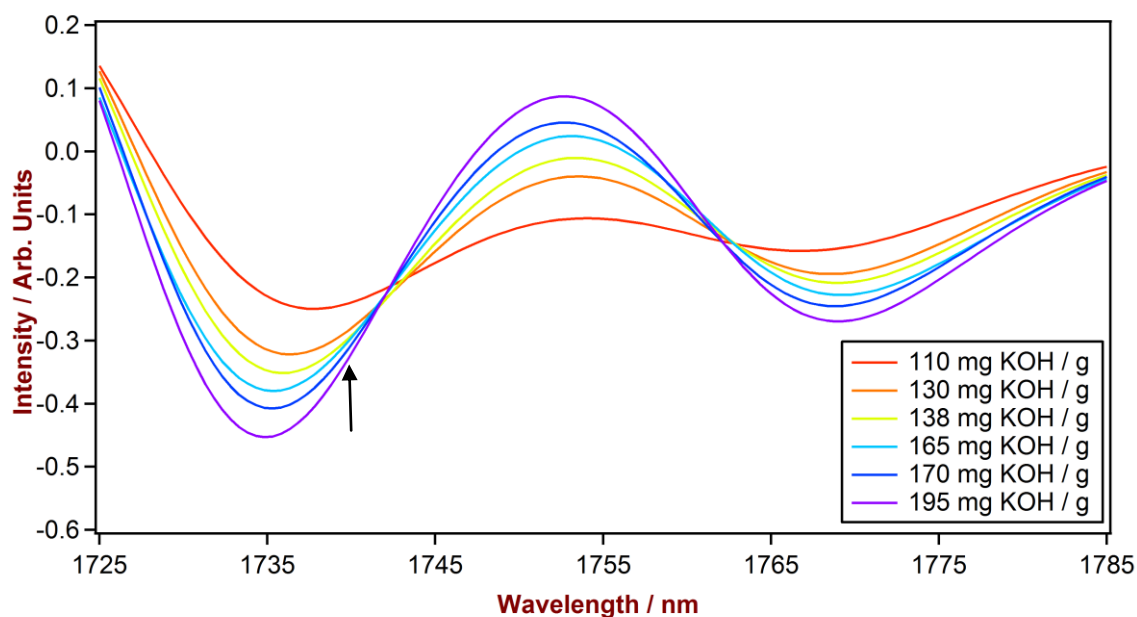# Hydroxyl number in liquid polyols by Vis-NIR spectroscopy

This Application Note shows that Near-Infrared Spectroscopy (NIRS) is a powerful tool to determine the hydroxyl number of liquid polyols. NIRS is a fast alternative to standard lab methods in quality control at the polyol producer and at the end-user.

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Method description

Introduction

Polyols are long-chain polymers, which can be produced through reaction involving organic oxides, acids, and multi-functional alcohols. Uses for the polymeric material include polyurethanes, surfactants, paint additives, adhesives, and foams. The particular use of the polymer is dependent on the molecular weight of the polyol product (which is proportional to the hydroxyl number of a given amount of polyol).

Hydroxyl number (number of mg of KOH equivalent to 1 mg of polyol as a measure of free hydroxyl groups) is the typical measure for determination of molecular weight for polyols. The laboratory analysis (according to ASTM E1899-08 or ISO 14900) involves titration of the hydroxyl end groups, which is time consuming and difficult to handle due to their inherent physical characteristics (i.e., high melting point and high viscosity).

Near-infrared (NIR) laboratory method have been developed as a rapid alternative and yield results, which are equivalent to those obtained by the reference laboratory method. It offers a quick, non-destructive analysis for determination of the hydroxyl number of polyols. The analysis is performed in a less then minute without any sample preparation and modification.

Fig. 1: A NIRS XDS RapidLiquid Analyzer equipped with 4 mm NIRS quartz cuvette with a screw top were used to generate the spectral data in true transmission mode.

The samples were placed into 4 mm quartz cuvettes and the temperature was kept constant at 32 °C ± 0.1 °C since the hydroxyl band is temperature sensitive. The reference values, necessary for the development of a quantitative model for the prediction of the hydroxyl number were provided from the customer.

Experimental

Polymer samples with OH numbers ranging from 92 to 205 mg KOH / g were analyzed. All NIR spectra were collected in the transmission mode over the full wavelength range of Vis-NIR spectroscopy (400 nm - 2500 nm) using a NIRS XDS Rapid Liquid Analyzer with sample heating option (**Tab. 1 / Fig. 1**).

Tab.1: Used equipment.

Equipment	Metrohm code
NIRS XDS Rapid Liquid Analyzer	2.921.1410
NIRS Quartz Cuvette Screw Top 4 mm	6.7401.020
Vision 4.03 Software	6.6069.102

Results

Band assignment in NIR spectra is rather complicated due to many broad and overlapping bands. The bands are overtones and combination bands of fundamental vibrations appearing in the mid infrared region. **Fig. 2** shows a spectral region (1680 nm – 1800 nm), where the spectrum indicates a correlation between increase of absorbance intensity and increase of OH groups.
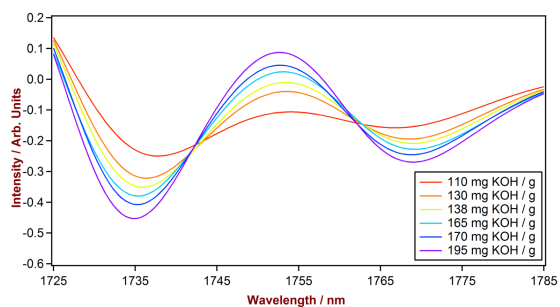

Fig. 2: Wavelength range from 1680 nm – 1800 nm of the 1st derivative spectra of the polyol samples with differing hydroxyl number.

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Method description

Vision, with its Partial Least Squares (PLS) algorithm, was used to develop quantitative prediction model for hydroxyl number in polyol samples in the range of 90 – 200 mg KOH / g. Therefore, absorption bands of the NIR range (1330 nm – 2080 nm) were chosen, because the statistical values show the best results using a broader wavelength range compared to just using the overtones and combination bands of OH. The spectral data were pre-treated using the 1st derivative to get rid of the baseline shift. Internal cross validation (leave-one-out method) was applied to verify the performance of the derived quantitative model.

The result of predicted values versus reference values can be seen in **Fig.3**.
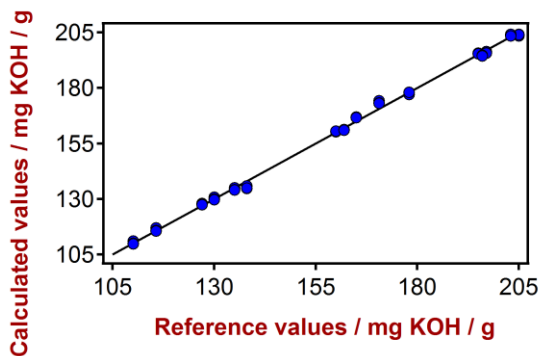

Fig. 3: Correlation of the NIR predicted values with the reference data as a result of a quantitative method development of the OH number in polyol samples.

The Figures Of Merit (FOM) shows a good correlation ($R^2 = 0.998$) predicted and calculated values. The comparison of the standard errors of calibration and validation (SEC = 1.38 mg KOH / g, SECV = 1.47 mg KOH / g) indicates that the model can be used to predict the OH number in polyols.

Conclusion

NIR spectroscopy can be used to accurately and rapidly determine the hydroxyl number in polyols. 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.

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