

Determining the Hydroxyl Value for Polyols Using FT-NIR

Steve Lowry, Ph.D., Michael Garry, Matthew Gundlach, Thermo Fisher Scientific, Madison, WI, USA

Key Words

FT-NIR Spectroscopy, Hydroxyl Value, Polyol, Polyurethane

Introduction

Polyurethane is one of the most flexible classes of polymers available on the market. Polyurethanes are found in numerous consumer products, including car upholstery, golf grips and tennis racquets. These unique polymers are produced by the reaction of a polyol with an isocyanate. As shown in Figure 1, the polyol and isocyanate reactants typically contain two or more functional groups.¹ The final polyurethane polymer is based on the carbamate, or urethane linkage.

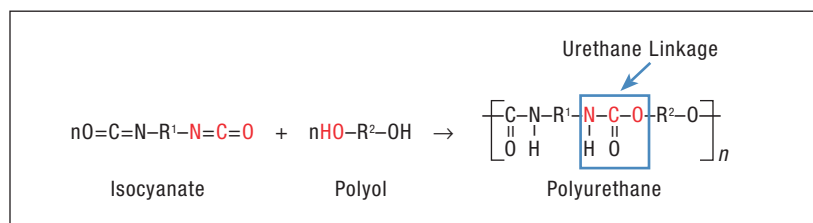
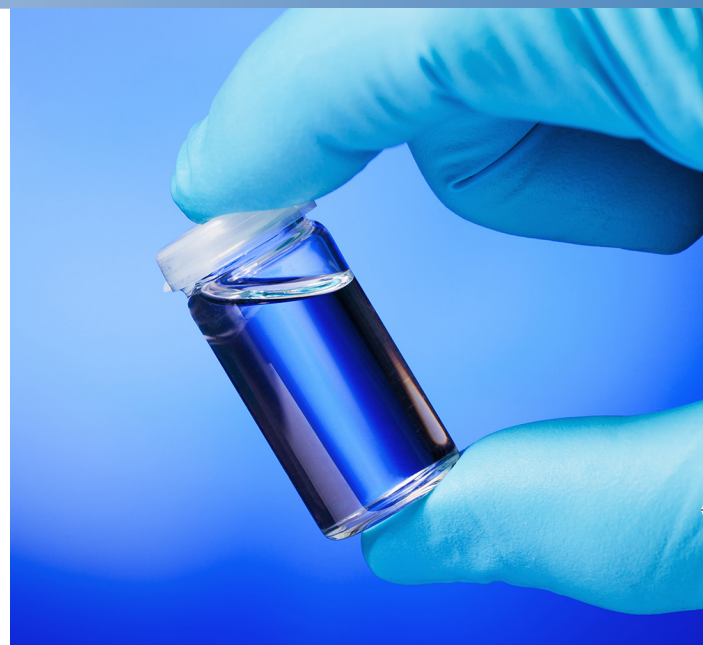


Figure 1: Reaction equation for polyurethane

The physical properties of polyurethane are controlled by a variety of factors during the manufacturing process, including the molecular nature of the polyol starting material. The number of reactive hydroxyl groups (-OH) on the polyol directly impacts the quantity of urethane linkages, which greatly influences the physical properties of the final polyurethane product. Traditionally, the number of hydroxyl groups on a polyol was determined by reacting the polyol with acetic acid and then titrating with potassium



hydroxide (KOH). The milligrams of potassium hydroxide required to neutralize one gram of the solution is called the hydroxyl value, as discussed in ASTM D4274-11.² This wet chemistry method is complicated, time consuming, and requires several reagents. More recently, Fourier transform near-infrared (FT-NIR) spectroscopy has been used to determine the hydroxyl value of various materials, per ASTM D6342-12.³ With modern FT-NIR instrumentation, small amounts of sample can be analyzed in less than one minute. In this application note, we describe a method used to analyze a series of polypropylene glycol samples with a variety of hydroxyl values using the Thermo Scientific™ Nicolet™ iS™5N FT-NIR spectrometer configured with an iD1H Heated Transmission accessory.

Experimental Conditions

A quantitative calibration for hydroxyl value was created using a set of six polypropylene glycol samples purchased from Sigma-Aldrich®. The hydroxyl values of the six samples ranged from 28 to 263 mg KOH/g. One milliliter of each standard was transferred into an 8 × 40 mm glass vial having an approximate sample pathlength of 6 mm. The vials were then placed into the iD1H Heated Transmission accessory, which holds the sample temperature constant at 40 °C to provide more consistent results by reducing sample temperature variability. The samples were allowed to stabilize for one minute in the iD1H Heated Transmission accessory before being analyzed on the Nicolet iS5N FT-NIR spectrometer, as shown in Figure 2. The instrument was configured with a CaF₂ beamsplitter, tungsten-halogen light source, and a high-sensitivity indium gallium arsenide (InGaAs) near-IR detector. Spectra were acquired from 11,000 to 4000 cm⁻¹ in less than one minute (90 scans at 8 cm⁻¹ resolution).



Figure 2: Nicolet iS5N FT-NIR spectrometer equipped with the iD1H Heated Transmission accessory

Once the spectra of the polyol standards were collected, they were opened in the Thermo Scientific™ TQ Analyst™ quantitative analysis software for calibration model development. TQ Analyst is a valuable chemometrics package that allows users to easily construct calibration curves for a given data set. In the TQ Analyst software, calibration curves can be built using a variety of quantitative models, from single variable methods to the most robust statistical analysis algorithms.

Results and Discussion

The most basic quantitative analysis model is known as Simple Beer's Law (SBL), which is useful for many single component calibration curves where peak shapes are well defined and only characteristic of the component of interest. When the SBL calibration model was applied to the hydroxyl value standards, a less than ideal calibration curve was generated. In Figure 3, the correlation coefficient for the standards is fairly strong at greater than 0.999, but the method lacked accuracy, as it did a poor job predicting the actual hydroxyl values. The poor prediction is manifest in the Root Mean Square Error of Calibration (RMSEC), which describes the error of each data point. The large RMSEC of 6.26 is indicative of an inaccurate model.

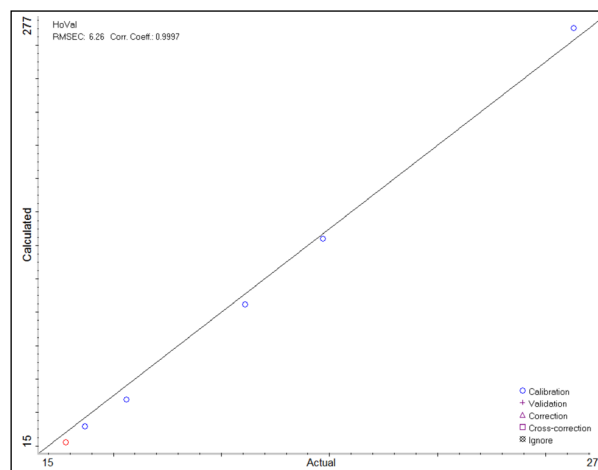


Figure 3: Calibration curve for hydroxyl value – SBL model

The SBL calibration had difficulty modeling the polyol standards set because the spectral features were broad, had regions of overlap, and exhibited chemical matrix interdependencies. In more complex quantitative calibrations, multivariate statistical analysis techniques are often required. The Partial Least Squares (PLS) mathematical model is one of the most popular statistical methods and can help optimize the calibration data. A PLS model successfully calibrates the data set even when spectral features overlap, multiple components of interest are present, and the relationship between component concentration and absorbance is non-uniform. PLS also allows statistical correlation of spectral features to other non-spectroscopic reference methods, such as wet chemical titrations or chromatography.

The PLS model can use multiple spectral regions to build the calibration. To simplify the process of determining the spectral regions to use, TQ Analyst software employs a region selection tool, which automatically analyzes the spectral data and selects the regions that best correlate to the number of alcohol functional groups. In this method, TQ Analyst software selected two wavenumber regions, as shown in Figure 4. The selected regions contained a high amount of variation in the peak intensities, which directly correlated to the number of hydroxyl groups on the polyol standards.

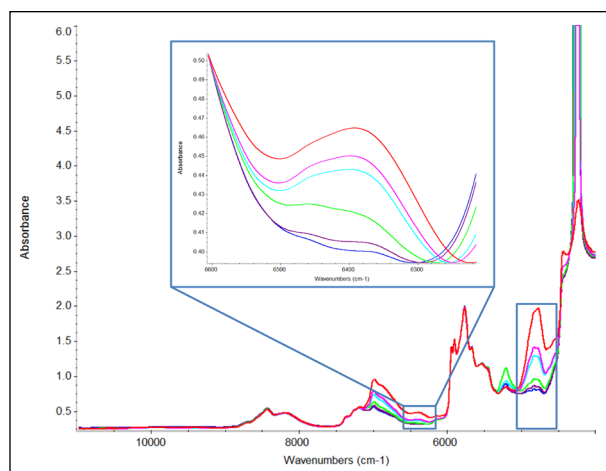


Figure 4: Automatically selected polyol spectral regions

Once the regions were selected and a 2nd derivative applied, the calibration curve from the PLS model was generated (Figure 6). The resulting correlation coefficient was 1.0000 and the RMSEC was only 0.652. As shown by the improved correlation coefficient and the drastic decrease in the RMSEC, the PLS statistical model provided a stronger representation of the polyol standard sample set than the SBL model. It should be noted that in many industrial situations, the sample matrix may vary over time. To construct a robust model that accounts for this variation, a more substantial calibration set that is periodically updated may be required.

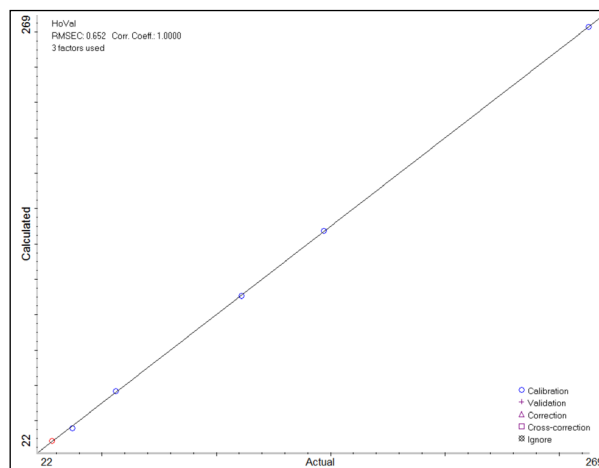


Figure 6: Calibration curve for hydroxyl value – PLS model

Before the calibration curve was generated, a Norris second derivative was applied to each standard. Taking the second derivative of the original spectra is a common practice to eliminate baseline effects and helps provide more accurate and consistent results. Figure 5 shows the original spectra from a polyol standard (red) and its resulting second derivative (blue).

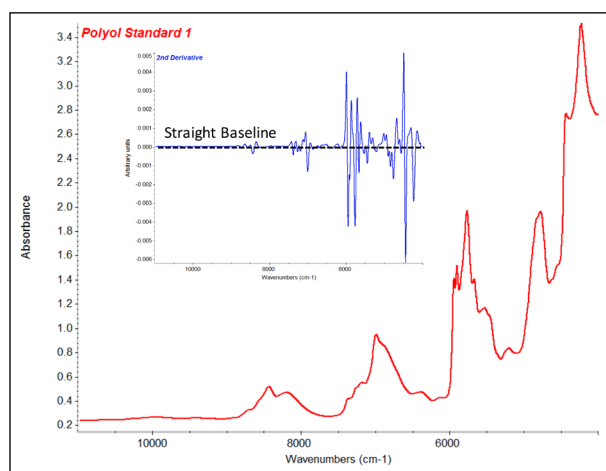


Figure 5: Original and 2nd derivative spectra

Once generated, the PLS calibration curve was used to calculate the hydroxyl value of a sample. The result for a single measurement of a polyol sample with a hydroxyl value of 111 mg KOH/g is shown in Figure 7. The PLS calibration calculated the hydroxyl value to be 111.08 mg KOH/g, resulting in a percent error of only 0.07%.

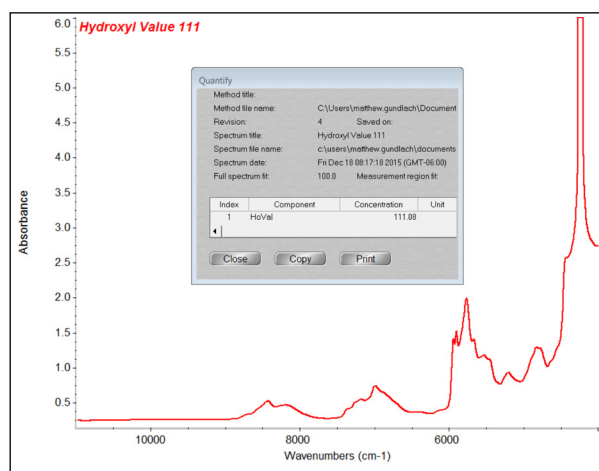


Figure 7: Polyol sample with quantitation result

To determine the precision of the Nicolet iS5N spectrometer and the iD1H accessory, the measurement was repeated 30 times over the course of two hours. To make analysis more efficient, an automated collection process was developed using the Thermo Scientific™ OMNIC™ Macros\Basic™ software program. Macros\Basic is a workflow generator available in the OMNIC software suite that is used in the quality control and process environments to automate standard operating procedures (SOPs). These automated SOPs simplify operation for non-technical users and ensure more consistent results. The Macros\Basic workflow and the stability study results are shown in Figure 8. The graph also contains the error limits for the hydroxyl value sample, defined as three times the standard deviation. These results indicate a stable prediction of the hydroxyl value over the time period tested.

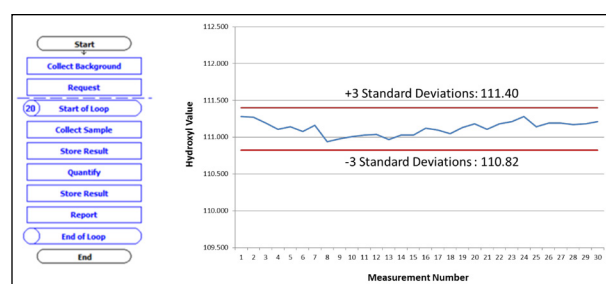


Figure 8: Macros\Basic command line and stability study results

Conclusion

Determining the hydroxyl value of the polyol reactants is a crucial step to ensure the polyurethane products exhibit the desired physical and chemical properties. The Nicolet iS5N FT-NIR spectrometer and the iD1H Heated Transmission accessory provided exceptional accuracy and repeatability in the prediction of hydroxyl value in polyols. While the SBL calibration model did not account for all variations in the data set, the PLS model with second derivative spectra produced much better results. By automatically selecting the best spectral regions and eliminating baseline effects, the PLS statistical model accurately determined the hydroxyl value in a wide variety of polyol samples. The automated workflow developed by Macros\Basic software allowed for an easy determination of instrumental precision. A similar automated workflow can be applied in a production QC environment to quickly and accurately determine the hydroxyl value of incoming or in-process materials.

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