

NEW PROCESS GAS ANALYZER FOR THE MEASUREMENT OF WATER VAPOR CONCENTRATION

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ABSTRACT

A new analyzer for the measurement of water vapor concentration based on Tunable Diode Laser Absorption Spectroscopy (TDLAS) was developed. The water-vapor line at 1854-nm was selected for the measurement, and the performance of the system was evaluated on different background gases to confirm that the measurement was free of interferences. An original feature of the instrument design is the use of an all-digital protocol for the modulation of the laser drive signal and the demodulation of the detector response. This innovation provides a simple means of varying the type of modulation protocol and all associated instrumental parameters. A reference cell is used in parallel with the sample cell to continuously validate the performance of the system. A limit of detection (LOD) of 5 ppmv and a range of 5 to 2500 ppmv were demonstrated.

INTRODUCTION

The measurement of water vapor in process streams has long been of key importance in a number of different industries. One of the most important applications is the measurement of

water vapor in natural gas. Most of the technologies employed for this application are based on chemical sensors, which have several limitations. The most severe limitation is fouling of the sensor, which can lead to inaccurate measurements and high maintenance costs associated with periodic replacement of the sensor. Spectroscopic measurements are relatively insensitive to the effects of sample fouling, and can help to reduce the long-term cost-of-ownership for moisture analyzers in many applications.

Tunable diode laser absorption spectroscopy (TDLAS) has been used for a number of industrial applications, measuring a variety of different analytes (1-2). Emission bandwidths for the tunable diode lasers are on the order of $10^{-4} - 10^{-5} \text{ cm}^{-1}$, giving the TDLAS technique extremely high spectral resolution, which results in the ability to isolate a single rotational-vibrational transition line of the analyte species. TDLAS offers extremely high specificity for the analyte, even in a complex sample matrix. A second advantage of TDLAS is the ability to rapidly tune the lasers, so techniques like wavelength modulation spectroscopy (WMS), which yield dramatic sensitivity enhancements over a direct absorption approach, are easily implemented (3). Because TDLAS is an optical technique, it also offers a very fast response speed. The high specificity, sensitivity, and response speed of TDLAS make it very suitable for the measurement of water in natural gas.

The principal objective of the work reported here is to characterize a new TDLAS-based instrument. In its initial configuration, the instrument has been set up to perform wavelength modulation spectroscopy (WMS). Using a simple WMS technique for this first study provides a better means of evaluating the system hardware. At the same time the instrument can be easily configured to implement other protocols, and the associated detection/signal-processing techniques. A key feature of this instrument is the use of a sealed reference cell, which contains a known amount of water vapor, for referencing the emission wavelength of the laser. Measurements of the reference cell are performed in parallel with measurements of the sample stream, providing a continuous validation of the system performance. Because the instrument is designed to measure a high-resolution spectrum of the absorption line, it has the capability to identify the presence of, and compensate for, minor background interferences that may be present in a complex sample matrix. Methane has minor background interference at the wavelength used for measuring water vapor, and as such, provides a good test for the system capabilities.

EXPERIMENTAL

THE INSTRUMENT

The TDLAS instrument evaluated in this work was a prototype of an AMETEK 5100 NCM. A schematic representation of the instrument is shown in Figure 1. A distributed-feedback (DFB) laser, operating with a wavelength range centered at 1854 nm, was used as the source in this instrument. This source produced an optical power of approximately three milliwatts, when

operated at the target wavelength for the water-vapor measurement (1854nm). Output from the laser was coupled into a single-mode fiber, which was connected to a fiber-optic splitter, used to divide the optical power in a 70/30 ratio and simultaneously connect the DFB laser to the sample and reference cells. Signals from the InGaAs 0.5 mm² photodiode detectors were input to separate channels of the electronics unit. It was now possible to make simultaneous measurements of unknown samples and a known moisture reference, which was used to lock the output wavelength of the laser to the 1854 nm absorption line of water vapor.

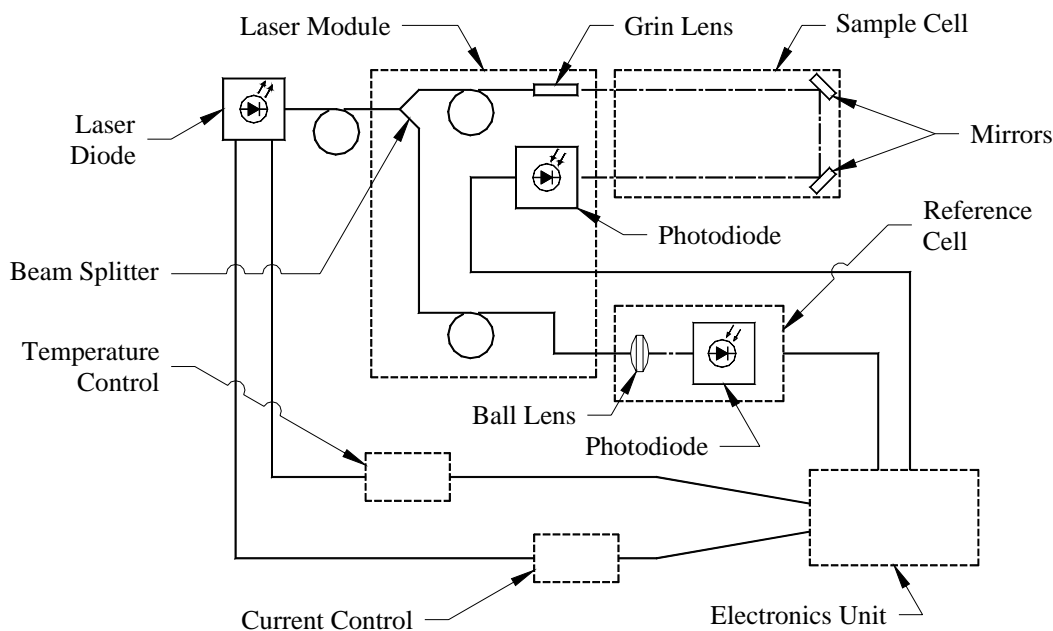


FIG. 1 - SCHEMATIC DIAGRAM OF TDLAS INSTRUMENT

This work describes a TDLAS-based instrument performing WMS. All aspects of the experiment were performed with a digital implementation of the technology. Specifically, the drive current for the laser was digitally synthesized with a single digital-to-analog converter. Further, signals produced by the detectors were digitized, prior to applying any signal processing (e.g., phase-sensitive detection, smoothing, etc.). Waveforms used to drive the laser and the associated demodulation/detection calculations were stored as files on the instrument, so changing the experimental protocol was simply a matter of downloading a file. Further, the duration for the discrete steps in the waveform is also stored as a setup parameter in the instrument, so the modulation/demodulation frequencies were software selectable. The TDLAS instrument described in this work was extremely flexible, and was easily modified to evaluate various modulation and demodulation/detection techniques.

METHODS

The moisture standard used to evaluate the performance of the TDLAS instrument was constructed by combining a two-pressure moisture generator and a dilution system. The two-pressure generator is similar in concept to those used as reference standards at national laboratories (4); the moisture concentrations produced by the two-pressure system are based only on the thermodynamics of the phase equilibrium established in its main saturation chamber (5-6). While the two-pressure system is a highly accurate and reliable device, changing the moisture output over a wide concentration range can be a cumbersome and time-consuming process. These difficulties were overcome by utilizing a blending system (Environics, Inc., Tolland, CT) to rapidly provide water vapor mixing ratios over a wide dynamic range, by diluting the “wet” output from the two-pressure generator with a dry-diluent gas. Traceability of the moisture standard was established through monitoring the conditions of the phase equilibrium in the main saturation chamber (i.e. – temperature and pressure), and through the controlled dilution stage (i.e. – volumetric flow rates). Air and natural gas were used as a background for the varying water vapor concentrations produced in the standard. Spectra for water and the natural gas components (methane, ethane, propane, etc.) were recorded with a JASCO FT-IR 6300 spectrometer, using an optical path length of 90 cm.

Evaluation of the TDLAS instrument was performed in several stages. The basic functionality of the system was evaluated in the first stage of testing. This portion of the work examined the relative performance, when using the fundamental (1F) and second harmonic (2F) signals for detection in the traditional WMS experiment. A calibration was developed for the instrument over a moisture concentration range of 0 – 2500 ppmv in nitrogen in the second phase of the evaluation. The limit of detection (LOD) was then determined. The testing was then repeated with natural gas as the sample matrix. The intended use of the instrument requires operation on samples over a modest pressure range, thus the effects of pressure broadening on the measurement were evaluated.

RESULTS AND DISCUSSION

Initial testing of the TDLAS instrument’s performance for measuring water vapor concentrations used nitrogen as the background gas. Nitrogen gas was selected, because it does not have any absorbance in the wavelength region around 1854 nm – the wavelength of the water vapor absorption peak selected for this study. Thus, the instrumental characteristics could be evaluated, without any complications from interferences in the sample matrix. This simplified background also facilitated comparison of the experimental data with the results of numerical simulations, used to model the instrument performance.

Prior to performing any quantitative studies with water vapor, the basic response of the TDLAS instrument was examined. WMS was implemented by using a digitally-sampled sine function summed with a staircase, and the resulting signal was used to drive the tunable diode laser (TDL). Specifically, the sine function was sampled at 21 discrete points, evenly spaced across

each period. This digitally synthesized signal provided a very close approximation to an analog WMS experiment. Results of a numerical simulation of the TDLAS experiment are shown in Figure 2. Figure 2a shows the power envelope received at the detector. The demodulated spectra are shown in Figure 2b. Spectra obtained from the instrument were in excellent agreement with expectations (3), and the results of numerical simulation performed by the authors.

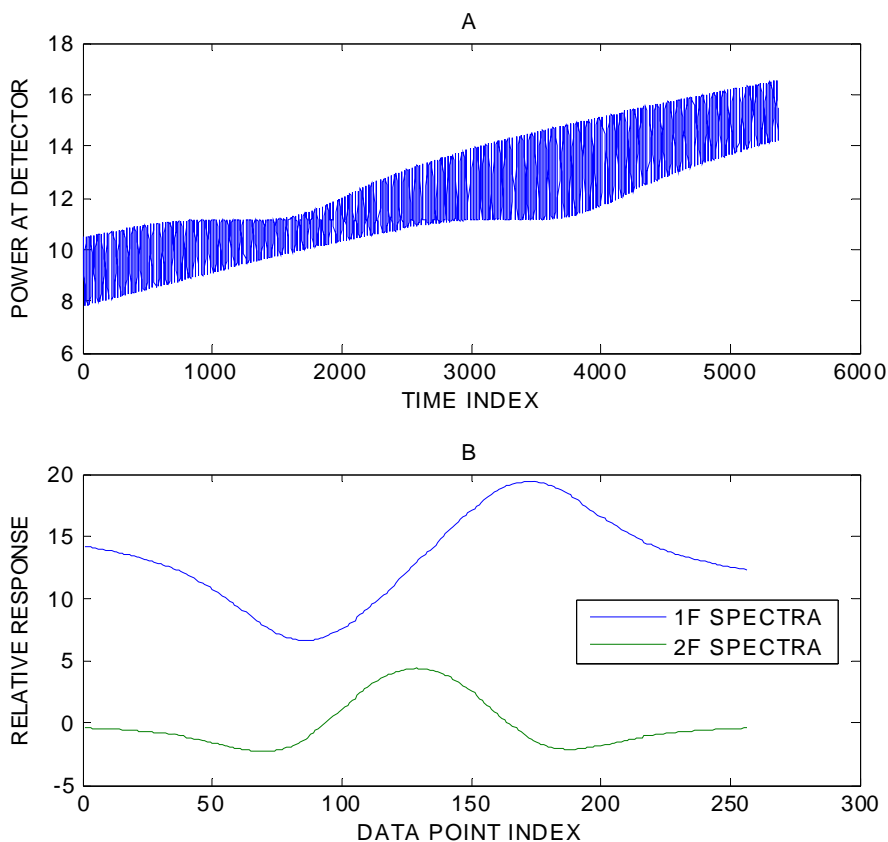


FIG. 2 – SIGNAL ENVELOPE AND DEMODULATED SPECTRA FOR THE WMS TECHNIQUE

While in theory any harmonic, or combination of harmonics, can be used in the detection scheme for a WMS experiment (7), most implementations of WMS focus on using the 2nd harmonic, or “2F”, signal. This practice is common for two main reasons (2-3): the 2F signal produces a peak that coincides with the absorption peak of the analyte, and using the 2F signal helps to remove the sloping backgrounds, which are caused by the non-linear power output of the TDL. Modifying the injection current to the TDL has been demonstrated by Kidd (8) to help remove the sloping backgrounds, but most researchers avoid using the 1F signals produced by WMS. However, because of the presence of these effects, the 1F signal actually contains more information than the spectra obtained at higher harmonics, which suppress these features. Specifically, the spectra produced by 1F demodulation contain the signal for the power envelope of the laser, superimposed on the analyte spectrum, which can be used to compensate for any

instrumental artifacts that impact the optical power received by the detectors (e.g., variations in laser output over time, fouling of optical surfaces, etc.). This contribution of the laser power is readily observed in the 1F spectrum, shown in Figure 2b, as the high and slightly-sloped offset from the baseline. Some instrument platforms have incorporated a separate signal for the power output of the laser. This signal is usually obtained by a separate measurement, rather than from the information that is readily available in the spectrum obtained by the 1F demodulation. The correction for power variations was implemented using the 1F spectrum in this study.

Calibration of the TDLAS instrument for the measurement of water vapor in nitrogen was performed by recording the 2F spectra for a series of different moisture concentrations, ranging from 0 to 2500 ppmv. In this initial calibration of the instrument all data were recorded with a sample pressure of 1.00 atmospheres in the sample cell. A series of spectra, recorded during the calibration of this first instrument, is shown in Figure 3. The clear progression in signal magnitude with increasing concentration of water vapor is readily observed. Using the calculated peak areas for these spectra, a calibration curve was generated; Figure 4 shows the results of the calibration developed from these data, with all points in close agreement to the unity line. A standard error of calibration of 2.2 ppmv was obtained for these data.

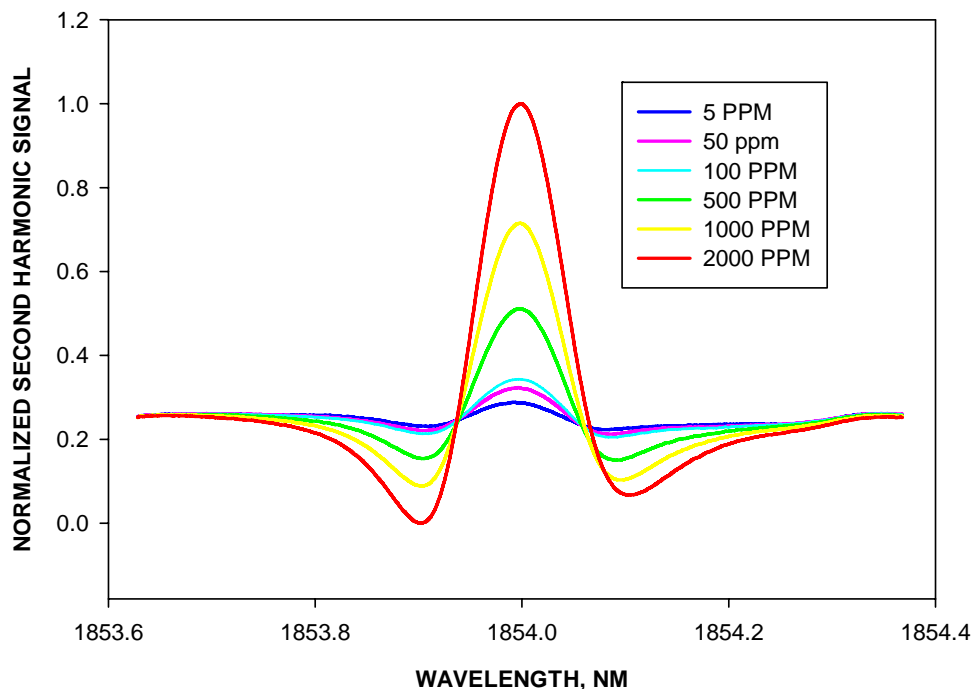


FIG. 3 – 2F SPECTRA RECORDED FOR CALIBRATION OF THE TDLAS FOR THE MEASUREMENT OF WATER VAPOR IN NITROGEN

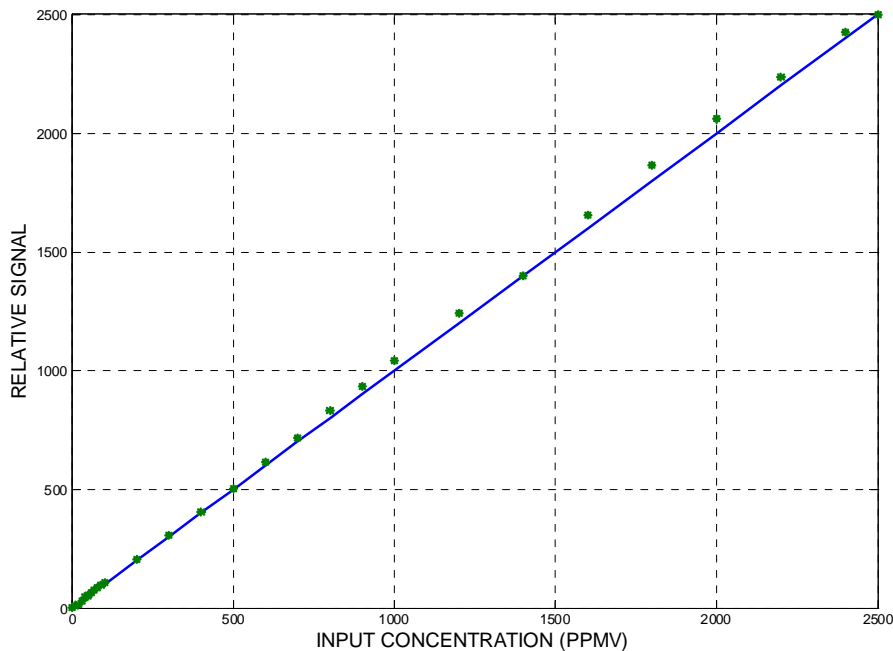


FIG. 4 – CORRELATION PLOT FOR RESULTS OF TDLAS CALIBRATION OF WATER VAPOR IN NITROGEN

The data shown in Figure 5 represent the typical response of the instrument to a series of moisture challenges. Each of the challenges in this series has duration of only 15 minutes, with a 15 minute return to the baseline value between challenges. The only exception occurs between hour 7 and 8, where the system was returned to baseline for a period of 75 minutes. The response of the instrument is both rapid and accurate.

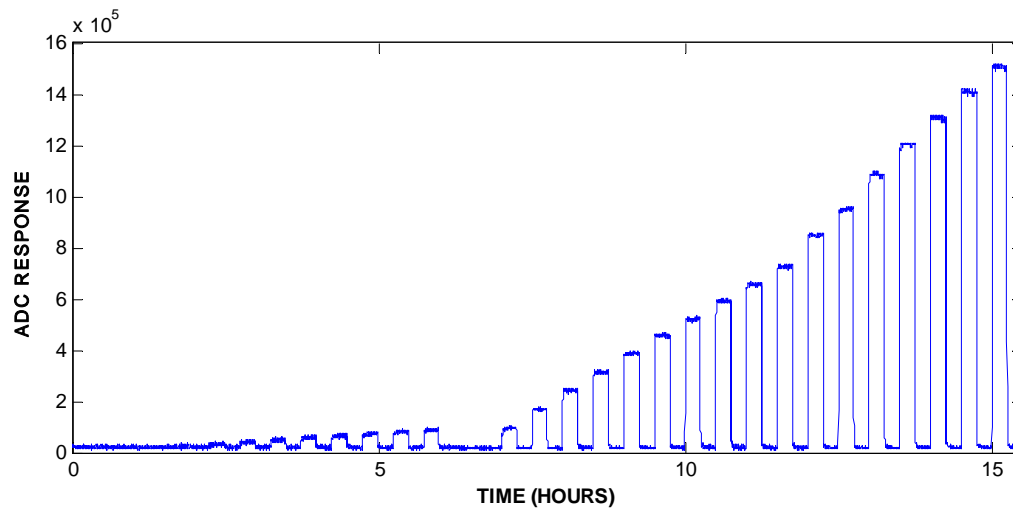


FIG. 5 – RESPONSE OF TDLAS TO A SERIES OF MOISTURE CHALLENGES

Using natural gas as the sample matrix introduces a slight increase in the complexity of the measurement. Specifically, methane will contribute a small amount of background interference to the measurement, which if uncorrected, will produce a bias in the measurements. Spectra recorded for water vapor are shown in Figure 6. These data were obtained with a path length of 90 cm, a pressure of 1.00 atmosphere, and a temperature of 21°C. Spectra of the hydrocarbons were recorded at 100% concentration, and the absorbance scales for these data are shown on the left-hand side of the plot. The spectrum of water vapor was recorded by saturating a stream of nitrogen, at a few degrees below the ambient temperature; no attempt was made to control the concentration of water vapor, as these data were used only for a qualitative evaluation of the relative peak position and line width. The absorbance scale for the water-vapor spectrum is shown on the right-hand side of the plot. Of the three hydrocarbons shown in the figure, only the methane had any substantial peak structure overlapping with the water-vapor line, which would interfere with the measurement of low concentrations of water vapor. These peaks in the methane spectrum were verified with HITRAN (9).

Making accurate measurements with low concentrations of water vapor in methane requires either finding another line in the water vapor spectrum, one without as much background interference (10), or accurately compensating for the background. A close look at Figure 6 reveals that the spectrum of methane contains a small peak at slightly longer wavelength (approximately 1854.17 nm) than the water-vapor peak. Compensation for the methane background required that peaks, water and methane, be recorded in the TDLAS spectrum. With the small methane peak included in the spectrum, the instrument was able to measure the methane concentration, and accurately subtract its contribution from the peak observed for the water vapor.

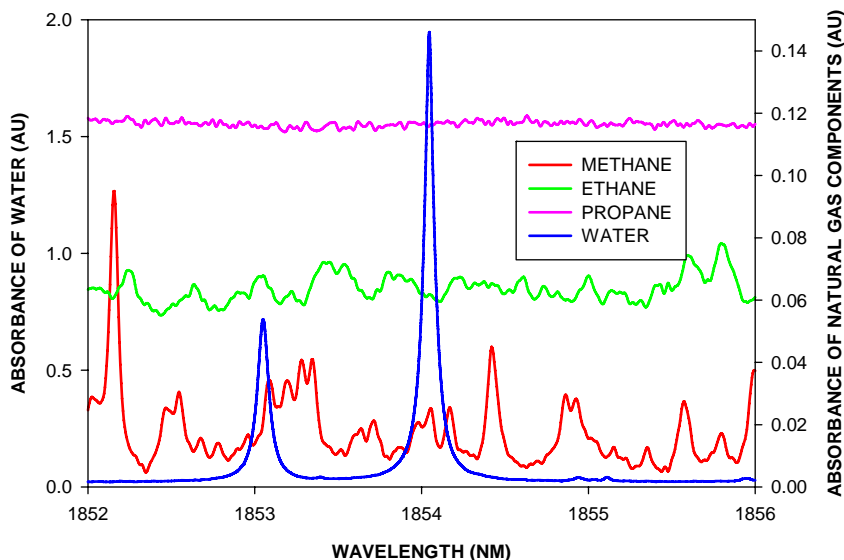


FIG. 6 – SPECTRA OF WATER VAPOR, METHANE, ETHANE, AND PROPANE

Calibration and testing of the instrument with natural gas as a sample was provided with described above methane compensation algorithm included in the software of the instrument. Bottled samples of natural gas were used for these measurements. Spectra for water vapor concentrations from 10 to 2500 ppmv in this sample matrix were recorded to develop the calibration. Spectra were recorded in 10 ppmv increments up to a concentration of 100 ppmv. Spectra were recorded in 100 ppmv increments from 100 to 1000 ppmv. Spectra were recorded in 200 ppmv increments for the 1000 to 2500 ppmv range. Results of this calibration yielded a limit of detection for water in natural gas of 5 ppmv. While these results were slightly inferior to the result obtained for nitrogen, they are adequate to meet the needs of most natural gas applications. However, because these signal levels are very small, some improvement would be easily achieved by simply increasing the optical path length for the measurement combined with further refinement of the compensation algorithm.

Instrument performance was also evaluated over sample pressures ranging from 5 to 25 psia. Collisional broadening increases the line width of the absorption line with increasing sample pressure. The relative increase in line width is 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. Examples of spectra recorded for water vapor in natural gas at both 5 and 25 psia are shown in Figures 7 and 8, respectively. Two features of these spectra require clarification. First, the spectra recorded at higher pressure (Figure 8) exhibit significant broadening and decrease in amplitude. Second, as the data shown in both figures were recorded with natural gas as the sample matrix, the background contribution of methane is clearly visible. It should be noted that the wavelength range shown in these plots has been narrowed to emphasize the line broadening of the water vapor line, so the second methane line is not present in these data. Even with the broadening observed at higher pressures, a limit of detection of 5ppmv was still observed at 25 psia.

The final series of tests performed to qualify the performance of the TDLAS instrument was to expose the system to a range of ambient temperatures. The system was exposed to an ambient temperature range of -20 to +50 C. Temperature control of the tunable diode laser was the critical metric in this test, as inability to maintain the laser at the proper junction temperature would have resulted in a failure to maintain the proper emission wavelength. The system was observed to maintain the proper laser temperature and continued to make accurate measurements of the water vapor concentration at all temperatures in this range.

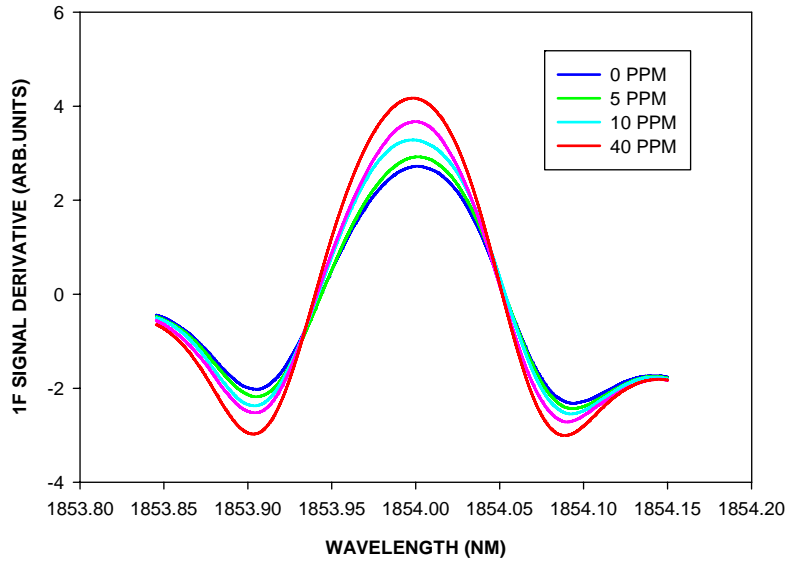


FIG. 7 – SPECTRA RECORDED FOR WATER IN NATURAL GAS AT A SAMPLE PRESSURE OF 5 PSIA

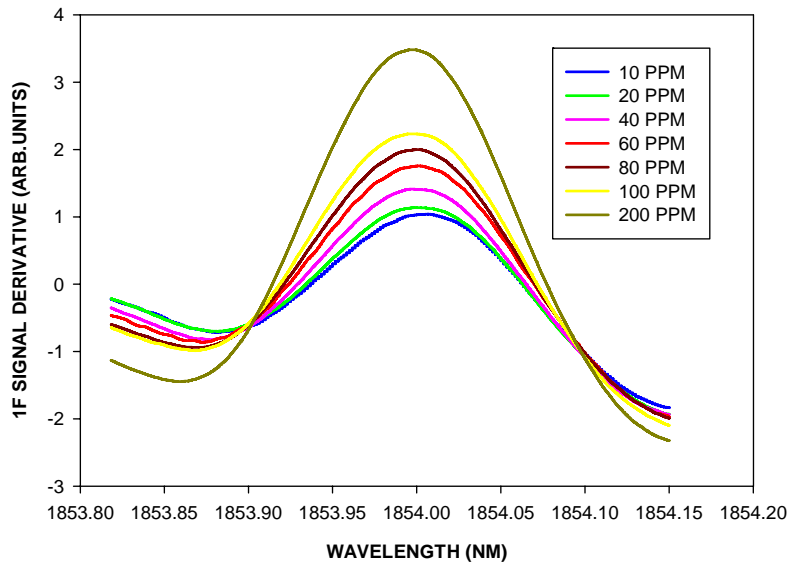


FIG. 8 – SPECTRA RECORDED FOR WATER VAPOR IN NATURAL GAS AT A SAMPLE PRESSURE OF 25 PSIA

CONCLUSIONS

A prototype of a new TDLAS-based analyzer was evaluated for the measurement of water vapor in nitrogen and natural gas. This instrument employed an all-digital measurement protocol, which was configured to replicate a conventional WMS experiment. Results presented in this study demonstrate that this digital implementation of the TDLAS experiment successfully duplicates the functionality of the conventional analog measurement. Further, the digital signal process methods employed in this system can successfully remove minor background interferences, caused by other absorbing species in the sample matrix. The instrument was able to obtain a limit of detection of less than 5 ppmv for both the nitrogen and natural gas samples.

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