Process Insights
Premium Insights Into Process

GuidedWave

Application Note:

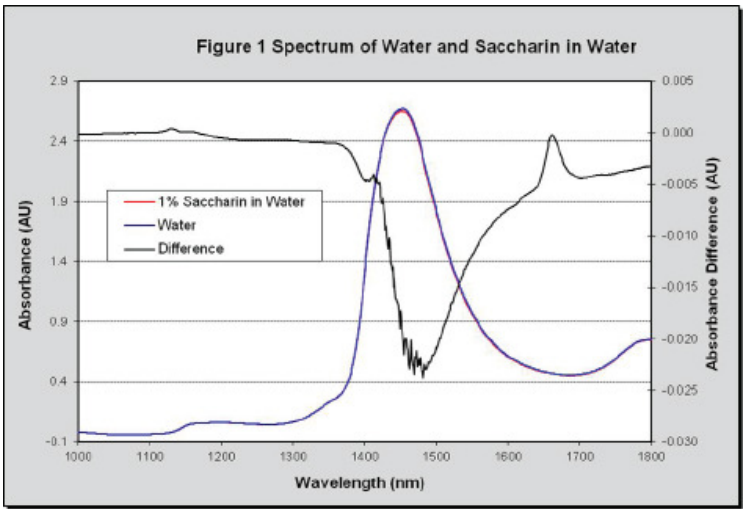
Low Level Organics in Water: Saccharin

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. These applications often require control of organic concentrations in water in the 100 ppm range and below. Another similar application is the measurement of total organics in wastewater streams. In that situation, NIR can be used as a high level alarm to detect breakthrough in wastewater treatment plants.

NIR-O™ Process Analyzer - Spectrometer

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 peak (C-H stretch) 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. This baseline absorbance is 100 times the saccharin absorbance at 1% and 10,000 times the saccharin absorbance at 100 ppm. This makes a low concentration measurement a challenge.



Water in the NIR

Water is a common solvent, but presents many challenges as a background material in the NIR due to its extremely strong NIR absorption. Water's highly polar nature also 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. In the 1660 nm region, the changes in the water spectrum with temperature are significant. This means that temperature must be controlled or its effects removed by appropriate modeling. Fortunately, the changes in the spectrum are well behaved and provide a means for removing the temperature effects.

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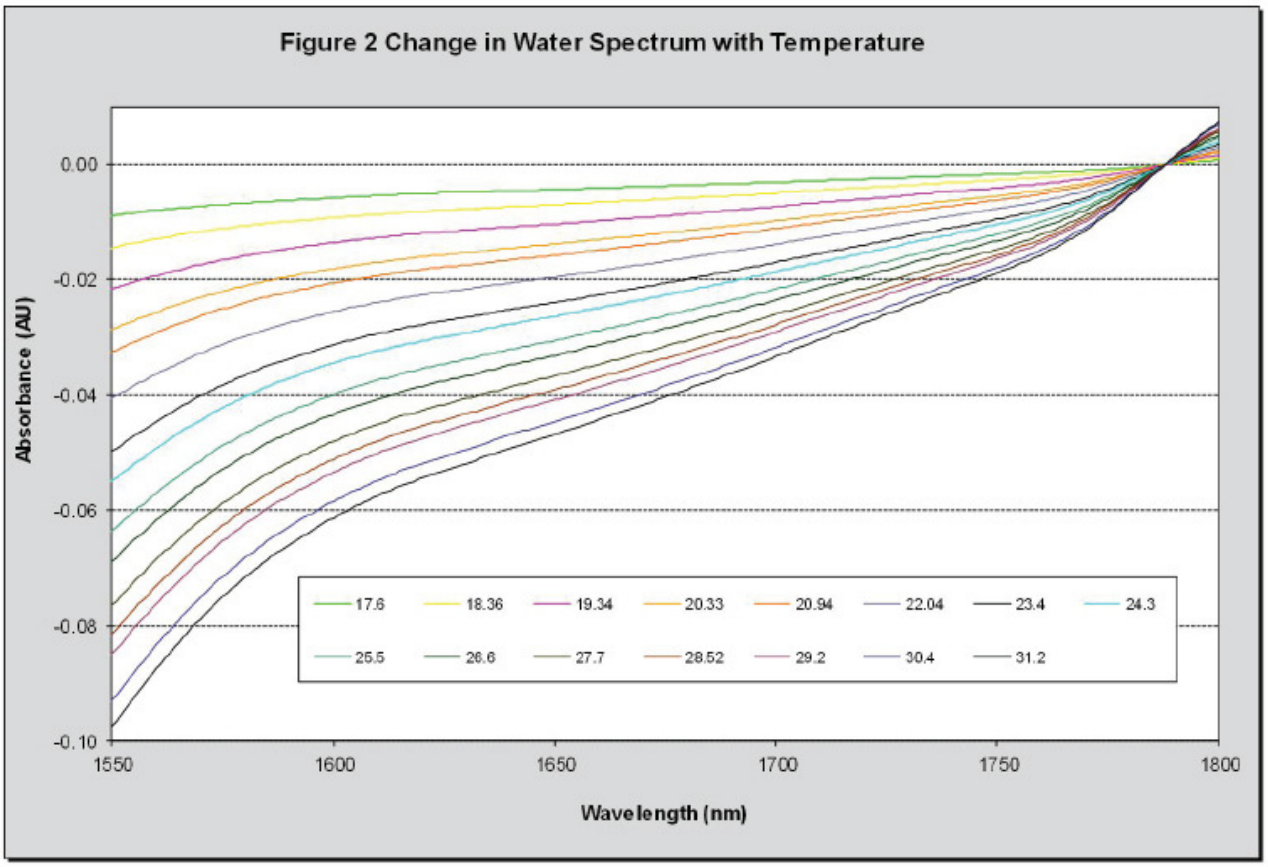

The Data Set

Samples, deionized (DI) water and sodium saccharin hydrate in DI water, were measured in a temperature controlled bath using a Guided Wave 2 mm SST probe along with a RTD temperature sensor. The SST probe was connected to the Guided Wave NIR-O extended range NIR spectrometer by 40 meters of 500 µm diameter single strand low-OH fused silica fiber optics. A total of 16 spectra of pure water and 368 spectra of saccharin solution were recorded over a concentration range of 0.0016 wt% to 1.014 wt% and a temperature range of 16°C to 32°C. The saccharin sample set consisted of 13 sample solutions, all prepared by weight from sodium saccharin hydrate. Each spectrum collected was an average of 32 scans, requiring 93 s to collect. Noise measured on this instrument, under these conditions was 13 µAU rms over the spectral range from 1550 nm to 1800 nm.

Removing the Water

After examining the data, it became clear that the RTD accuracy of ±0.1°C was not sufficient for this application. This implies that sufficiently 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.

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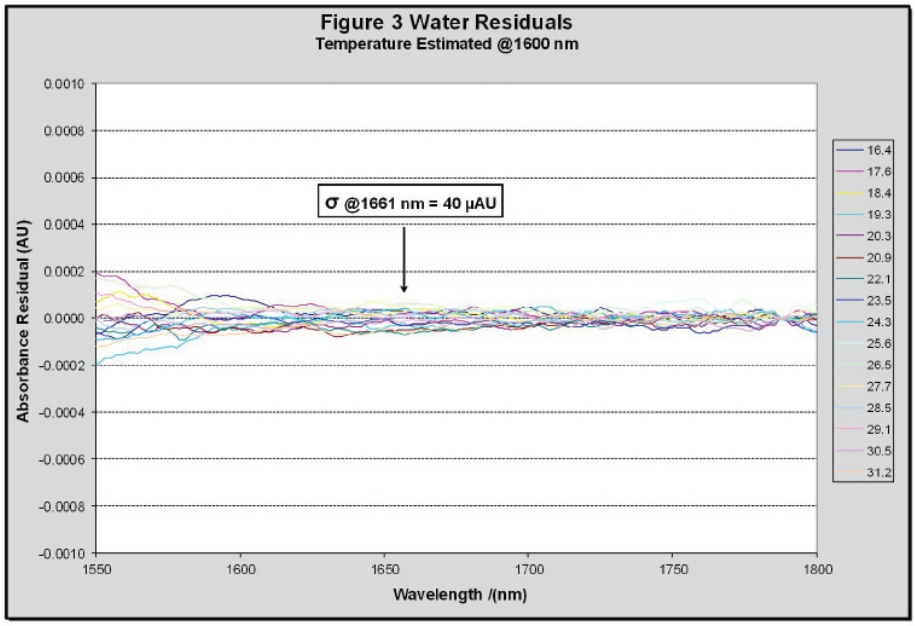
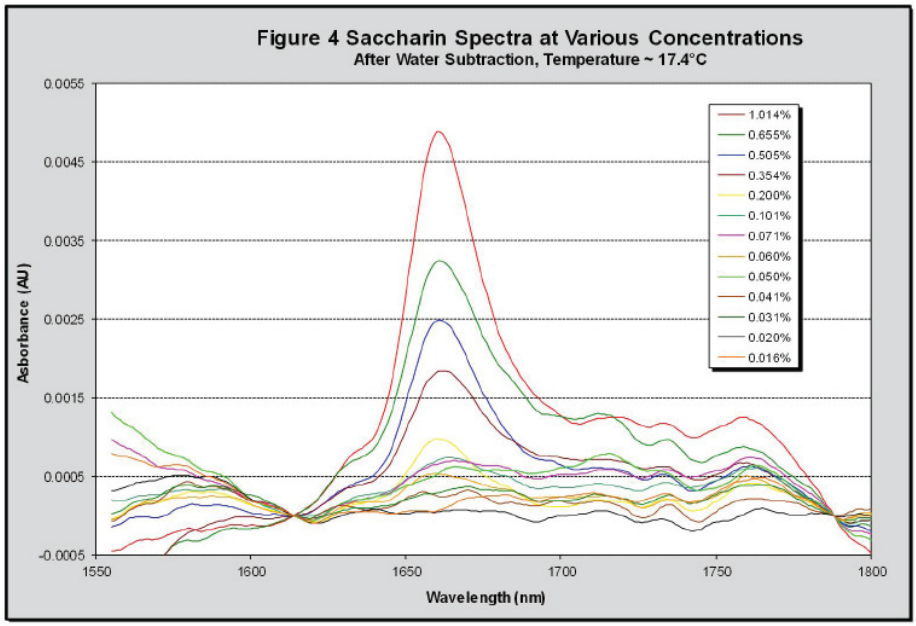
The spectral residuals for the water fit are shown in Figure 3. The residuals are approaching the noise floor of the analyzer; hence this method of removing the water background is quite effective.



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 4. The isolated saccharin peak at 1661 nm was then regressed against its concentration to yield the parity chart in Figure 5. This chart includes all data (368) collected at all concentrations and temperatures. This process resulted in a standard error of calibration of 0.023 wt% sodium saccharin hydrate or 19 ppm saccharin. Using 3σ as the conversion factor, this yields a detection limit of 57 ppm of saccharin in water by NIR spectroscopy.



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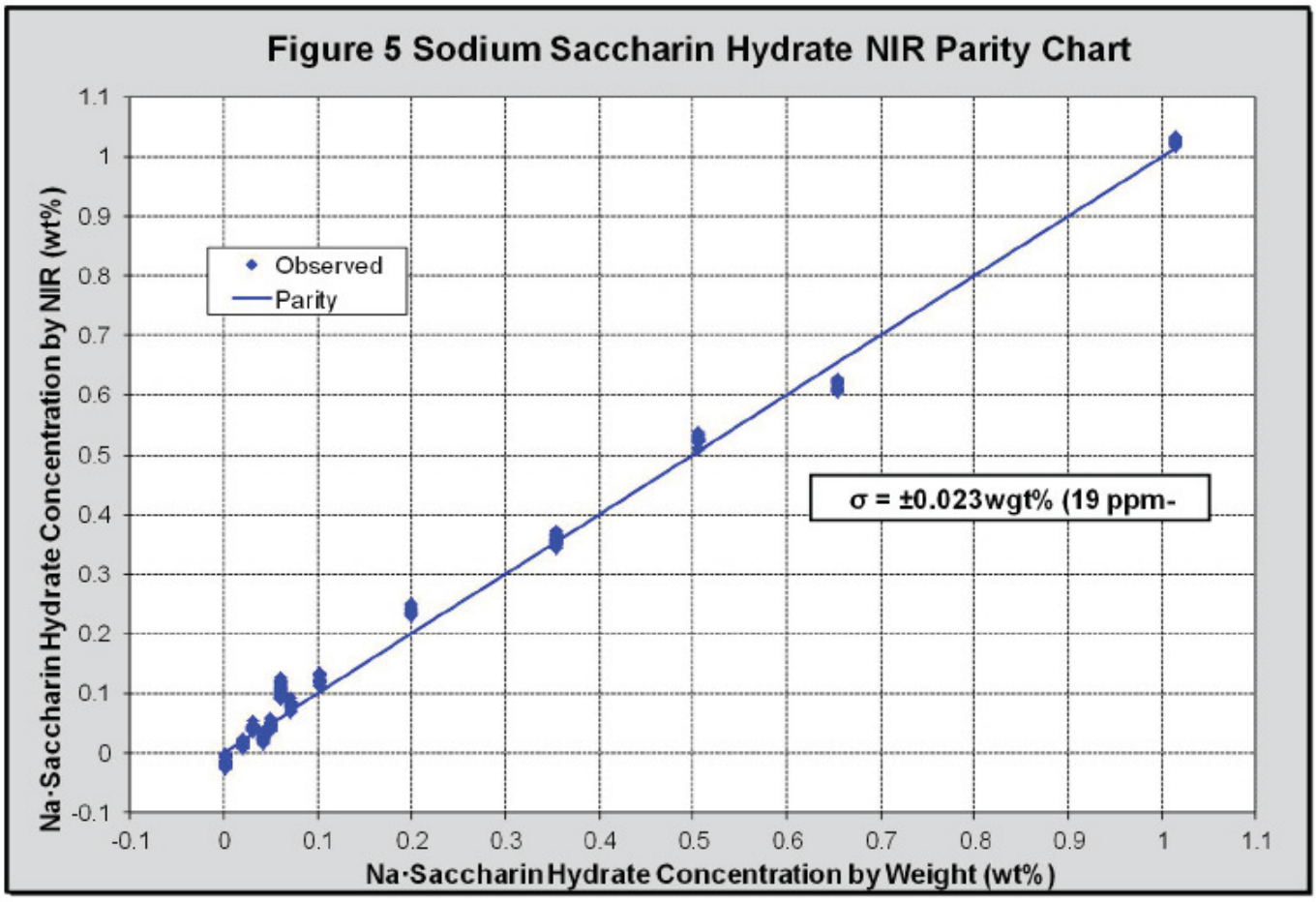

Conclusions

Modern NIR analyzers are quite sensitive, with extremely low noise and high wavelength stability. The characteristics facilitate the measurement of 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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