



Water in Solvents and Chemicals

Industry: Chemical
Product: NR800

Background Information

Water is often determined by FT-NIR in a variety of pure solvents and chemicals. Here we describe three such applications. Process streams for industrial solvents and pure chemicals are typically clear, free of particulate matter for the most part and easily measured using transmission cells.

Water in Methane

Figure 1 shows the spectrum of Methanol with water added in the 0-2000 ppm range. For Methanol, a very narrow range of the spectrum is actually used for calibration and measurement. The region from 5153 to 5369 cm^{-1} is used. Figure 2 shows a detail of this region and the difference between the spectra can be seen. To eliminate interference and error caused by shifts in the baseline, the spectra are first transformed by taking the first derivative. Figure 3 shows the first derivative spectrum in the same region.

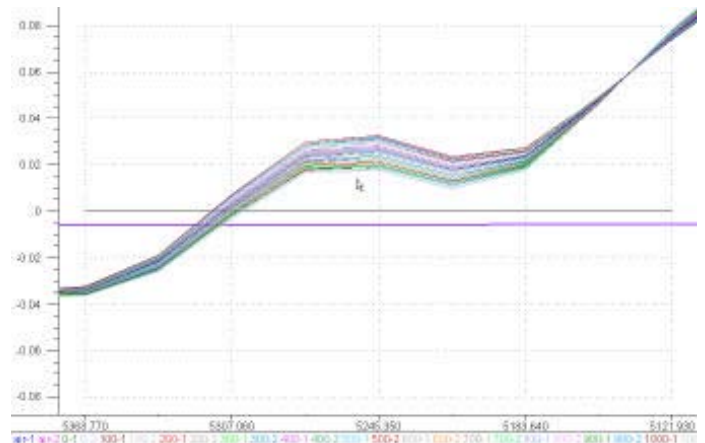


Figure 2: First Derivative Spectrum from 5153 to 5369 cm^{-1}

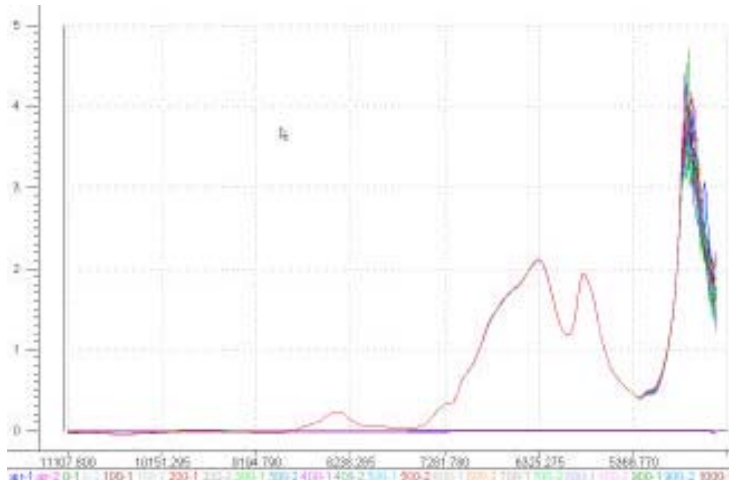


Figure 1: Spectrum of Methanol with 0-2000 ppm Water added

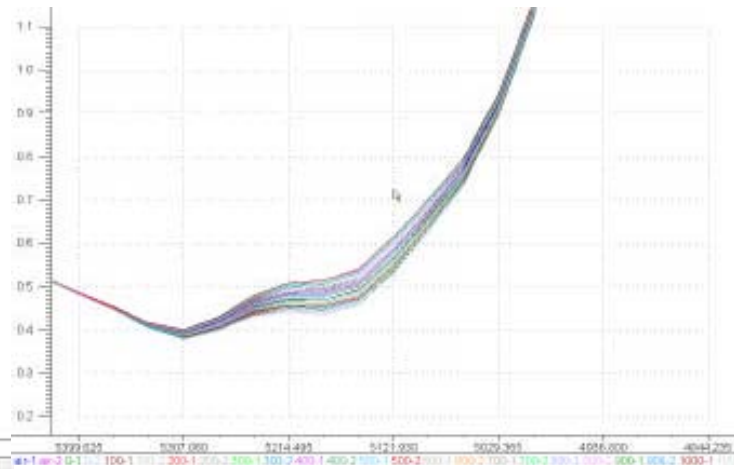


Figure 3: Detail of Spectrum from 5153 to 5369 cm^{-1}

Water in Solvents and Chemicals

Methanol calibrates well using this region as shown in the Predicted vs. Measured plots from the calibration model, Figure 4.

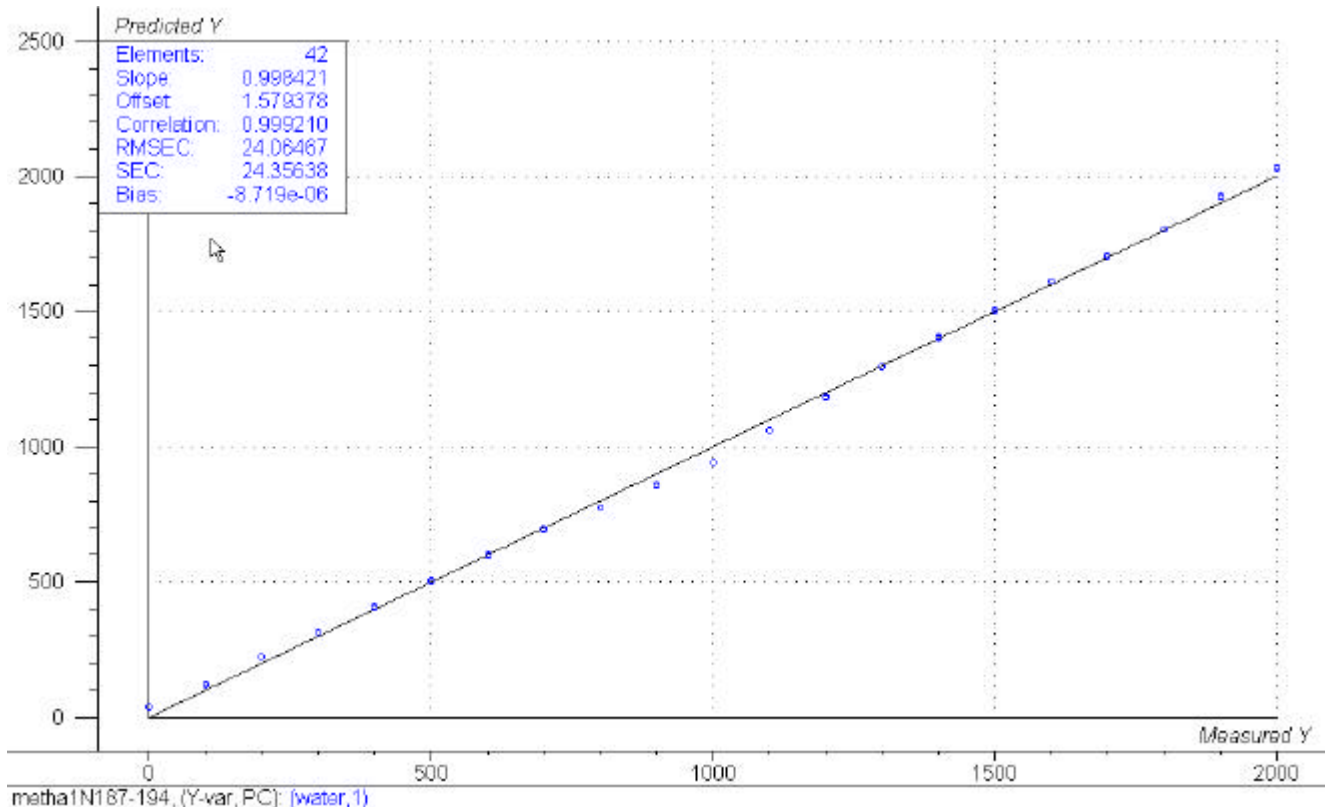


Figure 4: Predicted vs. Measured Water in Methanol

These measurements were performed using a 2 mm cell path length and 40 cm⁻¹ resolution.

The RMSEC (Root Mean Square Error of the Calibration) is a “1 s” measurement of the difference between water concentrations predicted by the FT-NIR and the actual water measurements determined in the lab. Thus the typical accuracy of the FT-NIR calibration can be said to be +/- 48 ppm at the 95% confidence level (2 s). Two spectra were

used at each concentration level for make the calibration model. The standard deviation of duplicate spectra was +/- 3 ppm H₂O. As is often the case, the repeatability of measurements by FTNIR is much better than the accuracy when compared to lab data. This is because the RMSEC includes the variations in the lab data, as well as the variations due to the FT-NIR. The repeatability is dependent only the ability to the FT-NIR to produce the same spectrum for the same sample.

Water in Solvents and Chemicals

Water in Acid

Similarly, water can be determined in Acetic Acid, but Acetic Acid has a very large absorbance in the 5153-5369 cm⁻¹ range due to the R-COOH functionality. Therefore the region 6665-7220 cm⁻¹ is used. Figure 5 shows the full spectrum of Acetic Acid with 0-2000 ppm Water added. Again the first derivative is taken as the basis for the model and the Predicted vs. Measured plot shows excellent accuracy.



Figure 5: Spectrum of Acetic Acid with 0-2000ppm Water Added.

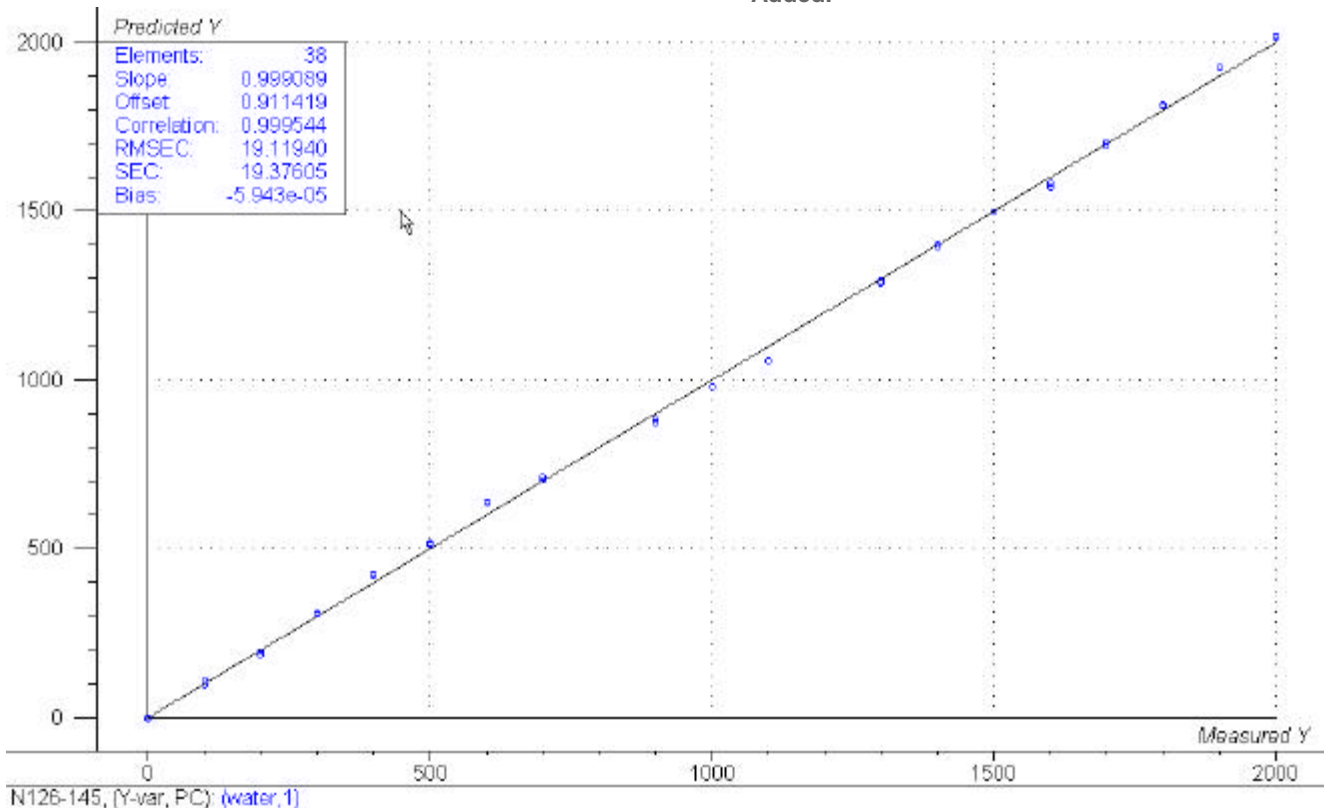


Figure 6: Predicted vs. Measured Plot for 0-2000 ppm Water in Acetic Acid

Water in Solvents and Chemicals

Note that in order to compensate for the weaker absorbance of water in the 6665-7220 cm^{-1} region, a 10 mm cell was used. The RMSEC was approximately +/- 19 ppm H_2O , and the standard deviation of duplicate spectra was 7.4 ppm H_2O .

Water in Acrylonitrile

In this example, we demonstrate some features of The Unscrambler® which can make for a more precise and robust calibration model. Note in Figure 7 that the baseline of raw spectra deviate from zero substantially. As in the previous cases, we transform the data by taking the first derivative of the spectra, which eliminates the baseline offset. See Figure 8.

Next, we create the PLS 1 calibration model using the spectral range 4813–5646 cm^{-1} and examine it. The RMSEC for our first attempt is 148 ppm, which is not bad, but we ask The Unscrambler to mark the outliers. Outliers are data points which are sufficiently different from other data to make them suspect. In this case, The Unscrambler marks all the lower concentration data, leading us to suspect that these points may have inaccurate lab data or some bias that is not in the other data points. See Figure 9. We recalculate the PLS1 calibration model without the suspect samples (easily done in two clicks) and the model improves substantially. The RMSEC of the new model is 49 ppm. See Figure 10.

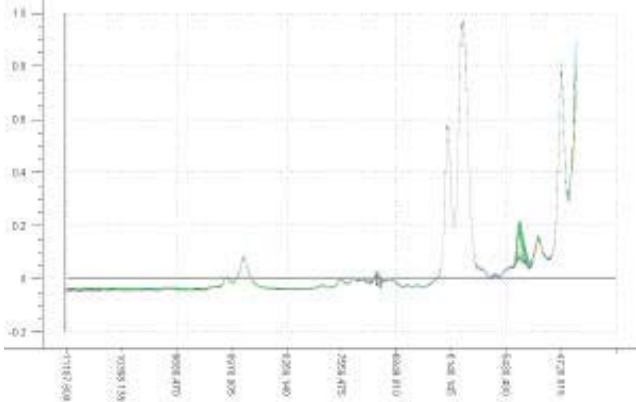


Figure 7: Spectra of Acrylonitrile with 0-5000 ppm water added

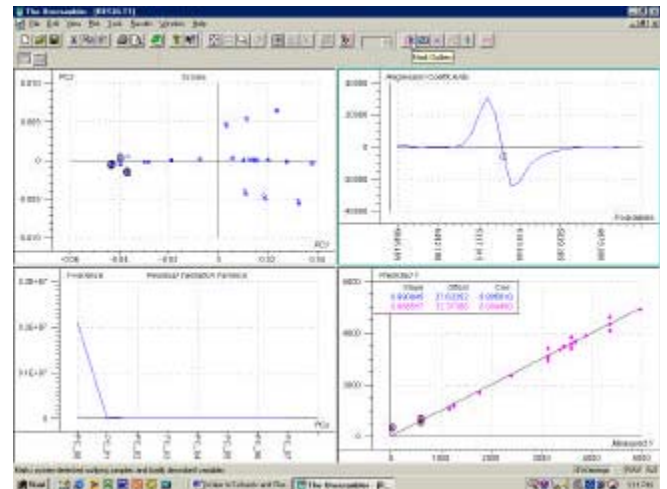


Figure 8: PLS1 Calibration Summary

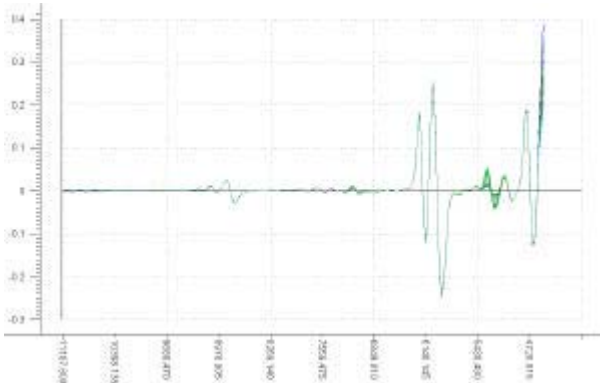


Figure 9: PLS1 First Derivative Spectra of Acrylonitrile

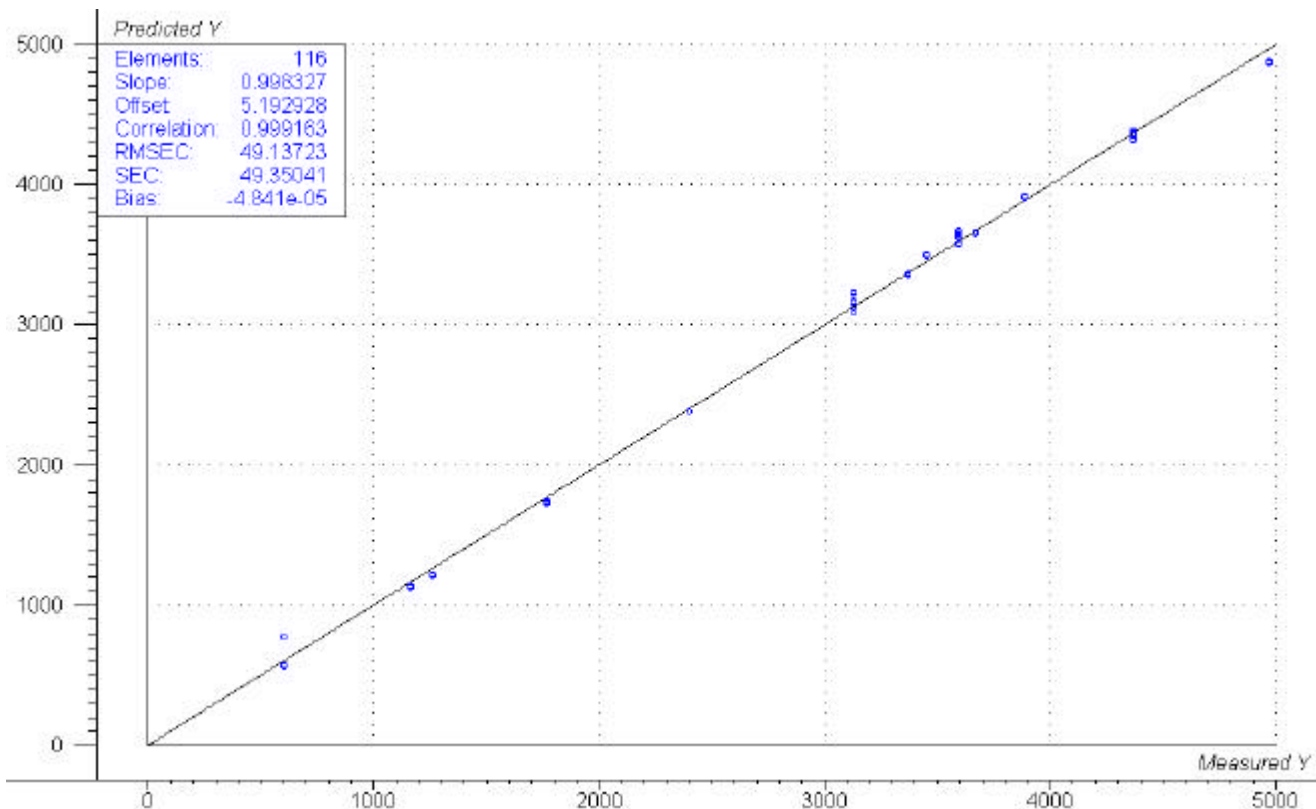


Figure 10: Summary of final Water in Acrylonitrile calibration

Conclusion

Water in Methanol and Acetic Acid is readily measured using FT-NIR in the 0-2000 ppm range with accuracies of about +/- 20 ppm H₂O. Water measurements in the range 0 – 5000 +/- 49 ppm has also been demonstrated in Acrylonitrile streams. Different spectral regions and cell path lengths may be

required for different sample streams, and each calibration initially requires custom application engineering. The simultaneous multi-channel capability of the NR800 makes simultaneous measurements of water in widely different sample streams possible