

## Optimising process NIR analysis with the tuneable-pathlength Spyder™ process flow cell

**In this note:** the Spyder™ process flow cell is used to determine the optimum pathlength for on-line FT-NIR measurement.

The optimal pathlength for an on-line FT-NIR process measurement needs to be determined by experimentation. Here we demonstrate the feasibility of measuring water in acetone by NIR spectroscopy at various pathlengths using an adjustable Spyder™ process flow cell, as a prelude to full-scale implementation of NIR process analysis on a production line.



### Introduction

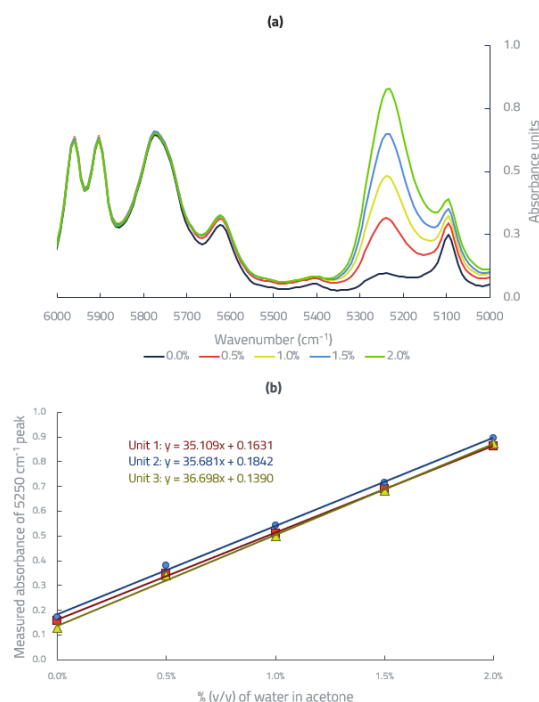
Monitoring the composition of a flow stream during production is key to ensuring the quality of the final product. Within the framework of Process Analytical Technology (PAT), efforts have been made to continuously monitor specific indicators such as the presence of contaminants, concentration thresholds for constituents during production, by-products, or properties of the final product. FT-NIR analysis provides these parameters through spectroscopic absorption measurements. By positioning process flow cells at different stages in the production unit, the flow stream can be continuously monitored.

FT-NIR relies on the detection of the absorption of molecular vibrational modes which, depending on the area of the spectrum they appear in, can be associated to a specific molecule. Monitoring the absorbance of spectral peaks associated with molecules that need to be tracked allows near-instantaneous control of the process. When conducting absorbance measurements, it is important to have enough dynamic range in peak intensity to monitor a range of concentrations; however, too much absorption will saturate the detector and lead to erroneous estimates of concentration. The main tool for controlling the intensity of peaks in the spectrum is the optical pathlength of the flow cells employed.

### Optimising pathlength in highly absorbing media

To showcase the tuneable-pathlength capabilities of the Spyder™ flow cell, we will follow a standard monitoring situation that can be especially tricky due to the nature of the contaminant: to monitor small concentrations of water

within a process. Dealing with water via FT-NIR is always a complex matter due to its high absorption compared with other molecules. For this reason, only a little water in a sample can lead to total saturation over the wavelengths absorbed by it. Nevertheless, in many production processes the amount of water content is important in the reactions that lead to the final product. In this example, we will be monitoring small concentrations of water in acetone using the absorption peak located around 5250  $\text{cm}^{-1}$ .



**Figure 1:** (a) Water in acetone at different concentrations for a nominal 2 mm pathlength and (b) the measured height of the 5250  $\text{cm}^{-1}$  for three different Spyder™ flow cells.

## 1. Consistency between process cells:

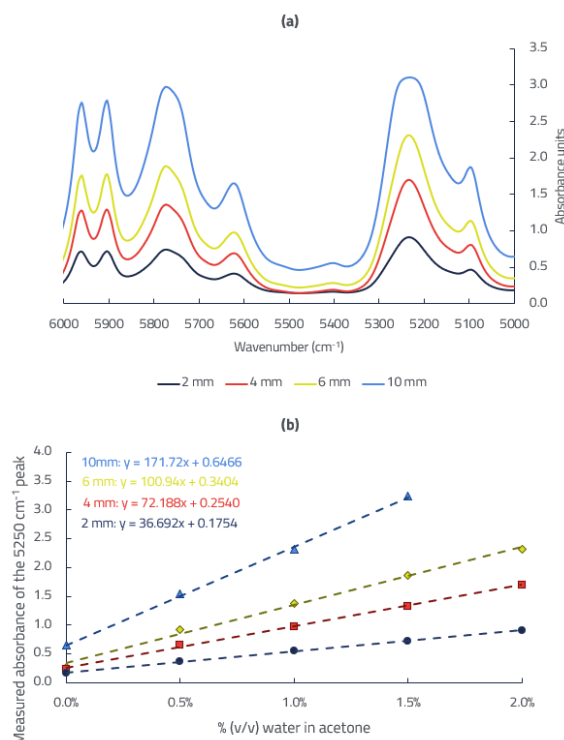
Preliminary tests at a nominal pathlength of 2 mm are plotted in Figure 1 for concentrations of water in the 0–2% (v/v) range typical of chemical process streams. Figure 1a shows spectra of samples with different water concentrations measured with the same Spyder™ flow cell, while Figure 1b shows the absorbance of the 5250 cm<sup>-1</sup> peak at different concentrations for three different Spyder™ flow cells.

Following Beer-Lambert's law ( $A = \epsilon cL$ ), the absorption ( $A$ ) is linearly proportional to the concentration ( $c$ ), whose slope is determined by the absorptivity ( $\epsilon$ ) of the attenuating component (water, in this case) multiplied by the optical pathlength ( $L$ ). Two observations can be made from the linear fit of the data in Figure 1b: first, the high and consistent  $R^2$  values (>0.998) in all samples shows that the data fit the expected linear relationship between concentration and absorbance predicted by the Beer-Lambert law. Second, the consistent slope and small standard deviation for all three cases ( $35.8 \pm 0.8$ ) demonstrates sample to sample reproducibility.

## 2. Changing the pathlength to ascertain optimal dynamic range:

Once the consistency of different process cells is proven, different pathlengths are explored to maximize the dynamic range of the discussed water peak. The range in absorbance values falls between 1.0 and 3.0 for the four different pathlengths at the higher concentration of 2% water in acetone shown in figure 2a. Since higher absorbance values imply less light reaching the detector we must be able to satisfy ourselves that the measured absorbances remain proportional to concentration. Absorbance values of 1.0 to 1.5 are considered safe as a "rule of thumb" but detailed consideration of the whole system may give us confidence at levels of 3.0 absorbance or more.

As before, Figure 2b shows the different linear fits for the different pathlengths measured. Again, the high  $R^2$  values obtained (>0.994) show the reliability of the method and technique. In our example, the 10 mm pathlength saturates for concentrations close to 2%. To limit the absorbance values to <1.5 a pathlength of 2 or 4 mm could be set. This will keep the calibration strictly linear and would allow for some margin should conditions in the field (for example fouling) impact the light-throughput negatively.



**Figure 2:** (a) 2% (v/v) water in acetone at varying pathlengths in a Spyder™ cell and (b) linear fits of the 5250 cm<sup>-1</sup> peak across various pathlengths.

## Conclusions

This exercise is required during a normal process, either to decide the optimal pathlength before proceeding to pilot or production implementation. The pathlength of a Spyder™ cell can be locked in place using the Stainless-Steel ferrules provided with the Spyder™ flow cell, enabling its use at the high pressures and temperatures of a chemical process. Alternatively, the results may be used to specify a bespoke high-performance process flow cell such as the Vortex™. Tuning the optical pathlength through testing for a precise application is key before planning and setting a production plan. Spyder™ allows this process before locking it in place for a set pathlength and monitoring of the process using the best conditions.

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