

Low Level Organics in Water: Saccharin

Under appropriate conditions, near-infrared (NIR) spectroscopy can be used to measure low levels of organics in water. This application note will discuss measuring saccharin to levels below 60 ppm over a temperature range of 16°C to 32°C. Saccharin is used as a sweetener and preservative in pharmaceuticals, nutraceuticals, and food and as an agent in semiconductor plating baths. Molecules similar to saccharin, *i.e.* benzo substituted heterocyclic rings, are used in semiconductor cleaning solutions. Hence, it is often required to know and control organic concentrations in water in the 100 ppm range and below. Another application is the measurement of total organics in wastewater streams. NIR can be used as a high level alarm to detect breakthrough in wastewater treatment plants.

Saccharin in Water

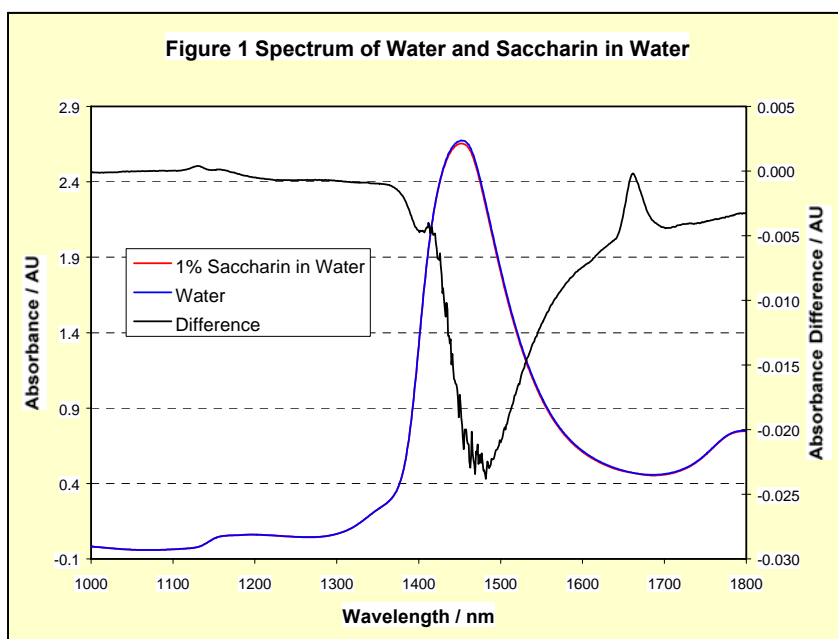
Figure 1 shows the spectrum of water and 1% sodium saccharin hydrate in water at a 2 mm path. Saccharin's first overtone aromatic C-H stretch peak occurs at 1661 nm and is clearly visible in the difference spectrum. However, it occurs in a region where water has a baseline absorbance of 0.5 AU, which is 100 times the saccharin absorbance at 1% and 10,000 times its absorbance at 100 ppm.

Water in the NIR

Water is the most frequently used solvent. However, it is not often associated with NIR spectroscopy because of its extremely strong NIR absorption. Its highly polar nature leads to a very large spectral thermal coefficient. Figure 2 shows a portion of the NIR spectrum of water over the temperature range of 17°C to 32°C relative to its spectrum at 16°C. In the 1660 nm region, the changes in the water spectrum are nearly 0.05 AU, or 10% of the baseline absorbance and 1000 times the saccharin absorbance at 100 ppm. Clearly, temperature must be controlled or its effects removed by appropriate modeling. Fortunately, these changes are well behaved and fit a quadratic equation in temperature quite nicely. Even better, the spectrum itself can be used to determine the temperature of the sample; thus neither temperature sensors nor costly control is required.

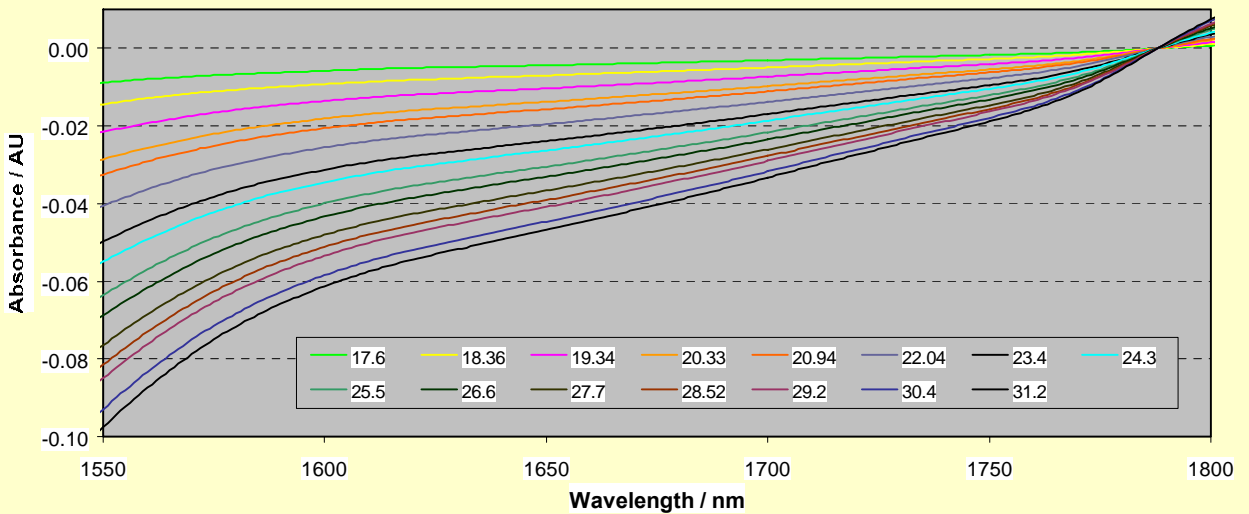
The Data Set

Samples (deionized (DI) water and sodium saccharin hydrate in DI water) were placed in a glass test tube, which was immersed in a temperature controlled circulating water bath. A Guided Wave 2 mm [SST probe](#) was inserted into the sample along with a RTD temperature sensor. Spectral data was collected over 40 m of 500 μm diameter single strand low-OH fused silica [fiber](#) on a Guided Wave [Lab 412](#) extended range NIR spectrometer. In all, 16 spectra of pure water and 368 spectra of saccharin solution were recorded over a concentration range of 0.0016 wgt% to 1.014 wgt% and a temperature



range of 16°C to 32°C. The saccharin sample set consisted of 13 solutions, all prepared by weight from sodium saccharin hydrate. Each scan was an average of 32 scans, requiring 93 s to collect. Noise measured on this instrument, under these conditions was 13 μ AU rms over the spectral range from 1550 nm to 1800 nm.

Figure 2 Change in Water Spectrum with Temperature



Removing the Water
After examining the data, it became clear that the RTD accuracy of $\pm 0.1^\circ\text{C}$ was not sufficient for this application. This implies that sufficiently

Figure 3a Water Coefficient Intercept

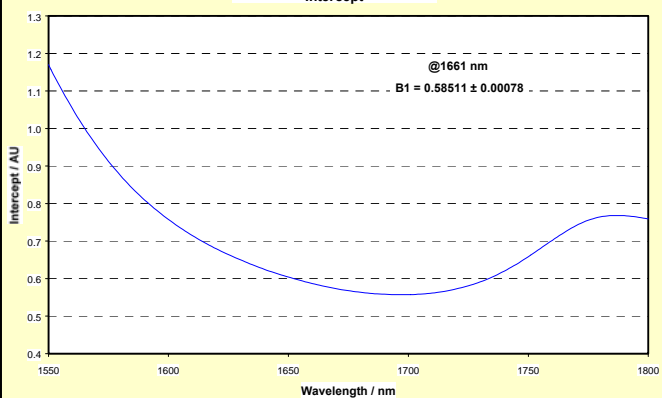


Figure 3b Water Coefficient Slope Term

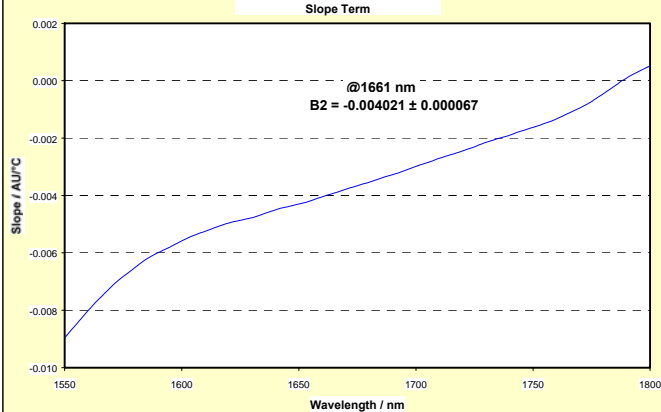
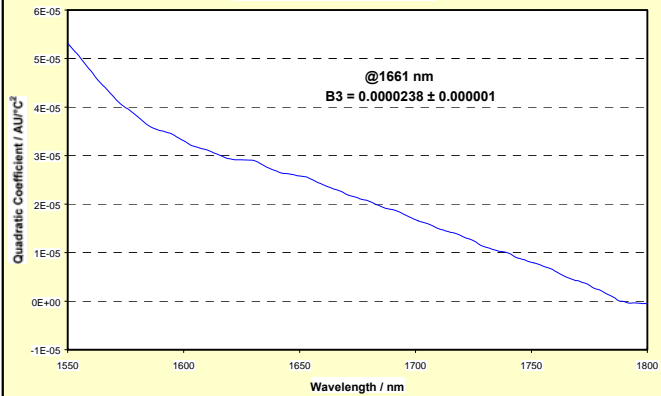


Figure 3c Water Coefficient Quadratic



accurate temperature control would be impractical. Using the pure water data, a quadratic regression model was built relating absorbance at 1600 nm to the RTD temperature. The residuals of this model were random, thus proving that prediction of temperature from the spectra would be more accurate than the RTD measurement, since the spectra were quite repeatable. Using the predicted temperatures, the absorbance at each wavelength was regressed again using a quadratic model. The regression coefficients are shown in Figure 3. The spectral residuals for the water fit are shown in

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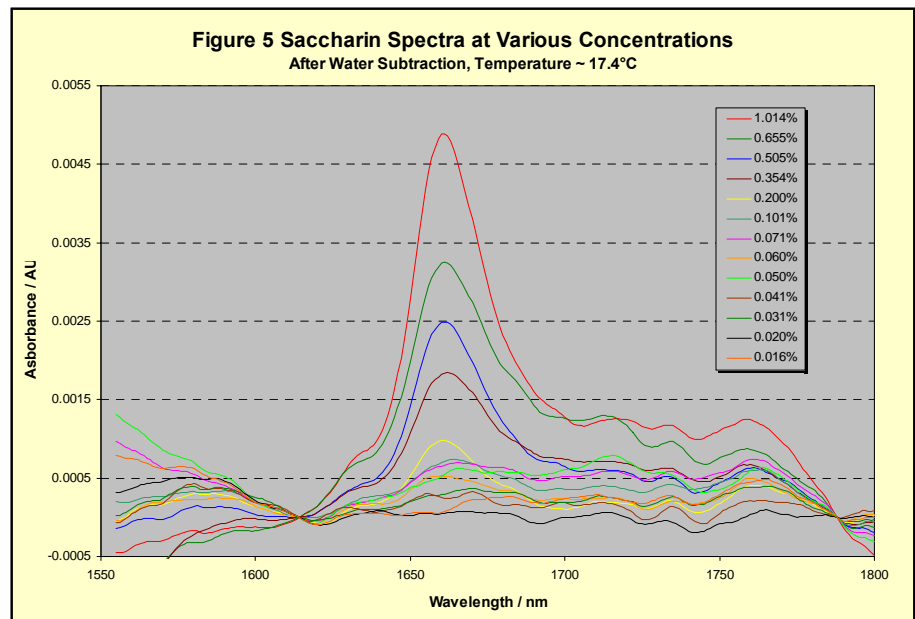
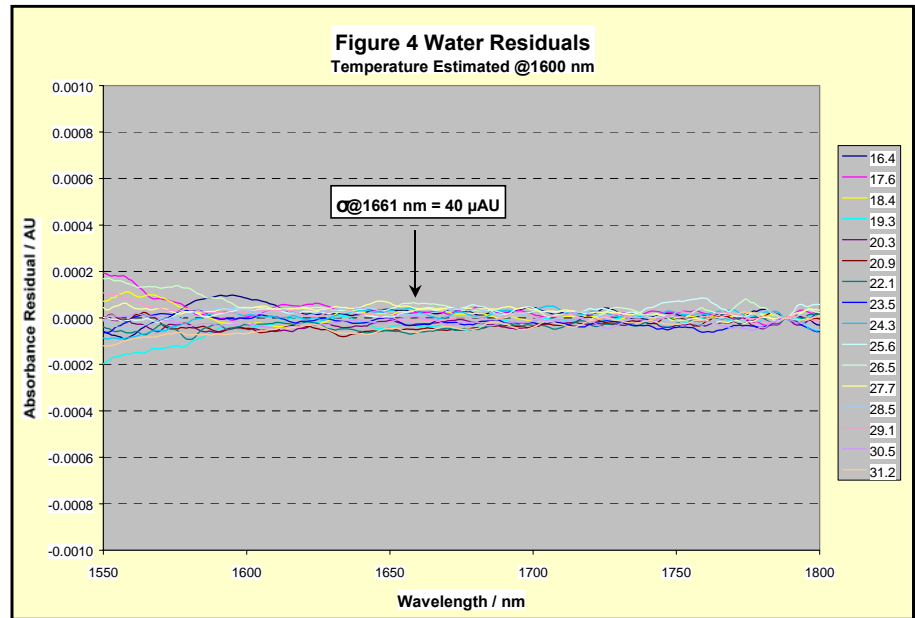
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Figure 4. The residuals are approaching the noise floor of the analyzer; hence this method of removing the water background is quite effective.

The Saccharin Solution

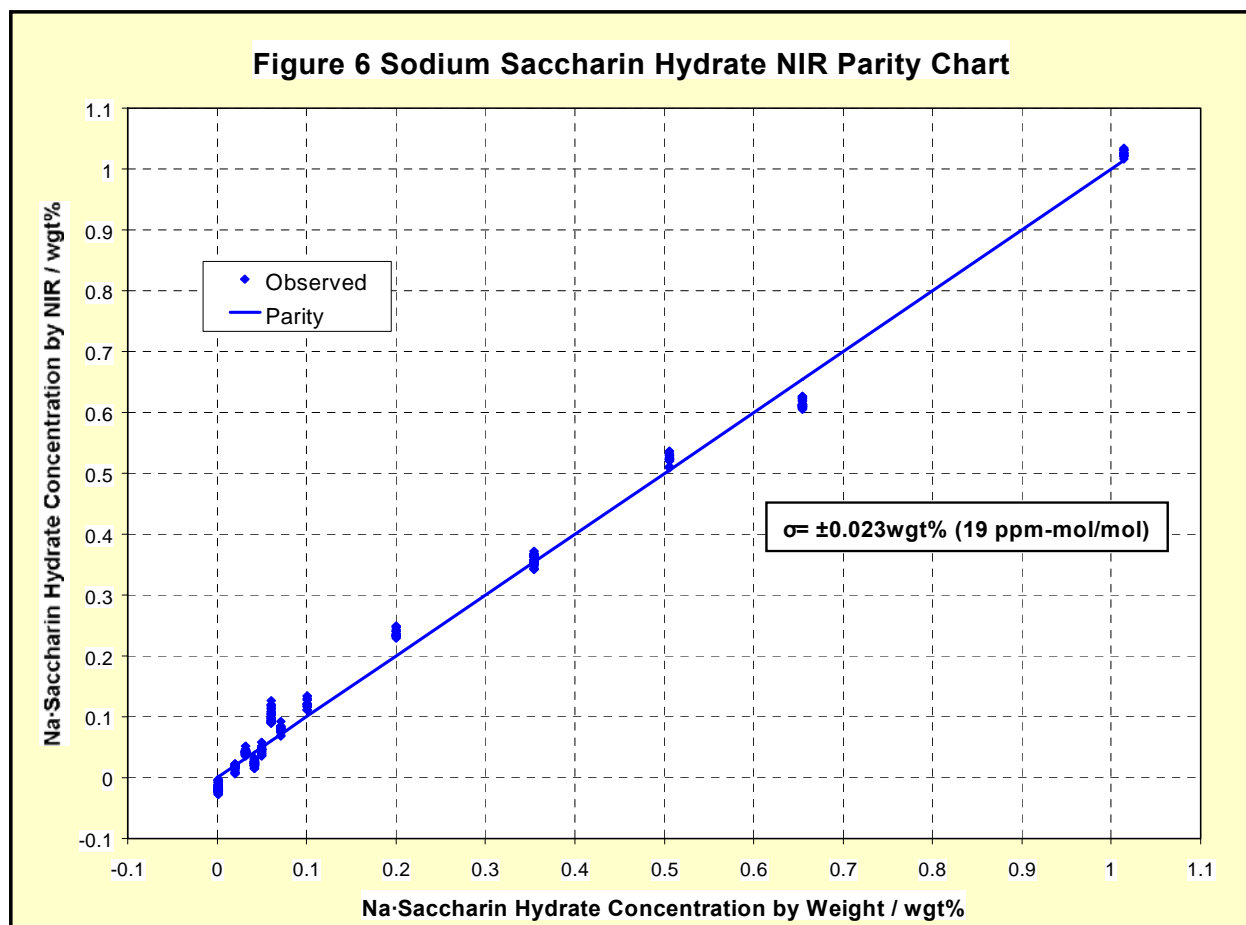
Using the initial regression of pure water absorbance at 1600 nm vs. temperature, a predicted temperature for each saccharin spectrum was computed. Using the predicted temperature and the quadratic regression equations for water vs. temperature at each wavelength as noted above, the underlying water baseline was generated and subtracted from each solution spectrum yielding a pure saccharin spectrum. Samples of the resulting spectra at approximately 17.5°C are shown in Figure 5. The isolated saccharin peak at 1661 nm was then regressed against its concentration to yield the parity chart in Figure 6. This chart includes all data (368) collected at all concentrations and temperatures. This process resulted in a standard error of calibration of 0.023 wgt% sodium saccharin hydrate or 19 ppm saccharin. Using 3σ as the conversion factor, yields a detection limit of 57 ppm of saccharin in water by NIR spectroscopy.



Conclusions

Modern NIR analyzers are quite sensitive, with extremely low noise and high wavelength stability; hence are capable of measuring low levels of organics dissolved in water at concentration levels below 100 ppm. Under appropriate conditions, the large change in the background spectrum of water due to temperature can be removed without the need for expensive temperature control hardware or measurement devices. All the necessary information is contained in the spectra.

The methods discussed here can be easily implemented on-line using current NIR analyzers. The approach applies to any molecule similar in structure to saccharin.



Reference

Todd, T. R. and R. Muegge, "Measuring Low-level Organics in Water using NIR Spectroscopy," Seventh International Forum Process Analytical Chemistry, Scottsdale, AZ, paper I-034, Jan. 23, 2003.

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