Quality control of silane mixtures with low-field NMR spectroscopy

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Introduction

In recent years, functional trialkoxy silanes have proven their versatility. After hydrolysis with water or alcohols, modified silanes are applied in numerous applications: from weather protection of buildings to bonding-imparting properties in the glass fiber industry, for sealants and adhesives, for coatings and paints to the modification of polymer materials.

Commercial benchtop NMR spectrometers have the potential to be used in silane chemistry as an online method for reaction monitoring and quality control [1] thanks to the presence of [29]Si nuclei and the characteristic ^{1}H fingerprints of the components.

Application

The products are formulated by blending and dissolving silanes, organic stabilizers, peroxides and other additives. The variety of these compounds is shown in Figure 2.
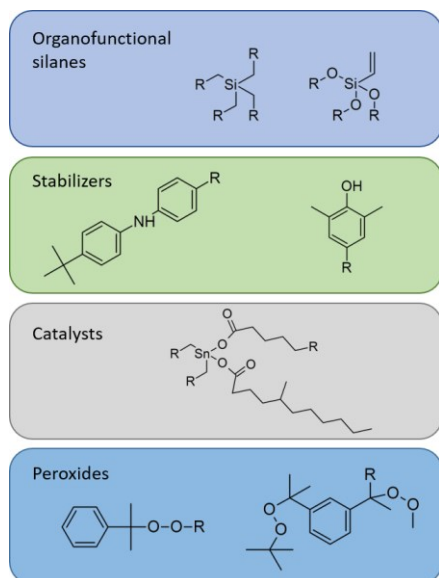

Fig. 2: Components examples used in product mixtures containing trialkoxysilanes.

Fig. 1: Laboratory set-up for the monitoring of the dissolution kinetics of additives in trialkoxy silanes.

Measurements

[1]H spectra (60 MHz) were acquired for calibration pur-poses in standard NMR tubes. The quantitative model was then transferred to a continuous flow setup in lab scale (Figure 1). Therefore, all components of the product mixture were placed into the stirred tank (liquids as well as solids). After switching on the stirrer, the product mixture was circulated through the NMR spectrometer with a flow rate of 1.5 mL/min.

Modelling

The acquired NMR spectra were treated in PEAXACT 5 using built-in NMR-specific functions, i.e. zero filling, apodization (exponential line broadening) and automatic phase correction. Additionally, an aligment of the spectral axis to the silane signal at 3.5 ppm was applied. Typical pretreated spectra are shown in Figure 3.

An automatic analysis method based on Indirect Hard Modeling (IHM) was developed. For each of the four additives Pure Component Models were set up based on measured pure component spectra (Figure 4).

Ratiometric calibration was performed using 15 training samples and 9 independent test samples for validation. Beyond the silane, also the additives – summing up to 2 mol-% only – could be quantified correctly with validation errors (RMSEP) of 0.01 - 0.03 mol-%.
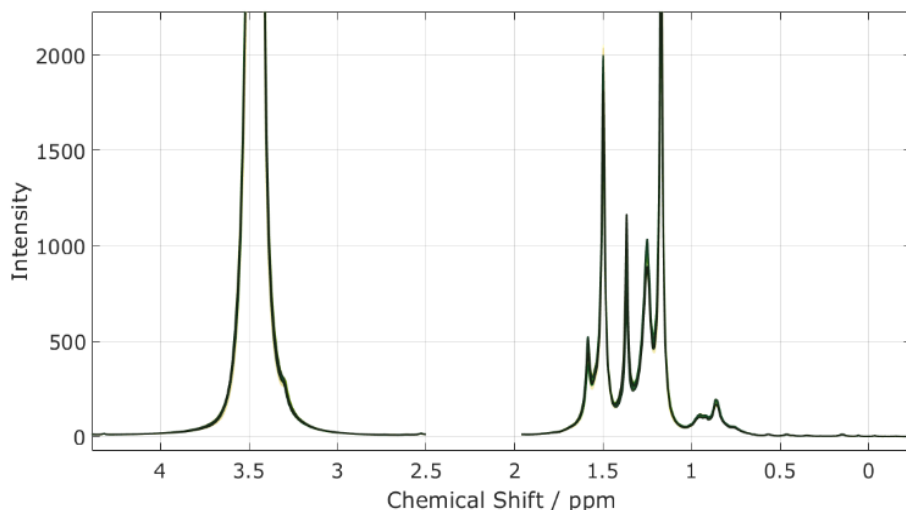

Fig. 3   Aliphatic region of ^{1}H NMR spectra of silane mixtures (processed in PEAXACT 5).

Analysis

NMR spectra were measured during the dissolution of additives within a silane every 4 minutes and were analysed in real-time using ProcessLink. The concentration profiles are shown in Figure 5.

The respective mole fractions can be used to optimize the time for mixing and enable the quality control of the final product within the blending vessel. The time required for the release of batches was easily reduced from hours to minutes.

Summary

In this case study it was shown how low-field NMR spectroscopy extends the application range of chemical analysis to new applications where established technologies such as NIR, Raman, UV/VIS, etc. cannot be used quantitatively due to lack of specificity for the intended application.

Especially with respect to unsupervised and automated use in the field, the applied NMR setup easily fulfilled all requirements of robustness and reliability. The connectivity with the process control system realised via the ProcessLink OPC interface allowed a straightforward and powerful access to the real-time analysis results, and a subsequent exploitation for the optimisation of the blending process. With this, a Return of Invest (RoI) of less than 12 months can be achieved.

References

Application developed by Evonik Resource Efficiency GmbH, Rheinfelden (M. Abele, S. Falkenstein) and Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin (K. Meyer, S. Kern, M. Maiwald).

[1] K. Meyer et al., Process control with compact NMR, TrAC Trends Anal Chem. 83a (2016), 39–52.
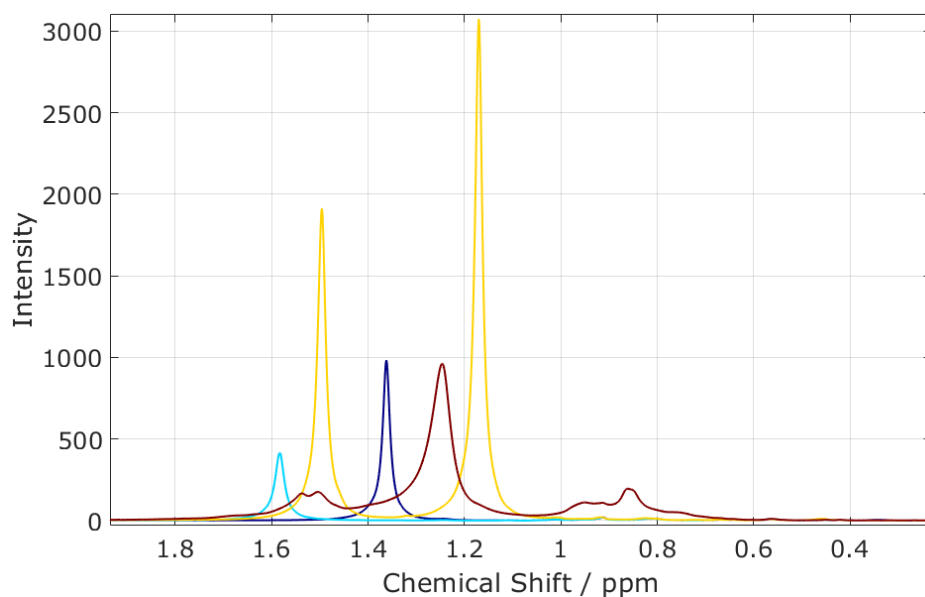
Fig. 4: ^{1}H-spectra of pure components (additives).
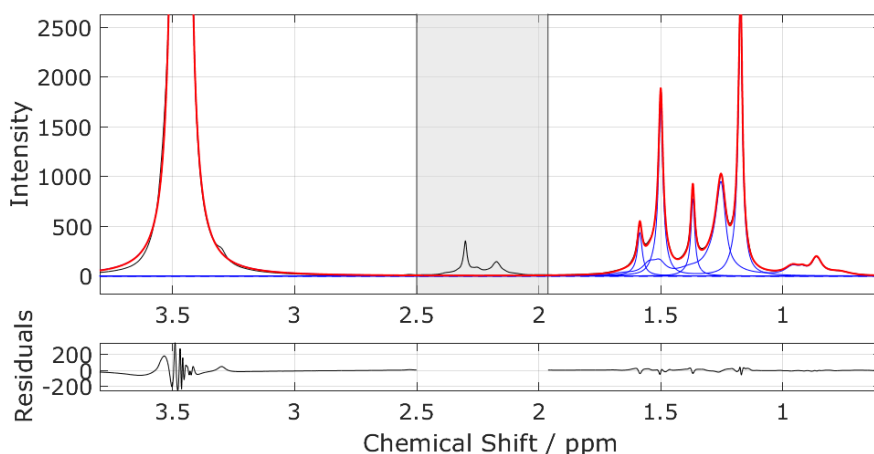

Fig. 5:   Hard Model (blue and red) fitted to a product mixture (black) containing a trialkoxy silane (3 - 4 ppm) and several additives (0 - 2 ppm).
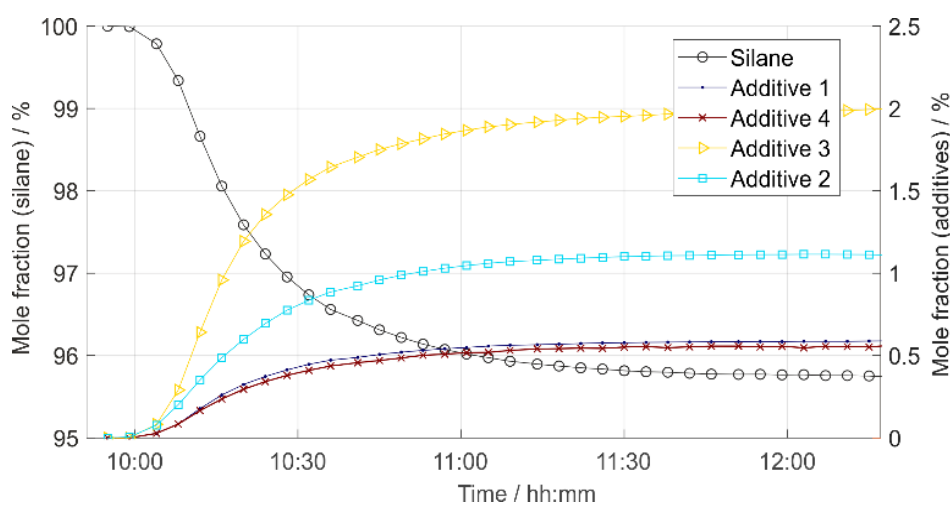

Fig. 6:   Prediction of mole fraction during online monitoring of a dissolution process.