

APPLICATION NOTE

Low Level Organics in Water: Saccharin Using a NIR-O™ Spectrometer

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.

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 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 16 °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.

The Data Set

Samples, deionized (DI) water and sodium saccharin hydrate in DI water, were measured in a temperature controlled bath using our GUIDED WAVE™ 2 mm Single-Sided Transmission (SST) Probe along with a RTD temperature sensor. The SST probe was connected to our GUIDED WAVE NIR-O™ process analyzer, extended range 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 scans to collect. Noise measured on this instrument, under these conditions was 13 µAU rms over the spectral range from 1550 nm to 1800 nm.

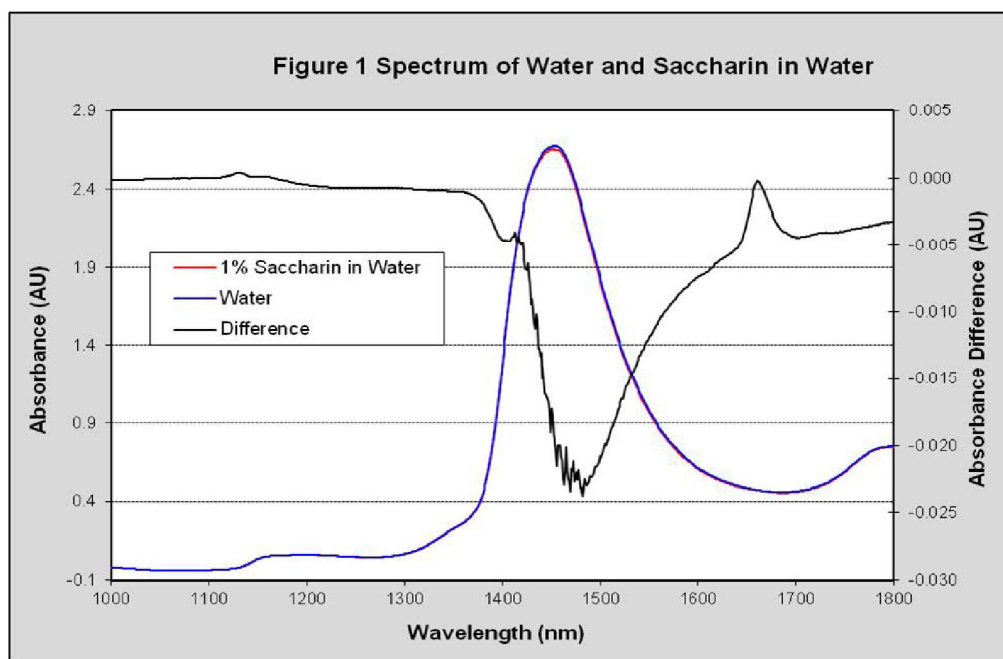


Figure 1: Spectrum of Water and Saccharin in Water

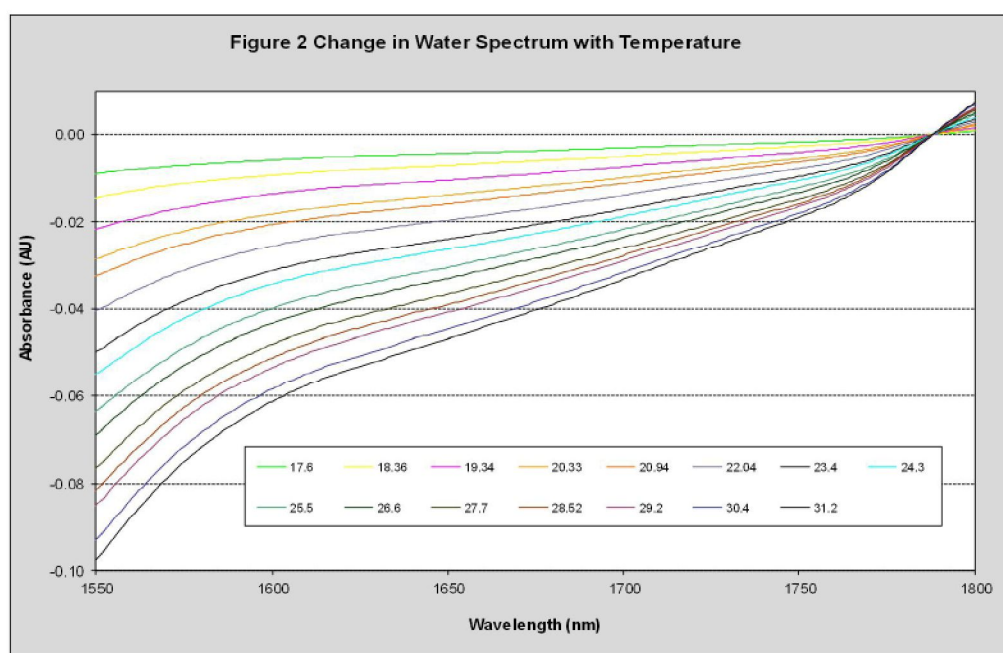


Figure 2: Change in Water Spectrum with Temperature

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. 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.

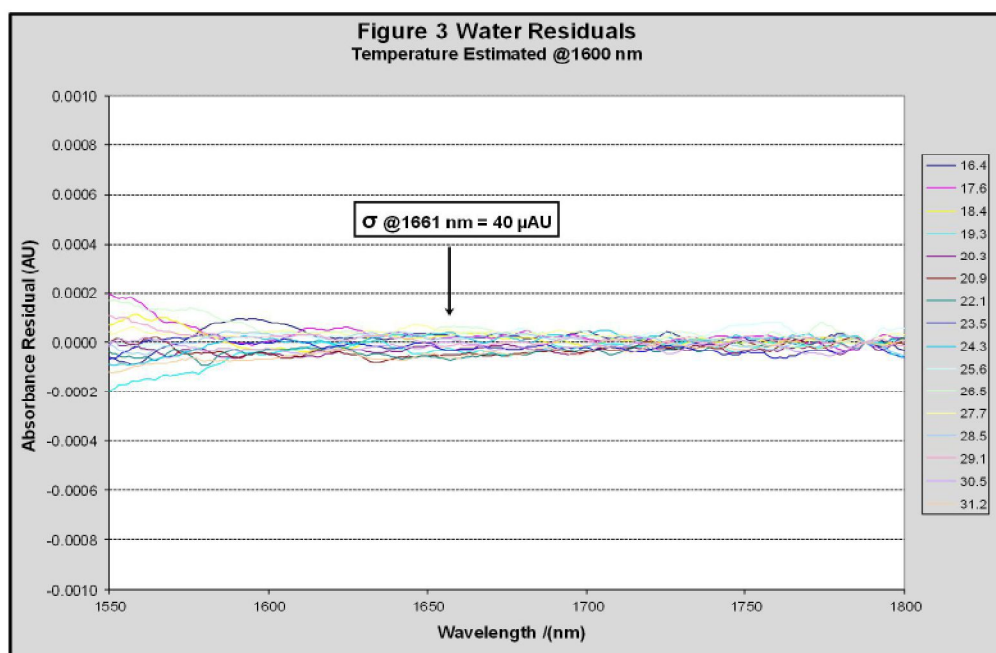


Figure 3: Water Residuals

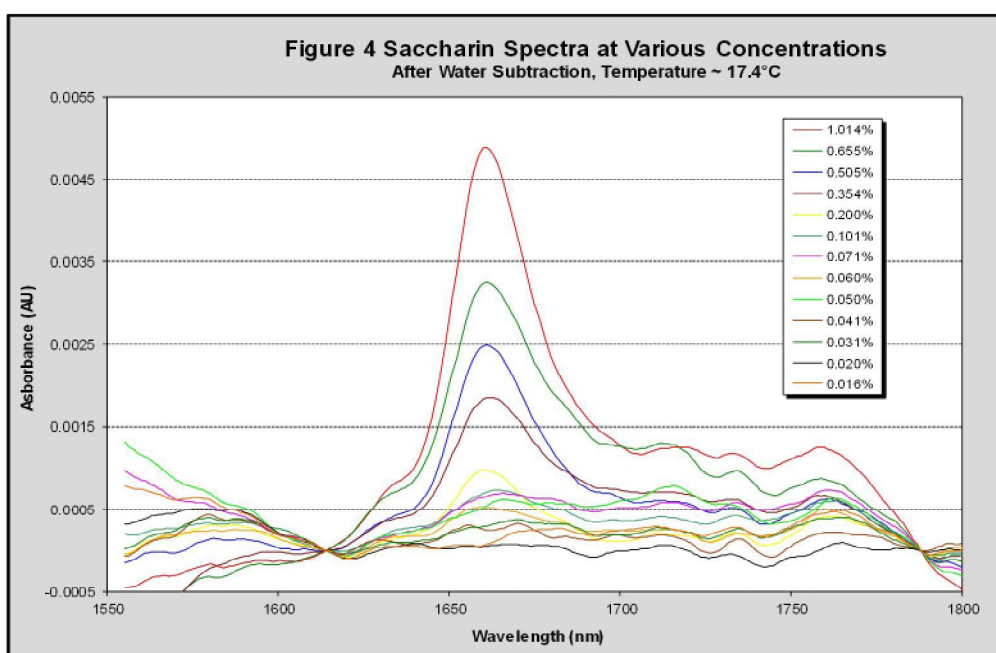


Figure 4: Saccharin Spectra at Various Concentrations

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.

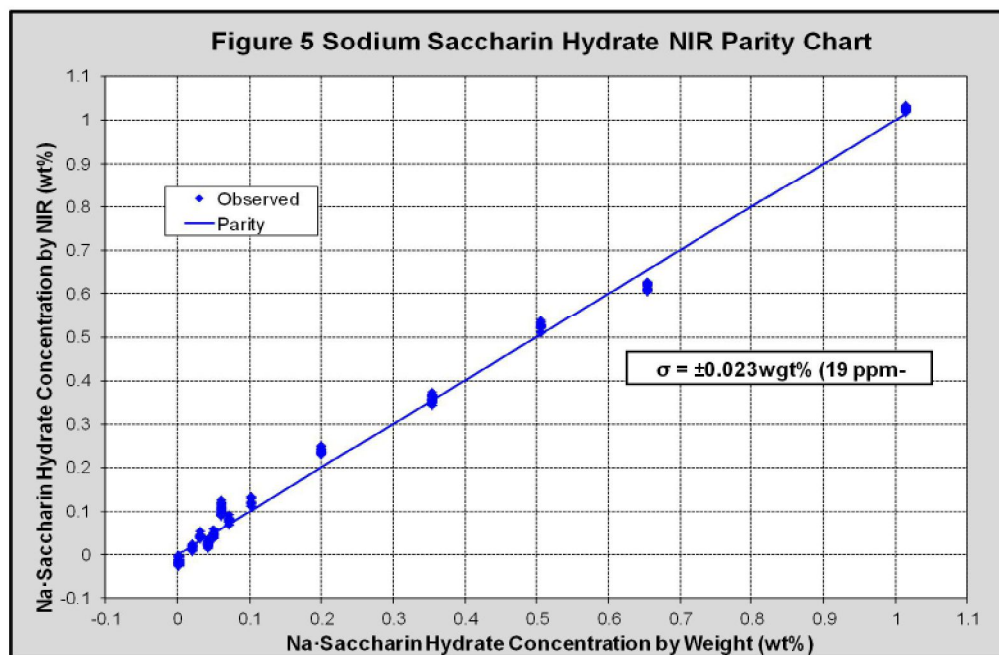


Figure 5: Sodium Saccharin Hydrate NIR Parity Chart

Conclusion

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. For more information on this or other applications, please contact Process Insights™ for sales or technical support.

References

1. 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

GAIN REAL-TIME INSIGHT INTO YOUR PROCESS

Process Insights manufactures and delivers premium sensors, monitors, detectors, analyzers, instrumentation, and software that are mission-critical to keep your operations, personnel, and the environment safe – every day across the globe.

Get the most reliable, precision analytical technologies available on the market today. We will work to match your needs and budget, and provide the optimal, and most stable process analysis solution for your application.

CENTERS OF EXCELLENCE | PROVIDING PROVEN SOLUTIONS

Process Insights is committed to solving our customers' most complex analytical, process, and measurement challenges everyday.

Process Insights – The Americas

4140 World Houston Parkway Suite 180, Houston, TX 77032, USA +1 713 947 9591

Process Insights – EMEA

ATRICOM, Lyoner Strasse 15, 60528 Frankfurt, Germany +49 69 20436910

Process Insights – APAC

Wujiang Economic and Technology, Development Zone, No. 258 Yi He Road, 215200 Suzhou, Jiangsu Province, China +86 400 086 0106

For a complete range of products, applications, systems, and service options, please contact us at: info@process-insights.com

For a complete list of sales & manufacturing sites, please visit:
<https://www.process-insights.com/about-us/locations/>

COSA Xentaur, Tiger Optics, Extrel, Alpha Omega Instruments, ATOM Instrument, MBW Calibration, MGA, Guided Wave, ANALECT and LAR TOC Leader are trademarks of Process Insights, Inc.



REVOLUTIONIZING MEASUREMENT

EVERYWHERE