

Rapid analysis of key chemical products in the Haber-Bosch ammonia synthesis process

Industry/application

Chemical manufacturing / petrochemical processing (ammonia production); Relevant to agriculture (fertilizer production), explosives, refrigerants, and pharmaceuticals

Products used

- Thermo Scientific™ Antaris™ II FT-NIR Analyzer
- Transmission fiber optic probe (1 mm pathlength) for sample measurement
- Thermo Scientific™ TQ Analyst™ Software for calibration/model development

Goals

Enable rapid, accurate measurement of ammonia concentration directly in the process while replacing time-consuming, operator-dependent, and hazardous traditional methods. Support safer workflows and use real-time insights to optimize reactions, reduce chemical consumption and reprocessing, and improve overall process efficiency.

Key terms

- FT-NIR
- Haber-Bosch process
- Real-time process monitoring

Key benefits

- Rapid analysis enabling near real-time decisions
- High accuracy and reliability
- Non-destructive and safer method (eliminates hazardous reagents used in titration)
- Reduced operator variability through automated spectral analysis
- Cost savings and process efficiency improvements via reduced waste, shorter reaction times, improved process control, and scalability with easy model transfer

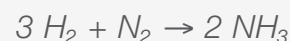
Authors

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Introduction

Ammonia is one of the most widely produced chemicals in the world because of its many uses in fertilizer, explosives, refrigerants, and pharmaceuticals. Over 80% of the ammonia produced is used for fertilizing agricultural crops. The entire nitrogen content of all manufactured organic compounds is ultimately derived from ammonia. A quick, easy and accurate analysis for determination of ammonia concentration is invaluable considering the far reaching influence ammonia has on different industries and the volume used and produced every day.

The typical modern ammonia-producing plant converts natural gas (methane), liquefied petroleum gas (propane or butane), or petroleum naphtha into gaseous hydrogen and other by-products. The hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop and referred to as the Haber-Bosch process. Ammonia can then be oxidized to make nitric acid, nitrates, or nitrites, which are essential for the production of nitrate fertilizer and munitions.



Haber-Bosch reaction.

One of the traditional methods for determining ammonia concentration is titration with an acid until an indicator's color change is reached. Titrations involve hazardous chemicals and require an analyst to make a subjective determination of when the endpoint has been reached. In addition, titration results are time-consuming, require a trained chemist, and vary from operator to operator. Ammonia concentration can also be measured by the Baume test which is a measurement based on density. The Baume test result is highly dependent on temperature and requires correction and conversion factors, making its implementation troublesome. Ammonia is also classified as an eye and respiratory tract irritant even at concentrations less than 10%, and is corrosive and dangerous to the environment at concentrations above 25%, making the search for a rapid, safe and accurate methodology for measuring ammonia of pressing importance.

Determining the concentration of materials with CH, NH or OH bonds has been radically simplified with the adoption of Fourier transform near-infrared (FT-NIR) spectroscopy, a technique based on measuring the characteristic vibrations of molecules. Ammonia concentration is easily quantified using a Thermo Scientific™ Antaris™ II FT-NIR Analyzer (Figure 1) because of the strong and distinct absorptions by the N-H bond (Figure 2) in the 1st overtone and combination band regions of the NIR portion of the spectrum. The normal absorption band overlap seen in the near-infrared region for organic compounds is caused by the many different C-H bond vibrations with very similar energies (frequencies). For the quantification of an aqueous ammonia solution this interference will not be present, so developing models is much simpler.



Figure 1. Antaris MDS FT-NIR Analyzer.

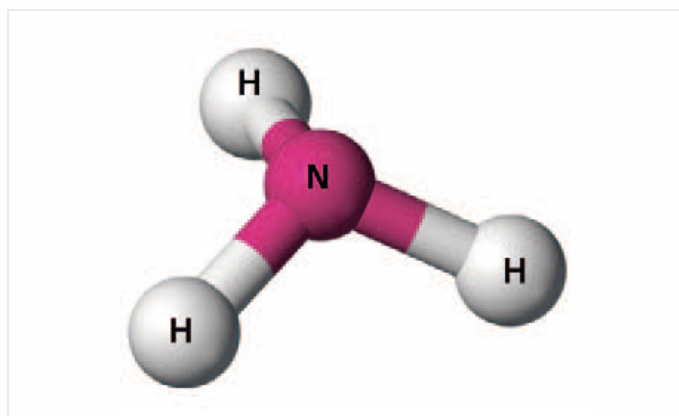


Figure 2. Ammonia molecule.

Experiment

The samples used to develop this method came from a storage tank prior to the ammonia being added to a reaction vessel. Knowing the concentration of ammonia in real time will help the customer optimize the reaction which will save on chemical and reprocess cost. The ammonia samples analyzed for this study ranged from nearly colorless to yellow to burnt orange, so spectra could be easily collected by transmitting light through the samples. A 1 mm pathlength transmission fiber optic probe was used for spectral collection by dipping the probe into the standard solution container. The 1 mm pathlength was used to allow inclusion of the N-H combination band region around 4500 cm^{-1} . For better flow through an online probe, calibrations would rely more heavily on the first and second overtone regions.

For this application, 32 scans were collected at 8 cm^{-1} resolution in approximately 15 seconds. Spectra were collected from $10,000\text{--}4,000\text{ cm}^{-1}$ using an air background taken through the fiber optic probe to eliminate any changes in the equipment or environment during the spectral collection. A total of 85 spectra were collected, of which 64 were used for calibration development and 21 were retained as independent validation samples. The ammonia concentration in the standards varied from 0.1–7.0%. As seen in Figure 3, the calibration (designated by o) and validation (designated by +) standards were evenly spread across the whole range of concentrations.

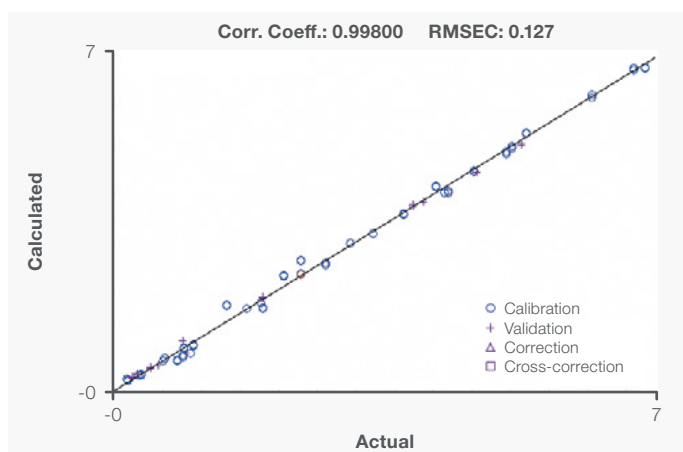


Figure 3. Calibration plot for ammonia.

A partial least squares (PLS) model was developed using the regions from and $6,718\text{--}6,365\text{ cm}^{-1}$ and $4,705\text{--}4,290\text{ cm}^{-1}$. These wavenumber ranges were chosen for model development because the spectra show peaks corresponding to the 1st overtone and combination bands for the N-H bond in these two regions (Figure 4 and 5). Building a model including other spectral regions would correlate primary ammonia concentration information to spectral information that is not caused by the N-H bonds. The spectra were processed by a 2nd derivative in order to narrow the spectral peaks while retaining peak position. In addition, a Norris derivative filter, with segment length = 11 and gap length = 10, was added to smooth out the small amount of random noise in the spectra.

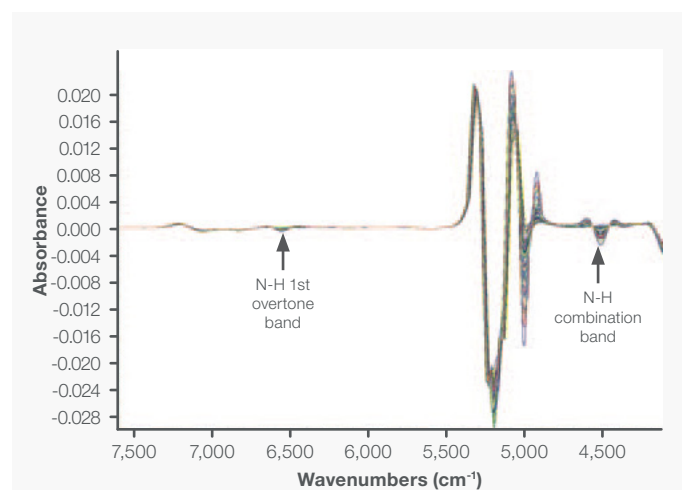


Figure 4. Second derivative spectra of ammonia.

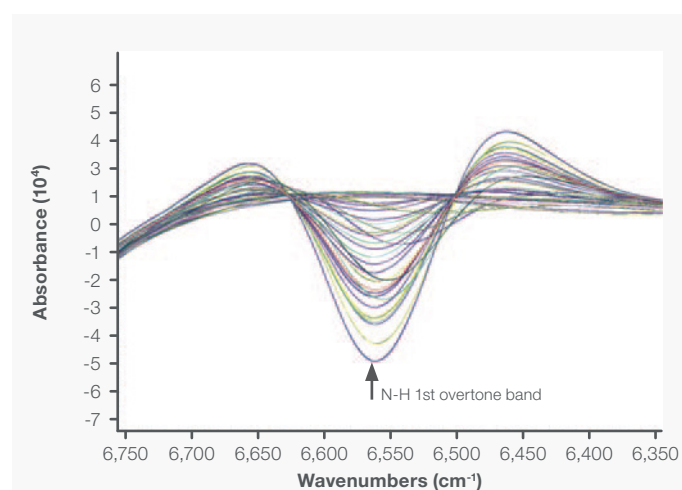


Figure 5. Second derivative for 1st overtone region of interest.

Results and discussion

The calibration in this study was developed using Thermo Scientific™ TQ Analyst™ Spectroscopic Analytical Software. The results show excellent cross-validation (RMSECV = 0.143) and independent validation (RMSEP = 0.079) errors compared to the calibration error (RMSEC = 0.127). The calibration (Figure 3) and crossvalidation (Figure 6) plots both show excellent correlation coefficients of 0.998 and 0.997. Both plots also show calibration and validations points that fall very closely to the ideal fit line across the whole concentration range. Figure 7 is the residual plot for the cross-validation. This plot shows the difference (predicted-actual) vs. actual results for all samples in the calibration. It is a useful plot for seeing if the prediction errors are randomly distributed across the whole concentration range and whether there is good linearity in the model. Figure 7 reinforces that the model developed is linear and has the same prediction error across the whole range in ammonia concentrations. A summary of the actual (lab) ammonia concentration versus the FT-NIR predicted results for the independent validation samples can be seen in Table 1.

Sample	Lab	FT-NIR	Difference
V1-A	0.812	0.656	-0.156
V1-B	0.812	0.662	-0.150
V2-A	0.758	0.92	0.162
V3-A	0.437	0.407	-0.030
V3-B	0.437	0.395	-0.042
V4-A	1.79	1.829	0.039
V4-B	1.79	1.841	0.051
V5-A	0.1	0.147	0.047
V5-B	0.1	0.155	0.055
V6-A	3.74	3.77	0.030
V6-B	3.74	3.745	0.005
V7-A	0.342	0.341	-0.001
V7-B	0.342	0.354	0.012
V8-A	0.171	0.214	0.043
V8-B	0.171	0.214	0.043
V9-A	3.88	3.833	-0.047
V9-B	3.88	3.833	-0.047
V10-A	4.57	4.471	-0.099
V10-B	4.57	4.461	-0.109
V11-A	5.14	5.082	-0.058
V11-B	5.14	5.041	-0.099
Bias		-0.017	
SEP		0.079	

Table 1. Independent validation results Lab vs. FT-NIR.

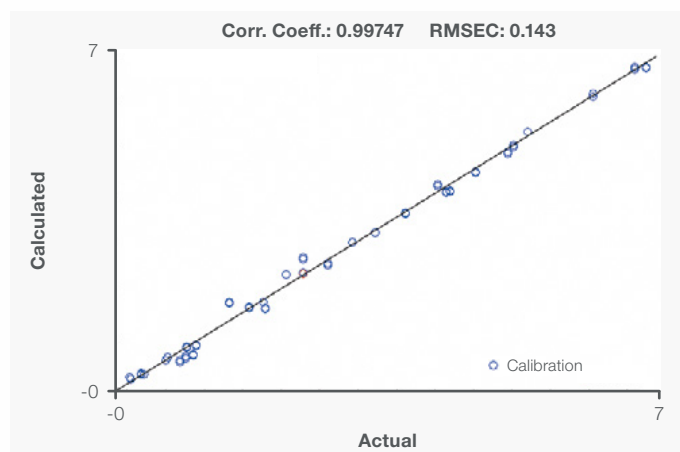


Figure 6. Cross-validation plot for ammonia.

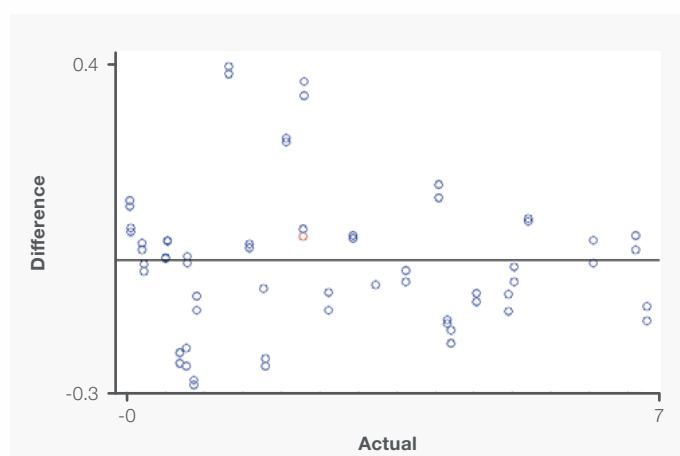


Figure 7. Residual plot for cross-validation.

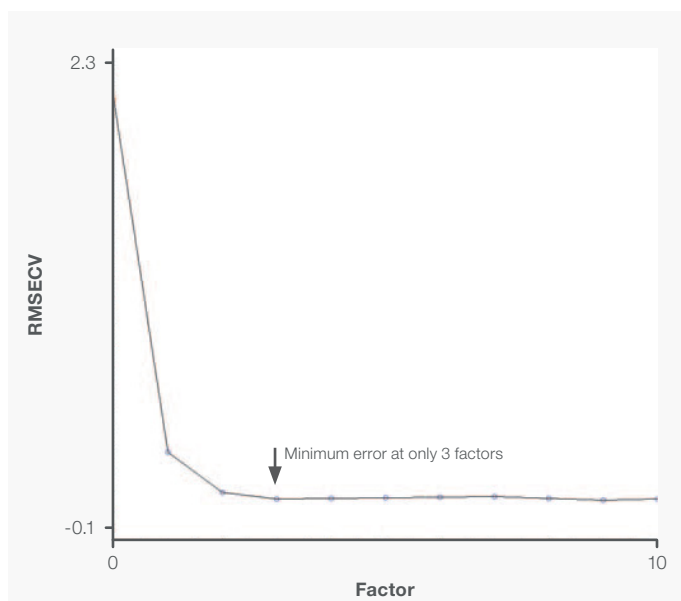


Figure 8. PRESS plot for ammonia.

For ammonia in aqueous solution, very good calibration and prediction errors and correlation coefficients were attained using only 3 PLS factors. The Predicted Residual Error Sum of Squares (PRESS) plot (Figure 8) shows that only 3 factors were needed in order to correlate the spectral and concentration variation for ammonia in this study. The PRESS plot aids in choosing the optimum number of factors in a PLS model. It shows the relationship between the number of PLS factors and the cross validation error (RMSECV). For this model using more than 3 factors resulted in a higher RMSECV (overfitting the data) meaning 3 factors is the ideal number for the model.

The factor loading plot (Figure 9) shows the relationship between concentration and spectral information for the 1st factor in the PLS model. Factors are ranked by the amount of variance described with the 1st factor being the most important and describing the most variation. The 1st factor contains the most common information in the standards. An ideal factor loading plot will have points distributed evenly along a line that is 45°. Standards on the 45° line are contributing evenly to the model meaning that no standard has significantly more influence on the model. Points (standards) that are close to the ideal line are well described by that factor. In this case factor 1 shows high concentration and spectral correlation to the standards. Sample points that are a far distance from the ideal 45° line could be outliers but the factor loading plot does not indicate any outliers for this method.

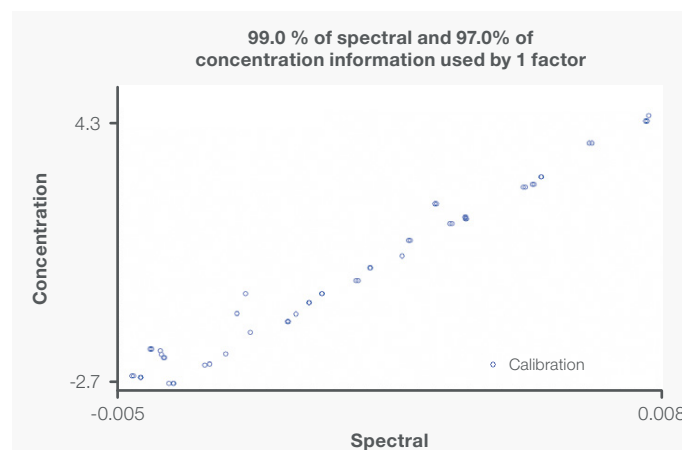


Figure 9. Factor loading plot for ammonia.

Conclusion

The calibration model developed for ammonia shows very good correlations as well as low calibration, cross-validation and independent validation errors while using only 3 factors. The combination of good PRESS and factor loading plots indicate the FT-NIR spectral data can easily be correlated to the primary lab ammonia concentrations. The 1st factor in the factor loading plot described over 99% of the spectral and 97% of the concentration variation. Pearson's coefficient of this model was excellent with a value of 0.998. The cross-validation and independent validation errors were very close to the calibration error. This indicates no loss in prediction power for samples not in the calibration, which will make for easy implementation of the model for predicting unknowns in the plant without loss of accuracy. The model was developed using a transmission probe in the lab. Transfer of the model into the process can easily be accomplished between Antaris instruments due to the common optical layout, precision engineering and ruggedness built into all Antaris analyzers. The ability to predict ammonia or other chemical concentrations in real time is a huge advantage over traditional time intensive tests that often involve hazardous chemicals. The capability to trend chemical concentrations in a process line or tank can save in chemicals costs, reduce reaction times and overall improve process efficiency. This study shows that ammonia concentration can be quickly, easily and accurately predicted using the Thermo Scientific Antaris II FT-NIR analyzer.