

# Development of a Rapid On-Line Acetylene Sensor for Industrial Hydrogenation Reactor Optimization Using Off-Axis Integrated Cavity Output Spectroscopy

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A spectroscopic analyzer has been developed for rapid, accurate quantification of acetylene and methyl acetylene in hydrocarbon cracked gas processing plants. The system utilizes off-axis integrated output cavity spectroscopy to measure the near-infrared, cavity-enhanced absorption spectrum of ethylene, methyl acetylene, and acetylene and employs a chemometric data analysis strategy to quantify the respective constituents. Initial tests verified that the instrument is capable of measuring <0.050 ppmv of acetylene, has a precision of  $\pm 0.025$  ppmv, and can accurately determine acetylene concentrations with comparable accuracy to a gas chromatograph ( $\pm 0.1$  ppmv) in an actual process stream composition matrix under plant operating conditions. Subsequently, the prototype analyzer was installed in a hydrocarbon facility for field-trials, where its rapid response ( $\leq 30$  seconds or better) allowed it to measure transient acetylene and methyl acetylene fluctuations that were too fast for conventional methodologies. Moreover, the analyzer showed an extended dynamic range that enabled measurement of very high acetylene levels (0–1000 ppmv) during abnormal plant operations. Finally, two commercial acetylene analyzer systems with stream-switching capabilities were implemented in an industrial facility and initial results are presented.

Index Headings: Acetylene; Ethylene; Diode laser absorption spectroscopy; Off-axis ICOS; Cavity ringdown.

## INTRODUCTION

Ethylene is a major building block used in many industrially important manufacturing processes including polyethylene, ethylene-propylene elastomers, and other high volume derivatives.<sup>1</sup> The control and optimization of the process used to manufacture ethylene has significant economic consequences to the chemical industry. One of the unit operations within a modern olefins cracker is the hydrogenation reactor, where careful control is needed to minimize the presence of acetylene impurity produced in the cracking process. Moreover, over-conversion of ethylene back into ethane results in loss of product and reprocessing costs; thus, it is critical to monitor acetylene ( $C_2H_2$ ) for optimization of the hydrogenation reaction. However, rapid analysis of  $C_2H_2$  impurity in crack gas has been a significant technology gap in the olefin industry for many years.

The speed, reliability, and accuracy of this analysis in hydrogenation reactors are critical to optimizing product yield and improving quality specification. The continuous and real-time measurement of trace acetylene provides insight into process run conditions to better control the reactor and reduce reactor upsets, which can improve the efficiency and lifetime of

process catalysts. Additionally, since acetylene is a product impurity that can cause process problems or poison the end-user's reactor catalyst, downstream users of the finished ethylene will not accept product that has off-specification acetylene levels (e.g., typically less than 2 ppmv of contamination). As a result, there is a need for a rapid on-line analysis of acetylene in both cracked gas at the hydrogenation reactor and in the finished ethylene product.

Currently, the olefin industry uses gas chromatography (GC) to quantify acetylene, with measurement times of 90–300 seconds, and enhances measurement frequency by using multiple units in tandem. However, in order to achieve real-time process control, an analyzer must provide much faster data (e.g., 1–30 seconds) while retaining adequate sensitivity (e.g., <0.1 ppmv), making conventional GCs inadequate for this application. One potential alternative involves using miniature GCs with MEMs-based separation columns. These devices have the potential of providing faster analyses of a wide range of constituents in a cost-effective manner. Preliminary research has demonstrated the ability to detect acetylene in pure ethylene with measurement times of 20–40 seconds.<sup>2,3</sup> However, these instruments are still being developed, making them currently unsuitable for industrial deployments.

## TECHNICAL APPROACH

**Off-Axis Integrated Cavity Output Spectroscopy.** Alternatively, near-infrared laser absorption spectrometry can be used to probe acetylene via overtone transitions near 1510–1540 nm. These transitions are readily accessible using standard, telecommunications-grade DFB diode lasers and are very well characterized;<sup>4–6</sup> however, the strongest absorption features in this region have integrated line strengths of only  $10^{-20}$  cm/molecule, making it difficult to detect low levels of acetylene in a single optical pass. Moreover, other flow constituents, including ethylene and methyl acetylene, have broadband absorptions in the same spectral region, reducing the selectivity and sensitivity of lower-resolution instruments (e.g., nondispersive near-infrared detectors) and commonly used noise cancellation schemes (e.g., wavelength modulation spectroscopy).

In this study, off-axis integrated cavity output spectroscopy (Off-Axis ICOS)<sup>7–9</sup> was used to quantify acetylene concentrations in the multi-component matrix of a hydrogenation reactor stream outlet.<sup>10</sup> This technique provides long effective optical path lengths (e.g., 500–10 000 meters typical) while retaining a robust off-axis alignment that is suitable for industrial applications. In off-axis ICOS, the laser is coupled into a high-finesse optical cavity comprising two highly reflective

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mirrors (e.g.,  $R = 99.9\text{--}99.999\%$ , typical) in an off-axis fashion. A small fraction of laser light enters the cavity through the first mirror and makes multiple passes through the gas sample while gradually attenuating due to sample absorption and transmission through the cavity mirrors. Light transmitted through the second mirror is then focused onto a highly amplified detector and digitized for analysis. The net result is that cavity enhances the single-pass sample absorption,  $A$ , and the fractional change in transmitted intensity,  $\Delta I/I_0$ , is given by<sup>9</sup>

$$\frac{\Delta I}{I_0} = \frac{GA}{1 + GA} \quad (1)$$

where  $G = R/(1 - R)$  is the cavity gain parameter. Thus, the high-finesse optical cavity provides an effective optical path length of  $L_{\text{eff}} = GL_0$ , where  $L_0$  is the distance between the mirrors. The off-axis alignment helps suppress coherent interferences by making the laser beam exceed its coherence length before overlapping with itself inside the cavity. Moreover, since concave mirrors (e.g.,  $\text{ROC} \sim 1 \text{ m}$ ) are used to form a stable resonator, the exact trajectory of the incoming beam is not critical, making the technique suitably robust for long-term industrial deployments.

**Chemometric Data Analysis.** As noted above, there are several gases present in an ethylene cracked gas process stream, including ethylene, methyl acetylene, propylene, methane, carbon dioxide, and acetylene. Fourier transform infrared (FT-IR) spectra of this region clearly indicate that many of these components absorb in the same near-infrared spectral window (e.g., 1510–1540 nm) that is targeted for acetylene detection.<sup>11</sup> Therefore, the data analysis routine must be capable of simultaneously fitting several absorbing species, and a chemometric model<sup>12,13</sup> was developed to address this issue.

In this model, the total per-pass absorption spectrum,  $A(\nu)$ , is expressed as a weighted sum of the absorption spectra of the mixture components:

$$A(\nu) = c_0 A_0(\nu) + c_1 A_1(\nu) + c_2 A_2(\nu) + \dots \quad (2)$$

where  $\nu$  is the laser frequency,  $c_n$  are coefficients related to the concentration of the  $n$ th species, and  $A_n(\nu)$  is the absorption spectrum of the  $n$ th species in the absence of other contaminants. Note that in order to achieve good fitting results, the absorption spectrum of the mixture components,  $A_n(\nu)$ , should be measured under similar conditions (e.g., composition components and concentrations) to the actual process gas sample. In this work, these basis-set spectra were obtained by filling the instrument with certified dilutions of mixture components and measuring the cavity-enhanced absorption spectra shown in Fig. 1. The selected concentrations were based on typical values found in a Dow Chemical Company light hydrocarbon cracker process stream. Note that, with the exception of methane, the other hydrocarbon constituents at their anticipated concentrations have absorption features that are similar in strength to acetylene at its contaminant level (e.g., 0–10 ppmv). Moreover, many of the larger hydrocarbons have broad absorption features.

The measured transmitted intensity through the optical cavity,  $I(\nu)$ , can be expressed by rearranging and combining Eqs. 1 and 2 above to give:

$$I(\nu) = \frac{I_0(\nu)}{1 + G[c_0 A_0(\nu) + c_1 A_1(\nu) + c_2 A_2(\nu) + \dots]} \quad (3)$$

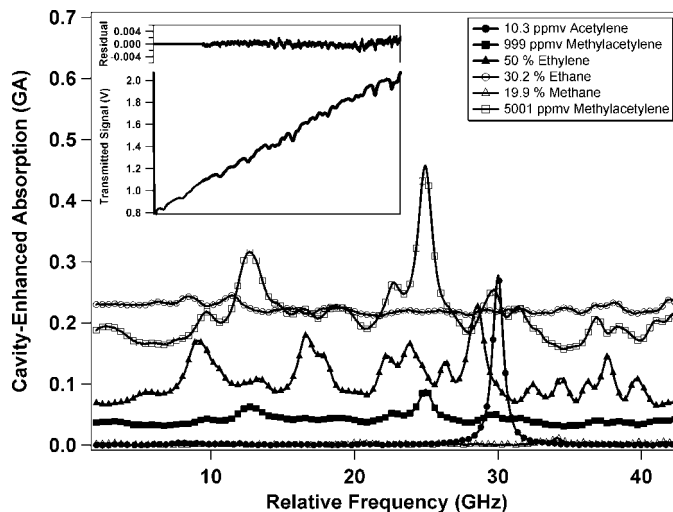


FIG. 1. Measured cavity-enhanced absorption spectra of ethylene process stream constituents diluted in nitrogen. Only every tenth data point has been shown for clarity. These spectra are used as the basis set functions for the chemometric fitting algorithm described in the text. The inset (top left) shows the measured cavity-enhanced transmission spectrum (gray line) fit to the chemometric model function described in the text (black line). The fit residual, shown at the top of the inset, indicates that the model function is in good agreement with the measured data.

where  $I_0(\nu)$  is the cavity transmission in the absence of any absorption and can be well approximated by a second-order polynomial. The actual cavity transmission is measured as a function of time (e.g.,  $I(t)$ ), and an etalon trace, which provides a measure of  $\nu(t)$ , is used to convert  $I(t)$  to  $I(\nu)$ . Because some of the absorbing species have relatively featureless spectra, the empty transmission spectrum,  $I_0(\nu)$ , cannot be determined from the measured transmission spectrum of process gas and must be measured during calibration intervals. The measured transmission spectrum is fit to a function of the form indicated in Eq. 3, resulting in values for the fitted coefficients  $c_0$  through  $c_n$ . These fit results are then directly used to quantify the constituent concentrations by comparing the measured coefficients to coefficients determined from calibrated standards. A typical fit of the cavity transmission spectrum is shown in the inset of Fig. 1, where the fit residual is limited by the measurement noise, verifying the chemometric fitting strategy. Complete model validation was accomplished by quantifying several calibrated standards and is presented below.

## EXPERIMENTAL

The acetylene analyzer consists of electronic and optical subsystems housed in the two National Electric Manufacturers Association (NEMA) enclosures. The top enclosure, Electronic Control Unit (ECU), includes a single-board computer that provides an output voltage to tune the laser, an A/D converter that digitizes and stores the detector output signal, software to analyze the cavity-enhanced transmission signal, and capabilities to report the resulting data via a variety of methods (e.g., RS-232, TCP/IP). User interface is provided through a front-panel display and ruggedized keypad. The enclosure also houses a custom laser driver card that controls the laser temperature and current to within  $\pm 0.01 \text{ }^\circ\text{C}$  and  $\pm 0.1 \text{ mA}$ , respectively. The output voltage from the computer is connected to the laser driver card and sweeps from 4 to 6 volts at a frequency of 100 Hz, resulting in a laser tuning of

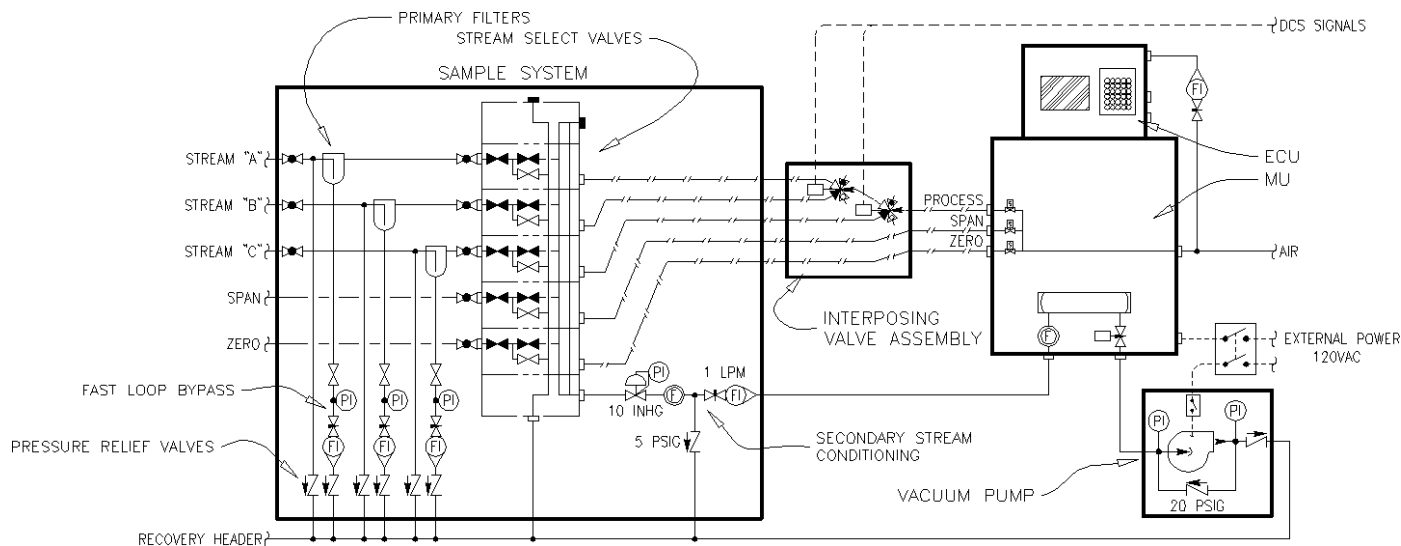


FIG. 2. Schematic of the gas handling system using symbols defined by the American National Standards Institute (ANSI) Y32.11 Process Flow Diagrams in the Petroleum and Chemical Industries Standard. The gas manifold includes hardware to select between the inputs for three process control streams ("A" through "C"), zero air, and a span gas. The gases are filtered and the input pressures are limited via pre-set relief valves. Digital control signals (DCS) are used to control solenoid valves and select a stream for analysis. The selected stream is conditioned prior to being drawn through the off-axis ICOS analyzer, which consists of a Main Unit (MU) and Electronics Control Unit (ECU), by a diaphragm pump.

approximately 50 GHz in 0.01 seconds. A secondary computer control signal sets the laser temperature and provides feedback based on the measured absorption features to provide long-term stability of the laser frequency. The ECU also includes electronics to drive the pneumatic signal solenoid valves, control the measurement cell temperature and pressure, and provide power to all necessary systems from incoming 120 VAC.

The bottom enclosure houses the off-axis ICOS instrument and peripherals. This subsystem consists of a 22 cm long, 5 cm diameter optical cell bounded by two highly reflective mirrors ( $R = 99.94\%$ , loss = 600 ppm) that provide an effective optical path length of  $\sim 367$  meters. In order to permit field-serviceability, the mirrors are housed in flanges that can be removed and replaced without realignment or optimization. A telecommunications-grade DFB diode laser producing 20–30 mW near 1531.6 nm is fiber-coupled and launched into the cavity in an off-axis fashion to probe the  $P(11)$  transition of the  $\nu_1 + \nu_3$  band of  $^{12}\text{C}_2\text{H}_2$ . Light transmitting through the cavity is focused onto a custom amplified InGaAs detector with a gain of  $3 \times 10^6$  V/A and a bandwidth of 30 kHz. In order to reduce the measurement noise, 100 cavity-enhanced transmission spectra are averaged (e.g., 1 second of data collection) prior to analysis.

The intensity and shape of absorbing features depends on the sample temperature and pressure.<sup>14,15</sup> Although this can be accurately measured for the isolated acetylene absorption feature, the temperature and pressure dependence of more complex broadband spectra cannot be readily measured or calculated. Therefore, in order to avoid these effects, the gas temperature and pressure are precisely controlled to match the conditions under which the basis set spectra were acquired. The former is accomplished by sheathing the optical cavity in a heated, insulated blanket that maintains the sample temperature at  $38 \pm 1$  °C. Note that the elevated temperature is chosen to obviate the need for cooling. The sample pressure is controlled by a downstream pressure controller that is mounted onto the

cavity outlet and keeps the sample pressure range of 1.5–2.5 psi to within  $\pm 0.02$  psi. The optimal measurement temperature and pressure were determined through quantification of a comprehensive test series. Although the setpoint temperature is not critical, the pressure must be chosen to allow for maximum absorption signal (e.g., higher pressure provides more signal) while maintaining adequate contrast ratio between the different absorption spectra (e.g., lower pressure provides sharper, more contrasting absorption features). The bottom enclosure also includes solenoid valves for sample introduction.

The sample system consists of primary stream conditioning, stream selection, secondary stream conditioning, and a vacuum pump. Sample and calibration gases are regulated to  $\sim 20$  psig before entering the sample system and are limited to  $< 50$  psig by a pressure relief valve that vents to a recovery header. The sample gas passes through a filter containing a sintered metal element configured for coalescing action. The bypass flow exiting the bottom of the filter carries away any coalesced liquids and provides shorter sample propagation time. The stream select valve assembly, illustrated in Fig. 2, consists of double-block and bleed valve modules, one for each stream. A valve module is activated by a pneumatic signal provided by the off-axis ICOS analyzer. The pneumatic signal for process stream selection passes through interposing switching valves that are controlled from a distributed control system. This arrangement allows the analyzer to control valve selections for calibration while permitting stream selection control from a plant operations console. The selected stream pressure is regulated to 5 psi and filtered. Pressure is limited by a pressure relief valve that vents to a recovery header when pressure exceeds 5 psig. Sample flow is set to  $\sim 1$  L per minute by a rotometer prior to entering the lower cabinet of the analyzer, providing a sample residence time of approximately 2 to 3 seconds in the measurement cell. An explosion-proof dual-head diaphragm pump is placed downstream of the analyzer to pull gas samples through the system.

The instrument software package permits analyzer operation

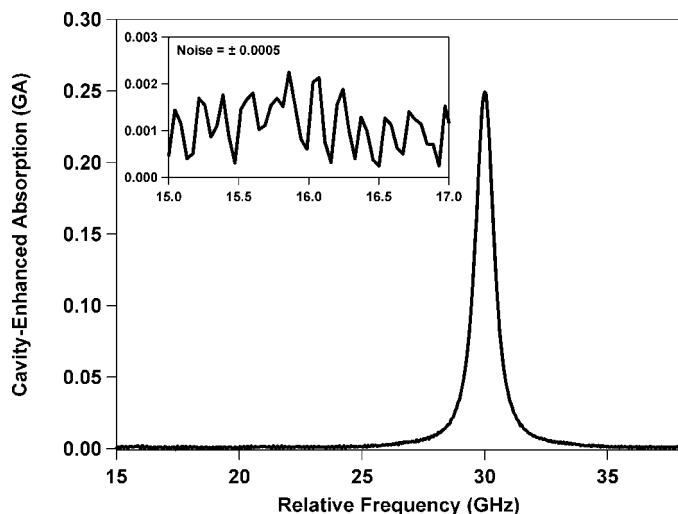


FIG. 3. Measured cavity-enhanced absorption spectrum of 8.7 ppmv acetylene/nitrogen and associated baseline noise (inset). The measurement signal-to-noise ratio exceeds 500:1, providing a detection limit of <0.020 ppmv acetylene.

through a ruggedized keypad on the front panel of the electronics control unit. In standard operating mode, the screen displays the acetylene and methyl acetylene concentrations, instrument status, and measurement parameters. The Basic Menu allows the user to access many common functions, including downloading data files, reviewing alarms, and data trends. The Advanced Menu panel, which is password protected to prevent inadvertent modifications, includes several features required for on-line diagnostics, including instrument configuration, calibration, data handling, and data trending. For example, the Laser Spectra & Control screen allows the user to view the raw transmission data and cavity-enhanced absorption spectrum while controlling the laser current and temperature setpoints. The instrument calibration routine measures the transmitted intensity in the absence of any absorption to determine the detector and data acquisition voltage offsets. The routine also introduces an acetylene standard and performs a single-point calibration to determine the cavity gain factor,  $G$ , and transmission baseline,  $I_0(\nu)$ . The latter is the cavity transmission spectrum in the absence of any absorption and can be readily determined by fitting the spectrum of acetylene in the absence of other higher hydrocarbons.

## RESULTS AND DISCUSSION

**Off-Line Data.** Prior to the field trial phase, the off-axis ICOS prototype was tested off-line at The Dow Chemical Company's R&D laboratory (Freeport, Texas) to empirically determine the system's performance specifications, including zero drift, precision, detection limit, and accuracy.

As noted above, the ICOS analyzer periodically measures the transmission baseline in the absence of absorbing sample,  $I_0(\nu)$ . Any drift of this baseline between calibration periods may result in an inaccurate measurement of acetylene or other sample constituents. In order to gauge the magnitude of this zero drift, a sample of dry nitrogen was flowed through the system for over 12 hours. The results indicate that the baseline drift changes the measured acetylene concentration by  $\pm 0.005$  ppmv. The small magnitude of this effect is largely due to the low correlation between the sharp acetylene feature and broad

TABLE I. Gas mixtures used to develop and validate the chemometric model. The mixtures span a wide range of anticipated process gas stream compositions. The acetylene concentrations of mixtures 1b, 5, and 6 were independently verified by Dow Chemical Company and the measured values are shown parenthetically.

Sample	Acetylene (ppmv)	Methyl acetylene (ppmv)	Ethylene (%)	Methane (%)	Ethane (%)
1	0.50	1017	40.1		
1b	0.50 (0.40)	1000	40.0		
2	0.96	3022	39.9		
3	1.48	5144	40.0		
4	1.50	990	40.0		
4b	1.50	1000	4.0		
5	2.86 (2.59)	1021	39.9		
6	8.0 (8.0)	999	40.1		
7	0.99	5024	40.0	20.0	30.0

baseline, and the zero drift for more featureless absorptions (e.g., ethylene, methyl acetylene, ethane, etc.) is expected to be larger.

The instrument's precision and stability was gauged by continuously measuring a flowing  $C_2H_2$  standard for more than 40 hours. The analyzer provides a  $1\sigma$  measurement precision better than  $\pm 0.025$  ppmv and is capable of maintaining such precision for long time periods. The acetylene detection limit is related to the signal-to-noise ratio on the measured absorption feature. The cavity-enhanced absorption spectrum of 8.7 ppmv of acetylene in nitrogen is shown in Fig. 3 along with an expanded view of the baseline noise (figure inset). The absorption has a GA  $\sim 0.25$  with a  $1\sigma$  baseline noise of  $\pm 0.0005$ , providing a detection limit of 0.050 ppmv (peak signal/ $1\sigma$  noise = 3). Note that this limit is comparable to the detection limit for GCs in the same application.

The accuracy of the instrument was determined by obtaining seven mixtures from British Oxygen Company (BOC) that mimic typical plant operating conditions, including steady state, alarm level, and plant upset (Table I). The mixtures were measured by BOC using gas chromatography with a relative uncertainty of  $\pm 5\%$  for components less than 5 ppmv in concentration and  $\pm 2\%$  for components greater than 5 ppmv in concentration. The acetylene concentrations of three of the mixtures (e.g., mixtures 1b, 5, and 6) were independently verified by Dow Chemical Company using optimized GC, and the measured values, which are also listed in Table I, show a slight deviation for mixture 5. Test data were collected over a period of 14 days during which mixtures were introduced into the analyzer one at a time to simulate changes in process run conditions. Additionally, in order to test hardware and software auto-calibration routines, zero and span checks were scheduled daily. The results, which represent a 6-second response time for the ICOS analyzer, are summarized in Table II and compared to typical GC specifications for the optimized on-line GC method. For methylacetylene, the slow response time of GCs has limited their use in acetylene hydrogenation process optimization control, and comparison data is not available.

**Field-Trial Data.** Subsequent to the successful laboratory demonstration, the ICOS prototype was installed in a Dow hydrocarbon plant (Oyster Creek, TX) where it was operated in parallel with two pre-existing GC systems for the trial duration of five and a half months. The GC response times for acetylene and methyl acetylene analysis were  $\sim 5$  minutes/analysis and  $\sim 20$  minutes/analysis, respectively. The ICOS instrument was

**TABLE II.** Measured values of several gas mixtures from both the off-axis ICOS analyzer and a gas chromatograph. The latter's specifications were obtained for a short-term study consisting of 30 consecutive analyses.

Acetylene					
BOC reported (ppmv)	Off-axis ICOS (ppmv)	3 $\sigma$ precision ( $\pm$ ppmv)		Accuracy/bias ( $\pm$ ppmv)	
		ICOS	GC	ICOS	GC
0.50	0.49	0.03	0.06	0.01	0.08
0.99	1.02	0.04	0.06	0.03	0.08
1.48	1.51	0.07	0.14	0.03	0.20
2.86	2.58	0.06	0.14	0.28	0.20
8.00	7.74	0.14	0.14	0.26	0.20

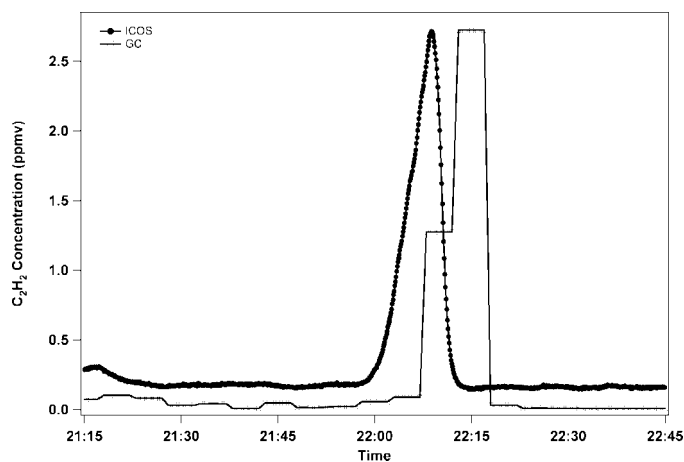
  

Methylacetylene			
BOC reported (ppmv)	OA-ICOS (ppmv)	3 $\sigma$ precision ( $\pm$ ppmv)	Accuracy (%)
1017	1020.9	5.8	0.4
1021	1021.1	13.9	0.0
3022	3082.3	63.0	2.0
5349	5144.0	130.7	3.8

shown to provide substantially faster data with comparable accuracy over a much wider dynamic range and, in some instances, tracked events that were too rapid for GC quantification. Moreover, the unit exhibited less measurement drift over the course of the field trial and provided visual verification of process excursions.

Prior to the field trial and after its completion, baseline instrument performance data was collected for both the ICOS and GC analyzers. Mixture #5 was run on both instruments for approximately 2.5 hours to confirm that each analyzer would meet its performance specification for measurement stability. The ICOS system averaged  $2.38 \pm 0.015$  ppmv with over 1500 individual measurements (6 seconds/analysis), whereas the GC measured at  $2.43 \pm 0.025$  ppmv and provided 30 analyses (5 minutes/analysis). After the field trial was completed (approximately five and a half months) both analyzers were again calibrated and another baseline run of approximately 2.5 hours was performed. The results indicate that the ICOS and GC acetylene measurements drifted by  $+0.17$  ppmv and  $+0.33$  ppmv, respectively.

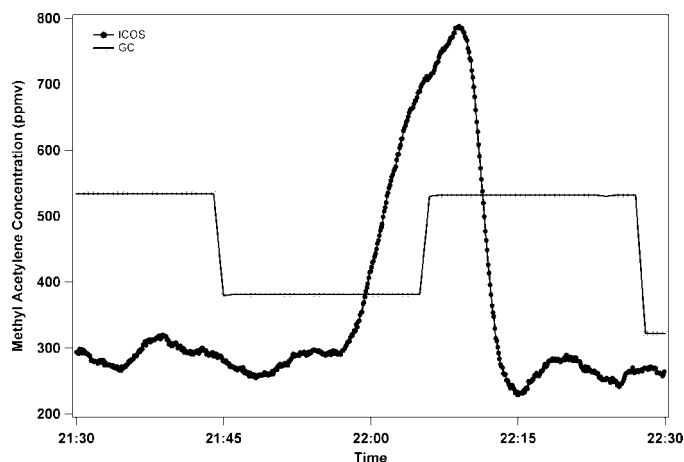
The chief advantage of the ICOS analyzer is its rapid intrinsic response time relative to the GC (e.g.,  $\leq 30$  seconds for ICOS versus 5 and 20 minutes for conventional GC). This parameter is critical for process control where a rapid process excursion (e.g., a measured acetylene or methyl acetylene value exceeding a control or alarm limit) can occur and requires immediate detection for mitigation. Plant operation protocol generally prohibits making changes to process conditions until a sufficient number of data points (e.g., a minimum of 2–3) indicate a consistent or trending alarm condition. For example, the data shown in Fig. 4 illustrate a process spike in which the acetylene concentration rises from  $\sim 0.2$  ppmv to greater than 2.50 ppmv in less than 2 minutes. The ICOS analyzer clearly resolves this behavior with a high sampling frequency. Conversely, the GC, which is a batch measurement method that requires  $\sim 5$  minutes/analysis, does not detect the spike until it is well underway (or expired altogether), and other, non-optimal process variables (e.g., reactor temperature, pressure, or flow rates) must be used to determine whether an excursion is taking place.



**Fig. 4.** Measured on-line process data for both the off-axis ICOS analyzer and GC in tandem. In this instance, the acetylene rapidly spikes for less than 10 minutes. Whereas the ICOS analyzer clearly resolves this behavior with redundant measurements, the GC only provides two anomalous values, well after the excursion has subsided.

Similarly, the ICOS analyzer also provides fast simultaneous quantification of methyl acetylene in the process stream (Fig. 5). Here, the methyl acetylene concentration spikes from  $\sim 300$  ppmv to  $> 500$  ppmv in approximately 5 minutes. The ICOS instrument detected the excursion as it occurred and made approximately 200 measurements during the ten minute period of the excursion. Therefore, the measurement quality of the ICOS analyzer gives plant operators enough confidence that the data reflects actual process conditions to take action to control and optimize the reactors. Again, the GC reported a measurement exceeding the alarm condition almost ten minutes after the excursion took place with only one measurement value at this level. Therefore, this GC measurement was not considered reliable and no corrective action would have been undertaken.

The rapid response of the ICOS analyzer also enables more accurate process measurements. In the example shown in Fig. 6, a series of very rapid acetylene spikes takes place in a 2-hour



**Fig. 5.** Measured on-line methyl acetylene data for both the off-axis ICOS analyzer and GC in tandem. During this rapid spike in methyl acetylene concentration, the ICOS analyzer provided real-time data and clearly resolved the event with over 200 measurements. Conversely, the GC misses the event entirely due to its slow response time.

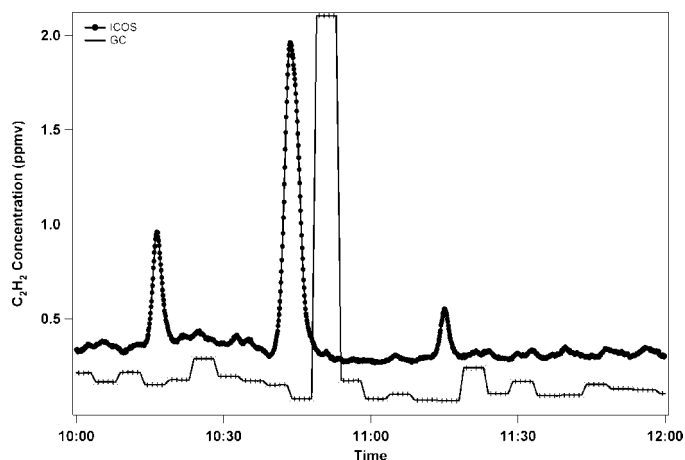


FIG. 6. Measured on-line acetylene data for the off-axis ICOS analyzer and a GC in tandem. During very fast acetylene fluctuations, the GC either misses the event entirely or misreports it after completion. Conversely, the ICOS analyzer reports it with high fidelity.

time-span. Each spike occurs so rapidly (e.g., <5 minutes) that the GC either misses the event entirely or reports it after it has expired. The ICOS analyzer, however, resolves the spikes with minimal time lag and reports changes in process conditions in real time. While these process spikes do not represent a plant upset or excursion, they indicate that process conditions fluctuated.

The rapid analysis of the ICOS analyzer can also help avoid “feedback looping” caused by reacting to a process value too late or by too much. In this case, the methylacetylene measurement shown in Fig. 5 deviated above the alarm point of 350 ppmv for approximately 10 minutes, and the process had already recovered prior to GC detection. In addition to speed and accuracy, the ICOS analyzer’s signal-to-noise ratio enables it to be sensitive enough to reliably report small changes in the measured values that may be difficult to differentiate from baseline noise using traditional methods. Some process spikes, like those in Fig. 6, are not large enough to warrant process control actions, but can be useful for correlating other process events for troubleshooting.

Occasionally, plant operation can result in acetylene values that exceed 10 ppmv. For example, during the field trial, an unplanned process outage occurred that commonly produces conditions that surpass the measurement capability of many instruments. While the ICOS analyzer was calibrated over a measurement range of 0–10 ppmv acetylene, it was capable of detecting acetylene concentrations up to 1000 ppmv. During the plant restart, the instrument measured acetylene concentrations far above the reporting range of the GC (max = 10 ppmv without reconfiguration) as shown in Fig. 7, thus providing additional data about the plant during the startup process.

At approximately 11:04 p.m., a downward spike occurred in the acetylene concentration as indicated in the Fig. 7. Typically, even if the GC had been properly reconfigured to address these conditions, the validity of the reading would have been questioned due to the operating conditions of the plant (e.g., fast fluctuations). However, the ICOS analyzer also records the cavity-enhanced absorption spectrum at each measurement to allow for visual confirmation of such abnormal events. The recorded spectra, shown in the inset of Fig. 7, were extracted at intervals representing (1) the high concentration

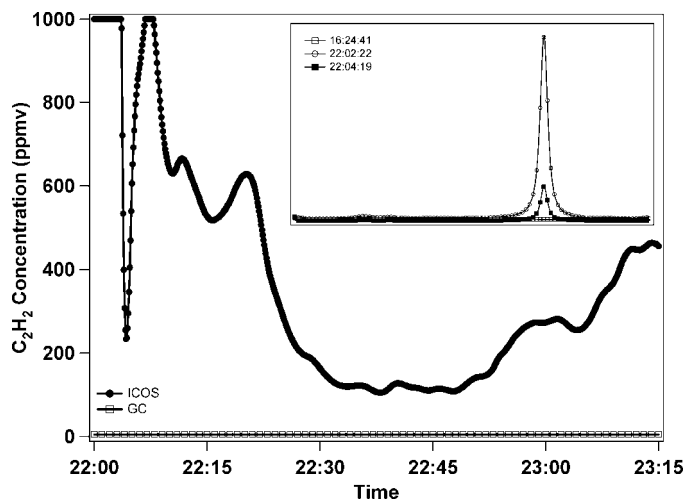


FIG. 7. During plant startup and other unconditional events, the acetylene concentration can reach very high levels. Unlike the GC, which cannot measure more than 10 ppmv acetylene without optimization, the off-axis ICOS analyzer can extend to 1000 ppmv acetylene and monitor these high levels in real time. Moreover, the absorption spectra can be viewed to further verify the measured data (inset, with markers spaced by a factor of 10 for clarity). The spectra indicate that the acetylene dip near 22:04 is real and not an instrument error.

before the downward spike, (2) the concentration at the lowest point of the downward spike, and (3) normal concentration as measured before the plant upset occurred. The peak height and area indicate that the measured values accurately represent process conditions and are not an instrument malfunction. Because the spectra can be used to validate the analyzer’s measurements, these data records become a powerful troubleshooting and diagnostic tool.

**Commercial Implementation.** The field trial data and findings clearly demonstrate that the ICOS analyzer is capable of providing rapid, reliable, and accurate acetylene analysis for improving advanced process control and optimization of hydrogenation reactors. Dow’s Hydrocarbon business recognized this opportunity and, therefore, invested in the commercial implementation of the technology. In the third quarter of 2006, two commercial acetylene ICOS systems (ICOS-1 and ICOS-2, supplied by Analytical Specialties Inc.) were installed at the Freeport light hydrocarbon facility in Texas. The two analyzers have been in operation since mid-October 2006 in conjunction with newly installed GC systems that employ the latest hardware and optimized methods to achieve a 90-second cycle time.

Using information from the prototype development phase, software and hardware improvements were applied to the commercial analyzer, resulting in greater long-term reliability and a faster data acquisition rate. The commercial acetylene ICOS analyzer is capable of data reporting at a rate of 3 seconds (the total system response time depends on additional factors including factors such as sample transport system, flow rate, etc.). Additionally, the Freeport hydrocarbon plant’s reactor configuration, stream composition, and typical component concentrations are different than that of the Oyster Creek facility where the prototype field-trial took place, and the chemometric model was revised to address this different composition.

Moreover, the Freeport plant required the ICOS sample system to be designed with stream selection capability,

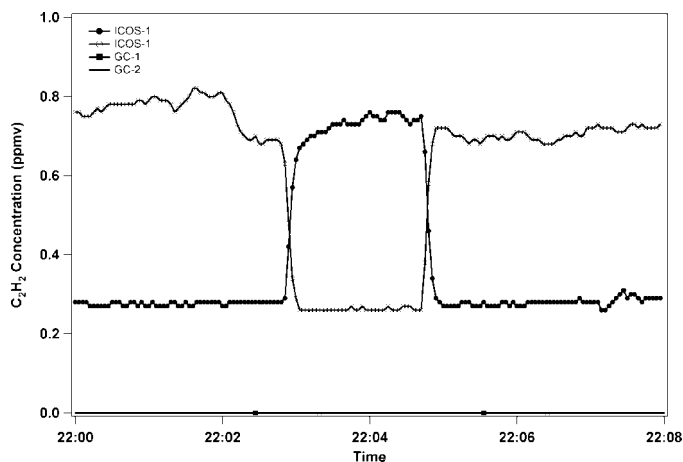


FIG. 8. Demonstrated stream switching between the two off-axis ICOS analyzers, ICOS-1 and ICOS-2. At 22:03, the sample streams into the two analyzers were switched for 2 minutes. Note that the two analyzers are in excellent agreement. Both process control GCs were monitoring the 0.28 ppmv acetylene stream and incorrectly reporting the acetylene concentration as 0.0 ppmv due to measurement error and drift.

providing the flexibility to monitor more than one reactor during critical plant operations with minimum transition time between analyses. The design also permits redundancy, allowing one analyzer to be taken out of service for maintenance without interrupting measurements. The low volume design of the stream switching assembly and transfer lines permit the ICOS analyzer to switch between two reactor streams and reach 90% of the actual value,  $T_{90}$ , in approximately 20 seconds and to stabilize at the actual value in about 55 seconds over the measurement dynamic range of 10 ppmv. Over the more narrow dynamic range, which occurs during reactor steady-state operation, the actual value was typically attained in only 20 seconds as illustrated in Fig. 8.

Regardless of the faster GC method ( $\sim 90$  seconds) and variations in reactor outlet composition, the rapid analysis of the commercial ICOS analyzer out-performed the optimized GC as shown in Fig. 9, and more correctly reflected actual process conditions. Recently, the ICOS measurements have been used to optimize the Freeport facility's startup operation and minimize recovery time during plant excursions, resulting in lower environmental impact and increased product quality.

## CONCLUSION

An analyzer has been developed for rapid, accurate quantification of acetylene and methyl acetylene in hydrocarbon cracked gas processing plants. The system utilizes off-axis ICOS to measure the near-infrared, cavity-enhanced absorption spectrum of ethylene, methyl acetylene, and acetylene, and employs a chemometric data analysis strategy to quantify the respective constituents. Initial laboratory tests verified that the instrument is capable of measuring  $<0.050$  ppmv of acetylene, has a precision of  $\pm 0.025$  ppmv, and can accurately determine

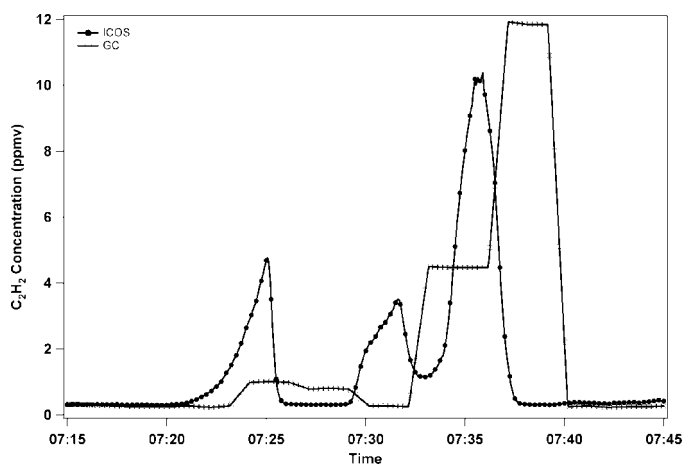


FIG. 9. Off-axis ICOS and GC measurements of a commercial ethylene process control stream. The GC clearly misrepresents the acetylene concentration during fast fluctuations and misses rapid alarm situations all together. Only every fifth data point has been shown for clarity.

acetylene concentrations with comparable accuracy to a GC in an actual process stream composition matrix under plant operating conditions. Future applications may include monitoring additional contaminants in ethylene gas flows or other near-infrared absorbers in complex background matrices.

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