APPLICATION NOTE

FT-IR Spectroscopy

AUTHORS

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Determination of Total Base Number (TBN) and Total Acid Number (TAN) in Lubricants Using FT-IR Spectroscopy and Multivariate Analysis

Introduction

Oil additives are chemical compounds that are added to lubricating oils to improve their performance for specific applications. Different compositions of additives can be used to tailor the lubricating oil for a particular use. The additives are designed to be consumed over the lifetime of the lubricant and, as such, will break down and form new compounds as the lubricant ages. The concentration of these breakdown products, which may be acidic or basic in nature, can be used to assess the quality of the oil.

The Total Base Number (TBN) is a measure of the alkaline concentration present in a lubricating oil sample whereas the Total Acid Number (TAN) is a measurement of the acidity of the sample. These factors can be used to determine whether the current lubricant needs replacing. It is highly important to continuously monitor the lubricating oil in a piece of equipment in order to provide proper maintenance and prevent any problematic issues occurring.

The current main methods for TBN analysis, ASTM D2896 and ASTM D4739, both use titration techniques to determine the basic content in the lubricants.[1] Similarly the current standards for TAN analysis, ASTM D664 and ASTM D974, use titration as well.[2] These methods require reagents which can be both expensive, corrosive and may produce hazardous chemical waste.

As an alternative, FT-IR spectroscopy combined with chemometric techniques can provide rapid TBN and TAN quantification without the need for solvents and other hazardous reagents. Using reference values collected using the traditional titration methods, chemometric techniques, such as Principle Component Regression (PCR), can be used to create a calibration model to rapidly determine the TBN and TAN value of unknown lubricant samples.

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Making a Successful Chemometric Model

In order to create a successful PCR calibration model, there are a number of steps that should be followed, as illustrated in Figure 1. Firstly, the dataset must be defined. Ideally, the dataset should contain approximately 150 - 200 samples that encompass all sample values of interest and give an even distribution of property value. The dataset must analyzed using both FT-IR spectroscopy and the ASTM titration method to obtain a reference value for each sample.

The collected spectra and reference values can then be used to create an initial calibration model. It is at this stage that any gaps in the property value range may be noticed and further samples may be collected and analyzed to fill these gaps in order to make the model more robust.

The number of principal components (PCs) used in the PCR calibration model is an important parameter to investigate. If too few PCs are used then the variation will not be sufficiently modelled and the model will predict poorly. On the other hand, if too many PCs are used then the model will begin to incorporate noise.

Validation should then be performed on the model using a separate set of samples with reference values. Validation gives an indication of how the model will perform on samples not included in the calibration. Throughout the calibration and validation process, outliers should be studied and removed. Outliers may arise from a variety of different causes, such as improper preparation of the standards, improper measurement or measurement error.

Finally, once calibration and validation of the model has been completed and all outliers have been identified and removed, the model can be used to predict values of unknown samples.

Experimental

For the TBN calibration 144 samples of lubricant were analyzed using a PerkinElmer OilExpress™ 4 system, using the parameters shown in Table 1. Reference TBN values were collected by titrating with perchloric acid, as specified by the ASTM D2896 method. This method measures the concentration of all basic dispersant and detergent present in the fluid, expressing the results as mg KOH required to titrate 1 gram of lubricant.

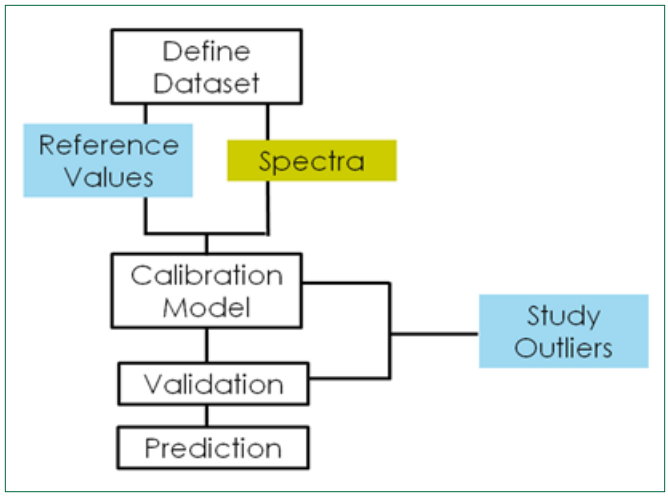

Figure 1: Workflow for creating a successful calibration model.

Table 1: Scanning parameters for TBN and TAN lubricant samples.

Scanning Parameters	
Spectral Range	4,000 – 400 cm^{-1}
Resolution	4 cm^{-1}
Number of Scans	1
Pathlength	0.1 mm

All collected spectra were pre-processed by blanking regions with absorbance values above the upper threshold of 1.5 as these regions are over-saturated. The spectra were also normalized to 0.1 mm pathlength to allow the method to be transferable. Raw and pre-processed lubricant spectra can be seen in Figure 2.

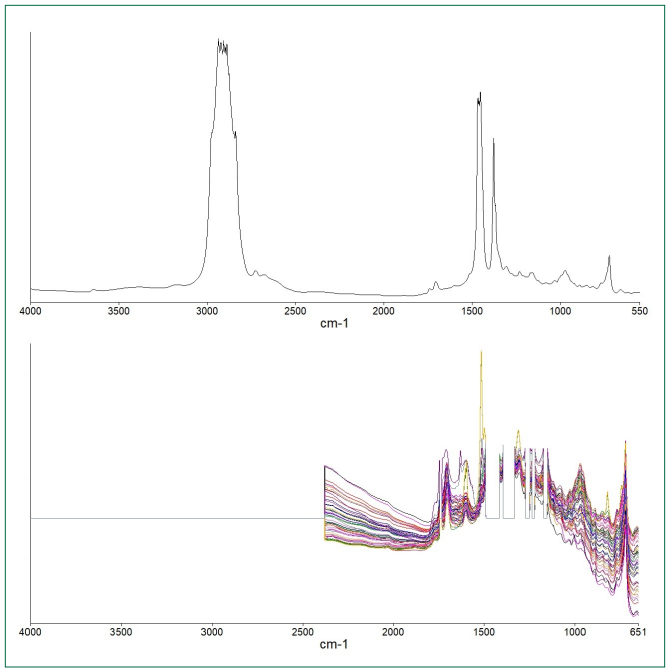

Figure 2: Example raw spectrum of lubricant (top) and pre-processed spectra for TBN model (bottom).

A PCR calibration model was created using PerkinElmer Spectrum Quant™ software. The samples were split such that 114 spectra were used to build the calibration and 30 spectra were used for independent validation of the model. Cross validation was also carried out for the model using the Leave-1-Out method.

Similarly, for the TAN calibration model 135 samples were used with the raw and pre-processed spectra shown in Figure 3. Data for the TAN calibration was processed in Spectrum Quant™ software and saved as a separate method to be run on its own or alongside the TBN method. 23 spectra were used for the independent validation of the TAN model using the Leave-1-Out method.

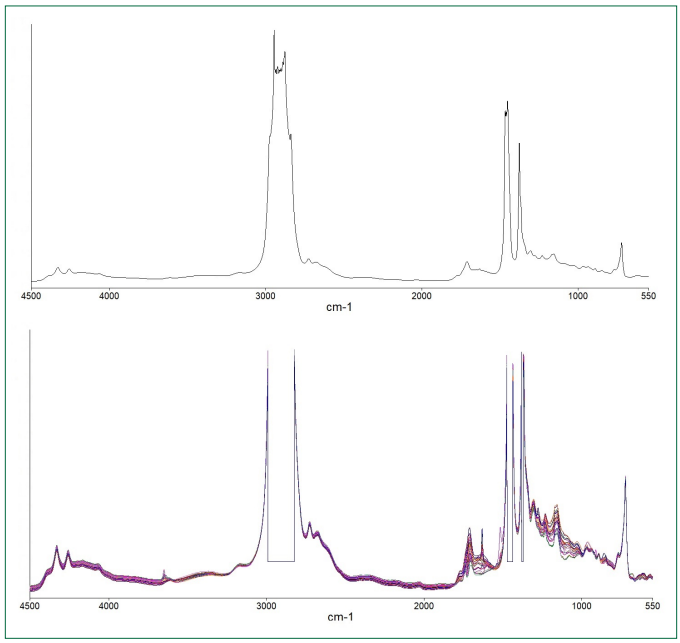

Figure 3: Example raw spectrum of lubricant (top) and pre-processed spectra for TAN model (bottom).

Reference values for the TAN method were collected by titrating with potassium hydroxide as specified by the ASTM D664 method with results expressed as mg KOH/g of lubricant to allow for direct comparisons of measurements.

Results and Discussion

Figure 4 shows the correlation plot for the TBN model, including both the calibration (points in blue) and validation data points (points in red). The data points are evenly distributed around the unity line, indicating a high level of agreement between the specified TBN value and the value predicted by the model.

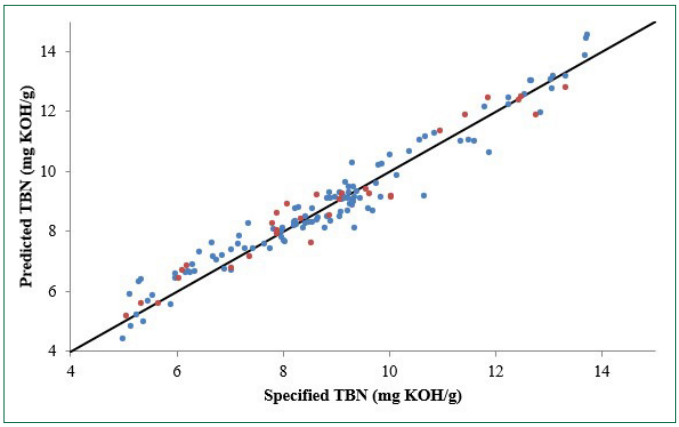

Figure 4: Correlation plot for TBN model showing calibration (blue) and validation (red) data points with solid black line indicating the unity line.

The regression data for the calibration model is highlighted in Table 2. The R^2 value is high, further indicating the good level of correlation between the reference and predicted TBN values. Additionally, the standard error of prediction (SEP) is relatively low.

Table 2: Regression summary for TBN model (where SEC is standard error of calibration, SEP is standard error of prediction and CVSEP is cross validation standard error of prediction).

R^2	SEC (%)	SEP (%)	CVSEP (%)
94.93	0.51	0.55	0.57

Table 3 shows the average independent validation results for the model. The average true and predicted TBN values are close in value which confirms the accuracy of the predictions of the model. In order to further improve the model, a greater number of samples with TBN values between 10.0 – 12.5 mg KOH/g could be used to create the calibration.

Table 2: Regression summary for TBN model (where SEC is standard error of calibration, SEP is standard error of prediction and CVSEP is cross validation standard error of prediction).

Average True TBN Value (mg KOH/g)	Average Predicted TBN Value (mg KOH/g)	SEP (%)
8.86	8.86	0.49

Figure 5 below shows the correlation plot for the TAN calibration model (points in blue) and validation results (points in red). The model built for TAN also demonstrates a high level of agreement between the specified and predicted TAN amounts. However, it is clear to see that the data set used for the TAN model would benefit from the addition of samples with TAN values of between 2.5 – 4 mg KOH/g to fill in the gaps in this calibration.

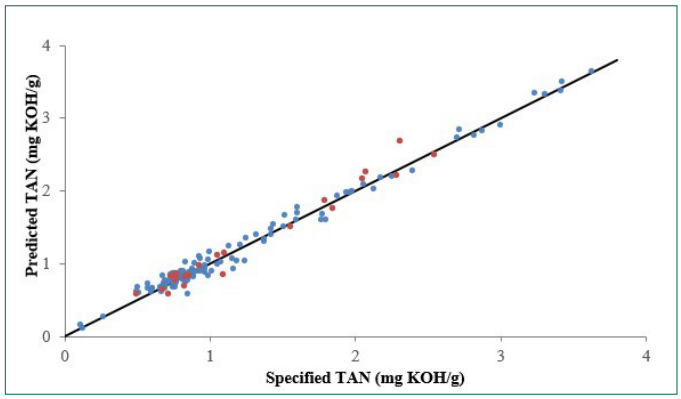

Figure 5: Correlation plot for TAN model showing calibration (blue) and validation (red) data points with solid black line indicating the unity line.

Table 5 displays the regression statistics for the TAN model in the calibration range specified. These stats are indicative of good correlation between the titration reference values and those predicted by the TAN model.

Table 5: Regression summary for TAN model (where SEC is standard error of calibration, SEP is standard error of prediction and CVSEP is cross validation standard error of prediction).

R^2	SEC (%)	SEP (%)	CVSEP (%)
98.45	0.088	0.098	0.103

Finally, Table 6 displays the validation results, further confirming the level of accuracy of our TAN calibration model with a low SEP for the validation data set.

Table 6: Independent validation results for TAN model.

Average True TAN Value (mg KOH/g)	Average Predicted TAN Value (mg KOH/g)	SEP (%)
1.25	1.26	0.12

Conclusions

The results show that FT-IR spectroscopy, with chemometric techniques, can provide an effective and rapid method for determining the TBN and TAN value of lubricants. Reference values collected using traditional titration methods can be used to create a calibration model which can accurately predict both the TBN and TAN value of unknown samples. Once the calibration model has been established, FT-IR spectroscopy can be used to rapidly determine TBN and TAN values of lubricant samples, without the need for solvents or the production of hazardous chemical waste.

It should be noted that the objective of a successful TBN or TAN chemometric model is not to replace the standard titration methods of analysis. The primary titration method will always be required but the chemometric model aims to reduce a significant portion of the titrated samples and, as such, reduce the usage of chemical reagents and consumables to ultimately yield significant savings for a laboratory.

References

1. ASTM D2896-15, Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration, *ASTM International,* West Conshohocken, PA, 2015.
2. ASTM D664 – 18e2, Standard test Method for Acid Number of Petroleum Products by Potentiometric Titration, *ASTM International,* West Conshohocken, PA, 2018.

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