REAL TIME MEASUREMENTS OF ACETYLENE IN ETHYLENE MANUFACTURING PROCESS. FIELD TRIALS OF THE TDLAS BASED ANALYZER

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ABSTRACT

The analyzer, based on near infrared Tunable Diode Laser Absorption Spectroscopy (TDLAS), was developed for the measurement of acetylene in process streams. Measurements of acetylene were made as under laboratory conditions and in different locations of the back end acetylene converter of the ethylene plant. 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, temperature, and background gas composition). Field trials were conducted over several months and the performance of the analyzer was compared with two gas chromatographs (GC) measuring acetylene in the same gas stream. A strong correlation of the TDLAS acetylene analyzer reading with gas chromatographs was demonstrated. One of the analyzer configurations for the field trials included simultaneous acetylene measurements in different locations of the converter with a goal to optimize production of ethylene. 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 $0 - 3000$ ppmv. The advantage of TDLAS acetylene measurements from the view point of the speed of the response in comparison with gas chromatography was also demonstrated.

INTRODUCTION

This paper describes the application of TDLAS for measurements of acetylene based on extractive sampling. The principal objective of the work reported here is to characterize new TDLAS-based extractive analyzer with an all-digital protocol for the modulation of the laser drive signal and the demodulation of the detector response. This analyzer was configured for

acetylene measurements in the gas stream typical for ethylene plant acetylene converter. Another objective of this work is to present the results of field trials of the acetylene analyzer at different locations of the acetylene converter and to demonstrate the benefits of using TDLAS analyzer for acetylene measurements in comparison with traditionally used gas chromatograph.

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. In modern ethylene production the most common method for acetylene removal is through selective hydrogenation in vapor phase. 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.

It is known that acetylene hydrogenates much faster than ethylene over the same catalyst when both acetylene and ethylene are present. The reason for that is preferential occupation by acetylene of active adsorption sites. This preferential adsorption of acetylene over ethylene assumes that there are sufficient amount of acetylene molecules to cover all active sites to minimize ethylene hydrogenation to ethane. However under conditions of industrial operations at the location near the bottom of the final bed where most of the acetylene molecules are already hydrogenated there is insufficient number of the acetylene molecules to maintain total active site coverage. In this situation carbon monoxide provide a means for blocking and inhibiting the adsorption of ethylene because adsorption rate for carbon monoxide is higher than that of ethylene. These facts are the basis for selective hydrogenation of acetylene to ethylene (1-3). To avoid incomplete conversion of the acetylene or undesired conversion of the ethylene to ethane the optimal conditions for the hydrogenation process may be determined by real time monitoring of acetylene concentrations at different locations of acetylene converter. 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 usually takes several minutes. TDLAS-based measurements provide real time monitoring with data acquisition rate of few seconds. It was also found (4) that during plant start up and other unconditional events the concentration of acetylene can suddenly reach very high levels. As was experimentally demonstrated in the environment of the ethylene plant during these fast acetylene fluctuations, the gas chromatograph either misses the event entirely or report it with delay after completion. It is critical to provide real time monitoring of the acetylene hydrogenation process at the required concentration levels and to control the time of the hydrogenation process.

INSTRUMENT DESIGN

The TDLAS instrument evaluated in this work was an AMETEK 5100 HD, which was modified to operate with multi-pass Herriott cells of different optical path length and to provide simultaneous measurements of acetylene at two different locations of the acetylene converter. A schematic representation of the instrument is shown in Figure 1. The measurement of acetylene

was performed with two 1521-nm distributed feedback (DFB) lasers. Laser diodes 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 fiber-optic beam splitters. The splitters were used to divide the optical power in a 50/50 ratio for use in the sample and reference measurements, respectively. Reference cell contained known concentration of the analyte in non-absorbing gas at wavelength of interest and was used to lock the output radiation wavelength of the laser.   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.

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 reference, which was used to lock the output wavelength of the laser.
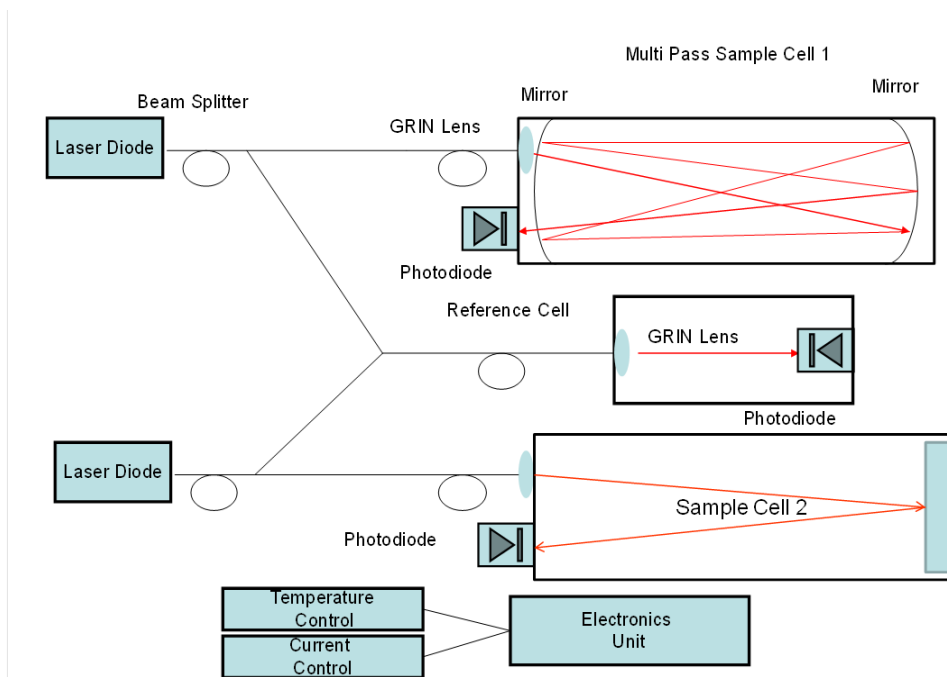

FIGURE 1. EXPERIMENTAL SET UP FOR TDLAS MEASUREMENTS.

The sample cells 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 lasers and photo diodes were also located in the main electronics compartment, isolated from the heated sample oven. It is should be noted that performance of the analyzer with two sample cells but based on single laser diode could be also provided.

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 (5-6). 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. Spectral lines widths were determined from the data published in HITRAN spectral library (7).

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 ro-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.

RESULTS AND DISCUSSION

LABORATORY TESTING

Initially, the analyzer performance was tested in the laboratory with samples of acetylene in a host gas containing 75% ethylene and 25% ethane, a gas stream composition typical for an ethylene plant acetylene converter. Three concentration ranges of acetylene, 0 – 15000, 0 - 3000

and 0 – 10 ppmv, were selected to match the conditions corresponding to the inlet, first and second bed outlets of the ethylene plant acetylene converter. Different concentrations of acetylene were created by mixing acetylene with the host gas in a gas mixer. Real gas stream through the acetylene converter also had hydrogen, methane, propane and propylene. Concentration of these components was on fraction of a percent level. 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 of 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. Spectral profile of the calculated regression vector is analyte specific and corresponds to spectral area where acetylene spectra are changing with concentration.
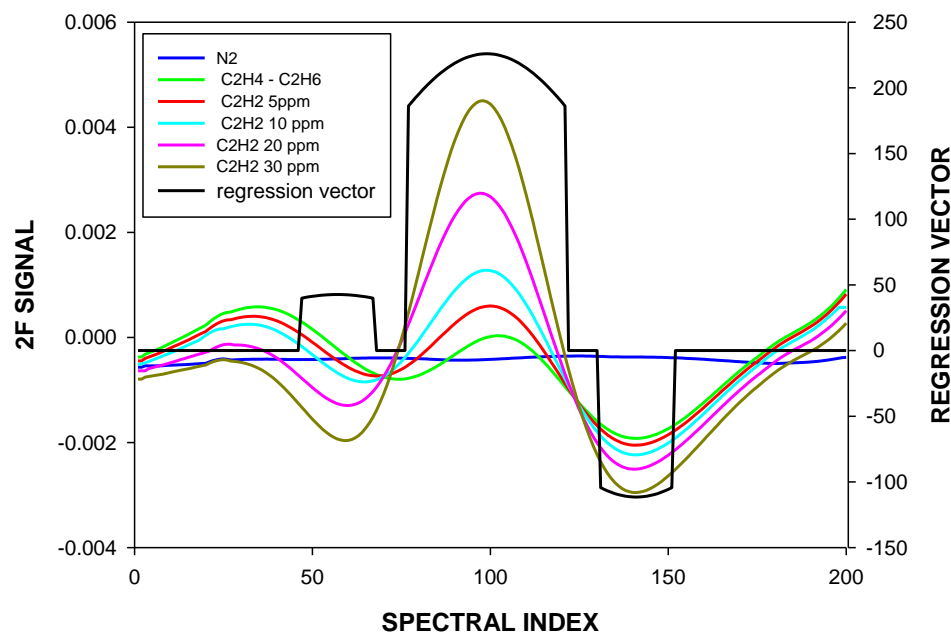

FIGURE 2. 2F SPECTRA OF ACETYLENE, ETHYLENE – ETHANE AND NITROGEN.

The data shown in Figure 3 and Figure 4 are the responses of the instrument to a series of acetylene challenges over the medium and high and low acetylene concentration ranges. The duration for each challenge was approximately 20 minutes. Return to the background gas baseline was also tested before and after validation measurements for each of the concentration

ranges. 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.
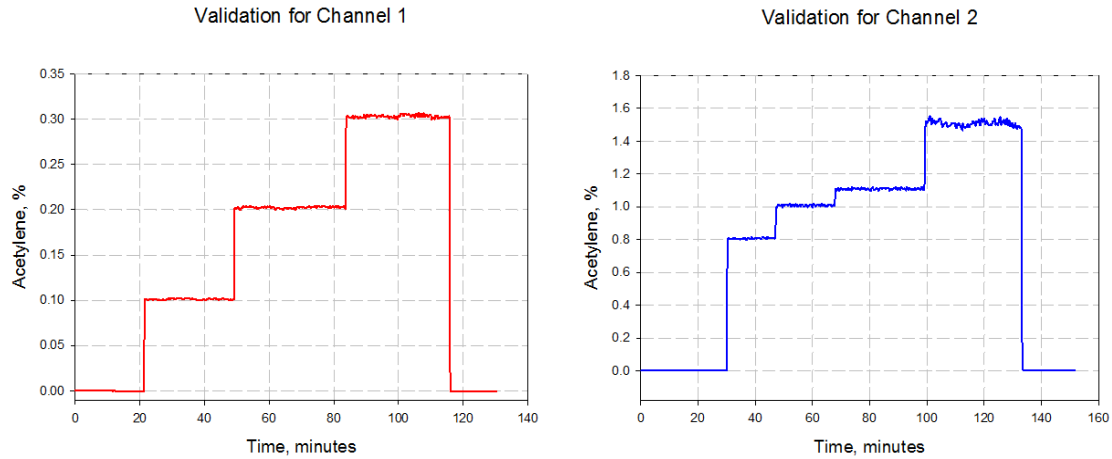

FIGURE 3. ACETYLENE READINGS. ETHYLENE–ETHANE BACKGROUND GAS. RESPONSE TO A SERIES OF CONCENTRATION CHALLENGES IN THE RANGES OF 0 - 3000 PPMV AND 0 – 15000 PPMV.
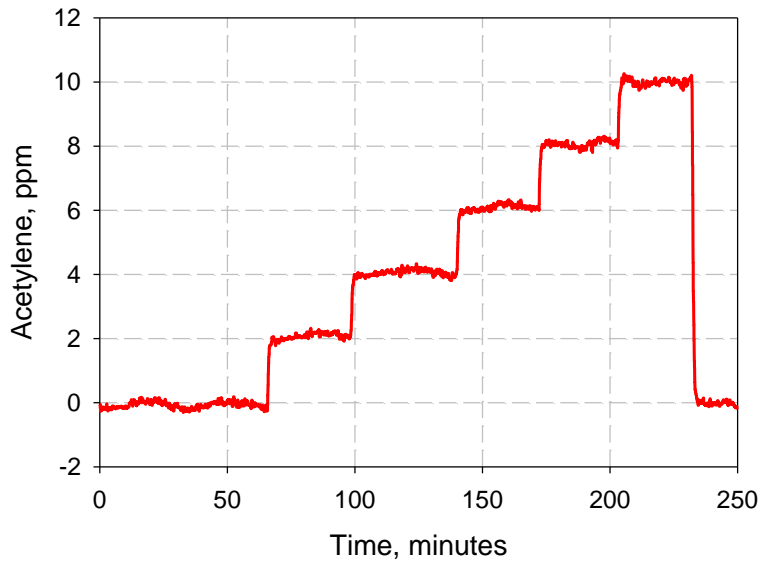
FIGURE 4. ACETYLENE READINGS. ETHYLENE–ETHANE BACKGROUND GAS. RESPONSE TO A SERIES OF CONCENTRATION CHALLENGES IN THE RANGE 0 - 10 PPMV.

The results of the validation test are summarized in the Table I.

TABLE I. PERFORMANCE OF THE ACETYLENE ANALYZER. LABORATORY TESTING

CONCENTRATION RANGE, PPMV	REPEATABILITY, PPMV	ACCURACY, PPMV	DRIFT 24 HOURS, PPMV	T90 TIME,SECONDS
0 - 10	0.1	0.3	0.18	30
0 - 3000	15	40	17	30
0 - 15000	150	300	180	30

Repeatability as a degree of agreement between replicate measurements of the same quantity was expressed in terms of standard deviation of the measurements. The value of the accuracy was calculated as the maximum positive and negative deviation of the readings from set value observed during validation test of the analyzer.

An example of the instrumental drift during 24 hours is shown in Figure 5 for the channel calibrated for measurements in the low acetylene concentration range. 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.
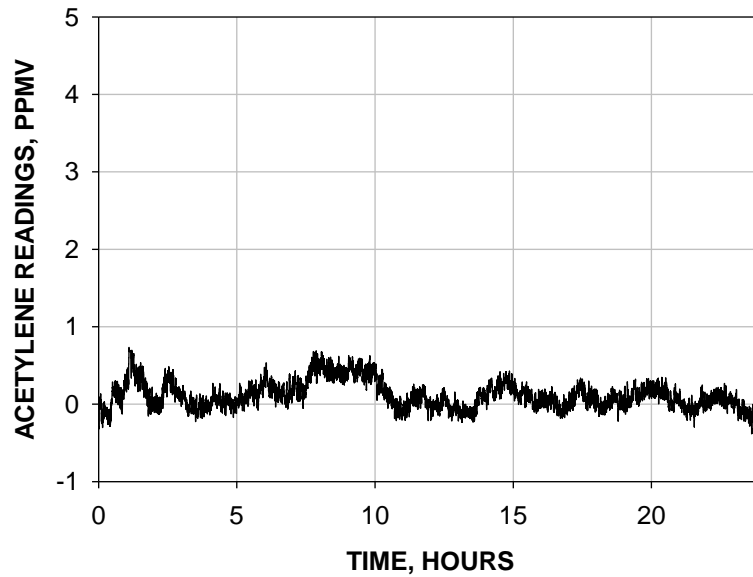
FIGURE 5. ACETYLENE ANALYZER DRIFT TEST.

FIELD TRIALS

Field trials of the acetylene TDLAS analyzer were conducted at Lyondellbasell ethylene plant at Corpus Christi, TX since May of 2013. Inlet, outlet of the first bed and outlet of the second bed of the back end acetylene converter were used as measurement sites during field trials. For each of the acetylene measurement site TDLAS analyzer was connected in parallel with respect to two gas chromatographs which were used to control the process. One of them had response time of 1 minutes, the response time of another GC was 3 minutes.Table II presents the gas stream running through acetylene converter.

TABLE II. BACK END ACETYLENE CONVERTER GAS STREAM

GAS, VOLUME ,%	STREAM 1			STREAM			STREAM 3		
	Normal	Max	Min	Normal	Max	Min	Normal	Max	Min
Acetylene	1.1	1.15	1.05	0.35	0.37	0.31	0.5 ppmv	0.6 ppmv	0.4 ppmv
C4S	0.01	0.03	0.00	0.04	0.04	0.04	0.06	0.07	0.06
Ethane	22.65	23.13	22.12	23.36	23.82	23.00	23.94	24.35	23.54
Ethylene	73.57	74.15	73.13	74.92	75.33	74.56	75.22	75.63	74.81
Hydrogen	1.67	1.79	1.61	0.59	0.64	0.52	118.66 ppmv	154.2 ppmv	99.00 ppmv
Methane	0.13	0.15	0.12	0.14	0.15	0.12	0.15	0.16	0.13
Nitrogen	0.05	0.15	0.00	0.00	0.02	0.00	0.01	0.04	0.00
Oxygen	0.01	0.05	0.00	0.00	0.00	0.00	0.00	0.01	0.00

Propane	0.26	0.73	0.11	0.13	0.17	0.11	0.13	0.18	0.11
Propylene	0.53	0.89	0.42	0.47	0.58	0.42	0.48	0.59	0.43
Pressure, PSIG	360	390	350	360	390	350	360	390	350
Temperature, °F	75	90	60	75	90	60	75	90	60

All tests were conducted under stable temperature of the sample cell compartment of 50°C. The pressure in the sample cell was around 19 psia.

Measurements of the acetylene at the inlet of the converter and at the first bed are shown on Figure 6 and Figure 7. In a period of one month the measurements were conducted continuously, without breaks. During first week of the test TDLAS analyzer had some 0.2% acetylene offset with respect to both GC analyzers. This offset was corrected by fine adjustments of the analyzer span factor. After that all three analyzers were following each other with high precision. Variation of the TDL analyzer readings with respect to GC was not higher than the difference between readings of GC analyzers with respect to each other. Acetylene readings at the outlet of the first bed of the converter did not require any adjustments. The difference between TDLAS analyzer and GC readings was less than 30 ppmv.
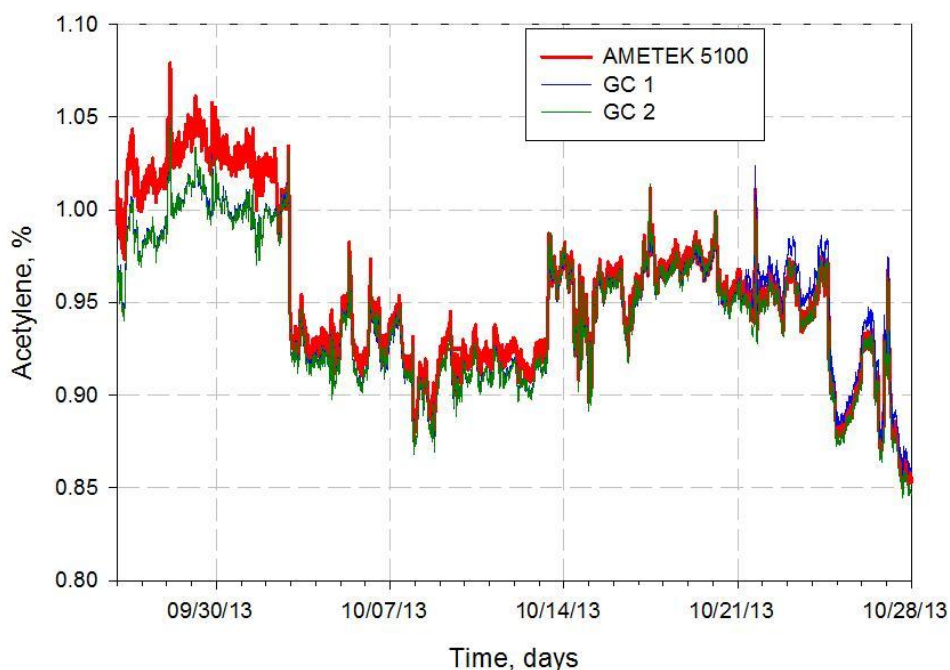

FIGURE 6. ACETYLENE MEASUREMENTS AT THE INLET OF THE CONVERTER.

FIGURE 7. ACETYLENE MEASUREMENTS AT THE OUTLET OF THE FIRST BED OF THE CONVERTER.
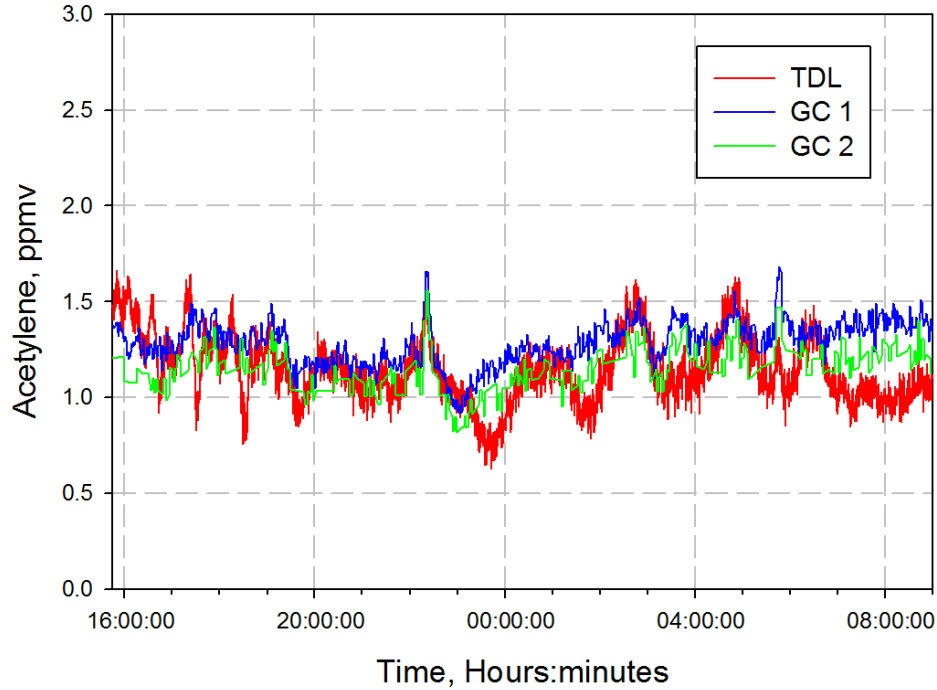

FIGURE 8. ACETYLENE MEASUREMENTS AT THE OUTLET OF THE SECOND BED OF THE CONVERTER.

Acetylene measurements at the outlet of the second bed of the converter are demonstrated in Figure 8. During 16 hours of the test acetylene readings were changing in the range around one ppmv. Again TDLAS analyzer was measuring acetylene being connected in parallel with respect to two GC analyzers. Despite of relatively narrow range of the acetylene concentrations all three analyzers had partial correlation of the measurement results without any significant variations of the readings.

To compare the speed of the response for GC and TDL analyzers the consequence of fast (less than 15 seconds) dilutions of the process stream corresponding to the outlet of the first bed of the acetylene converter was produced. For this purpose calibration gas with 250 ppmv of acetylene was injected in to process gas stream. It is should be noted that TDL analyzer and GC with 1 minute of cycling time were connected in parallel with respect to gas stream. As shown in Figure 9, the TDLAS analyzer was able to respond to all of these challenges. In contrast GC analyzer had response with delay or no response. It was found that the response of GC to acetylene depends on the time interval between the moment of dilution and injection of gas in to GC. It could match TDL readings with delay or could be zero as shown in Figure 9. It means that to provide reliable ethylene process control the process must slow down to match GC performance. Meanwhile TDL analyzer was able to provide close to real time process monitoring.
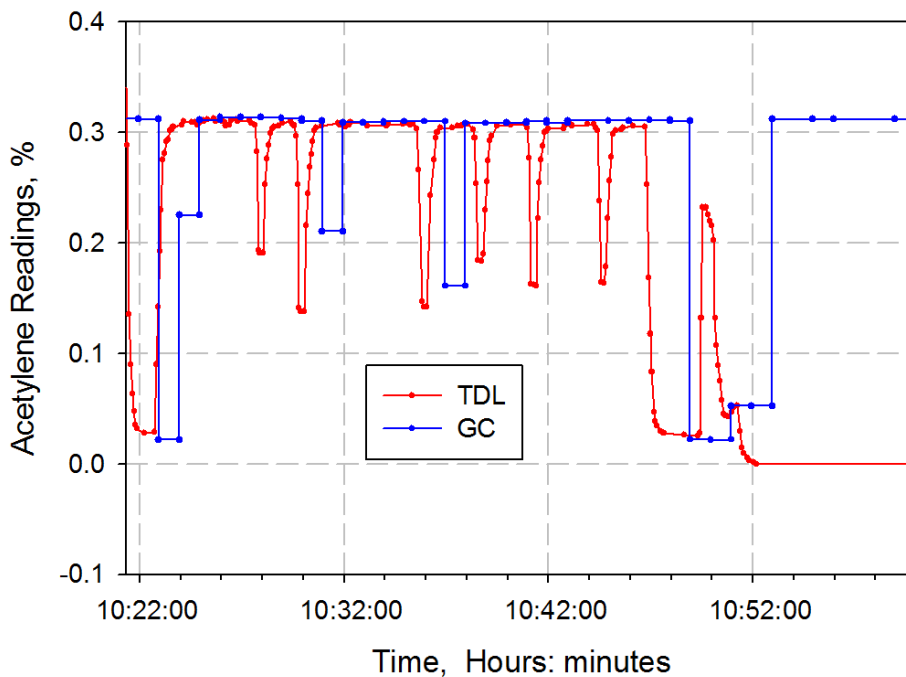

FIGURE 9. SPEED OF THE RESPONSE FOR TDLAS AND GC ANALYZERS.

CONCLUSIONS

AMETEK 5100 HD analyzer was built for the measurements of acetylene content in the inlet, outlet of the first bed and the outlet of the second bed of the acetylene converter. This analyzer 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. Performance of the analyzer in three investigated concentration ranges was matching requirements for the on-line monitoring of selective acetylene hydrogenation in ethylene plant acetylene converter.

Field trials of the acetylene analyzer demonstrated close match of the performance with gas chromatographs from the view point of required sensitivity. At the same time TDLAS based analyzer demonstrated better speed of the response which makes attractive use of the analyzer for closer monitoring of the hydrogenation process in ethylene plant acetylene converter. Specifically simultaneous measurements of acetylene at the inlet and outlet of the first bed of the converter are a way to optimize ethylene production by optimizing hydrogen injection and saving ethylene product.

ACKNOWLEDGMENTS

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