

## Application Notes AN N518

# Determination of Isocyanate Number using Near Infrared Spectroscopy

Isocyanate number is a critical parameter in the production of polyurethane based products.

Isocyanate number is an important parameter in the production of many different polyurethane based products including flexible and rigid foams, chemical-resistant coatings, specialty adhesives and sealants. Polyurethanes are formed by reacting a polyol (an alcohol with more than two reactive hydroxyl groups per molecule) with a diisocyanate or a polymeric isocyanate in the presence of suitable catalysts and additives. Using the appropriate

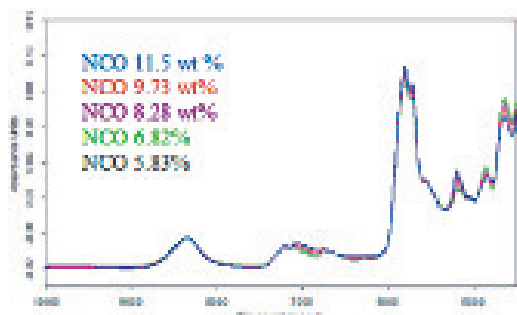
isocyanate and polyol, polymers can be precisely manufactured for specific application. The manufacture of polyurethanes requires a rapid and dependable QC method for the measurement of isocyanate number in both raw material and processing. The analysis of isocyanate number in raw material can prevent off-grade batches and appropriate adjustment could be made in time. While the control of the properties and processing characteristics of these polyurethanes requires good control of the process in order to obtain a consistent product.

Traditional wet chemical techniques are usually lengthy procedures involving derivatisation, titration and large quantities of chemicals. In this note, a spectroscopic method is outlined which is not only fast and accurate but is simple to apply since the measurement is performed remote from the spectrometer i.e. on-line. There are no solvents and reagents involved in spectroscopic method, which not only reduce the cost but also reduce the operator exposure to toxic materials. The results discussed were part of an on-line study that followed the isocyanate content during a polyurethane reaction.

### Experimental

The near infrared spectra of polyurethane samples were taken on-line while their reference isocyanate numbers were determined via a titration method. A MATRIX™-F FT-NIR spectrometer coupled to an AXIOM process transmission

Figure 1



FT-NIR spectra of polyurethane collected online after vector normalization

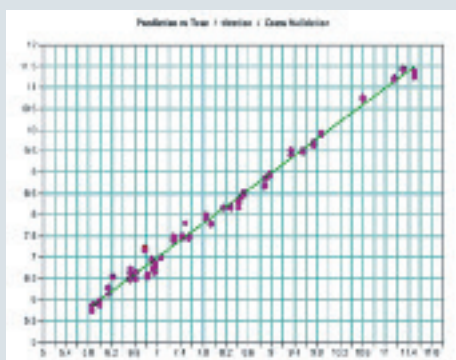
probe via 20m of fiber optic cable was used for these measurements. The probe had a 5mm gap and was installed directly into the polyurethane reactor. Spectra, consisting of 20 scans at a resolution of 16 cm<sup>-1</sup> were automatically collected at regular intervals during five isocyanate batches. The time stamp of the measured spectra were correlated to samples pulled from the reactor for wet chemical analysis in order to generate a good calibration model (see Figure 2). Samples from a further 2 production batches were used to test the predictive capability of the calibration model (see Figure 3).

For off-line analysis, sample could be measured in 5mm glass vials using a fiber coupled temperature controllable vial holder connected to the MATRIX™-F .

### Quantitative analysis

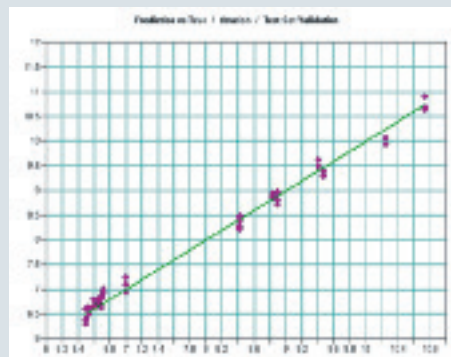
The on-line measurements of polyurethane samples with varying isocyanate content are shown in figure 2. Baseline variations in the raw data caused by air bubbles were removed by a vector normalization spectral preprocessing procedure. In a QA/QC lab environment or an off-line analysis these baseline offsets would not be present.

Figure 2



Cross validation result of the all samples from batches 1 to 5 using 2 PLS factors. R<sup>2</sup> = 98.38, RMSECV (Root Mean Squared Error of Cross Validation) = 0.20 % NCO

Figure 3



Independent external validation result of the all samples from batch 6 and 7 using 2 PLS factors. R<sup>2</sup> = 98.93, RMSEP (Root Mean Squared Errors of Prediction) = 0.15 % NCO.

The OPUS/QUANT-2 software package uses the full spectrum method of Partial Least Squares (PLS), which is suitable for near-IR spectra because of the generally overlapping nature of the spectra. The 1st overtone region around 5200 cm<sup>-1</sup> and the 2nd overtone region around 7000 cm<sup>-1</sup>, were used for the calibration. The data preprocessing option was set to vector normalization in order to remove various baseline shifts caused by air bubbles. An internal cross-validation in the leave-one-out mode (PRESS calculation) gave a recommended PLS rank of 2, a root mean square error of cross validation (RMSECV) is 0.2% by weight and an R<sup>2</sup> value of 98.4%. A graph showing the predicted and true values from this procedure is shown in Figure 2. In order to test the validity of the model, the NCO number of spectra from two additional batches, not included in the calibration data set, were predicted and compared with their true values. The results of the prediction are shown in Figure 5. The correlation coefficient of the validation was 98.9% and the root mean squared error of prediction was 0.15% NCO by weight.

● **Bruker Scientific LLC**

Billerica, MA · USA  
Phone +1 (978) 439-9899  
info.bopt.us@bruker.com

[www.bruker.com/optics](http://www.bruker.com/optics)

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**Bruker Optics GmbH & Co. KG**

Ettlingen · Germany  
Phone +49 (7243) 504-2000  
info.bopt.de@bruker.com

**Bruker Shanghai Ltd.**

Shanghai · China  
Tel.: +86 21 51720-890  
info.bopt.cn@bruker.com