

Determination of Ammonia Concentration in Water

Laboratory Testing and In-Line Monitoring Capabilities to Reduce Costs and Improve Quality

Process Control is a critical part of every optimization effort. It is key to making improvements in quality, achieving cost reductions and improvements in safety. Real-Time determination of NH_3 Ammonia concentration can be done in process and online providing manufacturers the critical information they need to optimize their process control reduce product variations and production costs.



Process Optimization with On-Line NIR Monitoring – Accurately Monitor Ammonia In-Process and in Real-Time

Background

Over 175 million tons of Ammonia are produced annually, making it one of the most highly produced inorganic compounds. It is used in the production of many other chemicals, plastics, fertilizers, and acids. Because Ammonia is both caustic and hazardous in concentrated form, sample extraction and lab testing pose safety and health risks, and with those risks come associated costs. Online monitoring offers both real-time process information to improve process control and eliminates the need for regular sampling.

Experimental Procedure

The purpose of this study was to demonstrate the ability of Verum Analytics' NIR technology to measure the concentration of Ammonia in water. Eleven samples were created spanning 0.50 – 3.20% (v/v/v%).

The results show clear and strong absorbance information for NH₃ indicating that the IsoChem NIR technique can be used to measure Ammonia at levels between 0.1 to 100%. The measurement could be applied for both laboratory and inline analysis.

The samples were scanned using a spectrometer with a SS316 transfectance probe (Figure 1) connected via NIR-grade fiber optic cables. Samples were scanned at room temperature and were lightly stirred during data acquisition. Probes are also available for use in high concentration and high temperature caustic solutions.



[Figure 1] IsoChem Laboratory Analyzer with Fiber Optic Cable and Transfectance Probe.

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[Table 1] Analyzer Configuration

Ammonia solution of 3.0% concentration was mixed with water to create the sample set. Accuracy of blending was approximately +/-0.02%.

Spectrum took 2 minutes to collect, and measurements were made in real time as concentrations were modified. Ammonia concentration was controlled to approximately +/- 0.02%. As will be seen in the results below this closely matches the accuracy of the models that were created. This indicates the accuracy of the calibration data was the limiting factor for the measurement accuracy. Higher accuracies would be achieved with more precise calibration values.

The performance statistics below were derived from 'leave one out' cross validation. This technique removes each sample from the model in turn, recreating the model each time and predicting the removed sample as a true blind validation sample. This technique is considered the most stringent of validation methods while maintaining a robust calibration set.

Data Analysis and Results

Calibrations were created using PLS chemometric calibration modeling. The results indicate a number of useful spectral peaks relating to the NH₃ molecule. Using Grams AI Chemometric Software, regions of the spectrum can be selected and as many peaks as needed can be used for the measurement. Due to the high concentration of water causing extinction of select wavelengths, some regions of the spectra were not beneficial and were removed.

The following peaks were observed to correlate highly with the concentration of NH₃:

- 1290nm
- 1385nm
- 1527nm
- 1626nm
- 1750nm

The strongest peak, 1527nm was influenced by its proximity to the water band, causing shifting of the absorbance peak. For this reason, it was excluded.

For the results below, the calibration model included the ranges of 1312-1422nm (capturing the 1385nm peak) and 1562-1664nm (capturing the 1626nm peak).

As can be seen in figure 2 below, spectral character related to Ammonia is present at many different regions in the spectra. This same information can be seen in Figure 3. Calibrations were successfully created using a number of different spectral regions before settling on those shown in the report. This indicates that the NH₃ molecule is detected at these various wavelength ranges.

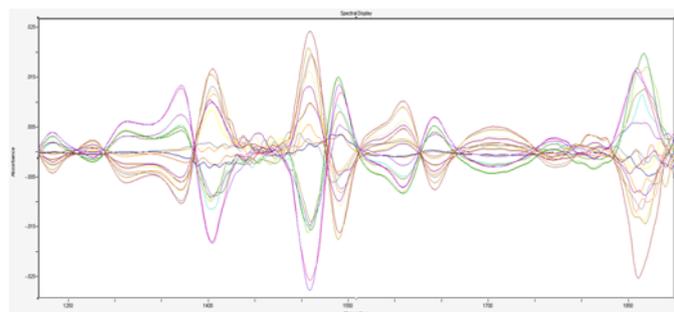


Figure 2: Absorbance spectra of all samples – 1st derivative and mean centered

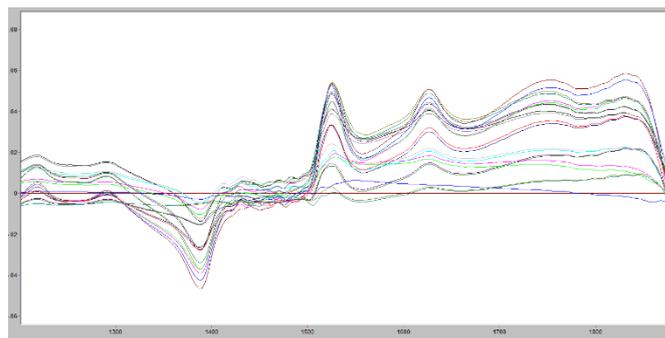


Figure 3: Absorbance spectra using water as a background

In order to more clearly see the spectral information of Ammonia, a spectra of pure water was used as a reference. This has the effect of removing all water and analyzer character from the spectra. As seen in Figure 3 above, the peaks of Ammonia are more easily seen. These same peaks are detected in the calibration process, however, after processing for first derivative and mean centering, the center of the peaks and their relation to each other is not easily observed.

Table 2 summarizes the results of the calibration. While the results presented are promising, they would be improved on by 1) using a higher accuracy known value in the calibration set and 2) using an online transmission probe in place of the laboratory transfectance probe.

For reference, SEP is the “Standard Error of Prediction” in the calibration (measurement accuracy) and R² is the correlation coefficient (fit). Strong NIR models will have low SEP as compared to the constituent value range, and high correlation (close to 1).

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Table 2: Calibration Results – Ammonia in Water

Spectra were processed and properties were modeled using the Partial Least Squares Regression Algorithm (PLS1) in the Grams Software Suite. PLS is a common chemometric algorithm, used to interpret datasets with a large number of datapoints and correlate them to chemical properties. For the reported measurements first derivative and mean-centering were utilized for data processing techniques.

Calibrations were cross validated, and results achieved matched the laboratory measurement method results. The accuracy of a chemometric calibration cannot exceed the accuracy of the samples used for calibration. The results indicate good correlation within the dataset to the known values and reaching the same level of measurement accuracy as the calibration set accuracy. The following actual vs. predicted graph demonstrates the measured values vs. the known values of each sample.

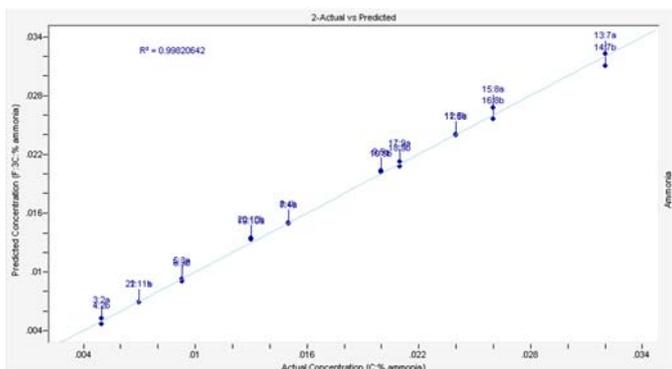


Figure 4: Ammonia Actual vs. Predicted (Lab vs. NIR) Measured Results

Summary

The results of this study indicate that the IsoChem Analyzer is well suited for the measurement of Ammonia in water or other chemical processes. Calibration models were developed with accuracies matching the accuracy of the known values used for calibration. These results provide an indication of the Analyzer’s abilities and results can be improved by increasing the accuracy of the primary measurement method and implementing the transmission probe in an online measurement.

It can also be seen that the measurement of Ammonia would have no obvious concentration limitations. The measurement would be equally accurate measuring at low and very high concentrations.

NIR (Near Infrared) spectroscopy provides a powerful process control tool. Providing in-process real-time measurement of sample chemistry, the technology offers a robust analytical technique directly in process streams.

Testing is non-destructive and measurements take only seconds. There is no per measurement cost and maintenance requirements are extremely low. The result is an ideal process control tool for Ammonia Production.



[Fig 5] Process NIR Analyzer (Verum Analytics IsoChem)

About LT-NIR

Analyzers Measure the Sample Chemistry

Using vibrational spectroscopy NIR analyzers detect and measure the bonds of molecules in the sample. Each bond vibrates in a bending, stretching, or rocking oscillation that is caused by exposure to the NIR light from the analyzer.

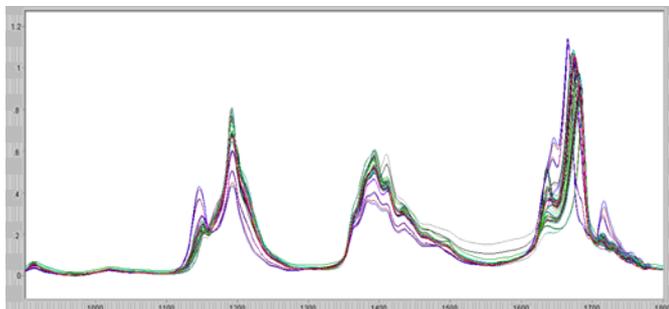


[Fig. 6] Example of rocking and bending oscillations

The vibration causes photons to be absorbed and the analyzer measures the absorption. In doing so it can detect the concentration of various bonds in the sample material, effectively seeing the chemistry of the sample.

The near infrared range is between 800-2400nm and the analyzer will generate a light source over a given part of this range. Ranges are selected that best suit the product and application. Earlier overtones have high absorbance and require small pathlengths, where later overtones have much lower coefficients of absorption and require larger pathlengths. For this reason, only a limited range of the spectra can be optimized using a single pathlength.

Generally, one octave allows for detection of multiple overtones and combination bands, offering extensive chemical information.



[Fig. 7] Sample spectra – various samples overlaid

Non-Destructive Analysis

The benefit of a light-based measurement is that the light is easily passed through most samples without the need for sample extraction. Light interacts with the sample on a molecular level, causing no change to the sample. This technique is non-destructive and easily implemented into most liquid stream measurements.

This provides the benefits of being an in-process measurement technique and one that is much faster and less labor intensive than standard laboratory analysis. Savings of online testing are multifaceted and different for each product, process, and customer. But a summary of the types of benefits, both financial and operational, are listed in table 3 below.

Fast, Real-Time Measurements

The quality of the measurement, that is the capability to achieve the desired accuracies and detection levels, is based on the amount of spectral energy gathered for the

measurement. For this reason, scanning times are customer adjustable. More gross measurements can be as fast as 10 seconds. Measurements requiring more accuracy and/or low levels of detection can take up to 3 minutes. This speed of analysis offers almost real-time continuous measurements of process conditions and key sample chemistry.

Category of Advantage	Typical Benefits
Reduced Lab Testing	<ul style="list-style-type: none"> • Savings on per measurement costs (columns, reagents, etc.) • Typical savings on cost of testing labor of >80%. • Free up lab resources for other priorities • Improved safety
Fast Determination of Reaction End Point	<ul style="list-style-type: none"> • Decreases in batch times or process throughput of 20% results in increased process capacity. • Saving in batch time and increases in process throughput result in energy savings.
Real-Time Monitoring of Quality Parameter	<ul style="list-style-type: none"> • Reduce occurrences of out-of-spec product for improved profitability and reduced losses. • Maintain consistent grade optimizing market value.
Optimizing Reactions	<ul style="list-style-type: none"> • Maximize usage of raw materials/feedstocks • Reduce utility consumption such as electricity

[Table 3] Advantages of Online Monitoring



Verum Website

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