FT-NIR for Online Analysis in Polyol Production

Abstract

Hydroxyl value and other related parameters are very important Quality Control (QC) measurements for manufacturers and users of polyols. Traditionally, these properties have been measured by titration methods. In the past five to ten years, near-infrared (NIR) spectroscopy has become the method of choice for these determinations. This note describes the use of Fourier transform near-infrared (FT-NIR) spectroscopy for these measurements. Examples are provided to demonstrate the precision and accuracy that can be expected when the Thermo Scientific Antaris™ FT-NIR analyzer is employed for these routine quality control measurements.

Introduction

The hydroxyl value is a critical parameter routinely measured by polyol manufacturers to determine the quality of their product. Users of these polyol products often depend on the manufacturer's certification of quality to confirm the appropriateness of the material for their own manufacturing processes. The hydroxyl value measurement is a key criterion for this certification because it reflects critical properties of the polyol, particularly the polymer chain length and purity. These properties, in turn, reflect the physical properties of the material. Ultimately, the physical properties of the product dictate its suitability for the purposes of the end user. Use of a material with inappropriate properties is usually very costly as it leads to the manufacture of products that are not within specifications, wasting production time and materials.

Polyol manufacturers often use the measurement of the hydroxyl value as a critical in-process test to indicate the completeness of a polymerization reaction. Traditionally, this test has been accomplished by a time-consuming titration analysis. In such a testing scheme, samples are collected at specified times during the reaction process. These samples are then taken to a process or QC lab and the titration is performed. The results are calculated and feedback is communicated to the process operator(s). At that point, any necessary adjustments are made.

There are several disadvantages to this type of protocol. The first is the fact that the results of the testing do not reach the process operators for a substantial period of time after sampling is performed. If the reaction has not progressed as expected, a significant period of time has then lapsed before an adjustment can be made. The longer the time lapse, the more disadvantageous such a protocol becomes. Similarly, if the reaction is found to be complete, the process cannot be terminated without risk until the analytical data are received. This results in less-than-optimal production efficiency. Another disadvantage is the fact that the titration analysis gives specific but limited information. This analysis might not show problems with the product if such issues do not affect the hydroxyl value measurement. Finally, titration analyses are labor-intensive and time-consuming. Purchase and disposal of the chemicals needed for titration are often costly. Exposure of the lab workers to these chemicals is also often a major concern.

Fourier transform near-infrared (FT-NIR) spectroscopy has become the method of choice, replacing titration for the measurement of the hydroxyl value in polyols. FT-NIR offers the advantages of speed, simplicity of operation and freedom from the use of noxious chemicals. Operators in the production area can potentially use the technique in an at-line mode. Such a method leads to rapid feedback which allows timely process adjustments and quicker detection of reaction end-points. This, in turn, saves time, improves efficiency and, ultimately, leads to cost savings. Another advantage is that worker exposure to chemicals is greatly reduced by the implementation of FT-NIR methods.

FT-NIR also has the potential to give analysts more comprehensive information about the product. Even if there is a problem that does not affect the hydroxyl measurement, FT-NIR can still detect deviations while a titration may not. Many times, polyol manufacturers must also measure other parameters related to the hydroxyl value. For example, polyester producers must measure acid number. FT-NIR has been proven to be advantageous for these measurements and other critical measurements for polyol products. Hence, the use of FT-NIR can help to streamline processes by allowing the measurement of multiple properties with one data collection event.

This note will show examples of the utility of the Antaris FT-NIR analyzer for the determination of the hydroxyl value and other critical polyol properties. The precision and accuracy of this technique for such measurements will also be demonstrated.

Experimental

Samples

Polyol samples were obtained from various proprietary sources. Both liquids and solids were used for this study.

Instrumentation

An Antaris FT-NIR Method Development Sampling (MDS) System was used to collect all of the data reported.

In the case of the liquids, the samples were transferred into standard 7 mm diameter disposable vials for measurement. The vials were then placed directly in the transmission sampling compartment using the three-position transmission holder (see Figure 1). The advantages of using these vials, in addition to the convenience of a disposable container, are that they are inexpensive and they do not have to be cleaned between measurements. This minimizes operator time and effort and increases sampling throughput. It also simplifies the measurement process allowing busy process personnel to accomplish the measurements without having to divert their attention from their main task for a long period of time.
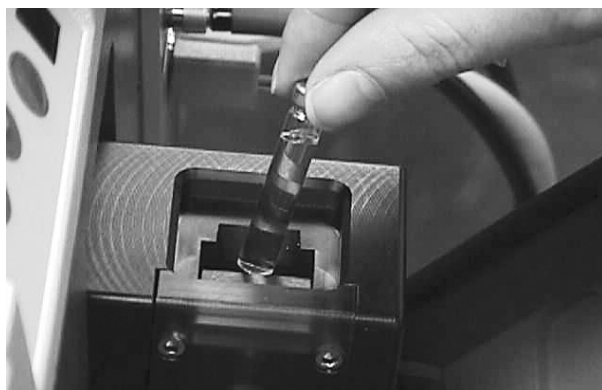

Figure 1: Transmission sampling module

The Antaris three-position heated transmission holder allows for precise control of the sample temperature during data collection, eliminating variability due to sample temperature. The temperature of the sample can be controlled to ± 0.1 °C with temperature control information clearly displayed by the Thermo Scientific RESULT™ data collection software (see Figure 2). A temperature equilibration delay ensures that the sample is at the proper temperature for the analysis. To increase sample throughput and reduce equilibration time, the samples can also be preheated using the external heater shown in Figure 3. This capability was employed for one of the sample sets in this study.
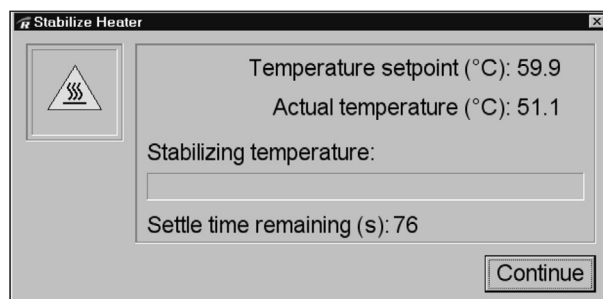

Figure 2: Temperature control in RESULT software

Figure 3: External heater for sample preheating

The solids used in this study were translucent resins. Data were collected for these samples using both transmission and reflectance. From these experiments, it was determined that the transmission data were superior. For the transmission measurements, the Antaris Tablet Transmission Module was used. Although this module was designed for transmission measurements of pharmaceutical tablets, it is also ideal for measuring many other types of translucent solids. The measurement is very convenient – it simply requires the placement of a solid on the plat-form as shown in Figure 4. To per-form the measure-ment, the detection module is lowered onto the sample.

Figure 4: Easy solid transmission sampling

For the study, spectra were collected from 4000-10,000 cm^{-1} and from 4000-12,000 cm^{-1} using RESULT software. Data were collected at 8 cm^{-1} resolution using 50-100 co-averaged scans. One of the principal advantages of the software is its simple end-user interface. RESULT allows a one-button actuation of a routine analysis to produce a customized report. The format for this report is prepared for the operator in advance by the method developer. All data analyses were performed using Thermo Scientific TQ Analyst™ quantitative analysis software. Second derivative normalization and/or Multiplicative Scatter Correction were used for baseline correction. Partial Least Squares (PLS) and Stepwise Multiple Linear Regression (SMLR) algorithms were used to derive quantification models.

Results and Discussion

Sample Set 1

The first sample set used for this study contained surfactants. A titrimetric reference method was employed to obtain data for the hydroxyl value and acid number. Figure 5 shows the spectra for these samples. Figure 6 shows the same spectra following transformation using a Norris second derivative (segment 19, gap 5).
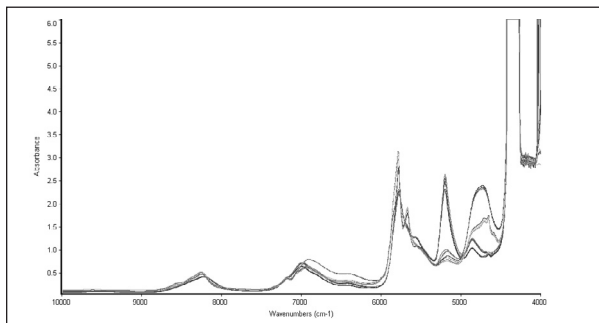

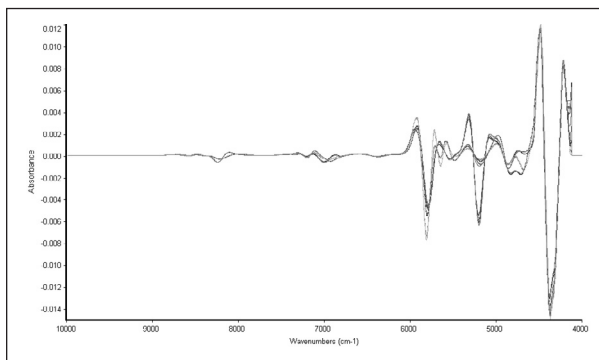Figure 5: Plot showing overlay of untreated spectra for samples from Set 1

Figure 6: Plot showing overlay of 2nd derivative spectra for samples from Set 1

From the data, it is evident that four classes of materials were used. The classes were functionally related but distinct. Samples representing five batches of each class were provided for calibration. A goal of this study was to determine if one calibration for each parameter could be constructed from these data or if the set would have to be divided to make multiple calibrations. One calibration would be preferable because it would reduce the amount of effort required for method development and long-term method maintenance.

Figure 7 shows the second derivative plots of the spectra in the region of the first hydroxyl overtone. An SMLR model employing data points at 6854 cm^{-1} and 8011 cm^{-1} was found to give the best results for this sample set for the hydroxyl number. In an SMLR calibration, the first data point normally provides information about the component of interest while the second data point often provides compensatory information about the matrix. Note that the primary data point is in the hydroxyl overtone region while the second data point is near an isosbestic point (the point where all the spectra intersect) in the region of the combination overtone bands. Isosbestic points often provide a good region to assess matrix variation. The calibration plot for this model is shown in Figure 8. The correlation coefficient was 0.9999 while the Root Mean Squared Error of Calibration (RMSEC) was 1.89 mg KOH/g. The RMSEC is essentially one standard deviation calculated for the NIR predicted values relative to the reference values. It represents one sigma for the expected method error. The Root Mean Squared Error of Cross Validation (RMSECV) was 2.59 mg KOH/g using a leave-one-out protocol. The fact that the RMSECV was relatively close in value to the RMSEC suggests that the calibration is viable. The range of reference values was 70 to 350 mg KOH/g. The precision (Percent Relative Standard Deviation or %RSD) of the results for five replicate measurements of the same surfactant was 0.55%.
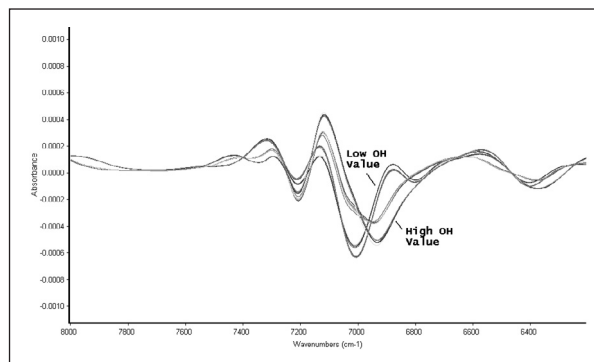

Figure 7: Plot showing overlay of 2nd derivative spectra in the O-H overtone region for samples from Set 1
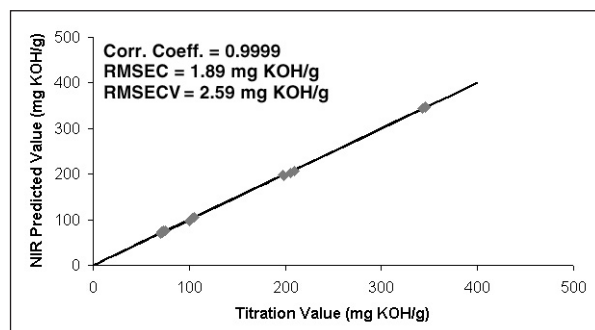

Figure 8: Calibration plot for hydroxyl value for Sample Set 1

For the acid number, a 3-factor PLS calibration model was used. When the whole data set was used for calibration, it was evident that an outlier was present (see Figure 9). However, when this outlier was removed, a good calibration was obtained using the data from 4500-8900 cm^{-1}. The calibration plot generated after the removal of the outlier sample is shown in Figure 10. A correlation coefficient of 0.9980 and a RMSEC of 0.129 were obtained for sample values ranging from 0.8 to 6.0 mg KOH/g. An RMSECV of 0.186 mg KOH/g was obtained with a leave-one-out protocol. The %RSD of five replicate measurements of the same surfactant was 1.65%.
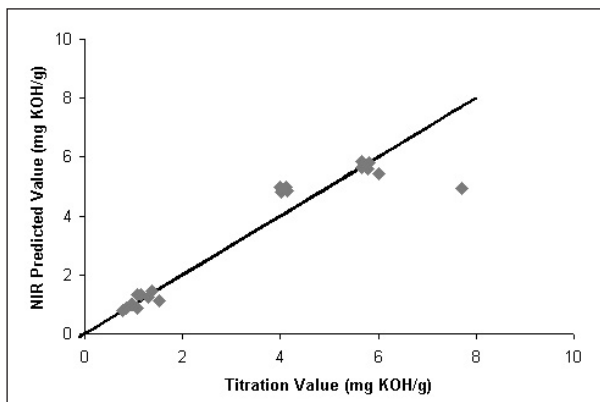
Figure 9: Effect of outlier on acid number calibration for Sample Set 1
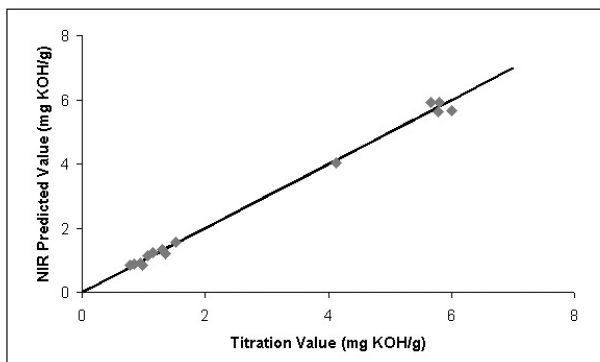
Figure 10: Calibration plot for acid number for Sample Set 1

It is important to note that the reference data for the two parameters of interest were not significantly intercorrelated. Two parameters are intercorrelated when, as the value for one parameter changes, the other also changes in a linear relationship. Parameter intercorrelation can be determined by plotting Parameter 1 values versus Parameter 2 values and calculating the correlation coefficient. A correlation coefficient of zero indicates that the parameters are not correlated. When the parameters such as hydroxyl and acid value are intercorrelated the more dominant spectral species will be used for both calibrations. This is an important consideration because it is often difficult to calibrate for constituents independently when the reference data are well correlated with one another. This is particularly true for the constituent with the weaker spectral response. In this case, the correlation coefficient between the hydroxyl value and acid number was 0.731.

Sample Set 2

For the second set of liquid samples, the important parameters were hydroxyl value and residual ethylene oxide (EtO). For the former, a titration method was used to obtain the reference data while a headspace gas chromatographic procedure was used to obtain reference data for the EtO.

In this case, the temperature was controlled by RESULT software at 50 ± 0.1 °C during data collection. This was done because two of the samples contained a significant amount of particulate matter. Upon heating, the particles disappeared which allowed for much better sample-to-sample consistency. Samples were pre-heated in a heating block to minimize the equilibration time required inside the sample block.

Figure 11 shows the full-range spectra for the calibration samples. For the hydroxyl value information, an SMLR calibration with three data points was used. Figure 12 shows the calibration plot for the hydroxyl value. This calibration resulted in a correlation coefficient of 0.9994 with an RMSEC of 0.780 mg KOH/g. The RMSECV was 0.951 mg KOH/g. The range of values was 23.40 to 116.0 mg KOH/g.
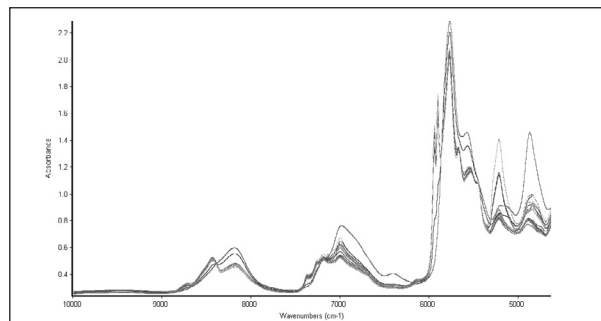

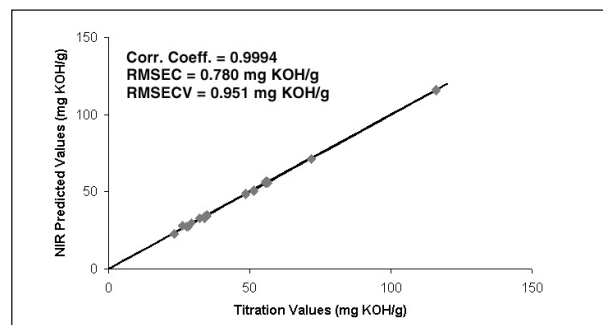Figure 11: Plot showing overlay of untreated spectra for Sample Set 2

Figure 12: Calibration plot for hydroxyl value for Sample Set 2

For the EtO information, a three-point SMLR calibration was also developed with a correlation coefficient of 0.9999 and an RMSEC of 0.400. The EtO data ranged from 1.78 to 100 parts per thousand (ppt). The RMSECV for this calibration was 0.460. Figure 13 shows a plot of the calibration results for the EtO component. The correlation between the two components was 0.624 indicating that there was little concern about the intercorrelation of the data.
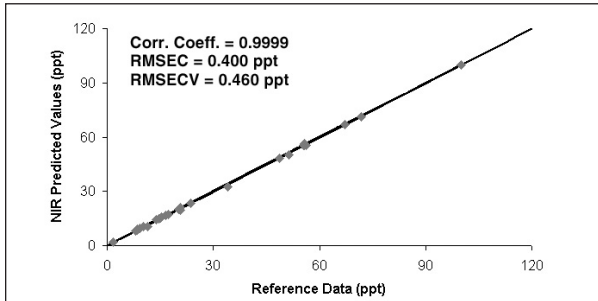

Figure 13: Calibration plot for EtO for Sample Set 2

Sample Set 3

The third sample set used in this study was composed of polyester resin materials obtained at various stages during the production process. These samples were hard, translucent solids. The objective of this study was to ascertain the utility of FT-NIR for: 1) the assurance that the esterification reaction is proceeding adequately, and 2) the determination of the reaction end-point. The samples were conveniently analyzed with the Standard Tablet Module on the Antaris analyzer. The ease of sampling allowed this analysis to be carried out at-line. The two parameters of interest for this set of samples were the hydroxyl value and acid number. The untreated spectra for these samples are shown in Figure 14. The expanded second derivative spectra are shown in Fig-ure 15. The data were pre-treated using a Norris derivative with a 17-point segment.
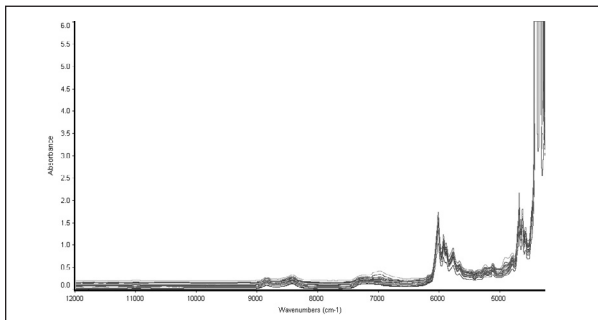

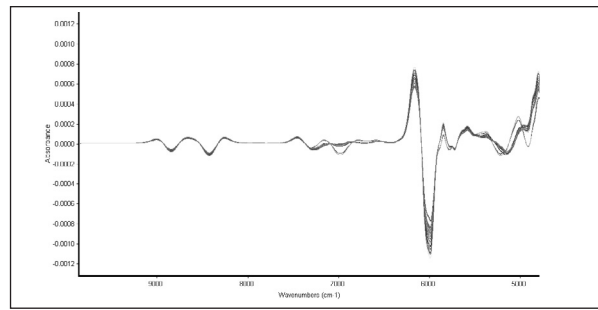Figure 14: Plot showing overlay of untreated spectra for Sample Set 3

Figure 15: Plot showing expanded overlay of 2nd derivative spectra for Sample Set 3

For the hydroxyl value calibration represented in Figure 16, a one-term SMLR model was used. The primary data point used was 5068 cm^{-1} while 5168 cm^{-1} was used as a denominator data point. The samples were collected for analysis by drawing the warm, liquefied production samples from the reactor and allowing them to harden in an aluminum pan. The pathlength for all of the samples was similar but could not be precisely controlled. The denominator data point is advantageous for this type of situation. It serves to compensate for the resultant pathlength differences among the samples. This is much easier than attempting to prepare samples with pathlengths that are consistent from one to the next. For this calibration, a correlation coefficient of 0.9995 was obtained. The RMSEC was 0.552 and the RMSECV was 1.99. The data ranged from 7.1 to 62.6 mg KOH/g.
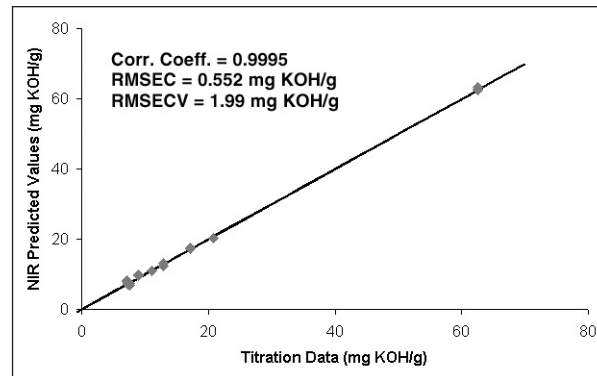

Figure 16: Calibration plot for hydroxyl value for Sample Set 3

For the acid number calibration, a two-term SMLR calibration model was constructed. The plot shown in Figure 17 represents the results for this model. Using 5315 and 5153 cm^{-1} as the primary data points and 4837 cm^{-1} as the denominator data point, a correlation coefficient of 0.9950 and an RMSEC of 1.31 mg KOH/g were obtained. The first data point at 5315 cm^{-1} is in the region of the relatively weak second carboxyl overtone. Not surprisingly, the second data point (5153 cm^{-1}) is in the hydroxyl region suggesting it might play a role in compensating for the matrix effects. The RMSECV for this calibration was 1.73 mg KOH/g for primary values that ranged from 8.6 to 47.8 mg KOH/g.
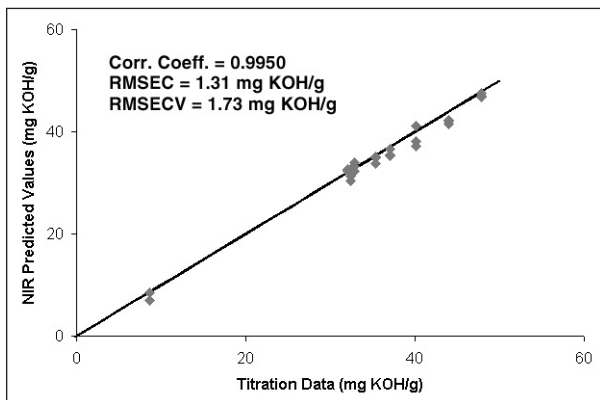
Figure 17: Calibration plot for acid number for Sample Set 3

It should be noted that the first chronological sample, which is taken prior to the final charge of acid, represents a critical data point particularly for the acid number calibration. This is due to the fact that the hydroxyl value and acid number data are otherwise intercorrelated (see Figure 18). The correlation coefficient for the total data set is -0.709 (acid number versus hydroxyl value). If the first sample is removed, the correlation coefficient becomes 0.996.
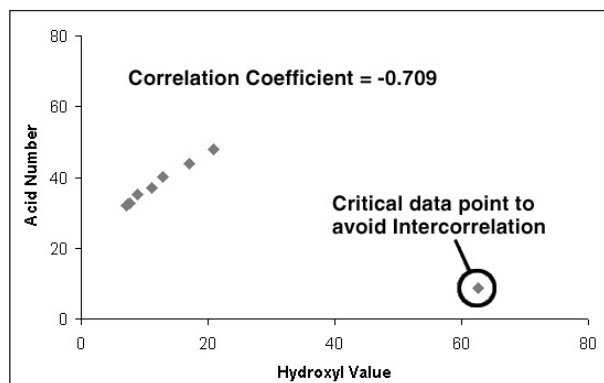

Figure 18: Plot showing correlation of hydroxyl value and acid number data for Sample Set 3

Conclusions

Calibration details for three sets of data have been presented in this note. For all three, the hydroxyl value is a critical parameter in determining the quality of the final product and/or the status of the chemical reaction used to produce the final product. In two out of the three cases, the acid number is also an important measurement while ethylene oxide monomer was an important parameter in the other case. Good correlations, calibration errors and cross-validation data were found for all of the calibrations. FT-NIR measurements for all of these properties were shown to be both accurate and precise for near-line, at-line or QC lab determinations.

For all six measurements, the Antaris FT-NIR analyzer was shown to be an excellent alternative to the reference method (titration or gas chromatography). The Antaris FT-NIR analyzer provides several advantages: faster sample analysis, accurate and reliable temperature control, reduced operator-to-operator variability and reduced costs by eliminating the use of solvents. Production efficiency will be enhanced with quicker availability of critical data, which can be used to make adjustments to the process. The use of Antaris for this purpose helps achieve goals for quality management programs such as Six Sigma or Total Quality Management (TQM).

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