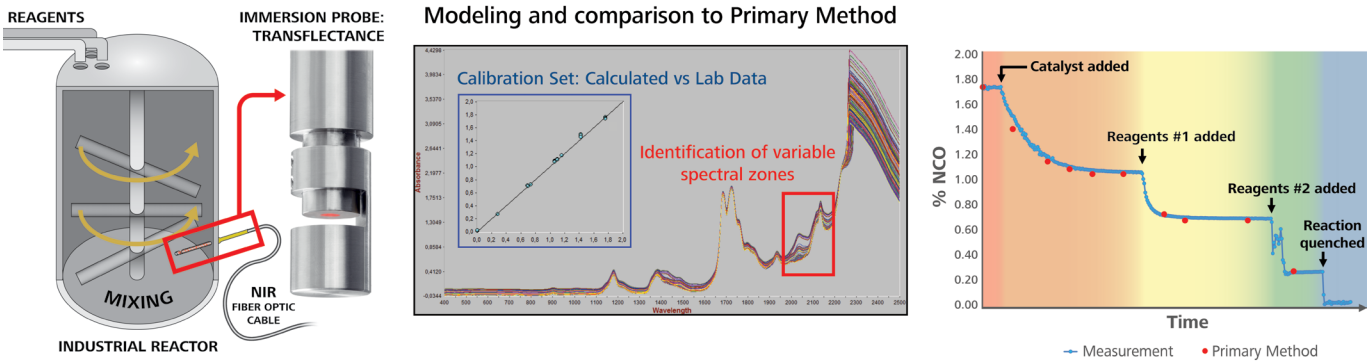
Process Application Note AN-PAN-1041

Inline monitoring of free isocyanate (%NCO) content in polyurethane

Polyurethanes (PU) are a class of synthetic polymers used to create solid or foam structures—flexible or rigid, such as mattresses, shoe soles, safety helmets, insulation, packing material, surfboards, wind turbine blades, and several safety features in cars to name a few. The variety of densities, hardness, and durability found in PU products is vast due to the sheer amount of additives and recipes available. PU are formed by reacting liquid di/polyisocyanates and polyols with a catalyst and various additives. The step additions of these chemicals occur in a reactor before the final mixture is spread on rollers or injected into molds to be further processed to customer specifications.

The reaction between polyisocyanates and polyols is quick and exothermic, beginning with the addition of a catalyst into the reactor. The process reaches an initial equilibrium, after which three stepwise chemical additions are made in the reactor to modify the PU properties. The final reagent quenches NCO functional groups from unreacted isocyanates; therefore knowing the precise concentration is crucial here.



Stylization of suggested placement for NIR probe in an industrial PU reactor with real data correlation between primary titration method and NIR model showing how different mixing steps can be shortened.

Determining the %NCO in the PU manufacturing process is a critical parameter to help determine the proper mixing ratio between the different reagents for optimized production of various PU characteristics. This is generally performed in the lab by titration methods. Spot samples are taken from the reactor at various points in the mixing process and %NCO is determined. Laboratory titration is slow and uses chemicals which need proper disposal. During transportation to the laboratory, sample properties have already changed as it is exposed to ambient conditions not representative of the reactor. A safer way to increase PU production, decrease waste, save time and money, monitoring %NCO inline in real-time is the way to go. Reagent-free near infrared (NIR) spectroscopic analyzers enable comparison of real-time spectral data from the process to the primary method (titration) to create a simple, yet indispensable model for your process needs. Gain more control over your production with a Metrohm Process Analytics NIR XDS system, capable of monitoring up to 9 process points with the multiplexer option.

Application: Wavelength range used: 1950–2080 nm. Inline analysis is possible using the properties of transflectance and the micro interactance immersion probe. The sample flows through the gap between the probe body and high-energy mirror tip, and adjusting the mirror tip defines the pathlength (equal to two times the gap) for analysis.

Typical Range: 0–30 %NCO

Keywords: PU, polymerization, coatings, NIR, spectroscopy, reaction monitoring, chemical free, XDS

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Remarks: A primary method must still exist as a check method. An appropriate range of samples covering the process variability should be analyzed by both methods to build an accurate NIR model. Correlations are made to process specifications.

Other Process NIRS applications related to PU:

- Moisture determination in drying step
- Hydroxyl number determination
- Monitoring the curing of polyurethane elastomer
- Determining percent linear expansion in polyurethane resins
- Water content of polyols (%)
- Determination of Acid and Alkalinity Numbers of Polyols
- Determination of Acidity as Acid Number (AN) for Polyether Polyols

NIRS XDS Process Analyzer

Related ASTM methods:

- **ASTM D2572**: Standard Test Method for Isocyanate Groups in Urethane Materials or Prepolymers
- **ASTM D6342 (ISO 15063)**: Determination of hydroxyl number
- **ASTM E1655**: Standard Practices for Infrared Multivariate Quantitative Analysis

Related Application Bulletin:

- **AB-414** Polymer analyses using near-infrared spectroscopy

Dedicated solutions for your sampling needs

Probe Type	Applications	Processes	Installation
Micro interactance reflectance probe	• Solids (powders, granules) • Slurries with > 15 % solids	• Bulk polymerization • Hot melt extrusion	• Direct into process line • Compression fitting or welded flange
Micro interactance immersion probe	• Clear to scattering liquids • Slurries with < 15% solids	• Solution phase • Temperature- & pressure-controlled extrusion	• Direct into process line • Compression fitting or welded flange
Micro transmission probe pair	• Clear to scattering liquids • Slurries with < 15% solids	• Solution phase • Temperature- & pressure-controlled extrusion	• Direct into process line or reactor • Into a side-stream loop • Compression fitting or welded flange
Micro interactance reflectance probe with purge on collection tip	• Solids (powders, granules) • Environments where sample amount is variable (e.g., fluid bed dryer)	• Drying of granules and powders	• Direct into the fluid bed dryer, reactor, or process line • Compression fitting or welded flange

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