

# Determination of Hydroxyl Number in Polyols by Mid-infrared Spectroscopy

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## KEYWORDS

FT-IR/polymers/polyols, hydroxyl number/ATR/Partial Least Squares (PLS), quantitative analysis

## INTRODUCTION

Quantitative infrared analysis of complex samples is often best accomplished using multivariate calibration techniques such as partial least squares (PLS).<sup>1,2</sup> PLS is superior to conventional peak height or area measurements for samples where severe spectral overlap or matrix interactions between components cause nonlinear changes in band intensities with concentration. PLS calibration models are tolerant to these conditions because they use wide spectral regions and make few assumptions about the effect of changing composition on sample spectra.

Although usually applied multi-component samples, PLS models can also be used to measure physical and chemical properties of nominally pure materials. This note describes how hydroxyl functionality in polymers, expressed in terms of hydroxyl number (mg KOH/g polymer), may be determined by mid-infrared spectroscopy using PLS quantitative analysis software.

Hydroxyl number measurements are an important part of process control and quality assurance programs in the production of many polymers including polyols, polyesters and polyurethanes. The results provide a measure of nominal molecular weight and the extent of polymerization reactions. The wet chemical methods normally used to measure hydroxyl number are expensive, use hazardous materials and require subjective judgments by the technician performing the test. It is highly desirable to develop rapid, safe and accurate spectroscopic techniques for this analysis.

## EXPERIMENTAL

A Nicolet spectrometer equipped with a horizontal 60° germanium attenuated total reflectance (ATR) accessory was used to analyze a set of polypropylene glycol polyol samples. The horizontal ATR is a convenient

way to make quantitative measurements on liquids because samples are easy to apply to the trough cell and the crystal is easily cleaned. Careful cleaning of the crystal between samples using a mild detergent solution following by a rinse with reagent alcohol was found to be an important factor affecting the precision of the analysis. All spectra were collected at 4 cm<sup>-1</sup> resolution.

## RESULTS

Variation in hydroxyl number causes only minor changes to the mid-infrared spectrum of polypropylene glycol as shown in Figure 1.

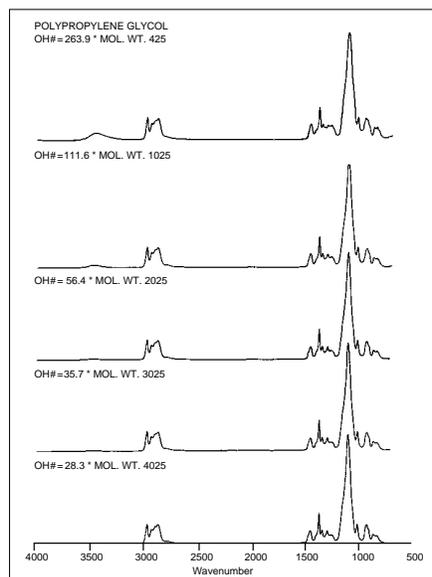


Figure 1: Comparison of polypropylene glycol spectra with different hydroxyl content as determined by titration

The O-H stretching band at 3470 cm<sup>-1</sup> shows the greatest variation as shown in Figure 2. This band alone can be used to measure hydroxyl number with moderate precision. Figure 3 shows a plot of the values predicted by a simple peak height method versus the value determined by titration. Each sample was analyzed five times. The precision of the method is reflected in the spread of the replicate measurements as shown in the bottom of Figure 3. For the four sets of five measurements, the average standard deviation was 1.0 hydroxyl numbers. Although perhaps not adequate as part of a thorough product evaluation, the peak height

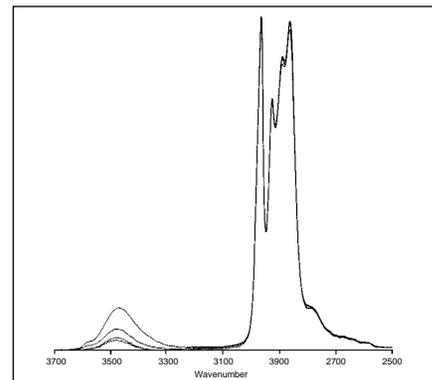


Figure 2: Polypropylene glycol spectra shown with expanded scale

method would be useful in some cases, such as screening of incoming chemicals.

Figure 4 shows the results of analyzing the same sample set above using a PLS method. Several different PLS methods were evaluated before the best set of experimental parameters were obtained. The spectral regions of 3585-3235, 1435-1200 and 1033-950 cm<sup>-1</sup> were finally selected for use in the analysis. The PLS method takes a considerably longer time to develop, but the average standard deviation of replicate measurements improves to 0.35 hydroxyl numbers, which is competitive with titration.

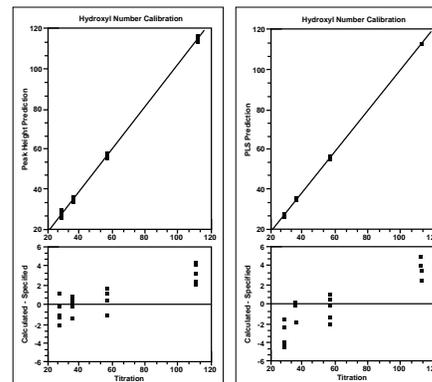


Figure 3: (left) Results of hydroxyl number determination using the peak height method. Figure 4: (right) Results of hydroxyl number determination using the PLS method.

## REFERENCES

1. M. P. Fuller, G. L. Ritter and C. S. Draper (1988) *Appl. Spec.*, **42**, 228-236
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