

Application Note – Water in Solvents

The measurement of low levels of water in hydrocarbon solvents is critical to many chemical processes. This note discusses the measurement of the water concentration in using fiber optic-based, Near-Infrared (NIR) spectroscopy. NIR can be applied in real time mode for continuous process monitoring, or as a laboratory procedure. In either case the NIR technique saves time and money through rapid non-destructive analysis. NIR also offers the benefit of increased safety over traditional methods.

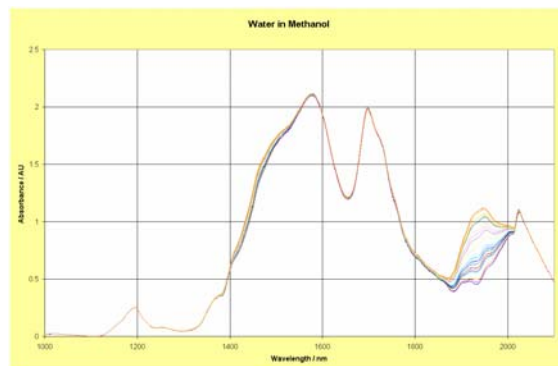
Measurement Background

The NIR region of the electromagnetic spectrum allows the use of the overtone and combination bands of the C-H, O-H, and N-H fundamentals. Water has two strong absorption bands in the NIR making it an excellent candidate for making low level measurements. The bands occur at 1400 nm and 1900 nm, the latter being the most intense. The choice of which band to use is determined by the background solvent and water concentration. By measuring the NIR spectra of a series of samples of known water concentration, a quantitative model can be developed which will allow the measurement of water in future samples based only on their NIR spectrum.

Experimental – Water in Methanol

The NIR spectra of a group of 22 samples of different levels of water in methanol were measured between 1000 and 2100 nm using a Guided Wave Model Process NIR Spectrophotometer and a 1 cm pathlength cell at constant temperature. Figure 1 shows the absorbance spectra of the samples with water concentrations ranging from 0 to 2%. The data from 1400 to 1800 nm has very high absorbance levels due to the Methanol. This region of the spectrum is not needed for water measurement and will be omitted from the regression analysis. The spectra were baseline corrected and submitted with the concentration data to Camo's Unscramblertm multivariate analysis software for calibration using Partial Least Squares (PLS) regression methodology. For a discussion of the PLS regression method and other multivariate calibration techniques

Figure 1 NIR Spectra of Water in Methanol 0-2%



please see Martens & Naes¹ and ASTM E1655².

Results – Water in Methanol

The results are shown in figure 2. The model RMSEP cv (root mean square error of prediction for cross validation) was 507 ppm over the entire range of values. This equates to about 1% relative error on average. This experiment was run at constant temperature. Changes in spectral data can be expected with temperature variation, but this can be compensated for by simply including samples measured at different temperatures in the model.

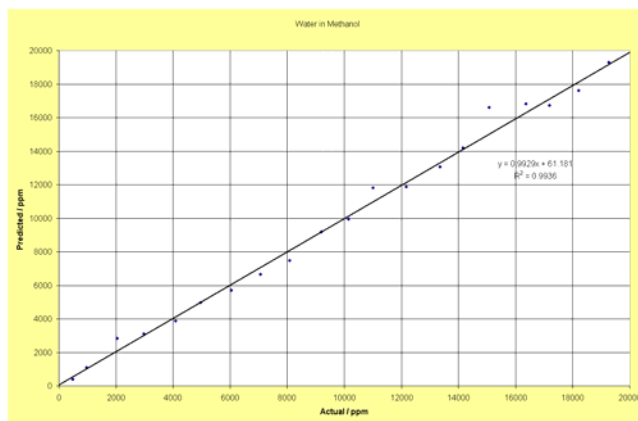


Figure 2 Predicted vs Actual water in methanol

Experimental – Moisture in Hydrocarbon (non-alcohol)

To demonstrate lower levels of water measurement the NIR spectra of a group of 17 samples containing different levels of water in a hydrocarbon background were measured between 1100 and 1600 nm using a Guided Wave Model Process NIR Spectrophotometer and a 3 cm pathlength cell. The longer pathlength is used to allow the use of the 1400 nm peak. Figure 3 shows the absorbance spectra of the samples with water concentrations ranging from 0 to 1500 ppm. The water band is observed in the 1400 nm area. This region of the spectrum was selected for the regression analysis. A first derivative was applied to the spectral data to correct for baseline offsets and the resulting data submitted with the concentration data to Camo's Unscramblertm multivariate analysis software for calibration using Partial Least Squares (PLS) regression methodology.

Results – Low Levels of Water in Hydrocarbon

The results are shown in figure 4. The model RMSEP cv (root mean square error of prediction for cross validation) was 16 ppm water. Water can be detected at much lower levels in non-OH

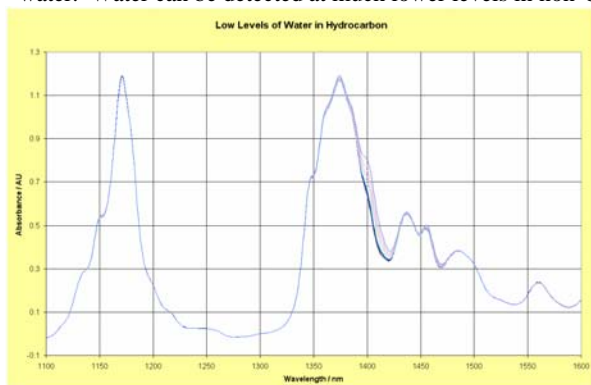


Figure 3 Absorbance Spectra - Low levels of water in hydrocarbon

References

1. H. Martens, T. Naes, Multivariate Calibration, John Wiley & Sons, 1989.
2. ASTM E1655 Standard Practices for Infrared, Multivariate, Quantitative Analysis.

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Guided Wave Incorporated

3033 Gold Canal Drive
Rancho Cordova, CA 95670
USA
Tel: 916.638.4944; Fax: 916.635.8458
gwinfo@guided-wave.com

www.guided-wave.com

Guided Wave BV

PO Box 427
7550 AK Hengelo (o)
The Netherlands
Tel: +31.74.2595390; Fax: +31.74.2595752
info@guided-wave-europe.com

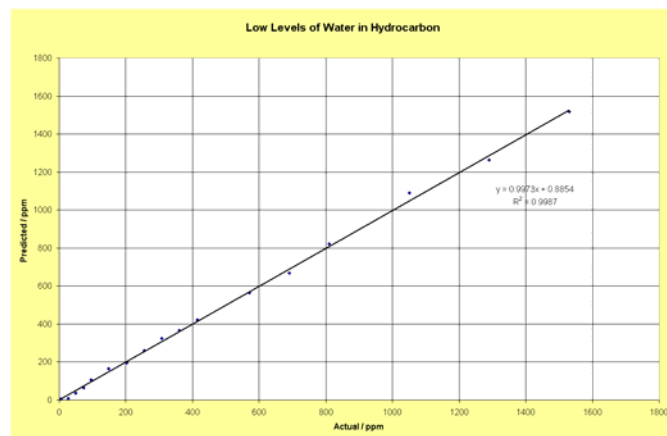


Figure 4 Predicted vs Actual water in hydrocarbon

containing solvents since there is less interaction between the base solvent and the water.

Conclusion

The measurement of the water levels in hydrocarbon solvents with NIR spectroscopy is both fast and reliable utilizing the Guided Wave hardware and software tools as described here. This method produces results that are available in real-time (seconds) thus making it a valuable tool for process measurement. This method can be applied in either a process or a laboratory environment. For more detailed information regarding system specifications please contact a Guided Wave sales or technical specialist.