

# **Reducing Mogas Reid Vapor Pressure (RVP) Giveaway Using Online Raman Spectroscopy: A One-Year Case Study**

Lee Smith, PhD, Process Instruments, 630 S. Komas Drive, Suite 310  
Salt Lake City, UT 84108

Robert Benner, PhD, Process Instruments, 630 S. Komas Drive, Suite 310  
Salt Lake City, UT 84108

Giancarlo Aguirre, Process Instruments, 630 S. Komas Drive, Suite 310  
Salt Lake City, UT 84108

Will Warkentin, Chevron, 100 Chevron Way, Bldg. 35, Room 1128  
Richmond, CA 94802

Angela Keys, Chevron, 100 Chevron Way, Bldg. 35, Room 1128,  
Richmond, CA 94802

Paul Singh, PhD, Chevron, 1400 Smith Street, Houston, TX 77002

## **KEYWORDS**

Reduce RVP Giveaway, Raman Spectroscopy, Hierarchical Modeling

## **ABSTRACT**

Butane costs 25% to 30% less than most other high-octane blend components used to produce gasoline in oil refineries. Being able to add more butane into summer gasoline blends while the blends remain below the highly regulated Reid vapor pressure (RVP) caps, which change seasonally, can greatly improve profitability. Unlike many other forms of spectroscopy, Raman scattering has repeatedly demonstrated excellent accuracy in predicting gasoline volatility over a wide range of RVP (i.e., 4.6 psi to 18.4 psi), using a single chemometric model. Breaking up a full-range RVP model into multiple sub-models with smaller ranges that match seasonal motor gasoline (Mogas) blends can greatly improve the online RVP standard error of prediction (SEP). Applying this hierarchical modeling approach to online Raman RVP measurements has allowed one Chevron oil refinery in Richmond, California, to target an RVP SEP of 0.1 pounds per square inch (psi) for its summer blends. This reduction in RVP giveaway yielded substantial annual savings.

## INTRODUCTION

Profitable gasoline production has always been a challenge for oil refineries because of numerous government regulations. A particularly difficult challenge is blending summer (June 1 through September 15) Mogas, which must maintain a sufficient high-octane rating to ensure that motor vehicles run efficiently, while keeping the RVP property, a measurement of volatility, beneath mandatory limits. The Clean Air Act requires the Environmental Protection Agency (EPA) to regulate summer gasoline blends to be lower in volatility in order to reduce evaporative emissions (1), which generally increase during warm weather and can cause unhealthy levels of ground-level ozone.

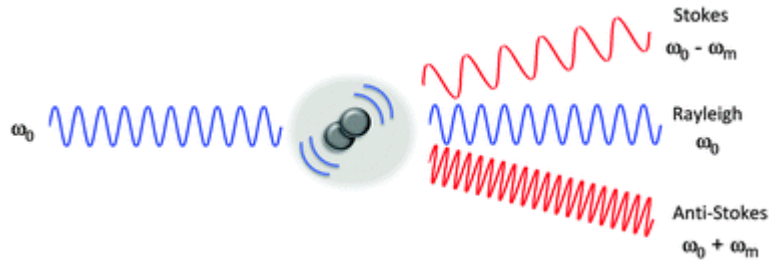
Refineries can often blend alkylate (2), a high-octane blend component with an inherently low vapor pressure, into their summer blends to meet these requirements. However, alkylate is one of the most expensive blend components, and some refineries do not have access to an alkylate stream. A more readily available, significantly less expensive solution for blending summer gasoline is to add in butane, which is approximately 30% less expensive than other blend components. Butane offers a high-octane rating but has a high vapor pressure, so it can be added only in small quantities to ensure the blend will not exceed the permissible RVP cap.

Online Raman (3) spectroscopy combined with hierarchical chemometric models is an accurate, continuous, online RVP measurement technique that allows a refinery to efficiently blend greater amounts of inexpensive butane into summer gasoline blends, reducing RVP giveaway while maintaining low RVP and high-octane requirements.

## METHODS

Vibrational spectroscopy involves the interaction of infrared radiation (IR) with matter. Raman scattering is a form of vibrational spectroscopy in which a change in the polarizability of a molecule with respect to a change in the normal coordinate of the vibration causes incident light to be scattered with a frequency shift that corresponds to the energy of the vibration. After this interaction, the scattered photons are shifted to either lower energy (Stokes) or higher energy (anti-Stokes), resulting in a unique "fingerprint" that can be observed in the Raman spectrum of the molecule (Figure 1). The Raman process is a light-scattering effect and has different selection rules than IR absorption.

Both Raman and mid-IR measure fundamental vibrational modes. The selection rules are different, so modes that are strong in Raman tend to be weak in mid-IR and vice versa. Because Raman scattering spectra are excited in the near-IR wavelength region (~ 785 nanometers [nm] to 800 nm) with laser excitation, Stokes Raman signal collection can be easily performed using conventional multimode fiber-optic cables. This allows for remote sampling from up to ~ 300 meters (1,000 feet) away, whereas with mid-IR/IR, fiber-optic cable lengths of only a few meters must be used.

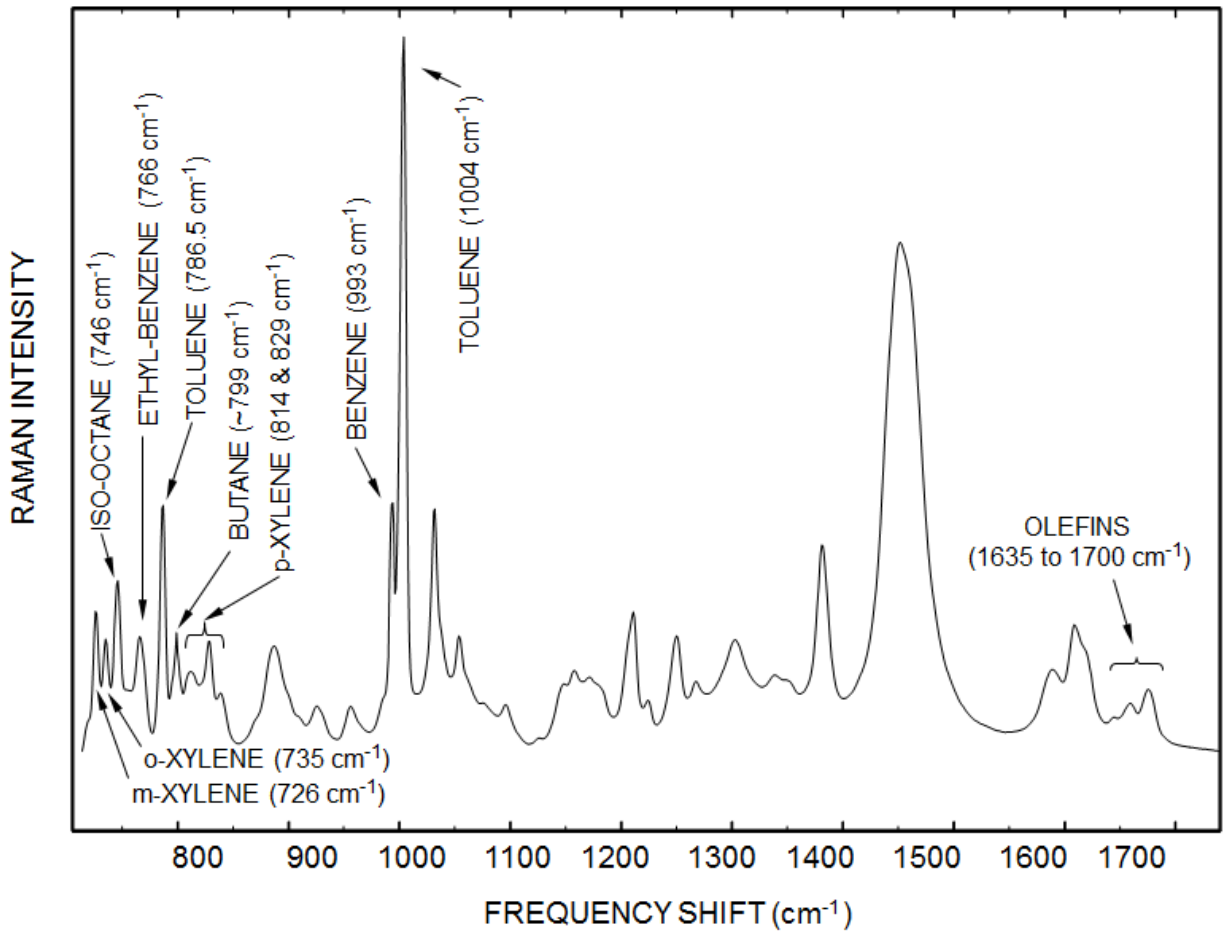


**FIGURE 1. RAMAN SCATTERING (REFERENCE 4)**

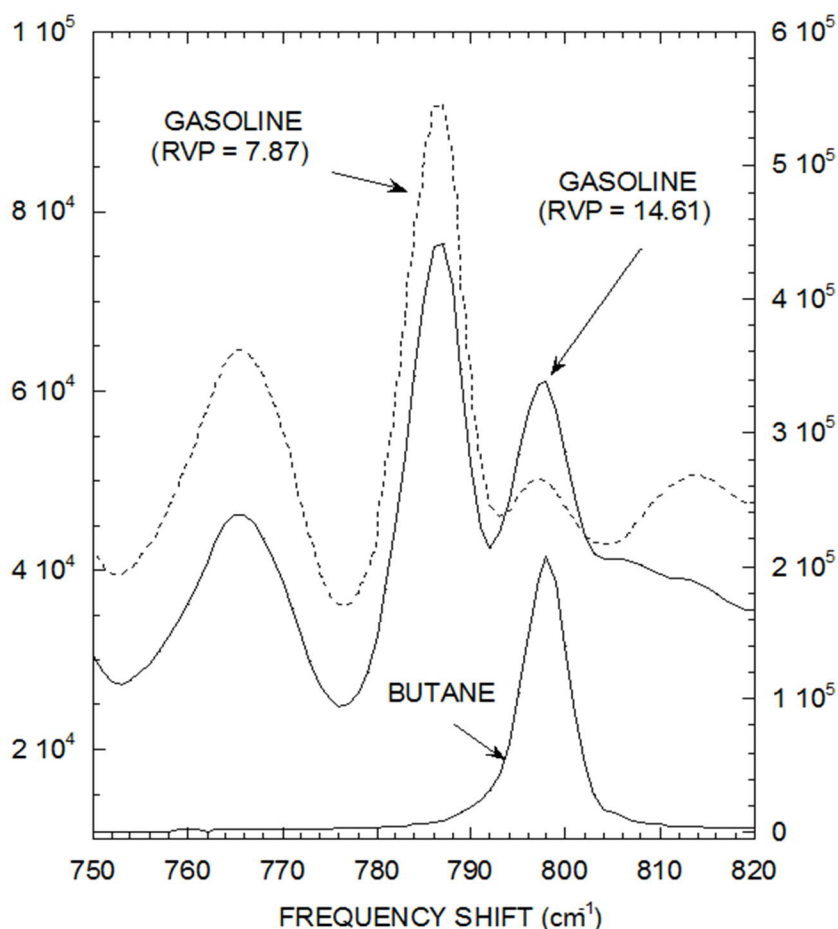
The Raman effect is rather weak but offers excellent spectral resolution and minimum overlap of components, resulting in maximum component specificity.

Raman scattering spectra are relatively easy to interpret. Peak frequency shift yields sample *composition*, and peak intensity yields *concentration* of components. Like all spectrographic methods, Raman scattering requires the collection of laboratory data using American Society for Testing and Materials (ASTM) laboratory methods and the building of chemometric models.

Unlike conventional near-IR spectroscopy, Raman scattering shows a unique and strong peak for butane at  $\sim 799$  wavenumber shift (Figures 2 and 3). This peak is discrete and does not overlap with the many peaks from other gasoline components. Consequently, Raman scattering used in conjunction with conventional chemometric techniques can easily be used to measure RVP.



**FIGURE 2. RAW GASOLINE RAMAN SPECTRUM**  
**NOTE BUTANE RAMAN PEAK AT ~ 799 WAVENUMBER SHIFT**



**FIGURE 3. NEAT BUTANE RAMAN PEAK (LOWER CURVE) AND BUTANE AS OBSERVED IN HIGH- AND LOW-VAPOR-PRESSURE GASOLINE**

## EQUIPMENT

Raman spectra were collected using an online analyzer from Process Instruments, Inc. (model PI-200-I-18). An InPhotonics Raman probe (model RPS 785/24/5) was configured in a flow-through sample cell (model PI-EN-S-2-2-A) that was plumbed into a speed loop. The sample flow rate was ~ 2 to 4 liters/hour. No sample conditioning was required. Laser excitation was at a wavelength of 785 nm, and power at the probe tip was ~ 250 milliwatts (mW). Spectrum collection time was ~ 3 minutes.

Online Raman spectra and ASTM laboratory data for ~2,200 data points were collected from a finished gasoline blend-header over a period of four years, ensuring that blends from many different crude slates, all seasonal variances, and a wide range of refinery conditions were represented in the data set.

The chemometric modeling software used was Solo version 8.1 (Eigenvector Research). Partial least squares (PLS) regression models were built using the steps below:

1. Background correction, area normalization of all spectra, and mean centering
2. Venetian blind cross-validation
3. Generalized least squares weighting (GLSW)
4. Outliers selected from leverage vs. studentized residuals
5. Conservative choice of latent variables determined from standard error of cross-validation (SECV) plot
6. Validation with an independent set of data

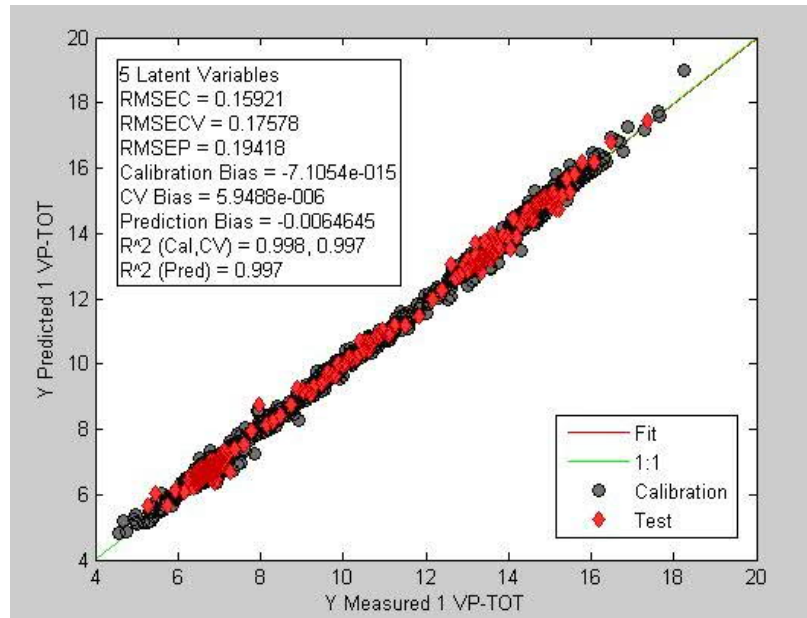
The training set included spectra from grab samples captured with a laboratory Raman spectrograph and online spectra captured with a separate online Raman unit. Laboratory grab samples usually have different RVP and octane profiles than online samples because of light-end losses during the grab sample collection process. Butane has a very high vapor pressure and a high-octane rating, and so is easily lost during the collection process. Thus, the RVP and octane values of a grab sample are often lower compared to their respective online samples. Because of these differences, online and laboratory Raman spectra were both included in the chemometric models.

Historically, grab sample collection times are often not accurately recorded, which makes it difficult to properly correlate grab sample collection times with their online spectra and predictions. For this reason, a flow sensor is always included on the grab sample collection circuit and connected to the online Raman system. When grab samples were collected, the event was time-stamped, and the respective online Raman spectrum was saved in a unique folder for use in model building.

Solo was chosen as the software for making chemometric models because it includes the GLSW technique. When compared with other commercial modeling packages, Solo models tend to have fewer latent variables (factors), the models tend to have lower SEPs, improved model robustness, and better model transference.

## **RESULTS AND DISCUSSION**

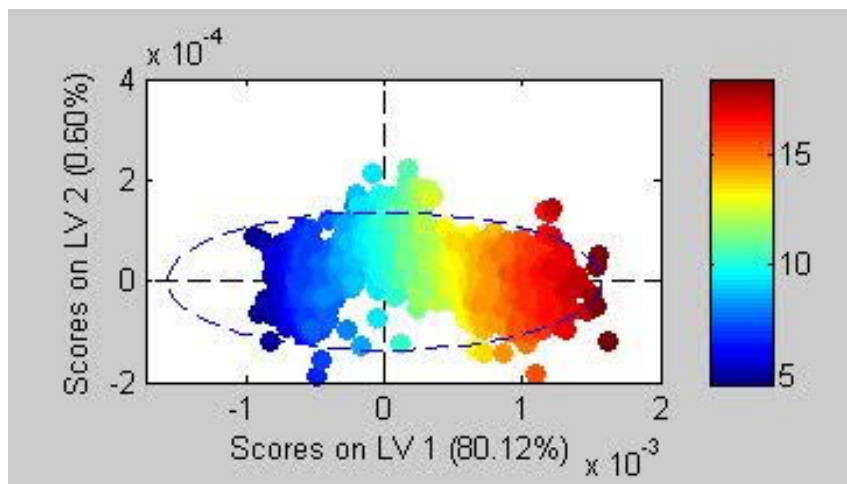
A full-range PLS model was built using a training set of 1,909 spectra, with 212 spectra reserved for an independent validation set. Twenty-one spectra were removed from the training set as outliers in preparing the model, and two spectra were removed from the validation set to obtain the results shown in Figure 4.



**FIGURE 4. FULL-RANGE RVP MEASURED VS. PREDICTED**

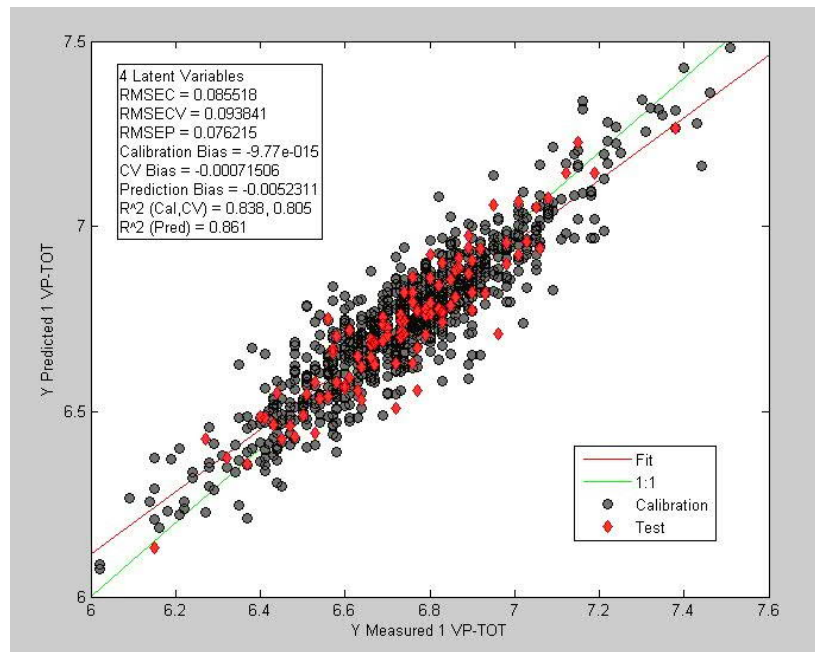
With five latent variables, the model provided an SEP of 0.19 psi, comparing well with the ASTM repeatability ( $r$ ) of 0.2 psi. The other parameter values (Figure 4) indicate that the full-range model is quite accurate.

Sub-models with better SEPs than the full-range model can be obtained by dividing the RVP data into smaller ranges. The scores plot for the full-range model (Figure 5) can be used to define the ranges for the sub-models based on the clusters of samples in the plot.



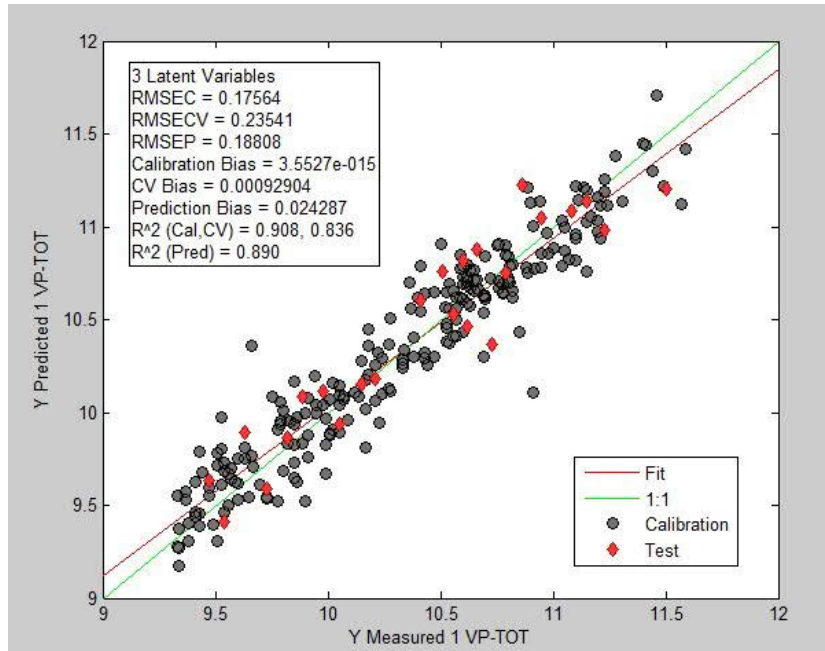
**FIGURE 5. FULL-RANGE RVP SCORES LV1 VS. LV2**

Alternatively, the ranges for the sub-models can be determined from the known ranges of the summer ( $6.0 < \text{RVP} < 7.5$  psi), transition ( $9.3 < \text{RVP} < 11.6$  psi), and winter ( $12.5 < \text{RVP} < 16.9$  psi) blends. Sub-models were made based on the known ranges, with the results illustrated in Figures 6–8. Compared to the SEP (0.19) of the full-range model, the SEP (0.08) of the summer model improved the most, but the SEP of the other seasonal sub-models (0.19 for transition-season blends and 0.16 for winter blends) also improved.

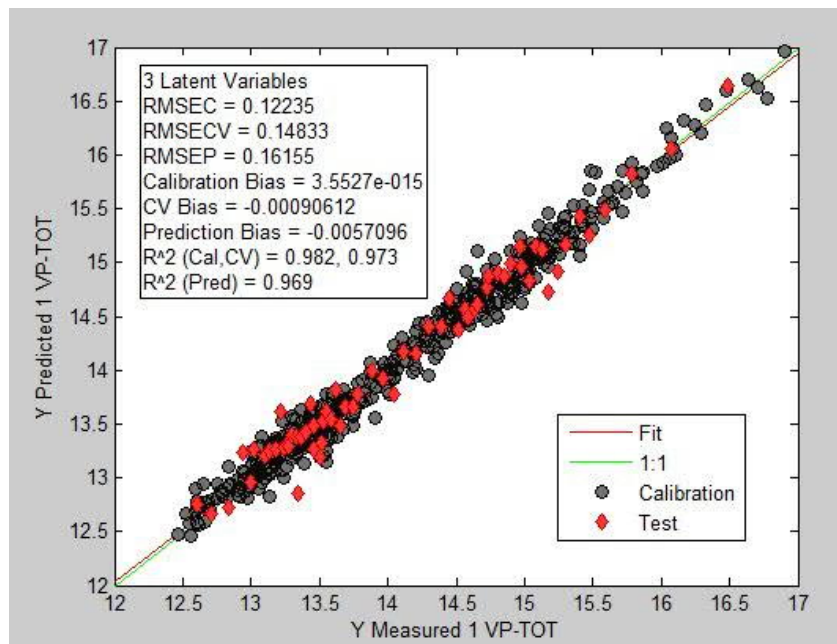


**FIGURE 6. LOW-RANGE RVP MEASURED VS. PREDICTED**





**FIGURE 7. MID-RANGE RVP MEASURED VS. PREDICTED**



**FIGURE 8. HIGH-RANGE RVP MEASURED VS. PREDICTED**

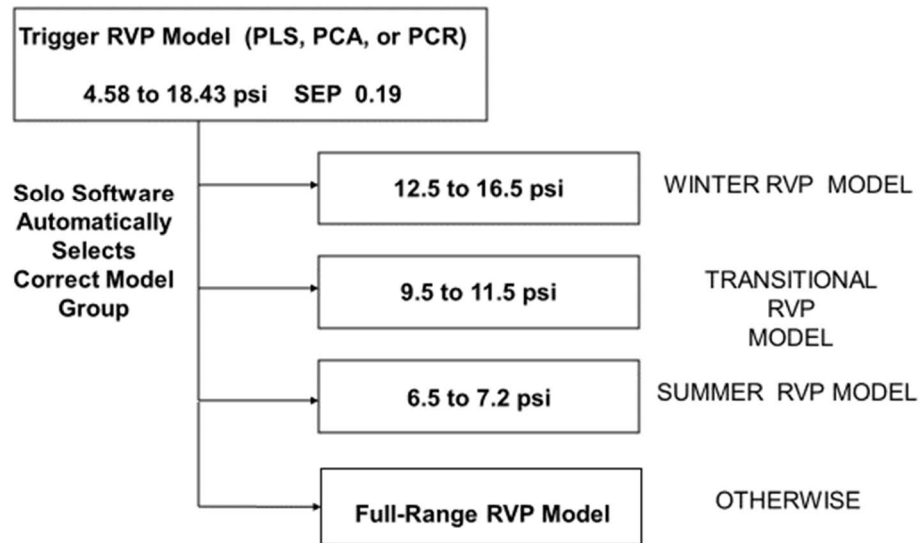
The RVP models were also tested with new data obtained in the months after the models were prepared. The validation results for the new data are shown in the table below:

**TABLE I. VALIDATION RESULTS FOR THE NEW DATA**

RVP MODEL	SAMPLES	SEP
FULL-RANGE	104	0.18
SUMMER	78	0.07
TRANSITION	20	0.23
WINTER	5	0.09

Although the number of new validation samples limits the statistics, the models appear to work well with future data. The SEP with the summer model (0.07) is even better than the SEP for the original validation set (0.08). These results are consistent with the goal of not only building reliable models, but also building models that are robust enough to increase the time between model updates.

The Solo software uses a hierarchical modeling tool that allows the appropriate seasonal target model to be automatically selected for a final RVP prediction that is based on the RVP prediction for a sample from the full-range model acting as a trigger. Although each model must be created, the models can be combined in a single hierarchical model that operates automatically according to the logic shown in Figure 9.



**FIGURE 9. HIERARCHICAL MODELING LEVELS**

The Chevron refinery applied these smaller-range models to its gasoline blending and documented RVP giveaway savings of \$6 million from twelve months spanning 2014 through 2015 by targeting

0.1 psi from specifications (5). The refinery was able to blend consistently to < 0.1 psi in summer grades. This means the refinery was able to blend significantly more butane into its fuels, especially during the critical summer season. A similar approach to its octane modeling resulted in additional savings.

## CONCLUSIONS

Raman scattering has repeatedly demonstrated excellent accuracy for predicting RVP values over a wide range (i.e., 4.6 to 18.4 psi), using a single chemometric model. It is shown that breaking up a full-range RVP model into multiple, smaller-range sub-models that match seasonal blends can greatly improve online RVP SEPs. Applying this hierarchical modeling approach to online Raman RVP measurements has allowed the Chevron refinery in Richmond, California, to achieve an RVP SEP of 0.1 psi for its summer blends ( $SEP \times 2 = \text{ASTM "R,"}$  where "R" = reproducibility). This reduction in RVP giveaway yielded an annual savings of \$6 million by allowing the refinery to blend in greater amounts of butane, which costs considerably less than other blend components.

Breaking down chemometric models into sub-models with smaller ranges, by season or perhaps blend type, can greatly improve model SEP. This modeling scheme can be applied using many commercial chemometric packages. However, not all chemometric packages include the hierarchical model feature that automatically switches models on the fly, according to the range of the predicted parameter.

Using this modeling technique for RVP and octane models, and from close observations, hierarchical models can be applied to many other fuel parameters, especially those where additional accuracy is desired, such as for distillation points. Hierarchical models may not be beneficial for all parameters, so it is recommended that appropriate scores plots be examined for specific situations to determine whether building multiple, smaller-range models is warranted.

## REFERENCES

1. United States Environmental Protection Agency, Federal Gasoline Regulations, <https://www.epa.gov/gasoline-standards/federal-gasoline-regulations>, (accessed February 22, 2017).
2. U.S. Energy Information Administration, Alkylation is an important source for octane in gasoline. <http://www.eia.gov/todayinenergy/detail.php?id=9971#>, (accessed February 22, 2017).
3. Larkin, Peter, "Infrared and Raman Spectroscopy", Infrared and Raman Spectroscopy: Principles and Spectral Interpretation, Elsevier, Waltham, MA, 2011, pp. 1-2.
4. Tipping, W., Lee, M., Serrels, A., Brunton, V., Hulme, A., "Stimulated Raman scattering microscopy: an emerging tool for drug discovery", Chemical Society Reviews, Vol. 45, No. 8, 2016, pp. 2075-2089.

5. Warkentin, Will, presenter, Chevron Users Group Meeting, Salt Lake City, UT. May 18–21, 2015.