated makes this an ideal method for monitoring the loading and unloading of trucks, tankers and barges, constantly assessing product quality, and eliminating loading errors.

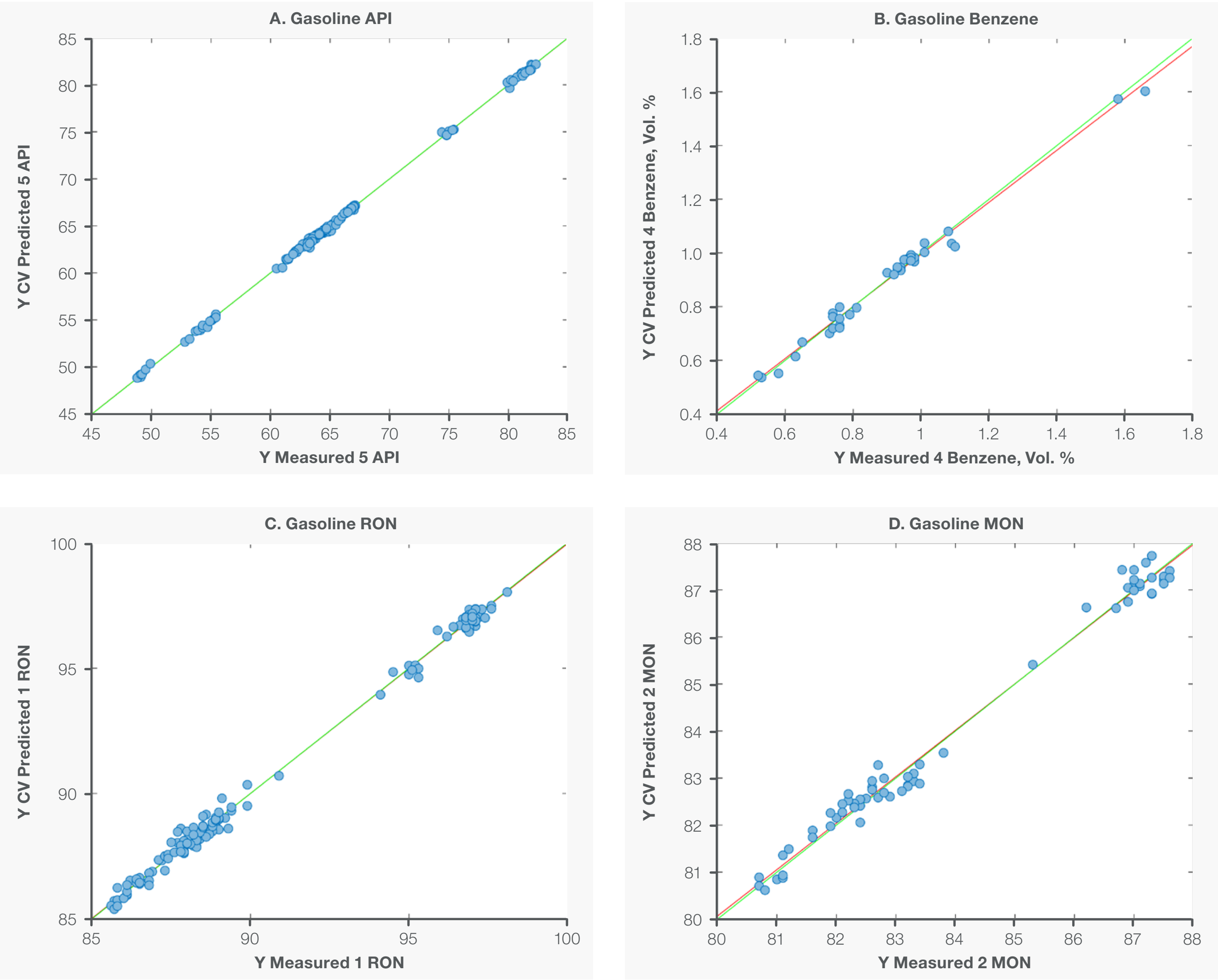


Figure 2. Gasoline property models for API (A), Benzene (B), RON (C), and MON (D).

Results and discussion

Diesel fuel properties

A total of 20 samples were available to build PLS models for seven properties of diesel fuels. Table 2 outlines the properties predicted and the ensuing model accuracy.

Property	Accuracy
API (°API)	0.06
Cetane number	0.40
Flash point (°F)	1.1
IBP	9.2
T10	2.9
T50	1.7
T90	2.2

Table 2. Diesel fuel properties and model accuracies.

Figure 3 shows examples of the models built using the diesel spectra. Unlike the gasoline models, there were significantly fewer samples available to build models. As more data becomes available, these models will continue to be maintained and developed. However, the initial models have good performance.

As with the gasoline models, the strong performance of the diesel models shows that Raman spectroscopy can complement current lab analyses with rapid screening times or replace costly time consuming distillation methods.

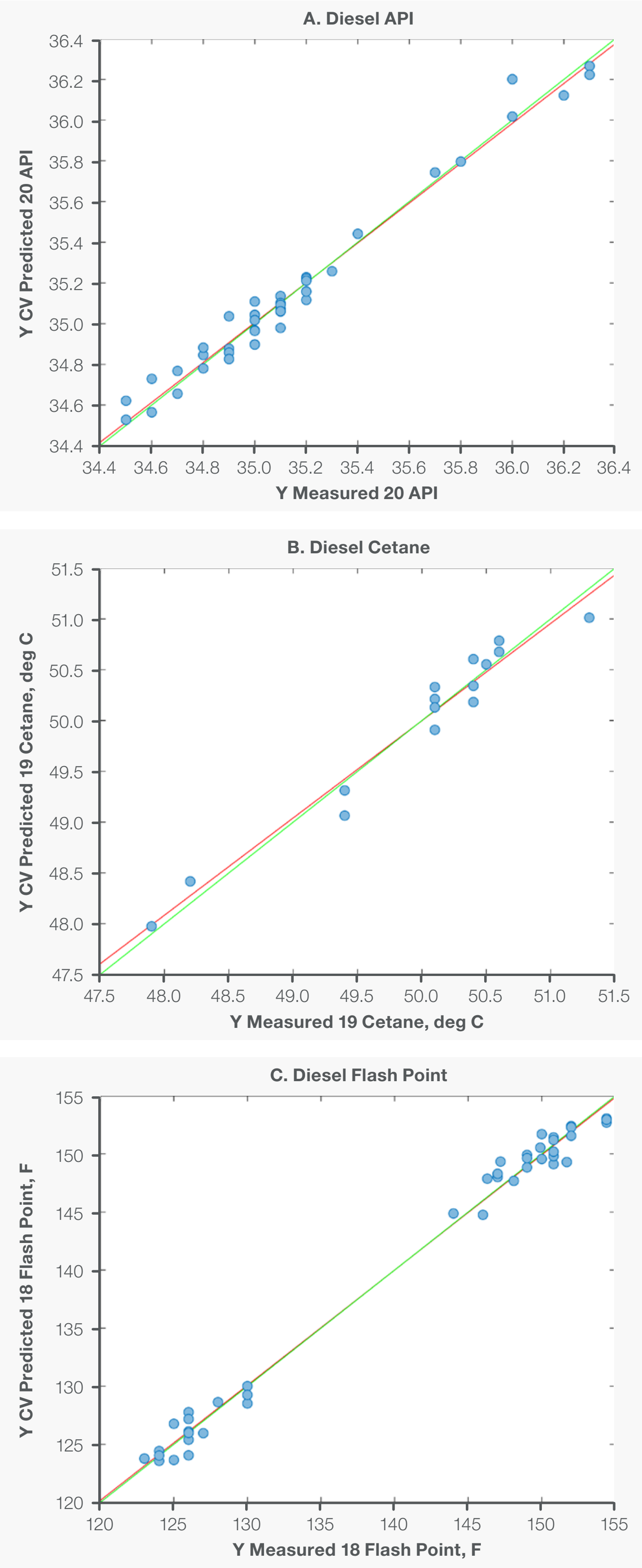


Figure 3. Diesel property models for API (A), Cetane (B), and Flash Point (C).

Results and discussion

Jet fuel properties

As with the diesel models, only 20 samples were available to be modeled. Table 3 shows the models built and the resulting model accuracies. Much like the diesel models, the jet models performed very well even with the limited number of samples.

Figure 4 displays a subset of the models built for the jet fuel samples.

As more samples are collected, the models will be expanded; this will improve the model robustness by expanding the working ranges and improving accuracy.

Property	Accuracy
API (°API)	0.09
Cetane number	0.26
Flash point (°F)	1.2
Freeze (°F)	1.0
IBP	3.5
T10	2.6
T50	1.3
T90	1.5

Table 3. Jet fuel properties and model accuracies.

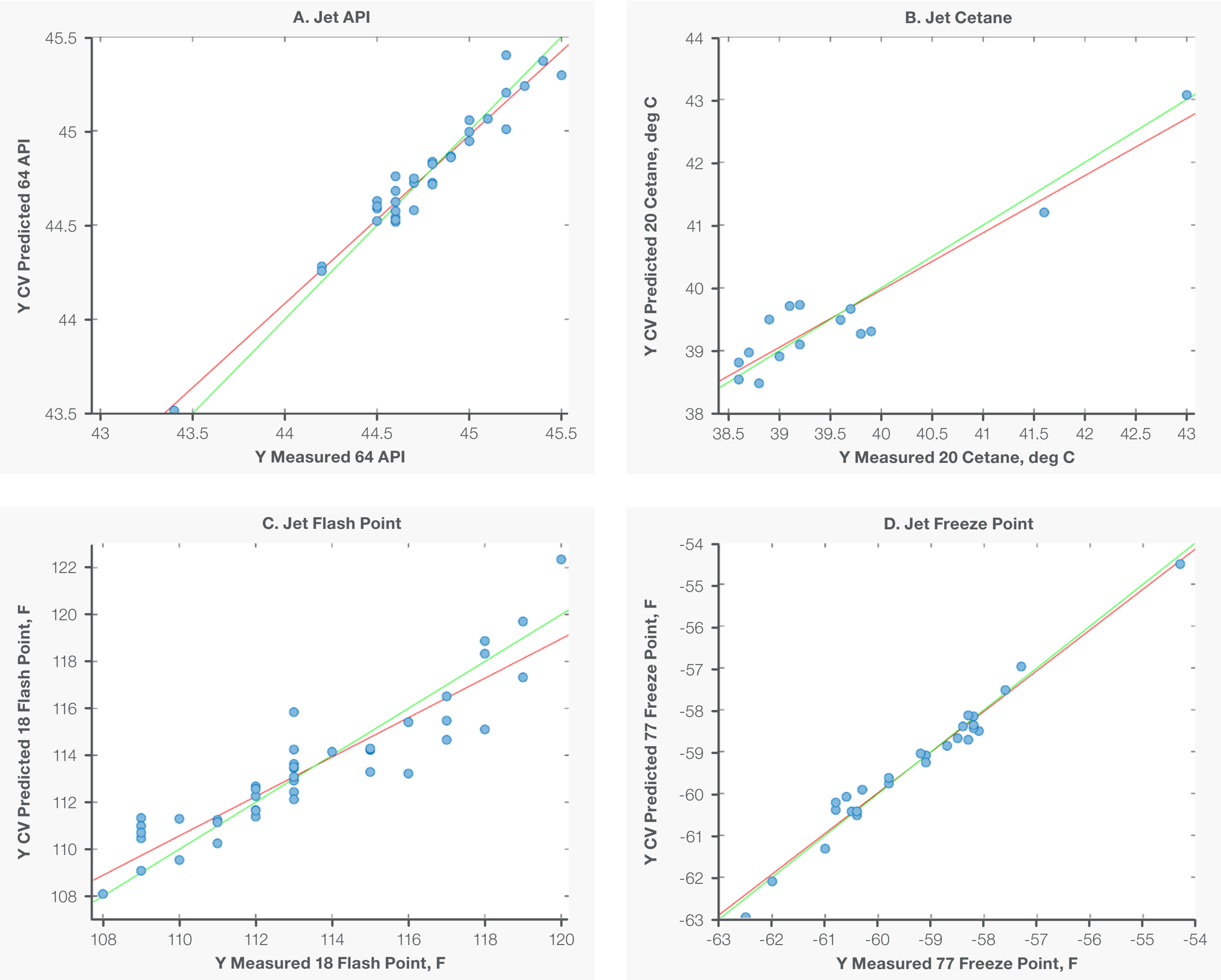


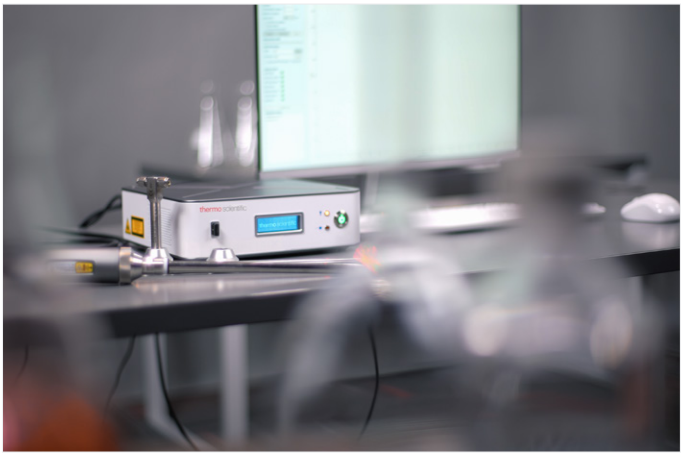
Figure 4. Jet fuel models for API (A), Cetane (B), Flash Point (C), and Freeze Point (D).

Conclusion

The investigations conducted demonstrate that Raman spectroscopy can be used to accurately measure various refined fuel properties of gasoline, jet, and diesel fuels.

The use of Raman spectroscopy in a refinery can increase throughput by a significant factor, reduce overhead, and improve the safety environment of a laboratory.

In addition, the transferability of the Raman methods allows models to be built in a lab and applied to process instruments in the field, increasing the return on investment using process analytical technology.



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