

RE-ENGINEERING CALIBRATION IN OPTICAL SPECTROSCOPY

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ABSTRACT

A project has been undertaken to assess how to reduce the amount of effort devoted to maintaining and optimizing spectroscopic model performance in support of refinery and chemical plant labs. Over the last five years, a series of algorithmic approaches have been examined with the goal of streamlining the process of chemometric model construction to make the models significantly more robust when put into routine practice. This effort generated the following observations:

1. Even though there are published “Best Practices” for generating chemometric models, these practices are infrequently followed;
2. Recalibration of an optical spectrometer is frequently required due to changes in crude slates and blending component composition;
3. Even if a calibration was performed properly during initial installation, staffing changes and lack of training has undermined recalibrations; and
4. It is of benefit to minimize software maintenance frequency to control product giveaway.

This paper focuses on a multi-organization effort leading to an improvement in calibration procedures for on-line and laboratory multiwavelength spectrometers. Here the authors detail the process of calibration and demonstrate a path to build calibrations that are more reliable and potentially less sensitive to process shifts. Much of this improvement can be attained without requiring replacement of either the hardware or software in place. Additional improvement in calibration quality is available through the use of well-referenced methods that constitute the best technologies available.

INTRODUCTION

Petroleum and petrochemical industries favor the use of optical analyzers for extracting detailed chemical information rapidly, allowing information to flow in a timely manner and improving process control. Chemometrics is employed to provide a calibration tying the spectral signals to specific chemical concentrations or physical properties. Indeed, industry has adopted a series of practices designed to perform this translation from spectrum to information. Unfortunately, it is not as simple as: pour in spectral data, subject it to an algorithm like partial least squares (PLS), and know that the analyzer will function as long as the light stays on. In order to use optical analyzers effectively, the analyst needs to consider the limitations that ultimately determine the eventual success and life-expectancy of any calibration. There are many areas that have an impact on the ultimate quality of a chemometrics calibration: outlier detection, selection of number of factors, and even choice of algorithm; some techniques, such as variable selection and sample handling, were addressed but are beyond the scope of this paper.

Spectroscopy is a powerful instrumented technique that is used effectively in all facets of the hydrocarbon processing industry. For some applications, like measuring small amounts of water in a hydrocarbon stream, the calibration of a spectrometer will be stable and can go without significant maintenance for extended periods of time. In other applications, such as differentiating relative concentrations of hydrocarbons or bulk properties, the calibration may drift such that the analyzer no longer tracks the process. This is caused by instrument variability, by changes in the blend due to fluctuations in the input hydrocarbons, and by process changes.

Three areas are of practical concern to the chemometrician: limitations of the analyzer technology; limitations of the reference technique; and choices inherent to the chemometrics processing. These concerns are summarized in Table I.

TABLE I. LIMITATIONS THAT DICTATE CALIBRATION QUALITY.

LIMITATIONS OF ANALYZER TECHNOLOGY	<ul style="list-style-type: none">• Works by inference (optical spectroscopy is a functional group counter)• Instruments have non-linear response• Instruments can vary over time on both a long and a short time scale• Instrument-to-instrument variability requires either separate calibrations or calibration transfer
LIMITATIONS OF REFERENCE TECHNIQUE	<ul style="list-style-type: none">• Error in the reference method can limit calibration model quality; reducing reference method error can improve model reliability• The impact depends on the precision of the reference method relative to the precision of spectral measurements
LIMITATIONS OF CHEMOMETRIC PROCESSING	<ul style="list-style-type: none">• Choosing which samples to use for calibration (consideration of range, outliers, swamping, masking)• Determining portions of the spectrum to exclude for modeling and predictions• Selecting the proper number of factors to properly balance the variance bias trade off without over-fitting• Selecting algorithmic parameters including which algorithm and appropriate preprocessing and transformations• Corrections for instrument variability over time and between instruments

This report summarizes eleven separate calibration efforts spanning four different analyzer technologies and five different end user companies. Ten evaluations involved motor fuel assessment, one stemmed from applications in chemicals. Five of the analyzers were FT-NIR, four were Raman systems, and one each came from dispersive NIR and mid IR. As a result, the primary focus is on the use of Raman and FT-NIR for the quality control of motor fuels, but, from this and many other investigations, the conclusions are broadly applicable.

In reviewing the data sets involved in this study, calibrations can be characterized by three philosophies. Common Practice is to spend only a small effort vetting the data looking for outliers and accepting the software-suggested number of factors based on a leave-one-out cross validation. Best Practices start the same as Common Practices, but more time is spent using software tools supplied with the instrument for eliminating outliers from the calibration data set and looking at additional diagnostics to identify the best number of factors to retain. Enhanced Practices apply the best available technology to significantly reduce the errors associated with preparing calibration models for routine use.

METHODS

The Partial Least Squares (PLS) method is the multivariate calibration method used for the Common Practices and Best Practices analyses in this report. The PLS method was developed around 1975 by Herman Wold [1] and has been extensively documented in the literature [2,3] along with more recent adjustments on the details of its implementation [4-7]. The PLS method addresses the regression problem in which there is strong colinearity among the variables and more variables than samples. It is ideally suited to deal with spectroscopic measurements.

Although PLS is a powerful regression method, it still suffers from undue influence by outlier samples due to its least squares nature. The effects of outliers on multivariate calibration methods, and the heretofore best practices for identifying them, have been documented in the literature [8-10]. Martens and Næs devote an entire chapter to the subject of outliers in their book [11]. One of the most promising approaches for outlier detection is robust analysis [12]. In this report we make use of the robust PLS method developed by Hubert [13] for the Enhanced Practices analysis.

Robust methods can improve on the selection of samples for the development of multivariate calibration models. Modeling nonlinear behavior can also be addressed using local modeling. For the Enhanced Practices, the method of locally-weighted regression (LWR), in which a regression model is developed on a reduced set of neighboring samples and is performed as reported by Centner and Massart [14]. For cases when Enhanced Practices uses genetic algorithms, the method developed by Leardi is used [15].

There are many metrics available to assess the correct degree of model complexity by choosing the number of factors to use in modeling. This is well-documented [11], but often very subjective, and selecting too many factors is frequently the cause of overfitting. When the regression vector starts to appear noisy or jagged, it is an indication that the model is overfit. A metric that characterizes jaggedness attempts to quantify the relevance of the noise compared to the overall

signal [16]. Error values are listed in this report as Root Mean Squared Error of Cross Validation (RMSECV).

All of the algorithms described are available as MATLAB[®] (Mathworks[®], Natick, MA) routines; most are implemented in the Pirouette[®] software (Infometrix[®], Bothell, WA).

RESULTS AND DISCUSSION

In processing the results of the data evaluations, three areas arose as being of primary concern in constructing a useful model. This section is divided into separate discussions of: model complexity (typically flawed in practice by choosing too many factors to include in the regression model), the handling of outliers (too many or inappropriate calibration samples), and the choice of algorithmic parameters. A brief discussion of each concern follows.

MODEL COMPLEXITY

One must balance the needs of adequately modeling the properties and/or concentrations of interest while avoiding overfitting the calibration data. This is done by setting the model complexity (that is, the number of factors) properly. Assessing how many factors are enough and where the model tips into overfitting can be performed with the aid of diagnostics, but the ultimate decision is usually subjective. Many end-users report spectroscopic models with 20 or more factors, almost always overfitting the data and compromising model flexibility and accuracy for what appears to be a lower calibration error. Selecting too many model factors seriously degrades the ability of the model to track the process and limits its usefulness in the future.

One common practice to decide on the number of factors is to use leave-one-out cross validation, which proceeds as follows. The first sample (spectrum and reference value) is removed from (*i.e.*, left out of) the calibration set and a model is built on the remaining samples. A prediction is made on the left-out sample and the difference between this predicted value and the reference value is recorded. This procedure is repeated until every sample in the data set is left out once and an overall calibration error is estimated based on all of the individual sample prediction errors.

Cross validation is critical, but a leave-one-out approach is most appropriate for small data sets. As the calibration set grows large (more than 50 samples, for example), the chance of having an equivalent pair of spectrum and reference value somewhere else in the data set increases and the error estimate may become overly optimistic. Because most of the calibration data sets used in motor fuel property prediction need to be big to span the variance in the process, a more realistic assessment is done by using a Venetian blind approach on the data, leaving out every n^{th} sample, such that 10-20% of samples are left out at a time. The process is repeated so that every sample is left out exactly once. This approach minimizes overfitting. To better understand how overfitting creates problems in using calibration models, consider the impact of a small spectral perturbation on a chemometric evaluation. Figure 1 shows a Raman spectrum with a minor peak added to an unimportant portion of the baseline.

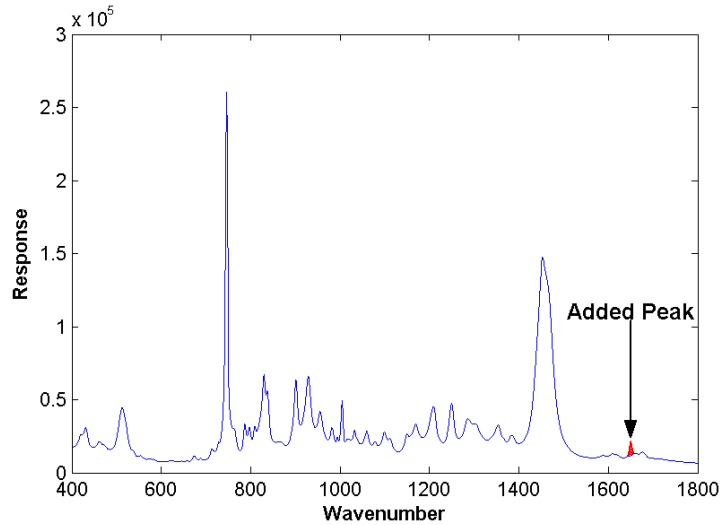


FIGURE 1. RAMAN RESPONSE VS. WAVENUMBER WITH PERTURBATION PEAK ADDED AT 1650 CM^{-1} .

As the concentration of the unusual peak is increased (shown as perturbation level in Figure 2), a model that is overfitting the calibration data will drift further from the expected value. The 24-factor model has a significant change in the estimated concentration compared with the 8-factor model as a function of the perturbation level.

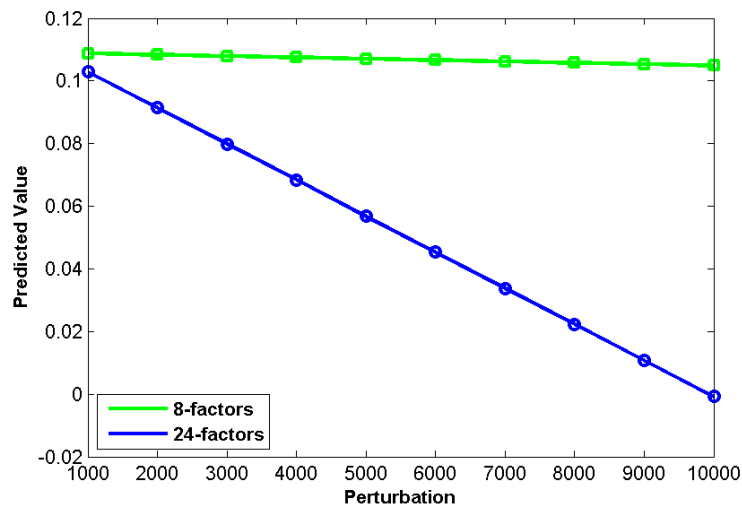


FIGURE 2. PREDICTED VALUE VERSUS PERTURBATION LEVEL. A 24-FACTOR MODEL DEVIATES FROM PREDICTION; AN 8-FACTOR MODEL IS STABLE.

Adding a small amount of noise to a spectrum that is overfit may also increase uncertainty in the predicted value. In another experiment, random noise with an intensity of 0.02% of the maximum

intensity is added across a spectrum, followed by a prediction. After repeating this process 50 times, the results are charted in Figure 3. This demonstrates the problem of overfitting: with each model, predicting the same 50 identical but slightly noise-altered spectra, the standard deviation of the predictions is 3 times larger using the 24 factor model compared to the 8 factor model.

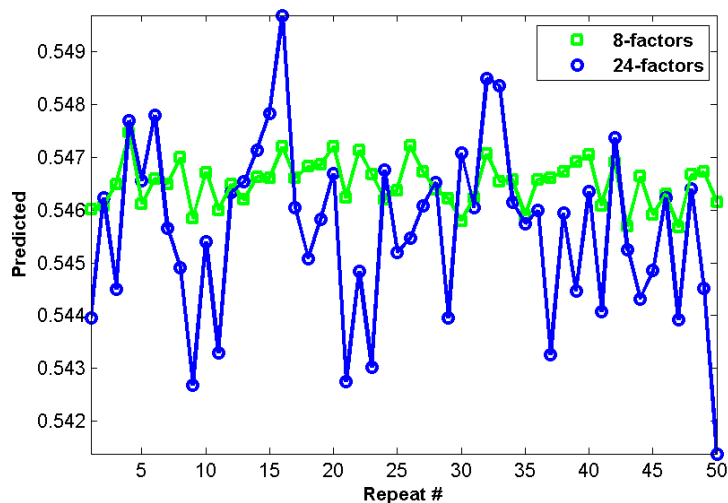


FIGURE 3. THE STANDARD DEVIATION OF PREDICTIONS IS SIGNIFICANTLY LARGER USING THE OVERFIT MODEL.

These examples show the problem that accompanies overestimating the correct number of factors in a PLS model. A metric known as jaggedness works well for avoiding the selection of too many factors. Jaggedness tests the effect of shifting the regression vector by one wavelength unit and computing the difference in the shifted and unshifted spectrum, looking for the point at which noise starts to become a major factor in the model. Combining the jaggedness criterion with the bias error found through the standard error of calibration guarantees a minimum which is a reasonable estimate of the optimal number of factors. The metric successfully balances the variance bias trade off that is implicit in the selection of the number of factors. All following discussions of model results and errors used jaggedness for determining the number of factors in the models.

HANDLING OUTLIERS

Another common mistake is the inconsistent, subjective removal of outliers via methods that are based solely upon visual inspection. Often outlier identification is restricted to an analyst's visual inspection of a model's Y/Y-plot and removal of samples that obviously deviate from the 1:1 ideal. This method of "outlier" removal is a non-statistical method that is likely to both remove samples that are important to the quality of the calibration and while retaining non-obvious statistical outliers. Best Practices removal of outliers should involve investigation of samples using statistically derived metrics, such as Mahalanobis distance, studentized residuals, F-ratio, and leverage. This Best Practices approach is depicted in Figure 4, where a Y/Y plot (left) and two

common outlier diagnostics (right) are examined to identify samples to remove. Outliers are identified with red stars. Note that some 1:1 outliers are still included, and other samples that follow the 1:1 line are separately identified as outliers.

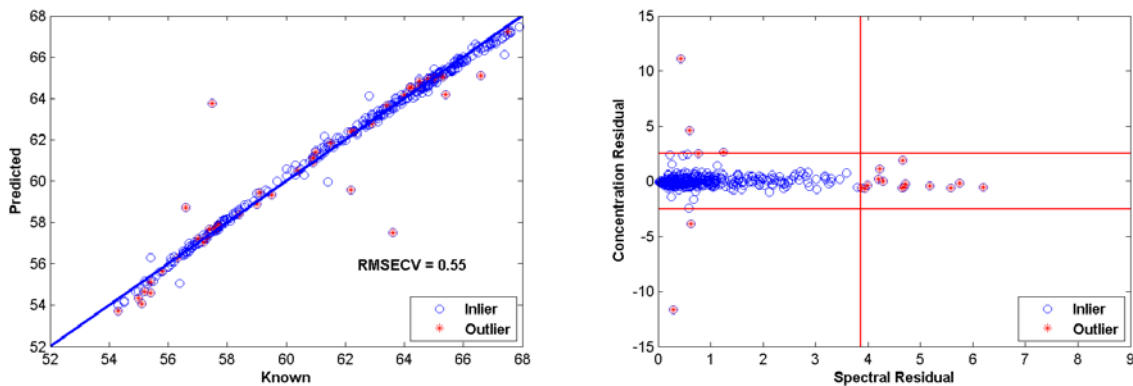


FIGURE 4. Y/Y PLOT (LEFT) AND OUTLIER DIAGNOSTICS (RIGHT) FOR A PLS MODEL; OUTLIERS ARE IDENTIFIED WITH RED STARS.

Without removal of outliers, the RMSECV is shown to be 0.55. After removal of these outliers, a new Y/Y plot (Figure 5, left) shows an improved RMSECV of 0.23. This is a significant improvement in model capability, but the new model also apparently contains further outliers as detected by the same technique (red stars on Figure 5, right and left). This often happens with Best Practices outlier removal approach. There is no consensus as to how many rounds of outlier removal is appropriate, and each round of outlier removal risks improper removal of samples. Even if such a process could be optimized, it is still subjective, can be time-consuming, and the approach will differ depending on the dataset and instrument technology.

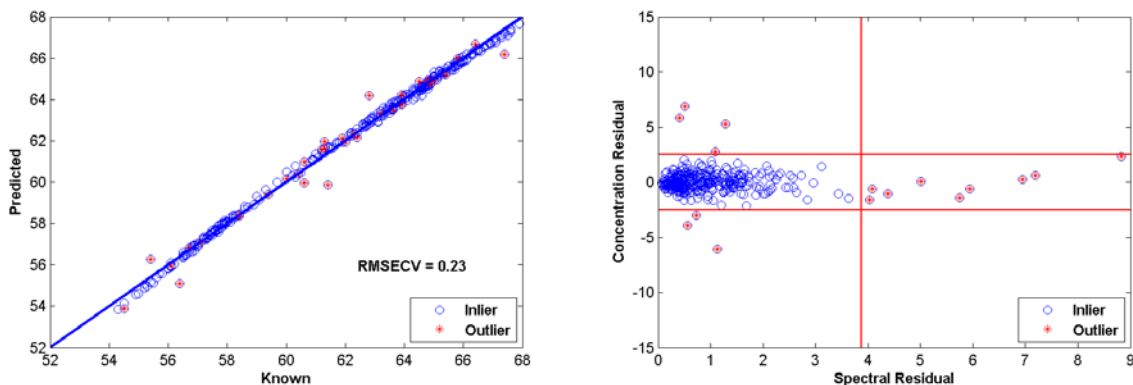


FIGURE 5. Y/Y PLOT (LEFT) AND OUTLIER DIAGNOSTICS (RIGHT) FOR A PLS MODEL THAT HAS ALREADY HAD OUTLIERS REMOVED; NEW OUTLIERS ARE IDENTIFIED ON BOTH PLOTS WITH RED STARS.

There is, however, an objective mechanism for identifying spectra that should not be retained for calibration: RobustPLS, an algorithm that identifies outliers in an automated fashion. Once optimized for a particular instrument and reference measurement, RobustPLS can rapidly define the calibration set with results comparable with, even superior to, analysis performed by an expert. Figure 6 shows diagnostic plots for the same dataset as above with a number of samples that are clear outliers, and also cases that are not identified by common evaluation techniques. This graphic shows the distribution of outliers identified by RobustPLS with the Y/Y plot clearly showing samples that are not normally detected as outliers. When samples are identified by RobustPLS as outliers, but those same samples are not identified by the common evaluation techniques, then masking is taking place. This can occur when there are multiple outliers and they work together to hide one another. When outliers are identified by the common evaluation techniques, but those same samples are not identified as outliers by RobustPLS, then swamping is taking place. This is in some respects even worse than masking because analysts believe they are removing outlier samples when in fact they are removing good samples.

To summarize, RobustPLS helps avoid two scenarios that confound outlier identification by visual means:

- Masking - when bad data points are hidden by other bad data points and thus appear to be good points.
- Swamping - when bad data points make good data points look like bad data points.

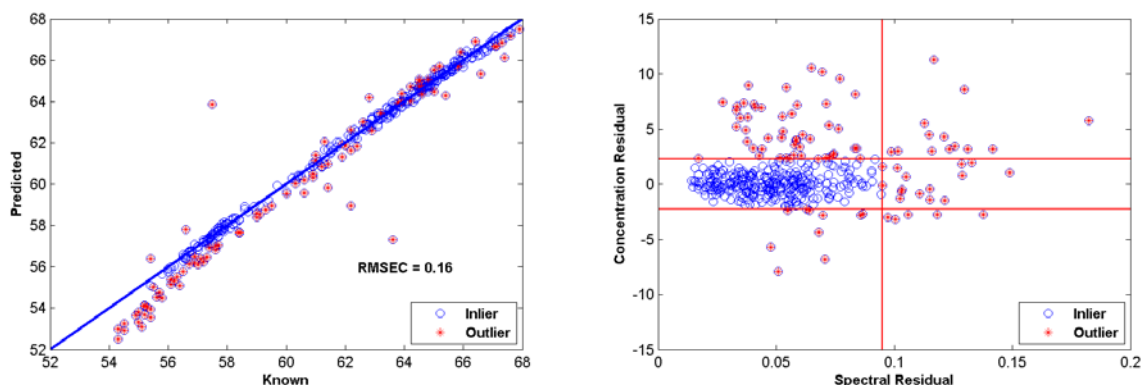


FIGURE 6. Y/Y (LEFT) AND TWO OUTLIER DIAGNOSTICS (RIGHT) PLOTTED FOR ROBUSTPLS MODEL; OUTLIERS ARE DETERMINED BY ROBUST STATISTICS AND ARE MARKED WITH RED STARS.

Removal of the outliers identified via RobustPLS results in the PLS model below in Figure 7 (left) which has cut the initial prediction error by more than 4 fold, from 0.55 to 0.12, and reduced the “best practices” error of 0.23 by half. Outlier diagnostics on this data (Figure 7, right) show results from the application of RobustPLS. These are ideal results that were attainable without multiple passes or operator judgment. Note that some samples that may be considered “outliers” by an analyst have still been included, indicating that RobustPLS identified these samples as statistical inliers. This process is easily automated, allowing for rapid and objective creation of calibration sets.

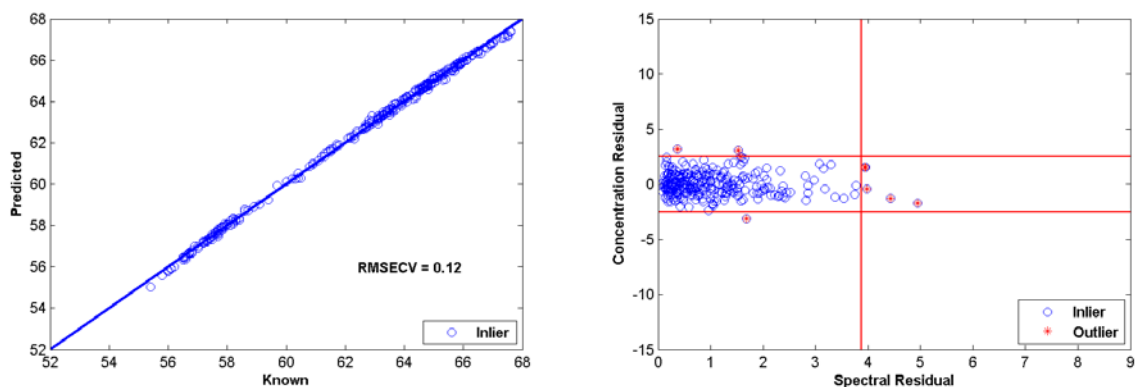


FIGURE 7. ROBUST PLS MODEL (LEFT), AFTER REMOVAL OF OUTLIERS IDENTIFIED IN FIGURE 5; OUTLIER DIAGNOSTICS (RIGHT) SHOWING TIGHT SAMPLE BEHAVIOR.

ALGORITHM PROCESSING

PLS is the modeling algorithm most often selected for spectroscopy systems. This choice is very reasonable in its application to motor fuel properties in that PLS allows for more variables than samples and addresses the colinearity problem and multivariate averaging. That does not mean, however, that selecting the proper number of factors and eliminating outliers are the only decisions that will impact model quality. Preprocessing and transformations are commonly applied and are not discussed here. Spectral range can also be restricted to improve the predictive capacity of the PLS model. Very important but less common is the restriction of the range of samples used during the prediction step; this Enhanced Practice is described here.

Through a large variety of projects, locally weighted regression (LWR) has frequently shown results that rival or improve results from standard PLS. This advanced technique can be found in many commercially available software packages, but is rarely used for motor fuel properties due to a lack of familiarity with the technique. When presented with a prediction task, LWR abridges the data by identifying those samples that most closely correspond to the prediction sample. It then uses this data subset to construct a calibration on the fly and apply it's model to this sample. LWR requires only setting the number of nearest neighbors to use for calibration and set the number of factors.

Using the same example dataset (including outliers identified via RobustPLS) as above, analysis (shown below in Figure 8) shows that cross validation error reaches an equilibrium around 6-8 factors, when using fewer than 150 nearest neighbors.

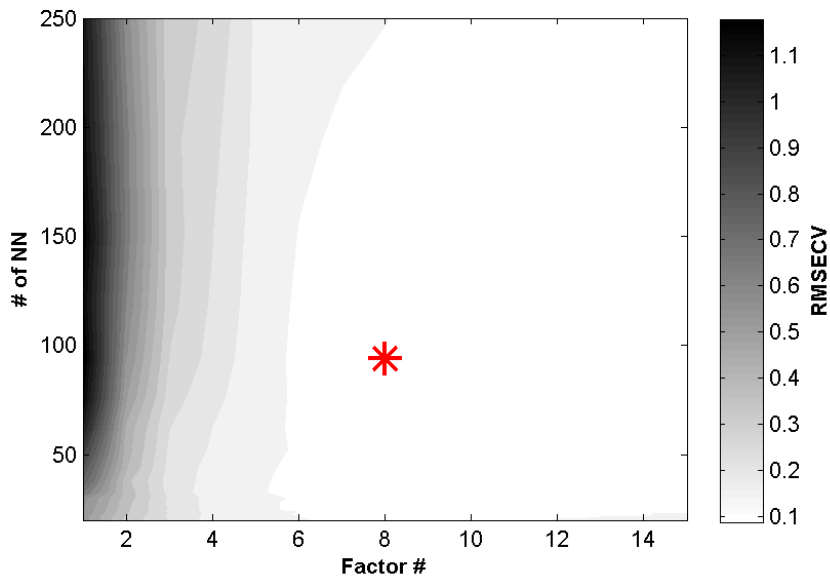


FIGURE 8. ERROR CONTOURS (RMSECV) VS. NUMBER OF FACTORS AND NEAREST NEIGHBORS FOR LWR ANALYSIS.

The final LWR model (Y/Y-plot shown below in Figure 9) used 8 factors and 94 nearest neighbors; final model prediction error was 0.096, one-fifth of the original (Figure 4) and a further improvement on the robust outlier set (Figure 7).

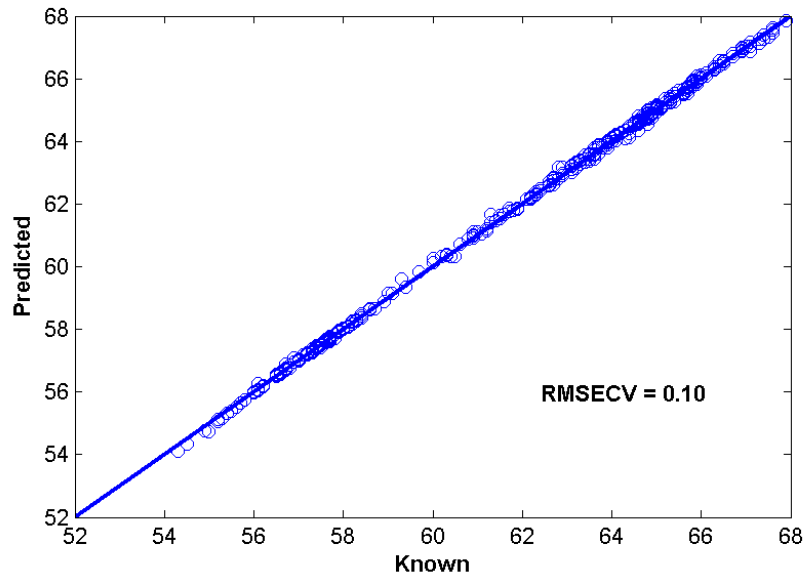


FIGURE 9. Y/Y-PLOT OF LWR MODEL.

Not all properties benefit from such a segmented approach, but there are often significant benefits both in lowering the prediction error and in making the model reliable in a process setting. The value of using LWR is a function of both the instrument type (Raman, NIR, FT-NIR, or mid-IR) and the property of interest.

THE RESULT OF ENHANCED PRACTICES ON MOTOR FUEL PROPERTIES

In review of the results of all of the property predictions, there are clear advantages to expanding the typical set of chemometric tools when performing calibrations. In Table II, we average the results of the five FT-NIR instruments and the four Raman systems into a single table. The numbers are not comparable between these two instrument types; the individual analyses that combine to form this table differ vastly.

The table should be examined for the level of improvement seen as one progresses from Common, through Best to Enhanced Practices. In general, the number of factors stays the same or decreases slightly through this progression. The reader should be careful not to compare the error values between the two instrument types. The errors are affected by a variety of site-specific problems and do not form the basis of a direct comparison. In fact, in one instance where we were able to compare the same samples on the two analyzer technologies, the results were substantially the same.

TABLE II. SUMMARY RESULTS FOR RAMAN AND FTNIR INSTRUMENTS.

Raman Summary Results

	COMMON PRACTICES			BEST PRACTICES				ENHANCED PRACTICES			
	FACTORS	ERROR	% ERROR	FACTORS	ERROR	% ERROR	% IMPROVED	FACTORS	ERROR	% ERROR	% IMPROVED
API	8	1.505	0.035	7	0.601	0.024	86%	8	0.510	0.020	99%
AROMATICS	6	2.720	0.082	6	1.140	0.037	82%	6	0.355	0.013	154%
BENZENE	9	0.106	0.046	8	0.036	0.022	97%	7	0.024	0.016	123%
IBP	9	3.250	0.079	8	2.850	0.091	13%	6	2.650	0.010	20%
T50	7	6.152	0.054	7	4.051	0.049	44%	8	3.220	0.038	65%
FBP	10	13.570	0.071	9	9.660	0.085	34%	9	9.260	0.078	38%
RON	9	1.054	0.069	9	0.652	0.056	45%	9	0.398	0.035	83%
MON	8	1.104	0.090	9	0.533	0.043	68%	9	0.452	0.049	82%

FTNIR Summary Results

	COMMON PRACTICES			BEST PRACTICES				ENHANCED PRACTICES			
	FACTORS	ERROR	% ERROR	FACTORS	ERROR	% ERROR	% IMPROVED	FACTORS	ERROR	% ERROR	% IMPROVED
API	6	0.55	4.0%	7	0.23	1.7%	82%	8	0.10	0.7%	140%
AROMATICS	9	1.08	3.3%	6	0.76	2.6%	34%	10	0.72	3.1%	40%
BENZENE	7	0.05	5.7%	9	0.04	5.5%	16%	9	0.03	4.3%	41%
IBP	6	2.37	4.1%	3	1.83	3.2%	26%	9	1.53	7.0%	43%
T50	7	2.72	4.7%	7	1.44	2.5%	65%	9	1.28	2.6%	71%
FBP	10	4.16	8.3%	4	3.26	6.5%	24%	9	3.32	6.9%	23%
RON	9	0.40	3.2%	8	0.29	2.4%	30%	8	0.24	2.3%	47%
MON	8	0.33	3.9%	7	0.26	3.3%	23%	6	0.20	2.7%	49%

A consistent application of Best Practices yields an improvement in the 30-50% range; Enhanced Practices can provide even greater improvements, depending on the property. Figure 10 shows representative results from one of the FT-NIR instruments.

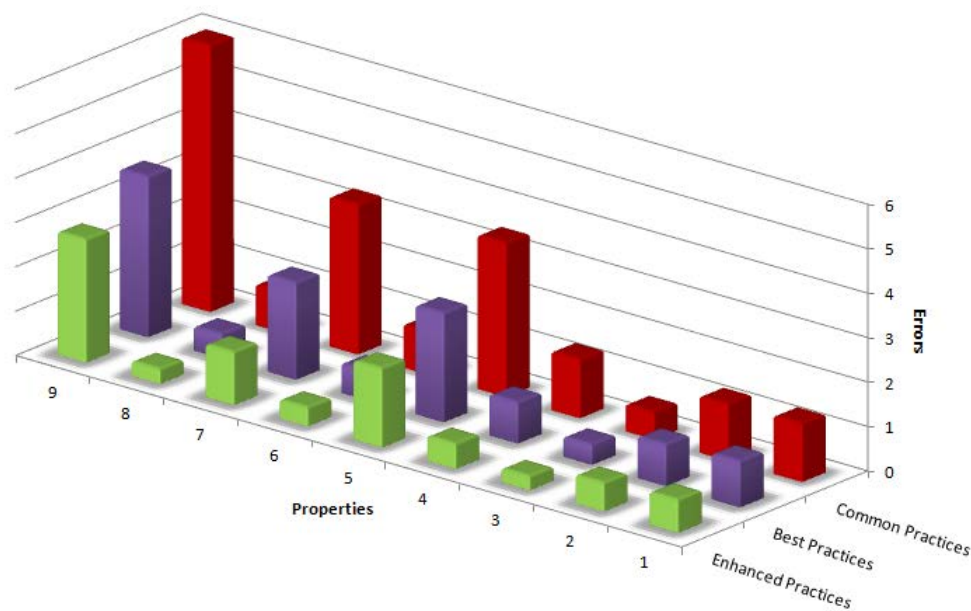


FIGURE 10. IMPROVEMENT OF ONE EXAMPLE INSTRUMENT PREDICTING NINE PROPERTIES USING ENHANCED PRACTICES.

CONCLUSIONS

Based on the processing of a number of data sets, the authors find that it is possible to improve on the standard approach to calibrating optical analyzers. Some benefits described in this paper can be realized without making any change to the existing hardware or installed software. Some improvements, on the other hand, are only available if the instrument company's software is augmented by a more-complete chemometrics package. Further day-to-day improvement is available by adding hardware and software to streamline, even automate portions of the calibration procedure.

Because the choice of samples to include in the calibration can be made outside of the legacy instrument, an optimum set of samples for calibration can be composed and brought into the analyzer software. In testing the RobustPLS approach to calibration sample set assembly, we found that this mechanism is automatable and delivers an objective collection of samples that duplicates or improves the model quality that a talented chemometrician would supply. The authors suggest using the approach embodied in the jaggedness criterion to compliment standard error calculations and avoid overfitting calibration models.

In addition, because of non-linearity in the spectral measurements and changes to the ingredient streams, this study has found that separating the data into smaller subsets can substantially reduce the calibration error for many of the properties being modeled. In general, results were improved by applying PLS to segments in the calibration data set either by using a global PLS model to

select a subsequent final model (hierarchical modeling), or by using the spectral features to identify appropriate samples to use and build the calibration subset on the fly (locally-weighted PLS regression). This is not common in instrument company software, but is available from several third-party suppliers.

Finally, there are areas where a change in procedure is beneficial. The data employed in creating the multivariate calibrations are often not stored in a consistent, orderly manner making it difficult to recreate models. The models are used and subsequently, upon replacement, never reused. Because there are cycles in the operating parameters of a chemical plant or refinery, there may be value in keeping old data either to update the existing calibrations or construct a longer-lasting evaluation schema.

Some specific suggestions:

- Outlier detection should be done on a property-by-property basis; it should not be done globally, and should employ robust methods. This is an objective mechanism to choose an optimal calibration set.
- Select the number of factors with a combination of jaggedness of the regression vector, spectral residuals, and the fit error (RMSECV).
- Use LWR when Y/Y plots exhibit nonlinearity. The calibration data with a reasonable cross validation scheme should be used to estimate LWR parameters and potential model performance improvements.
- Avoid using leave-one-out cross validation; instead, order the spectra by their property value and use a Venetian blind approach.

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