

FT-NIR Spectroscopy**Author:****Ian Robertson**PerkinElmer, Inc.
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The Determination of Hydroxyl Number in Polyols Using the Spectrum Two N FT-NIR Spectrometer

Introduction

Near-infrared (NIR) spectroscopy is an invaluable tool for the quantitative analysis of a wide range of chemical compounds. In combination with a number of chemometric methods, the technique provides a fast, non-destructive

route to the determination of physical and chemical properties. NIR sampling of both solids and liquids requires no sample preparation and can be performed using disposable sampling media such as glass vials.

This application note describes the use of FT-NIR spectroscopy in a typical polyol analysis with an outline of the development of the workflow designed for routine use and quantitative method used for the application.

Polyols are long-chain polymers which contain alcohol functional groups and are produced via reactions involving organic oxides, acids, and multi-functional alcohols. A wide range of products – including surfactants, foams, paint additives, and adhesives – are manufactured using polyols. The production of polyurethanes, for instance, involves polyol intermediates. Current analysis of the polyols produced normally take the form of back titrations. The resultant OH number is an average value over a number of titrations reported as the mg KOH per gram of sample. The ASTM titrimetric method takes approximately 12 minutes per sample, the DIN method approximately 40 minutes. These current methods for determining OH number are expensive, time consuming, and prone to human error and variability.

A typical NIR-based application is faster, more precise, and reliable than other methods. It also reduces the need to handle potentially hazardous substances. The bands in the NIR region (ca. 15000 – 3000 cm^{-1} , 667 – 3333 nm) are primarily overtones and combination bands normally associated with C-H, N-H and O-H bonds. Since organic polymers are composed of carbon, hydrogen, nitrogen and oxygen atoms, the NIR spectra of polymers feature sharp, strong absorbance bands. Polymer manufacturers can use NIR spectroscopy to perform analyses on the production site. This has obvious advantages in the area of quality assurance, giving instant results using a simple measurement. ASTM method D6342-08 gives guidance for the procedures to be used when developing NIR spectroscopic methods for determining hydroxyl numbers in polyols.

A typical NIR method development for OH determination consists of first assembling a set of reference samples that should span both the expected analyte range and spectral variance expected to be encountered once calibration is in use. Once a set of reference samples is obtained, it is advisable to divide these into two sets: a set for calibration, and others to be used as the validation set. The suitability of the samples used in the calibration set is particularly important since it must closely match the product being manufactured at the production site. A tradeoff exists between calibration sets covering a very wide range of OH numbers and the accuracy with which OH numbers can be predicted. Therefore, it has been found that the accuracy can be improved when using a method calibrated over a more restricted (ca. 50) OH number range. The PLS (Partial Least-Squares) method available in the PerkinElmer Spectrum™ QUANT software uses the NIR spectra recorded to derive a calibration. This equation is then used to predict the value of the constituent of interest of future samples using their NIR spectra. An application that is analyzed by using spectroscopy is often more precise than when measured by other methods. However, the accuracy of the method in predicting the

true value of the future samples is dependent upon the accuracy of the reference method. It is therefore important to stress that the results obtained from the reference method in setting up the calibration are crucial to the success of the NIR application. This is particularly true for the collection of suitable calibration standards, and the analysis of the calibration set by titration. This step should be carried out with an objective of producing the greatest possible accuracy.

The Spectrum QUANT software was used to derive a calibration matrix between the calibration spectra and their reference OH values. The technique of PLS extracts those spectral contributions which are correlated with OH value and eliminates the need to select specific wavelengths for the calibration. As previously stated, the near infrared region consists of many overlapping bands that contain overtone and combination bands involving the absorptions of mainly OH, NH, and CH bonds. The bands of interest in the determination of OH value are due to the OH first overtone at 7150 – 6670 cm^{-1} (1399 – 1499 nm), and the OH combination bands of 5260 – 4760 cm^{-1} (1900 – 2100 nm) as seen in Figure 2.

Experimental

Seven polypropylene glycol standards of known OH value were supplied to serve as a calibration set. The samples were run in duplicate to give 14 overall samples for the calibration and to account for any minor intra-batch variability. All samples were supplied with OH number values measured by the reference 'wet' chemistry method (titration). The infrared spectra of all samples were recorded on a PerkinElmer Spectrum Two N™ FT-NIR spectrometer equipped with a Heatable Transmission Module (shown in Figure 1).



Figure 1. Spectrum Two N with Heatable Transmission Module (HTM).

The samples were scanned in disposable glass vials with a nominal path length of 6 mm over a spectral range of 10000 – 4500 cm^{-1} using 20 scans at a resolution of 8 cm^{-1} . All spectra were ratioed against the open beam of the accessory to compute absorbance spectra. Sample temperature is an important experimental parameter to consider in the analysis of polyols as their NIR spectra are temperature sensitive. Heating was not necessary in this case as all the samples were liquid at room temperature. However, the temperature was set to 35 °C to ensure temperature control of the samples at a temperature comfortably above room temperature. All samples were allowed to equilibrate at temperature for an equivalent time of four minutes before each measurement was performed.

Results and Discussion

The absorbance spectra for the polyol standards and the unknowns were collected and two examples, representing extremes of OH number, are shown in Figure 2. Spectral features located at approximately 7200 – 6670 and 5300 – 4760 cm^{-1} (1389 – 1499 and 1887 – 2100 nm) correspond to polymeric O-H first overtone and O-H combination bands respectively. Spectral differences over O-H absorption regions between standards having low and high OH numbers highlight the sensitivity of NIR spectroscopy and its ability to distinguish OH number for polyol samples.

The Spectrum QUANT software is capable of modelling the OH number in terms of the spectral contributions relevant to OH number determination. The PLS algorithm was selected over the

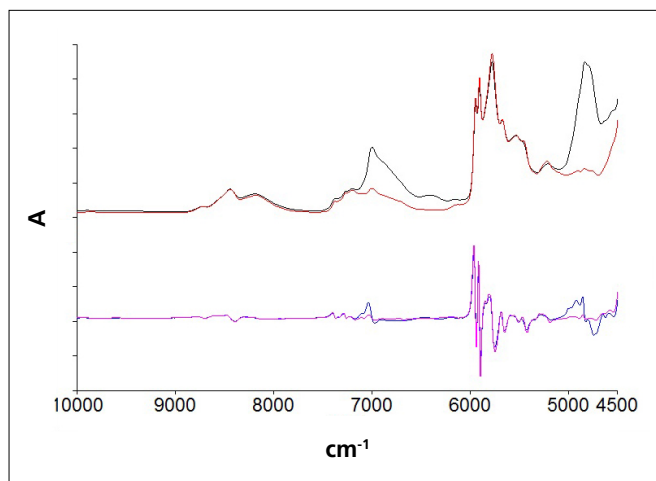


Figure 2. Absorbance spectra (top) and first derivative spectra (bottom) of high and low OH number samples. Top: high OH (black), low OH (red); Bottom: high OH (blue), low OH (pink).

full range of the spectra, using first derivative pre-processing to eliminate any baseline offsets that may occur within the spectra. The software will automatically select the optimum number of principal components to use for the calibration. Leave 1 Out Cross Validation was performed where the software drops one sample from the calibration set and performs an entire calibration with the remaining samples, then makes a prediction for the dropped sample. This process is continued until all samples have been left out of the calibration set. The cross validation plot of estimated versus specified OH number is shown as Figure 3.

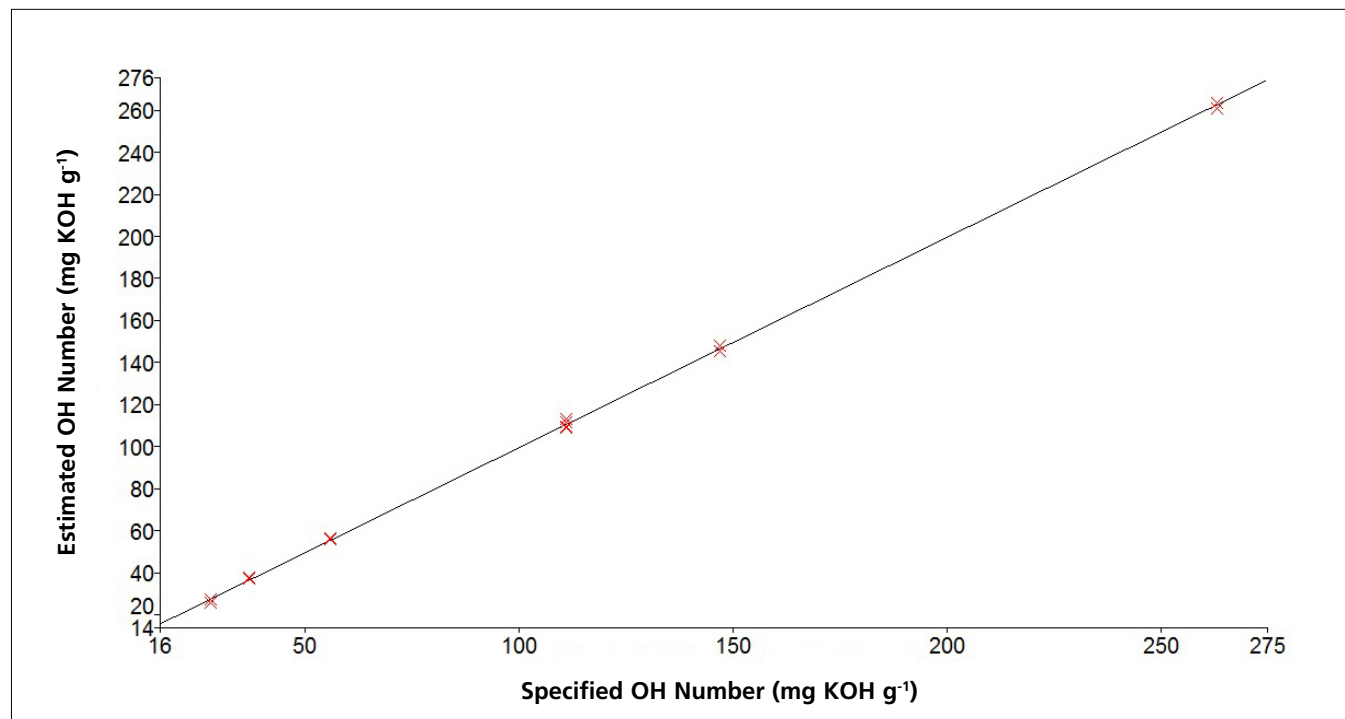


Figure 3. Cross validation plot for OH number standards.

By looking at the results tabulated in Table 1, 99.9868 % of the data can be explained using three factors with a standard error of prediction (SEP) of 1.105 OH number. The calibration was applied to a series of six sub-samples from the same batch of polyol with a reported OH number value of 111 mg KOH g⁻¹. The predicted results are shown in Table 2.

Table 1. Regression summary.

Property	Number of PCs	% Variance (R squared)	Std. Error of Estimate (SEE)	SEP	Cross Validation SEP	Mean Property Value
OH Number	3	99.9868	1.024	1.105	1.318	107.6

Table 2. Prediction of validation samples.

Sample Name	OH Number (mg KOH g ⁻¹)
Validation 1	110.3836
Validation 2	112.9022
Validation 3	110.4161
Validation 4	109.8288
Validation 5	109.3114
Validation 6	110.8284
Mean Value	110.6118
Std Deviation	1.2399

Once the calibration has been developed, it can be deployed using the Spectrum Touch™ software interface. Spectrum Touch software allows the components of an analysis, such as Instrument Setup, Data Collection, Data Analysis and Reporting, to be incorporated into a workflow including instruction screens or SOPs. The method is performed with a simple user interface that can be utilized by routine operators with minimal training. Example screens from the OH number analysis are shown in Figure 4.

Conclusion

The aim of setting up a NIR-based application is to provide an alternative method to the wet chemistry reference method with similar accuracy. Analysis of OH number in polyols is possible using NIR spectroscopy and provides a considerably faster and easier route to OH number than the current methods. From the calibrated methods presented here, it can clearly be seen that OH numbers covering a very wide range can accurately be predicted to ca. +/- 1 OH number which can be as good as the reference method itself, therefore proving NIR spectroscopy to be an extremely valuable, non-destructive technique for the rapid determination of physical and chemical properties.



Figure 4. Example screens in Spectrum Touch software from the OH number analysis.