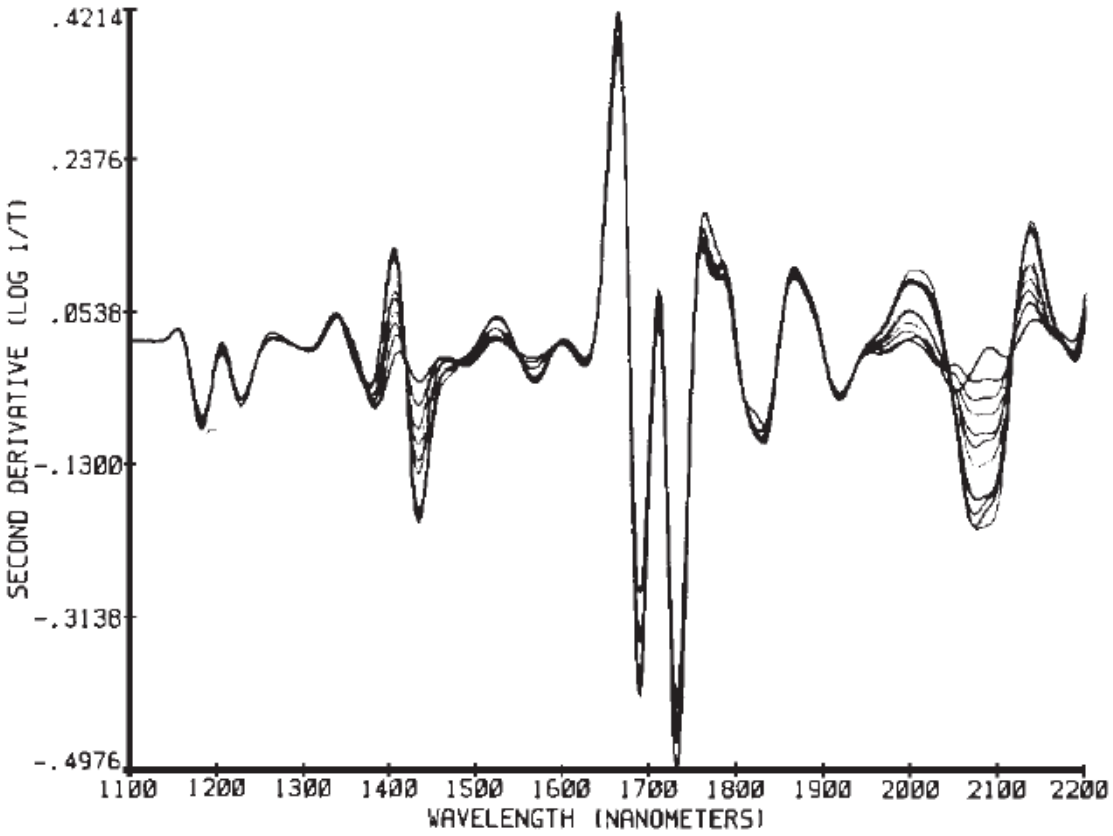
Near-Infrared Spectroscopy Application Note NIR–6

Near-infrared analysis of polyols



This Application Note describes a fast, nondestructive, and reliable NIRS method for the determination of the hydroxyl number in polyols. Results are available in real-time, for which reason NIRS is highly suited for in-process quality control. Second-derivative spectra and linear least-squares regression provided hydroxyl numbers that comply with those obtained by titration.

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Method description

Introduction

Polyols are long chain, liquid polymers, which can be produced from the polymerization of organic oxides (e.g., ethylene oxide, propylene oxide). Polyols are used in many manufacturing processes to form polymeric materials such as polyurethanes, which as a foam are used for cushioning and packaging, automobile seats, in household furniture, etc. The end use for the materials produced using polyols are dependent on the molecular weight of the polyols used. Molecular weight is inversely related to the number of hydroxyl end groups present in a given amount of polyol. Hydroxyl number (number of hydroxyl end groups per gram of sample) is the typical measure for determination of molecular weight for polyols. The laboratory analysis involves a titration of the hydroxyl end groups, which is relatively time consuming.

Near-infrared spectroscopy offers a quick, nondestructive method of determining the hydroxyl number in polyols. The analysis is performed in a matter of minutes on the whole sample without any sample preparation or modification.

Experimental

Samples of polypropylene glycol, ranging in hydroxyl number from 26 to 280 were used in this analysis. The NIR spectra were measured in transmission using a FOSS Model 6500 spectrophotometer from 1100 to 2500 nm. Since this instrument is not available anymore, the NIRS XDS Transmission Optiprobe Analyzer with sample heater or the NIRS XDS RapidLiquid Analyzer is recommended. The samples were placed into 4 mm quartz cuvettes for this analysis, and the temperature was held at 32 ± 0.1 °C since the hydroxyl band is temperature sensitive. Sample scans were generated from 32 co-added scans for each sample and referenced against 32 scans of air.

Results and discussion

The absorbance (log 1/T) spectra for the polyol samples are shown in Figure 1. The variation of the O-H combination band near 2070 nm and that of the first O-H overtone near 1460 nm are clearly evident from this figure. Figure 2 shows the second derivative spectra for these samples, which was calculated to compensate for any baseline variations which often occur in analyzing «real world» samples.

Figure 1
Polypropylene Glycol

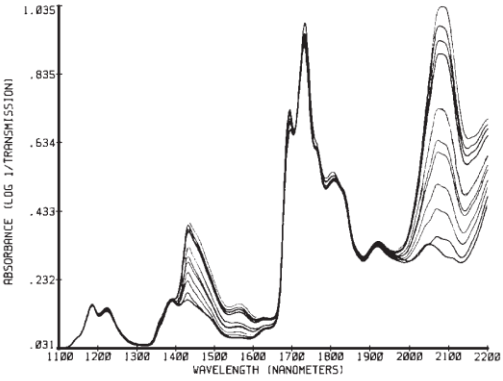
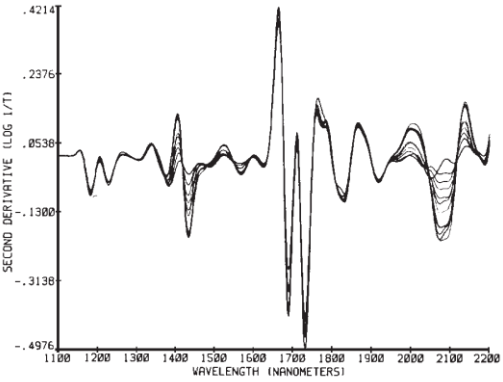


Figure 2
2nd Der. Polypropylene Glycol



It is observed in Figure 2 that variation near 2070 (hydroxyl combination band) and at 1460 nm (hydroxyl overtone band) are increasing with increasing hydroxyl number.

To demonstrate the ability to quantitate hydroxyl number by NIR, a linear least-squares regression was performed, using the second derivative spectra and the known hydroxyl numbers for each sample. A model was developed at 2070 nm, yielding a correlation (R) of 0.999 and a standard error of calibration (SEC) of 4.20 OH#s.

Figure 3 shows the scatterplot of NIR-calculated versus laboratory-reported results.

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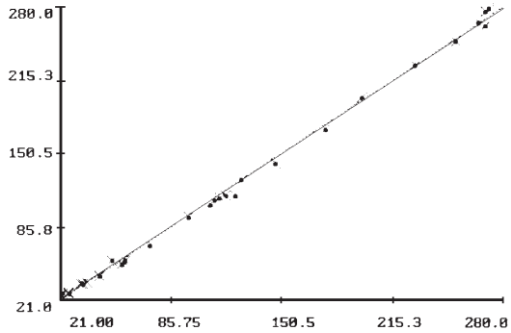
Method description

Figure 3
Lab vs. Calculated Percents



The NIR results agree to within 5 hydroxyl numbers of the lab data . The achievable error by the NIR analysis is limited by the accuracy of the lab analysis, which for samples with hydroxyl numbers in the hundreds is typically about ±5.

To increase the accuracy for those samples below 100 hydroxyl numbers (which have better accuracy in the lab analyses) a separate calibration equation for these samples is developed.

Conclusions

NIR spectroscopy can be used to accurately and rapidly determine the hydroxyl number in polyols. Other NIR measurements of interest for polyol manufacturers are polyols made from propylene and ethylene oxides, resulting in a «mixed polyols». NIR has successfully analyzed the hydroxyl number in mixed polyols, as well as the amount of primary hydroxyl (attached to an ethylene unit on the polyol) and secondary hydroxyl (on a propylene unit) groups.

The methyl substitution rating of the polymer backbone can be determined using the ratio of methyl absorption (due to the propylene portion), to that of methylene absorptions (due to both ethylene and propylene portions of the polymer).

Other successful NIR analyses include moisture, residual oxide, and primary and secondary amine levels in substituted polyols.

NIR therefore appears to be uniquely suited for analyzing the hydroxyl end groups of polyols (both for molecular weight information, as well as differentiation of the type of end group) and characterization of the backbone of the polyol. The analysis requires no sample handling, temperature correction or compensation. A number of analytical parameters can be monitored resulting in better control of the process of producing these materials.

Table 1: Typical measurements for polyols and polyols derivatives

Matrix	Analytes
Oxide-based polyols	Hydroxyl number Primary hydroxyl number Secondary hydroxyl number EO/PO Ratio Residual oxides Moisture
Ester-based polyols	Acid number Hydroxyl number Moisture
Substituted polyols	Primary amines Secondary amines
Polyurethanes	Isocyanate levels Hydroxyl number

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