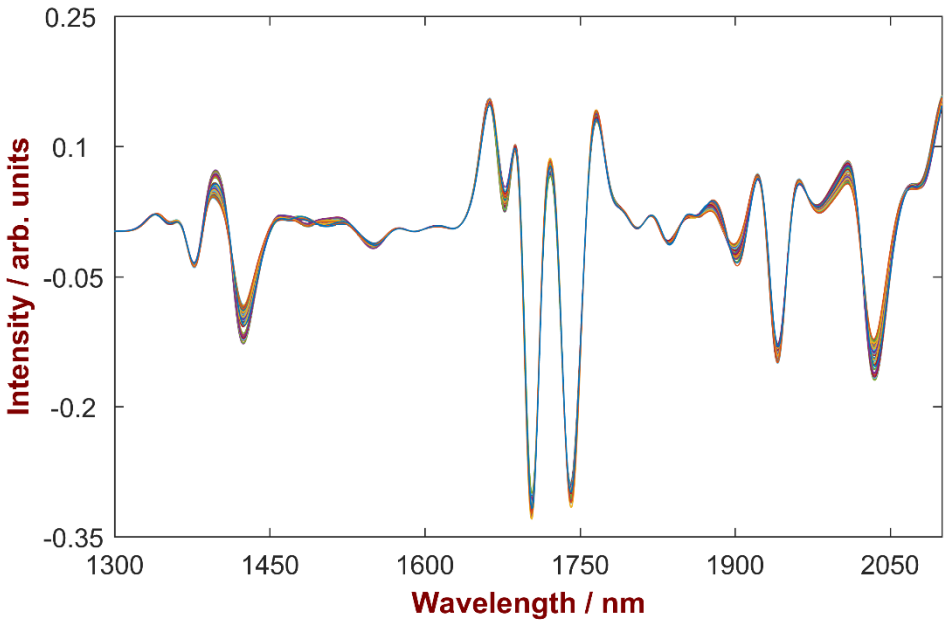
NIR Application Note NIR–065

Simultaneous determination of multiple quality parameters of polyols using Vis-NIR spectroscopy



This Application Note demonstrates different application possibilities of Metrohm Vis-NIR analyzers for the determination of multiple quality parameters of polyols. This unique analytical technique enables significant cost and time savings compared to standard reference analysis.

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Method description

Introduction

Polyols are a broad class of organic compounds characterized by the presence of two or more hydroxyl groups. Synthetic polyols are frequently used as raw materials in the production of polyurethanes. In a condensation reaction polyols form bridges between isocyanate molecules, leading to polyurethane with a polymeric structure. The properties of the final product can be influenced through a selection of appropriate raw materials with defined chemical and physical properties. Therefore, it indispensable to perform a quality control of raw materials prior to the polymerization in order to minimize risk of the out-of-spec products. In this step, it is important to determine multiple quality parameters such as hydroxyl value, acid value, moisture content and others. The classical way for the analysis is the use of titration. This method requires reproducible sample preparation, additional chemicals, and waste disposal, which result in increase of the running costs. The duration of analysis depends on the sample type and is usually at least 30 minutes per parameter.

Alternatively, the manufacturer can utilize near-infrared spectroscopy (NIR). Using this technique, the sample can be analyzed as-is without any sample preparation. Due to its multi-component capability NIR enables simultaneous determination of multiple quality parameters within a minute. This leads to significant time savings compared to the classical analysis methods. Additionally, this technique enables a possibility to reduce significantly running costs of QC lab since the analysis is performed without the use of chemicals such as solvents or reagents. NIR was recognized by regulatory bodies as a tool for quality control and can be used for the determination of hydroxyl values according to ASTM D6342 or ISO 15063 norms. The present Application Note demonstrates the application possibility of NIR for the quality control of polyols.

Experimental

140 samples provided by a customer were used in the present study. Samples were provided with reference values for acid and hydroxyl values as well as moisture content. A part of the samples were used for the method development. Remaining 25% of the samples were used for the validation of the developed methods. The spectra were collected in transmission mode on a NIRS XDS RapidLiquid Analyzer over the full wavelength range (400–2500 nm). Samples were pipetted in disposable vials and analyzed at 30 °C with 30 seconds as a delay time for thermal equilibration. The software package Vision Air 2.0 Complete was used for data acquisition, data management and development of the quantification method. **Tab. 1/Fig. 1** lists the used equipment.

Tab. 1: Used equipment and software.

Equipment	Metrohm number
NIRS XDS RapidLiquid Analyzer	2.921.1410
NIRS disposable glass vials, 8 mm diameter, 250 pcs.	6.7402.000
Vision Air 2.0 Complete	6.6072.208

Fig. 1: The NIRS XDS RapidLiquid Analyzer was used for spectral data acquisition over the full range from 400 to 2500 nm.

Results

Fig. 2 shows Vis-NIR spectra of polyol samples. Specific analytical methods were developed for each quality parameter in order to improve the analytical figures of merit. Redundant spectral information was excluded from the method development by the selection of analyte specific wavelength ranges combined with dedicated spectral pre-treatments. Example of such procedure is illustrated in **Fig. 3**, which shows spectra pretreated with a 2nd derivative.

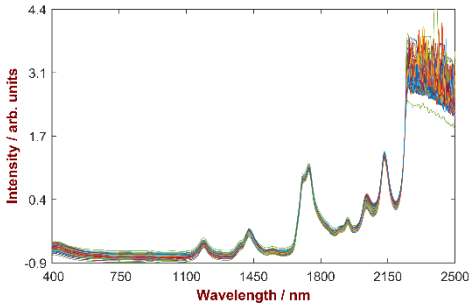

Fig. 2: Raw Vis-NIR spectra of polyols over the full wavelength range.

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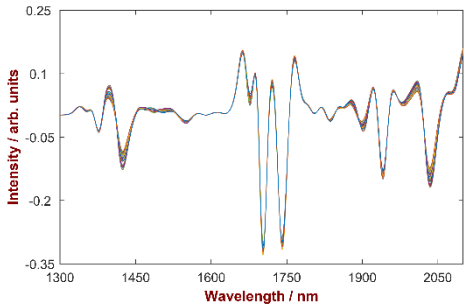

Fig. 3: 2nd derivative spectra of polyol samples.

The correlation plots, see **Fig. 4–6**, show high correlation between the parameters determined by the reference analytical method (x-axis) and the predicted values (y-axis) from Vis-NIR spectroscopy. The good correlation results are confirmed by the analytical figures of merit shown in **Tab. 2–4**. The estimated errors of predictions were found to be in the same range as the errors of the reference methods.

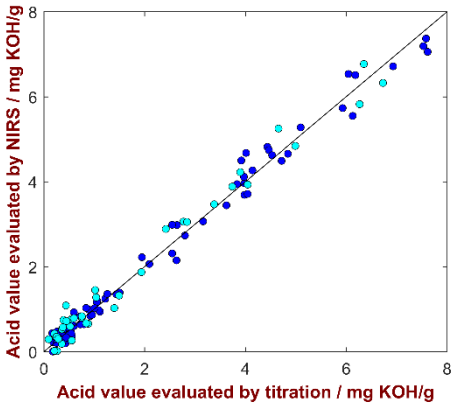

Fig. 4: Correlation plot of the acid value predicted by NIRS versus the reference values. The blue marks stand for samples used in the calibration set, the turquois marks are samples used in the validation set. A high correlation is observable.

Acid value:

Tab. 2: Results of the quantitative method development for acid value.

Range	0–8 mg KOH/g
Regression model	PLS, 9 factors
Pre-treatment	2nd derivative
Wavelength ranges	1366–1482 nm 1612–1828 nm 1900–2116 nm
R^2	0.989
SEC	0.23 mg KOH/g
SECV	0.33 mg KOH/g
SEP	0.38 mg KOH/g

Hydroxyl value:

Tab. 3: Results of the quantitative method development for hydroxyl value.

Range	70–125 mg KOH/g
Regression model	PLS, 6 factors
Pre-treatment	2nd derivative
Wavelength ranges	1350–1500 nm 1800–2100 nm
R^2	0.999
SEC	0.46 mg KOH/g
SECV	0.50 mg KOH/g
SEP	0.68 mg KOH/g

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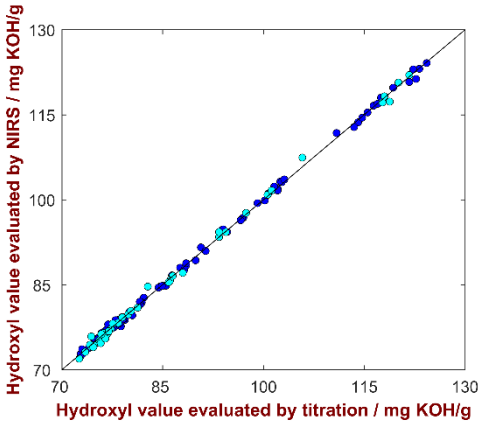

Fig. 5: Correlation plot of the hydroxyl value predicted by NIRS versus the reference values. The blue marks stand for samples used in the calibration set, the turquois marks are samples used in the validation set. A high correlation is observable.

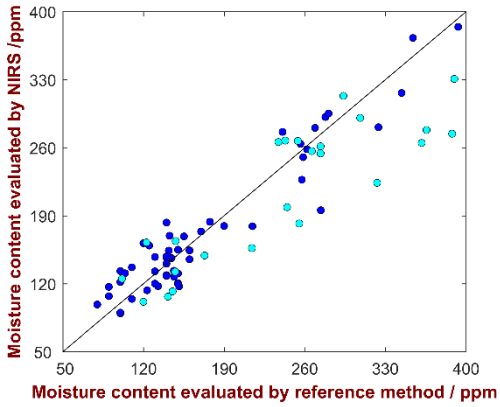

Fig. 6: Correlation plot of the moisture content predicted by NIRS versus the reference values. The blue marks stand for samples used in the calibration set, the turquois marks are samples used in the validation set. A high correlation is observable.

Moisture content:

Tab. 4: Results of the quantitative method development for moisture content.

Range	75–400 ppm
Regression model	PLS, 7 factors
Pre-treatment	2nd derivative
Wavelength ranges	1350–1600 nm 1800–2000 nm
R^2	0.902
SEC	25 ppm
SECV	30 ppm
SEP	52 ppm

Summary

The present application note demonstrates the possibilities of Vis-NIR spectroscopy for quality control of polyols. It was successfully demonstrated that this technique can be successfully utilized for the simultaneous determination of hydroxyl and acid values as well as moisture content. The estimated analytical figures of merit of NIR were comparable to those of reference methods. Additionally, it should be pointed out, that similar NIR methods can be developed for further quality parameters of polyols such as solvent or solid content, primary and secondary hydroxyl values and others.

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