Application Note AN M111

MIR-Spectroscopic Reaction Monitoring

Introduction

The spectroscopic monitoring of chemical reactions in the mid-IR is an established method to determine optimal reaction conditions, to identify the end-point of a reaction or to gather information about the reaction-order and -path. At the laboratory scale a reaction can be monitored via a series of manual measurements, for example by frequently drawing and measuring samples. This is, however, very laborious and error-prone. Furthermore it can happen that the sample disintegrates on its way to the spectrometer due to temperature change, air contact etc. Additionally the measurement intervals are much longer in this case, which reduces the temporal resolution significantly. The measurement in a flow-through setup, that passes the reaction medium constantly over an ATR-crystal in a closed cycle, constitutes an efficient alternative (see fig. 1). As reaction media can be chemically aggressive or might contain particles the ATR (Attenuated Total Reflection) technique usually is the more robust and therefore better approach than transmission. During the whole reaction, spectra are recorded software controlled at regular intervals.

The Bruker ALPHA FT-IR spectrometer in combination with the temperature controlled diamond ATR-unit und a specially designed flow-through cell is a cost effective, robust and compact combination for the monitoring of reactions with a temporal resolution of up to five seconds.

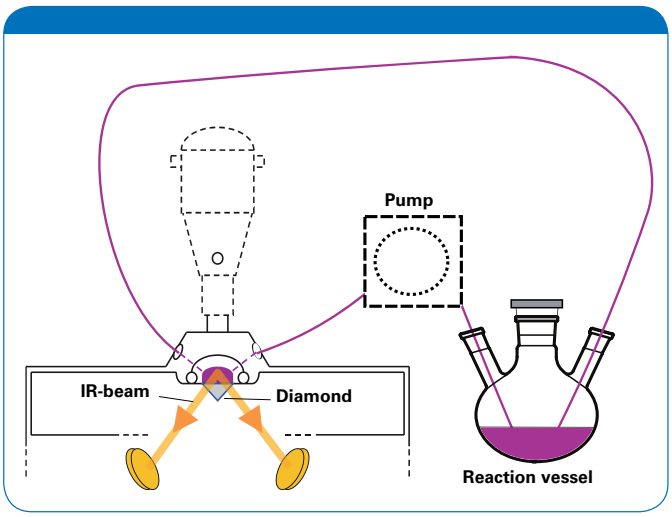

Figure 1: Schematic of the measurement setup.

Instrumentation

The example measurement was performed with the Bruker ALPHA FT-IR spectrometer in combination with a temperature controlled diamond ATR-unit. The tem-

Figure 2: ALPHA with heatable diamond ATR and flow-through cell.

perature at the ATR measurement element can be set to values between room-temperature and 120 °C. Figure 2 shows the stainless-steel made flow-through cell. The diamond of the ATR-unit is brazed in tungsten carbide and the O-ring material is Kalrez. This results in an extremely high tolerance to all kinds of chemicals. In our demonstration experiment the reaction medium was passed continuously over the diamond crystal. The automated measurement and the evaluation were performed by the function "Reaction Monitoring" of the OPUS spectroscopy-software.

Example measurement: Monitoring of an esterification

As an example reaction we show the monitoring of the synthesis of ethyl acetate from glacial acetic acid and ethanol. The reaction mixture was stirred over a period of 3.75 h at 40 °C. Finally the temperature was raised to 60 °C and held there for two more hours. During the whole reaction automated measurements were performed every five minutes. Figure 3 shows the OPUS evaluation view for time resolved measurements which contains four different fields. The field on the upper left shows the zoomed carbonyl band (C=O stretching vibration) in its temporal evolution in 3D-view, on the lower right the same is shown in 2D. The carbonyl band of the acetic acid is located around 1710 cm^{-1}, the band of the ethyl acetate is around 1740 cm^{-1}. It is clearly visible how the band of the carbonic acid declines and how the one of the ester is rising. For the evaluation of the temporal changes of the ester concentration the intensity at 1747 cm^{-1} was used. The change of the carbonic acid was evaluated by using the intensity at 879 cm^{-1} (see figure 4). The latter band results from the carbonic acid dimers that are formed by hydrogen bonding. The evaluation result is shown in figure 3 on the upper right. The red curve shows the formation of the ester and the blue curve the decrease of the carbonic acid. Also clearly visible is the increase of the reaction rate in the last third of the diagram due to the temperature rise from 40 to 60 °C.

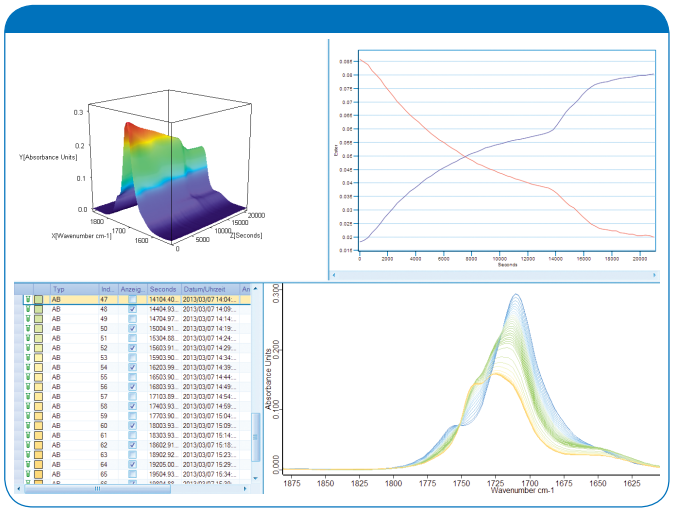

Figure 3: OPUS-analysis of the reaction process.

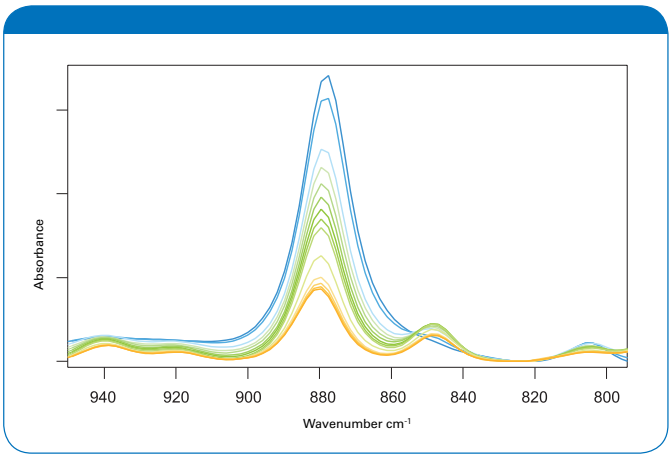

Figure 4: Band of the carbonic acid dimer.

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