PROCESS GAS ANALYZERS FOR THE MEASUREMENT OF AMMONIA AND ACETYLENE CONCENTRATION

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KEYWORDS

Tunable Diode Laser, Wavelength Modulation Spectroscopy, Analyzer, Acetylene, Ammonia.

ABSTRACT

New analyzers, based on near infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS), were developed for the measurement of ammonia and acetylene in process streams. Measurements of acetylene were made in sample matrices corresponding to acetylene converters at different locations in an ethylene production plant. Measurements of ammonia were made in sample matrices including percent levels of water vapor and carbon dioxide. In both cases reliable performance was demonstrated over a wide range of analyte concentrations and under a variety of experimental conditions (e.g., sample pressure and background gas composition). The acetylene measurements yielded an accuracy of 0.3 ppmv over a concentration range of 0 – 5 ppmv; an accuracy of 40 ppmv was observed for a range of 0 – 2000 ppmv. For the ammonia measurements an accuracy of 0.7 ppmv was observed for a concentration range 0 – 30 ppmv.

INTRODUCTION

TDLAS as a non-contact optical technique with long term stability, high specificity, and considerable sensitivity has found use in many applications in industrial process plants [1]. This paper describes the application of TDLAS for measurements of acetylene and ammonia based on extractive sampling. Acetylene is a byproduct of modern ethylene production processes and is considered an impurity of the process. Even in small concentrations, acetylene acts as a poison to the catalyst used for production of polyethylene from ethylene. Ideally, the maximum concentration of acetylene in an ethylene final product should be less than 5 ppmv.

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Most ethylene is produced by thermal cracking of hydrocarbons in the presence of steam. Ethylene plants use different feed stocks. Depending on the hydrocarbon feedstock for pyrolysis, the cracking furnace design and operating conditions the amount of acetylene byproduct can vary from 0.2 to 0.9% by weight [2]. When the acetylene content is significant, it can be recovered as a product or converted into ethylene by a selected hydrogenation system. In modern ethylene production the most common method for acetylene removal is through selective hydrogenation in vapor phase

$$C_2H_2 + H_2 \rightarrow C_2H_4 \quad (1)$$

It is should be noted that during the hydrogenation process other chemical reactions can occur in the hydrogenation unit, and as a result, ethylene can be converted to ethane if the reaction goes too far

$$C_2H_4 + H_2 \rightarrow C_2H_6 \quad (2)$$

To avoid an incomplete conversion of acetylene or an undesired continuing conversion of the ethylene to ethane, the optimum conditions for the hydrogenation process may be determined by real time monitoring of the acetylene concentration. Traditionally, gas chromatography has been used to provide acetylene monitoring in the ethylene production process. However despite the high sensitivity, which can result in the ability to measure sub ppmv levels of acetylene, gas chromatography's disadvantage is its cycle time requirement resulting in low speed of the response. The analysis time for a GC can take several minutes [3]. TDLAS-based measurements provide real time monitoring. It is critical to provide real time monitoring of the acetylene hydrogenation process to the required concentration levels and to control the time for hydrogenation process. It is also known that during plant start ups and other unscheduled events, the concentration of acetylene can suddenly reach very high levels. As was experimentally demonstrated in the environment of the ethylene plant [3] during these fast acetylene fluctuations, the gas chromatograph either misses the event entirely or report it with delay after completion. In contrast TDLAS based measurement provide real time monitoring of the process.

The main field applications for ammonia TDLAS-based measurements are air quality monitoring and emissions monitoring. The need to monitor air quality reflects the fact that ammonia is a toxic gas with a time weighted average exposure limit of 25 ppmv. It is essential to control the presence of ammonia for process optimization and hazard prevention. In an emissions monitoring application, the gas stream of the post combustion exhaust stack can have up to 20% carbon dioxide and water. Depending on the wavelength selected, both of these components have the potential to provide background interference for the ammonia measurement. The wavelength for TDLAS measurement should be carefully selected to minimize this interference.

The principal objective of the work reported here is to characterize new TDLAS-based extractive analyzers with an all-digital protocol for the modulation of the laser drive signal and the demodulation of the detector response. These analyzers were configured for acetylene and

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ammonia measurements in different background gases, with an environmental temperature range of -20°C to +50° C, and a sample cell pressure range of 10 – 25 PSIA.

INSTRUMENT DESIGN

The TDLAS instrument evaluated in this work was an AMETEK 5100 HD, which was modified to operate with a multi-pass Herriott cell, having an optical path length of 5 meters and a volume of 128 ml. A schematic representation of the instrument is shown in Figure 1. The measurement of acetylene was performed with a 1521-nm distributed feedback (DFB) laser, and the ammonia measurement was performed with a 1527-nm DFB laser. Both lasers produced an optical power of approximately ten milliwatts; optical attenuators were used to reduce the output power to usable levels. The outputs of both lasers were coupled into single-mode optical fibers, which in turn were connected to a fiber-optic beam splitter. The splitter was used to divide the optical power in a 50/50 ratio for use in the sample and reference measurements, respectively. Gradient refractive index (GRIN) lenses, with a beam divergence of 1.8 milliradians, were used to collimate the output of the single-mode fibers and direct the resulting beams through the sample and reference cells. The sample and reference cells each contained 0.5 mm^2 InGaAs-photodiode detectors, which were connected to separate input channels of the electronics unit. With this configuration it was possible to make simultaneous measurements of unknown samples and known references, which were used to lock the output wavelengths for both lasers.

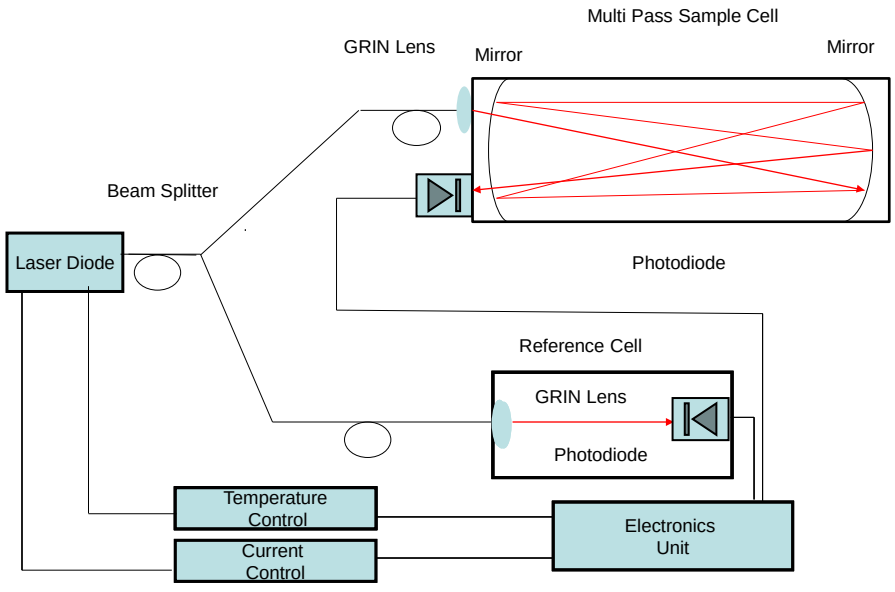


FIGURE 1. EXPERIMENTAL SET UP FOR TDLAS MEASUREMENTS.

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The sample cell temperature was controlled with accuracy of +/- 0.1°C and could be set in the range of 60°C – 120°C by setting the temperature of the oven in the sample cell compartment. The reference cell is not located in the sample compartment, but the temperature was maintained above 40°C. The laser and photo diodes were also located in the main electronics compartment, isolated from the heated sample oven.

A more detailed description of the TDLAS-based analyzer using the wavelength modulation spectroscopy (WMS) approach, with a digital implementation of the technology, is given elsewhere [4-5]. The WMS experiment was implemented by using a digitally sampled sine function, summed with a staircase, and the resulting signal was used to drive the tunable DFB laser diode. Signals produced by the detectors were digitized prior to applying signal processing (e.g., phase-sensitive detection, smoothing, etc.). In contrast with the common practice of using second harmonic detection (2F), the detection/demodulation in this analyzer was performed at the laser-modulation frequency (i.e., "1F" detection). Using the 1F-detection scheme enabled the normalization of the spectra, without the need for a separate measurement of the laser power. Specifically, the magnitude of the power envelope of the laser output is contained in the spectra produced by 1F demodulation. After the 1F spectra were normalized, they were differentiated; the resulting derivative spectra approximate the second derivative of the absorption spectrum of the analyte and were referenced as 2F signals in this work.

The scan parameters for the laser (e.g., injection current range, modulation depth, etc.) were set to match the desired wavelength range required to cover width of the ro-vibrational transition. Line widths were determined from published data published in HITRAN spectral library [6]. The wavelength-locking algorithm employed by the instrument was based on two nested levels of temperature control employed to maintain the operation of the laser diode at the proper wavelength. The first level was a simple PID control loop, which maintained the laser at a target temperature. In the second level, the outer control loop, the spectra of the analyte samples in the reference cells were monitored. Minor shifts in the observed peak positions were used as a feedback signal for the temperature set point of the inner control loop. Thus, the outer-control loop provided a fine adjustment for the inner-control loop.

Wavelength selection for acetylene measurements was dictated by the spectral position and intensity of the acetylene absorption bands in the near infrared range, the requirement of minimal spectral interference with other components of the gas stream at the ethylene plant acetylene converter (e.g., ethylene, ethane and methane), and of course by the availability of laser diodes. From this point of view acetylene rotational vibrational spectral lines in the vicinity of 1521 nm were the most attractive for measurements. In addition, this region of the spectrum corresponded to high sensitivity for InGaAs detectors and to maximum transmittance of telecommunication range fiber optics.

The main absorption bands for ammonia in the near infrared range are located in the vicinity of 1500, 2000, and 2300 nm [6, 9]. The compounds most likely to cause interference for air quality monitoring and emissions control are carbon dioxide and water. The concentration of water and

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carbon dioxide in air quality control monitoring should be between 1 – 2 % for water and 250 – 380 ppmv for carbon dioxide [7]. For emissions control monitoring, concentrations of carbon dioxide and water could reach 10 – 20%. In these streams ammonia needs to be monitored at low-ppmv levels. Of the three spectral regions the lines in the vicinity of 2300 and 1500 nm are the most useful for emissions monitoring of ammonia, due to the interfering species having relatively weak transitions in these regions [7]. In contrast, for the ammonia lines near 2000 nm water and carbon dioxide interferences are substantial, eliminating the region as a viable option for emissions monitoring [8]. Although the ammonia line strengths around 2300 nm are a few times larger than those of lines around 1500 nm, the commercial availability of room temperature laser diodes at the shorter wavelengths, the high spectral sensitivity of InGaAs detectors, and the high transmittance of fiber optics make the 1500 nm region a superior choice for commercial sensor development.

RESULTS AND DISCUSSION

ACETYLENE ANALYZER

Initially, the analyzer performance was tested with samples of acetylene in a host gas containing 65% ethylene and 35% ethane, a gas stream composition typical for an ethylene plant acetylene converter. Two concentration ranges of acetylene, 0 – 2000 ppmv and 0 – 5 ppmv, were selected to match the conditions corresponding to the mid-bed and the outlet of the ethylene plant acetylene converter. Different concentrations of acetylene were created by mixing acetylene with the host gas in a gas mixer. Examples of some measured 2F signals, corresponding to different acetylene concentrations, are shown in Figure 2. In these data the peak amplitude and area of the 2F acetylene signal were proportional to the concentration of acetylene in the cell. With increasing acetylene concentration, a common peak position at 1521.06 nm became more notable. The data in Figure 2 also contain the background spectrum of the sample matrix (i.e., the ethylene-ethane mixture). This background spectrum was significant in comparison with the absorbance of the acetylene at these low concentration levels. Hence, the spectra of the sample matrix components needed to be built into the calibration model. Utilizing an Inverse Least Squares regression, a calibration model was developed to accurately measure the acetylene concentrations in the presence of the ethylene-ethane sample matrix. The regression vector that was calculated as a result of the Inverse Least Squares regression is also shown on Figure 2. A concentration correlation plot is shown in Figure 3. All data points from both the calibration and validation sets follow the unity line without any notable deviations or trends. The standard error of calibration was calculated as 0.3 ppmv and the standard error of prediction was determined to be 0.4 ppmv.

The limit of detection (LOD) was defined as the concentration of the analyte required to give a signal equal to three standard deviations of the baseline. According to this definition, LOD characterizes the ability of the analyzer electronics, optics, and algorithm to distinguish the smallest detectable level of the analyte from the background spectra. For evaluation of the LOD, an acetylene-free 2F spectrum was used to define the baseline. An estimate for the LOD of 0.3 ppmv was calculated for the measurement, according to the following equation.

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$$LOD_{ppm} = \frac{3\sigma \times 30ppm}{M_{30}\sqrt{K}} \quad (3)$$

Where σ = standard deviation in the background spectra

M_{30} = magnitude of the 2F spectrum measured for 30 ppmv acetylene

K = number of data points in the spectrum used to calculate the area of the 2F signal

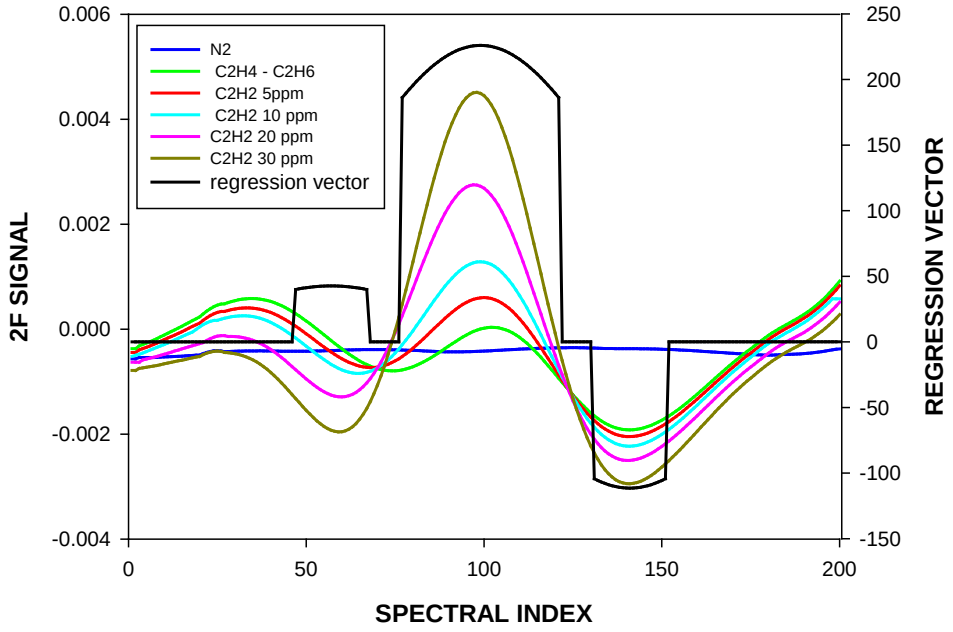


FIGURE 2. 2F SPECTRA OF ACETYLENE, ETHYLENE – ETHANE AND NITROGEN.

The data shown in Figure 4 are the responses of the instrument to a series of acetylene challenges over the concentration ranges of interest. The duration for each challenge was approximately 40 minutes with a return to the zero gas baseline value between most of the challenges. An ethylene–ethane gas mixture was used as the zero gas. The response time (T90) was measured to be 30 seconds and was limited by the propagation of the gas in the sampling system with a flow rate of 2L/min. The data acquisition rate was 2 seconds per measurement.

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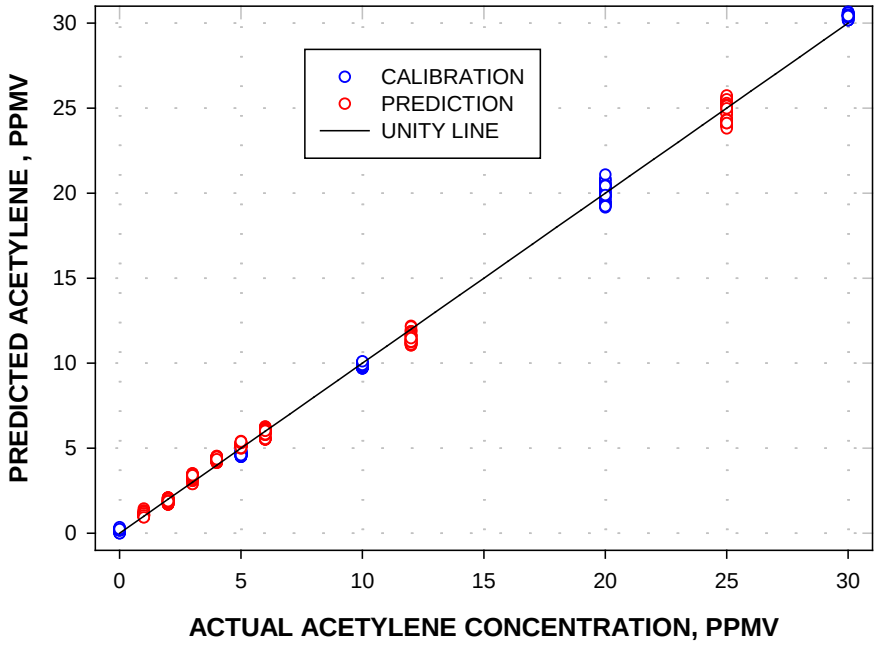


FIGURE 3. ACETYLENE CONCENTRATION CORRELATION PLOT.

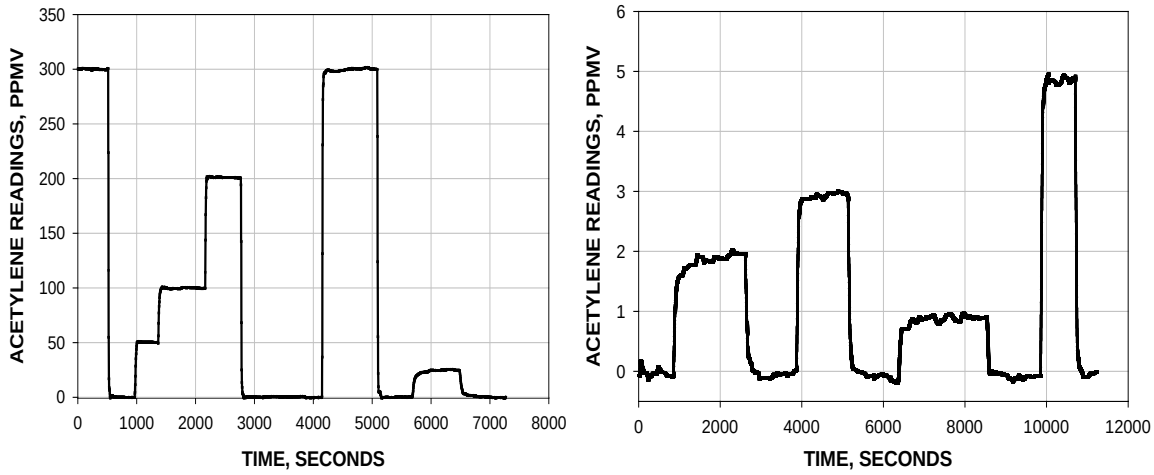


FIGURE 4. ACETYLENE READINGS IN AN ETHYLENE–ETHANE BACKGROUND. RESPONSE TO A SERIES OF CONCENTRATION CHALLENGES IN THE RANGES 0 - 300 PPMV AND 0 – 5 PPMV.

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Repeatability as a degree of agreement between replicate measurements of the same quantity was expressed in terms of standard deviation of the measurements. Standard deviation of the readings on each of the challenges was 0.08 ppmv. The value of the accuracy evaluated at the levels in the range 0 – 5 ppmv was 0.3 ppmv. While these data are reasonable for the 5 meter pathlength used in the prototype instrument, it is anticipated that substantial improvements could be obtained with a longer pathlength cell. The value of the accuracy over the full concentration range of 0 – 2000 ppmv was better than 40 ppmv.

Instrumental drift during 24 hours is shown in Figure 5. During the drift test, an ethylene–ethane gas mixture was run through the sample cell at a flow rate of 2L/min. No significant trends or correlations with the environmental temperature or sample pressure were observed in the data. Over the 24 hour period, a mean value of 0.11 ppmv, with a standard deviation of 0.18 ppmv, was recorded.

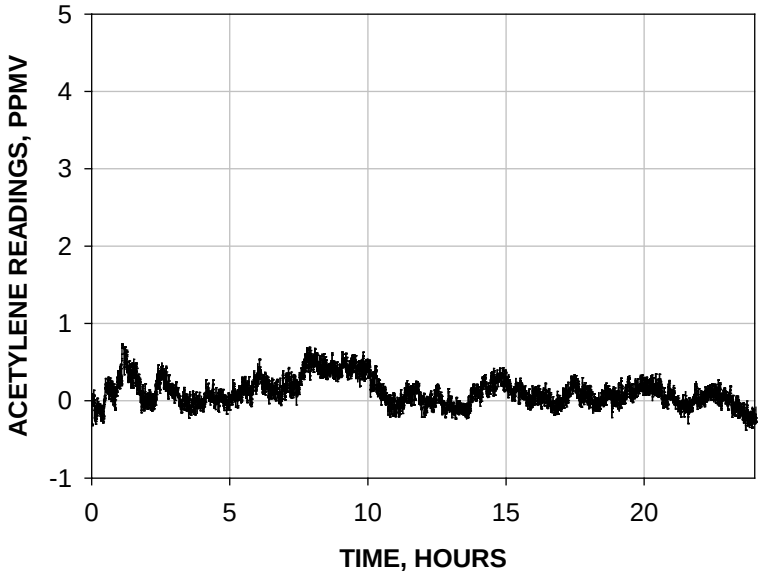


FIGURE 5. ACETYLENE ANALYZER DRIFT TEST.

AMMONIA ANALYZER

Temperature and cell pressure are critical to prevent water from condensing and adsorbing the NH3. Sample handling for this analysis is also difficult.

The near infrared spectrum of ammonia in the vicinity of 1527 nm is very crowded and contains many overlapping transitions [9]. The multitude of lines is a result of ammonia inversion doubling [10] and the overlap of several harmonic and combination bands, including $\nu_1 + \nu_3$, $2\nu_3$ and $\nu_3 + 2\nu_4$ bands [11,12]. Moreover, ammonia's strong dipole moment creates broad line shapes as a result of dipole-dipole interactions during collisions [13, 14], causing many of these

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neighboring lines to overlap. A 2F spectrum containing three ammonia lines (1527.04, 1526.99 and 1526.96 nm) [7], recorded for a 100 ppmv concentration in nitrogen, is shown in Figure 6. These three lines shown in the figure are not totally resolved under the conditions present in the sample cell of the instrument; specifically, these data were recorded at atmospheric pressure and a temperature of 60°C. For comparison, 2F spectra corresponding to different background gases including nitrogen, 10% water in nitrogen, and carbon dioxide are shown on the same scale with the ammonia spectrum. It is obvious that in this wavelength range the amount of spectral interference observed for water and carbon dioxide is negligibly small, compared to the absorbance of the ammonia over the desired concentration range. This means that detection of ammonia will be limited only by the optical noise of the system and could be improved by simply increasing the optical path length.

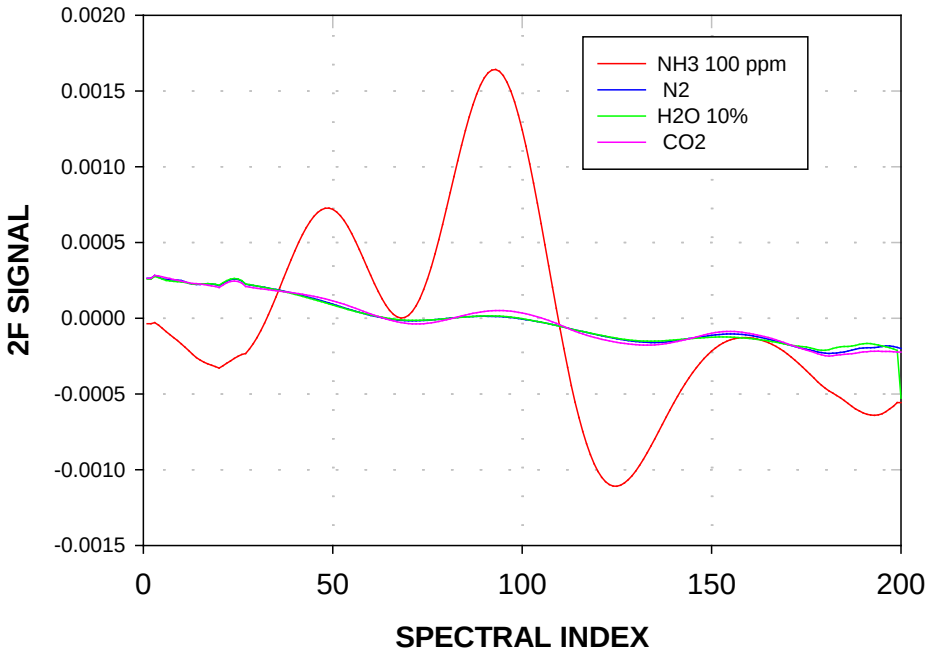
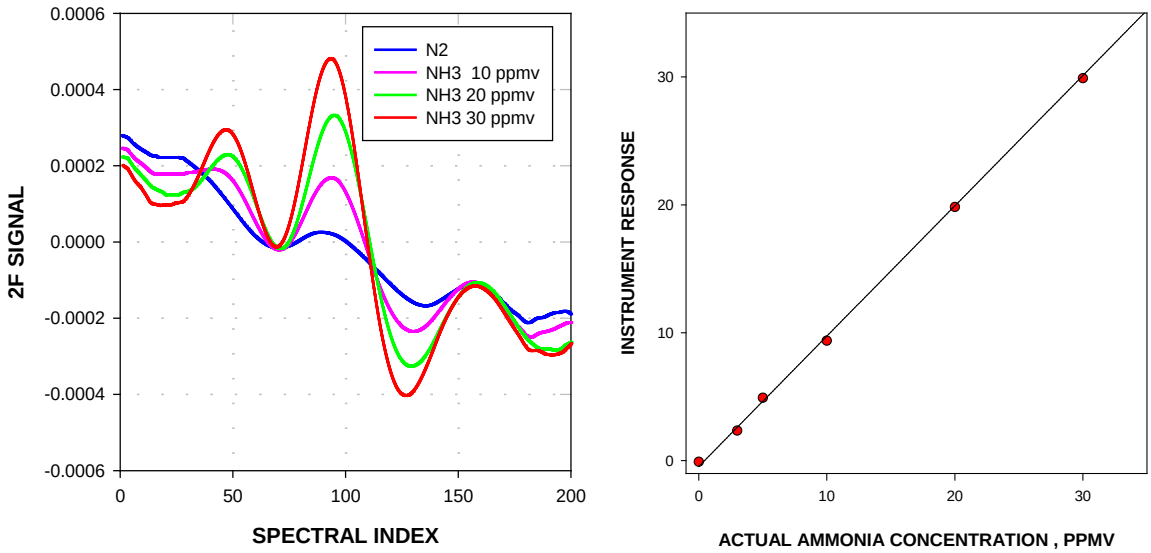


FIGURE 6. 2F SPECTRA OF AMMONIA, NITROGEN, WATER, AND CARBON DIOXIDE IN THE VICINITY OF 1527 NM.

Different concentrations of ammonia over the range of 0 – 30 ppmv were created by mixing ammonia with the background gas in a gas blender. To reduce the amount of adsorption of ammonia on the wetted surfaces, stainless steel tubing maintained at 80°C was used. Examples of some measured 2F signals corresponding to different ammonia concentrations are shown in Figure 7A. These data show that the peak amplitude and the area of the 2F ammonia signals are proportional to the concentration of ammonia in the cell. Using the calculated areas under these spectra, a calibration was generated.

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A) B)

FIGURE 7. 2F SPECTRA OF AMMONIA and NITROGEN (A), CONCENTRATION CORELATION PLOT (B).

The results of the calibration developed for the ammonia data are shown in Figure 7B. All experimental points are in close agreement with the linear regression line with a correlation coefficient (R^2) of 0.9996.

The response of the instrument to a series of ammonia challenges in the concentration range of interest is shown in Figure 8. The duration of each challenge was approximately 40 minutes with a return to the zero-gas baseline between challenges. The averaged response time (T90) was 250 seconds. Based on an examination of these data and the experimental setup, the increased response time observed for the ammonia was determined to be caused by a combination of the gas exchange rate in the sampling system and the time required for equilibration of the surfaces to the ammonia concentration. The data acquisition rate was 2 seconds per measurement.

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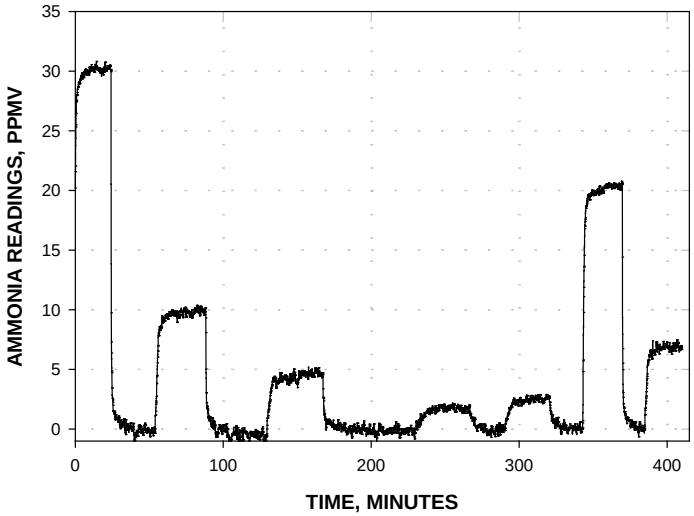


FIGURE 8. INSTRUMENT RESPONSE TO A SERIES OF AMMONIA CHALLENGES THE BACKGROUND MATRIX CONTAINED A COMBINATION OF NITROGEN, CARBON DIOXIDE, AND WATER VAPOR.

Repeatability as a degree of agreement between replicate measurements of the same quantity was expressed in terms of the standard deviation of the measurements. Standard deviation of the readings for each of the challenges was 0.25 ppmv. The accuracy of the ammonia measurements, evaluated over the 0 – 30 ppmv range, was measured as 0.7 ppmv.

The performance of the instrument was also evaluated over a range of sample pressures from 10 to 25 psia. Spectra recorded for ammonia over this pressure range are shown in Figure 9. Collisional broadening increased the width of the absorption line with increasing sample pressure. Decreasing the pressure in the sample cell resulted in better resolution of the three mentioned ammonia lines. The relative increase in line width was approximately equal to the relative increase in the absolute pressure. As a result of the collisional broadening, the spectra recorded by the TDLAS instrument were observed to broaden proportionally, with a corresponding decrease in amplitude.

After the calibration was carried out under normal atmospheric pressure (P_0), the analyzer response (C) for a fixed ammonia concentration (C_0) was recorded under several selected values of pressure (P) in the sample cell. To correct for the pressure dependence, a pressure compensation routine was implemented. The pressure-compensation factor was calculated from a third-order polynomial, which used the ratio of the absolute pressure under the measurement conditions to that of the standard value (i.e., 1.0 atmosphere). For the curve shown on Figure 10, polynomial regression was

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$$\left(\frac{C_0}{C}\right) = \sum_{j=0}^{3} a_j \left(\frac{P}{P_0}\right)^j \tag{4}$$

Where C_0 = fixed ammonia concentration
C = analyzer readings
P = pressure in the sample cell
P_0 =normal atmospheric pressure
(a_j)= the coefficients estimated for this instrument were in accenting order 0.8032, 0.217, -0.0032, and -0.0196.

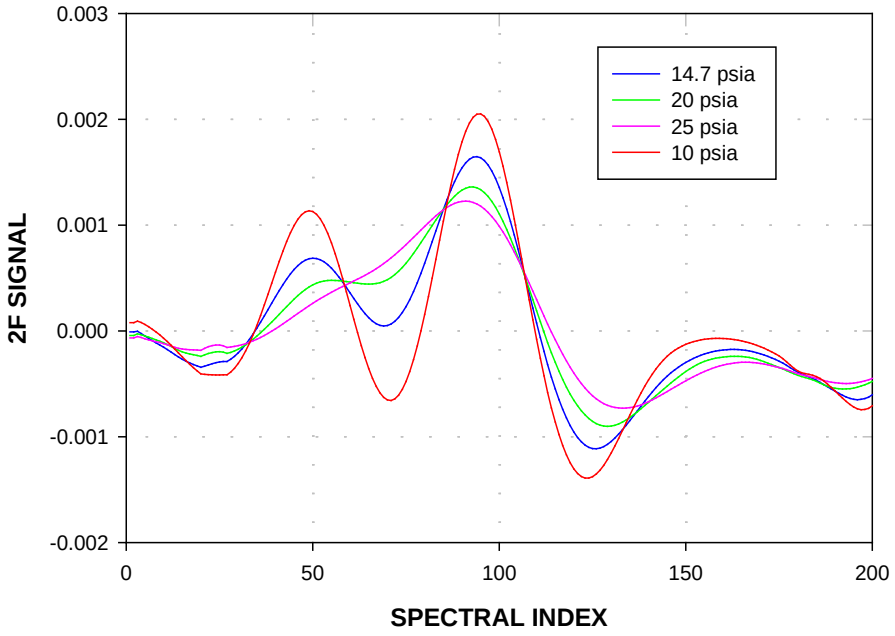


FIGURE 9. SPECTRA OF 100 PPMV AMMONIA UNDER DIFFERENT PRESSURES IN THE SAMPLE CELL.

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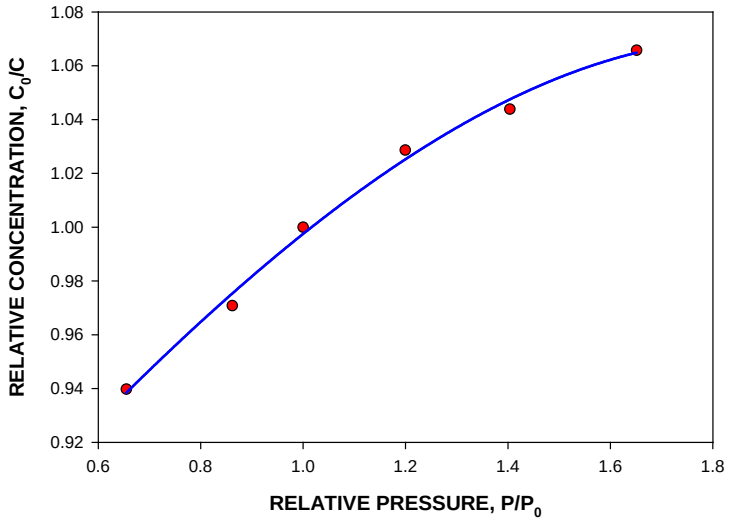


FIGURE 10. PRESSURE COMPENSATION CURVE FOR THE AMMONIA ANALYZER.

CONCLUSIONS

Prototypes of gas analyzers were built for the measurements of acetylene content in the mid-bed and the outlet of the acetylene converter and for emissions monitoring of ammonia. These analyzers employed an all digital measurement protocol which was configured to replicate a conventional wavelength modulation spectroscopy experiment. Further, the digital signal processing methods employed in this system successfully removed minor background interferences, caused by other absorbing species in the sample matrices. Specifically, the digital signal-processing methods employed in this system were used to successfully implement a multivariate calibration, enabling the instrument to accurately measure acetylene in the presence of the overlapped spectral responses for ethylene and ethane. The acetylene measurements yielded an accuracy of 0.3 ppmv over a concentration range of 0 – 5 ppmv; and, an accuracy of 40 ppmv was observed for a range of 0 – 2000 ppmv. For the ammonia measurements an accuracy of 0.7 ppmv was observed for a concentration range 0 – 30 ppmv.

ACKNOWLEDGMENTS

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Editor's Note

April 19, 2013

Reference:

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The paper provided here has been corrected from previous publications.

Its original publication was issued at the ISA Analysis Division Symposium in Galveston, Texas, on April 15 through 17, 2013. The original publication was in electronic form with files provided on a USB bulk memory device (aka "thumb drive" or "memory stick".) The paper that was provided with that issue contained publication errors on pages 7, 8 and 9. The formulas presented on those papers failed to render correctly in the published format and this error was not observed by the editor.

The authors actual paper, submitted to and approved by the AD Paper Review Committee was correct. The error in the published paper was strictly a technical error in the publication.

These errors have been corrected in the paper preceding this note. In this issue, the term "corrected" has been added to the electronic file name.

The editor extends apologies to the authors for this occurrence.