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Application Note

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Transmission Cells for the NIR Analysis of Liquid and Vapor Phase Process Streams

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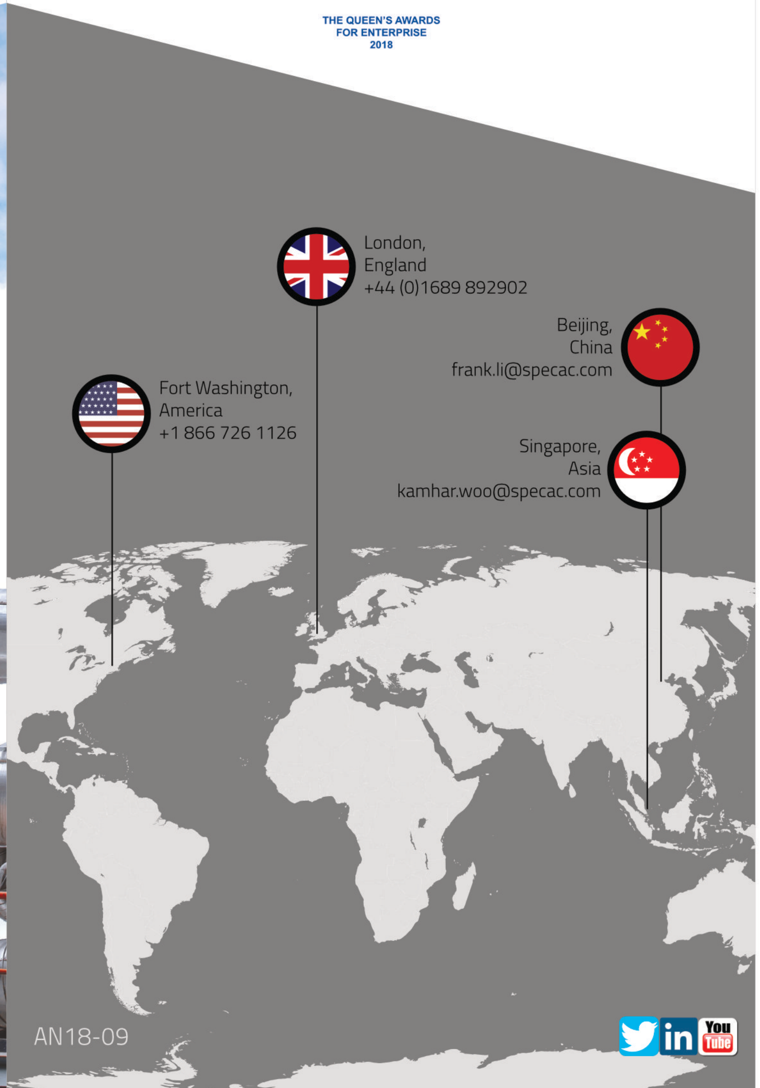

The fundamental advantage of using NIR analysis as the basis of industrial on-line process monitoring is that high quality spectra can be obtained remotely using optical fibres.

Near infrared (NIR) has bought many benefits to process plant operators as a wide variety of sampling protocols have been developed. Gas and liquid flow cells can be directly inserted into a process stream or inserted into a fast loop by-pass and monitored using a single remote spectrometer coupled to a fibre multiplier.

The benefits of in-line analysis are:

- Real time information
- Better process control
- Enhanced product quality
- Optimised plant throughout and efficiency
- Plant data for quality management
- Monitoring of plant safety
- Reduced amount of process samples for off-line analysis resulting in reduced exposure of plant personnel sampling equipment

Transmission flow cells have been developed which are capable of collecting both liquid and vapor phase NIR spectra over fibre optic runs many hundreds of metres in length.

Procell Typhoon (vapor phase) cell (Left). Procell Cascade (liquid phase) cell (Right)

Historically, the most important measurements have been for water at ppm or % levels in various solvents using the overtone/combination bands at 7150 and 5260 cm^{-1}. A 1 mm pathlength enables detection at up to 5000 ppm weight.

An important parameter in the batch manufacture of polyols is the hydroxyl number of the product. Polyol products from a wide variety of different precursors and with varying hydroxyl numbers can be correlated using the band at 4830 cm^{-1}.

More recently FT-NIR spectroscopy has been successfully used for in-line monitoring of the transesterification reactions for biodiesel production [1].

NIR has also been used to monitor the concentration of NaOH for the control of scrubbing process gases prior to stack discharge to ensure that acid gas surges do not break through.

Cell Design

The transmission cells used in this project have a high efficiency coupling into fibres of only 200 μm diameter. A commercially available NIR fibre optic spectrometer was used to obtain the spectra shown. Sapphire optics in these cells have the benefit of low fouling in harsh environments. For liquid cells, flat windows are desirable in order to avoid refraction effects at the liquid-window interface. Similarly with vapour streams at pressures of ~8 bar the linear increase in vapour density with increasing pressures has shown that flat windows are preferable in order to prevent refraction losses.

High performance process cells are ruggedized transmission units that must be designed for use in process main stream pipelines or in fast loop by-pass systems. For coupling to the fibre optic system, industry standard SMA connectors are used which allow a wide choice of fibre diameter.

The design of a process cell cannot simply be based upon the modification of a laboratory cell. These cell types have entirely different requirements due to the unique demands on them in a process installation such as continuous exposure to harsh conditions over periods of months or even years.

Seal design, particularly around the optical components, is crucial to ensure leak free operation under all conditions. This may even include extreme thermal shock such as when superheated steam is introduced for cleaning. The principal factors that must be modelled are the thermal expansion coefficients of the components, the manufacturing tolerances (and their build-up), as well as the swell, chemical compatibility and compression set characteristics of the seal materials under the process conditions. Very often the latter are not well known and may have to be specially measured. For security, an independent back-up seal of totally different construction may be added along with a tell-tale leak path to warn of failure of the primary seal.

Results and Discussion

Liquid and vapor phase spectra are shown for acetic acid (Figure 1). 32 scans were co-added at spectral resolutions of 2 and 16 cm^{-1}. At a cell pathlength of 300 mm, pressure of 8 bar and temperature of 160°C, excellent signal-to-noise data was achieved. The simplicity of vapor phase spectra give them a big advantage over liquid phase studies. There are no hydrogen bonding interactions and whereas liquid phase spectra are critically dependent on temperature, this has not been so far the case for vapor phase work. As the chosen measurement pressure is increased, both the vapor density and the absorbance intensity increase linearly. The implication is that one selects the pathlength depending on the pressure in the system. We expect to be able to relax the pathlength to around 50 cm for studies at atmospheric pressure based on our data.

Vapor phase spectra for ethylene under the same conditions show Q branching data at 2 cm^{-1} (Figure 2) whereas at 16 cm^{-1} resolution this branch is suppressed. Spectra for water at 2 cm^{-1} also gave good resolution of rotational fine structure and the sensitivity is higher than for liquid phase data (Figure 3).

Conclusions

We have illustrated the principal design features necessary for process transmission cells capable of collecting spectra of chemically aggressive species under conditions of high temperature and pressure. The key achievements were the highly efficient optical coupling of a 200 μm fibre into the process cells allowing cost-effective installations and the seal designs. The high-performance quartz fibres also play a major role in the quality of data obtainable.

References

[1] de Lima, S.M., Silva, B.F.A., Pontes, D.V., Pereira, C.F., Stragevitch, L., Pimentel, M.F., Fuel, 115, (2014), 46–53.

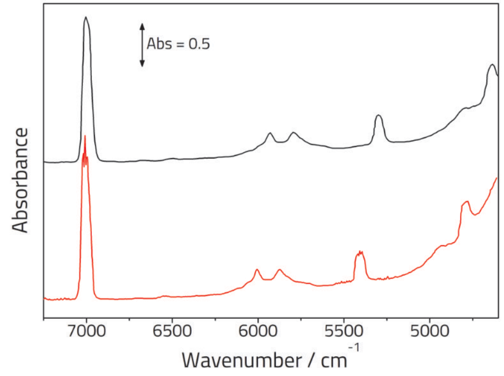

Figure 1: Acetic acid spectra. Liquid phase (top), Vapor phase (bottom)

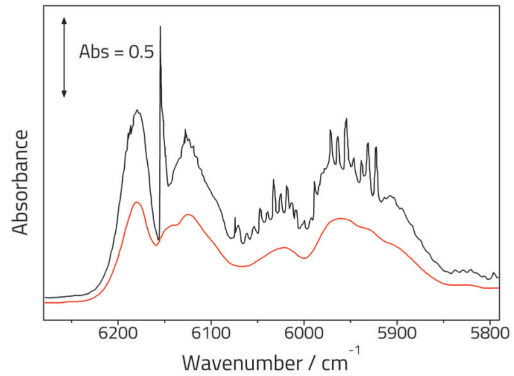

Figure 2: Vapor phase ethylene at 2 cm^{-1} (top) and 16 cm^{-1} (bottom) at 8 bar pressure and 160 °C, sampled remotely over a distance of 60 m.

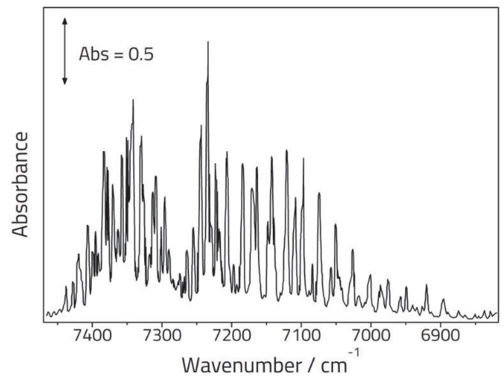

Figure 3: Vapor phase water spectra at 2 cm^{-1} resolution showing a good resolution of the rotational fine structure.