FINAL REPORT

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Date of Report: September 30th, 2013

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Project Title:	ADVANCED LASER-BASED SENSORS FOR INDUSTRIAL PROCESS CONTROL
Project Period:	10/01/2010 – 09/30/2013
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1. **Project Objective:** One to two succinct paragraphs stating overall project objectives and how it would help improve industrial energy efficiency.

To capture the potential of real-time monitoring and overcome the challenges of harsh industrial environments, Los Gatos Research (LGR) is fabricating, deploying, and commercializing advanced laser-based gas sensors for process control monitoring in industrial furnaces (e.g. electric arc furnaces). These sensors can achieve improvements in process control, leading to enhanced productivity, improved product quality, and reduced energy consumption and emissions. The first sensor will utilize both mid-infrared and near-infrared lasers to make rapid in-situ measurements of industrial gases and associated temperatures in the furnace off-gas. The second sensor will make extractive measurements of process gases.

2. **Background:** Outline the reason(s) for the project and its specific goals; the technical and commercial issues being addressed, and a brief summary of work in previous quarters or years (a few paragraphs).

The goal of the project is to develop, deploy, and commercialize advanced laser-based gas sensors for monitoring and process control. To achieve this goal, researchers will leverage insight gained from two previous projects:

1. A Small Business Innovation Research (SBIR) Phase I project utilizing room-temperature, mid-infrared quantum cascade lasers and other laser technologies to record in-situ measurements of gas temperature and key combustion species.

2. An SBIR Phase II project that developed a heated, extractive gas analyzer for fast, sensitive measurements of multiple trace gases in process control applications.

In this SBIR Phase III effort, the Phase I project will serve as the basis for a gas sensor that will utilize both mid-infrared and near-infrared lasers to make rapid, in-situ measurements of carbon monoxide, carbon dioxide, oxygen, water, and gas temperature. The Phase II project will serve as the basis for an analyzer that will make extractive measurements of multiple process gases and trace pollutants.

3. **Accomplishments:** List any major accomplishments achieved during the life of the project.

During the course of this DOE project, Los Gatos Research (LGR) fabricated, tested, and deployed both in-situ tunable diode laser absorption spectrometry (TDLAS) analyzers and extractive Off-Axis Integrated Cavity Output Spectroscopy (Off-Axis ICOS) analyzers.

3.1   TDLAS Analyzers
During this DOE program, LGR has successfully used mid-infrared quantum cascade lasers (QCLs) to extend the Tunable Diode Laser Absorption Spectrometry (TDLAS) technique to accurately quantify additional species and gas temperature in high-temperature flows. These QCLs have recently become commercially available, though they still require substantial evaluation and are still difficult to obtain at the custom wavelengths required for the industrial applications.

During this program, LGR received and mounted the QCL shown in Figure 3.1.1. The QCL is fully-packaged and integrated into a water-cooled housing.
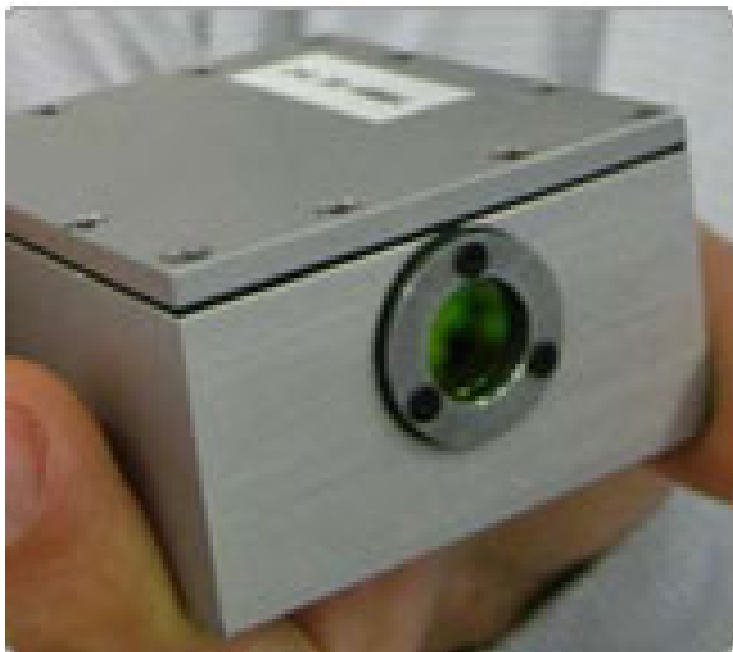
Figure 3.1.1:   Fully-packaged quantum cascade laser received and tested by LGR.

The laser was directed through LGR's flat-flame burner to monitor CO concentration, H_2O concentration, and gas temperature. A sample measured absorption spectrum is shown in Figure 3.1.2. The spectrum contains strong absorption features from both CO and H_2O, allowing for accurate quantification of the gas densities. Moreover, since each of the absorption features arises from a different molecular quantum state (with different ground-state energies), the absorption spectrum also provides gas temperature.
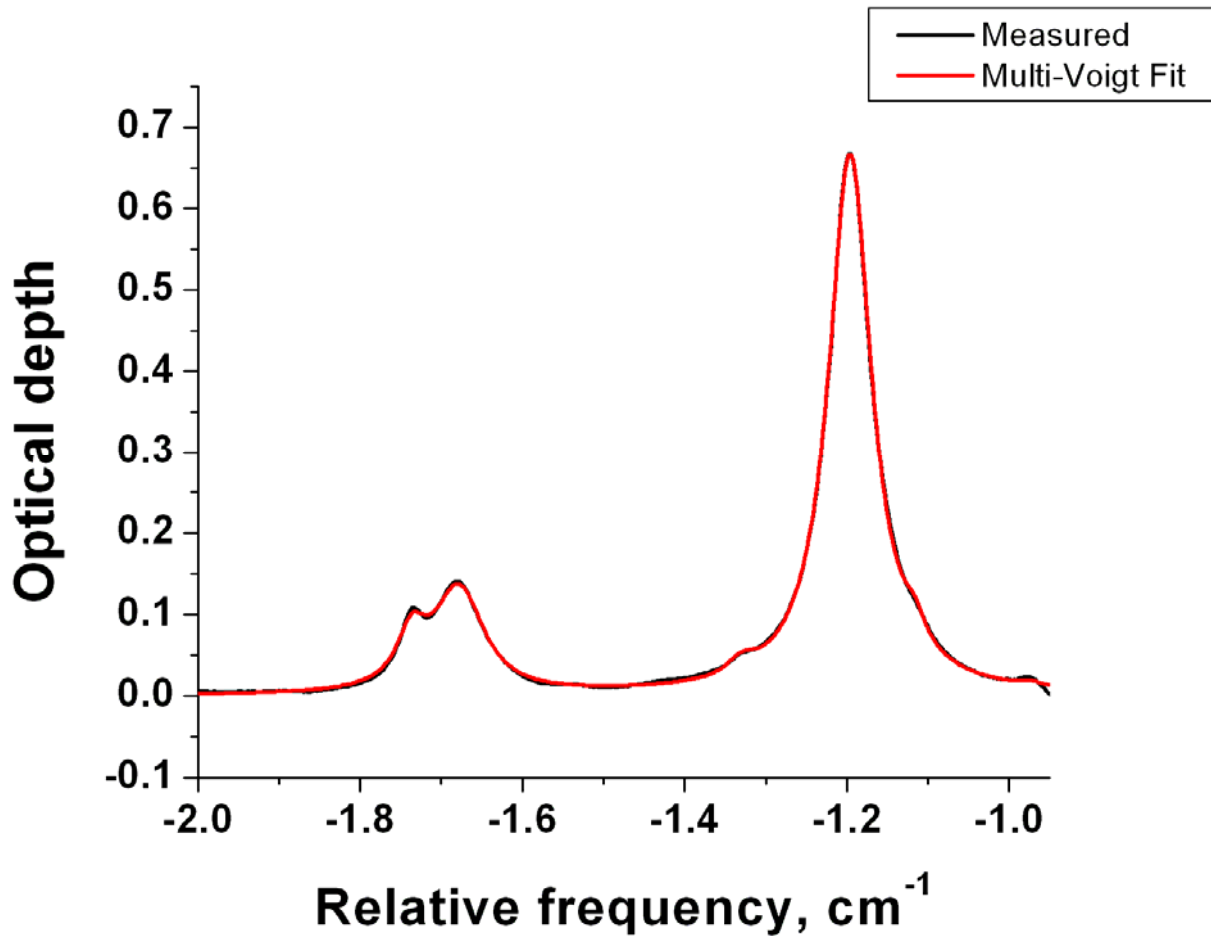
Figure 3.1.2: Measured absorption spectrum of CO and H_2O near 5.15 microns in LGR's flat-flame burner facility. The spectrum was acquired using a quantum cascade laser and operating the flame in a fuel-rich mode (e.g. high CO levels) to emulate industrial furnace conditions.

In order to prove that the Phase III mid-infrared TDLAS sensor provides accurate data, LGR introduced a known amount of carbon monoxide into a high-temperature furnace. The furnace temperature was actively controlled and accurately measured via a thermocouple inserted into the gas.

Figure 3.1.3 shows that the sensor provides the correct carbon monoxide temperature independent of gas temperature.
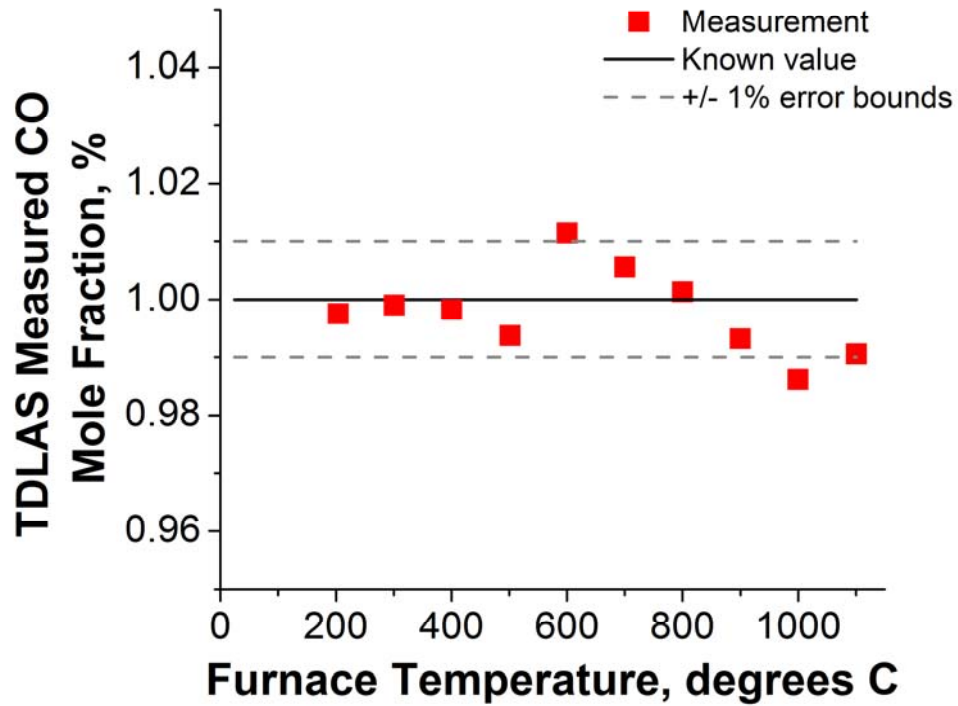
Figure 3.1.3: The Phase III TDLAS sensor provides an accurate carbon monoxide gas concentration independent of furnace temperature.

The sensor was then used to determine the gas temperature from the measured absorption spectrum. The measurements (Figure 3.1.4) were in excellent agreement with the thermocouple readings.
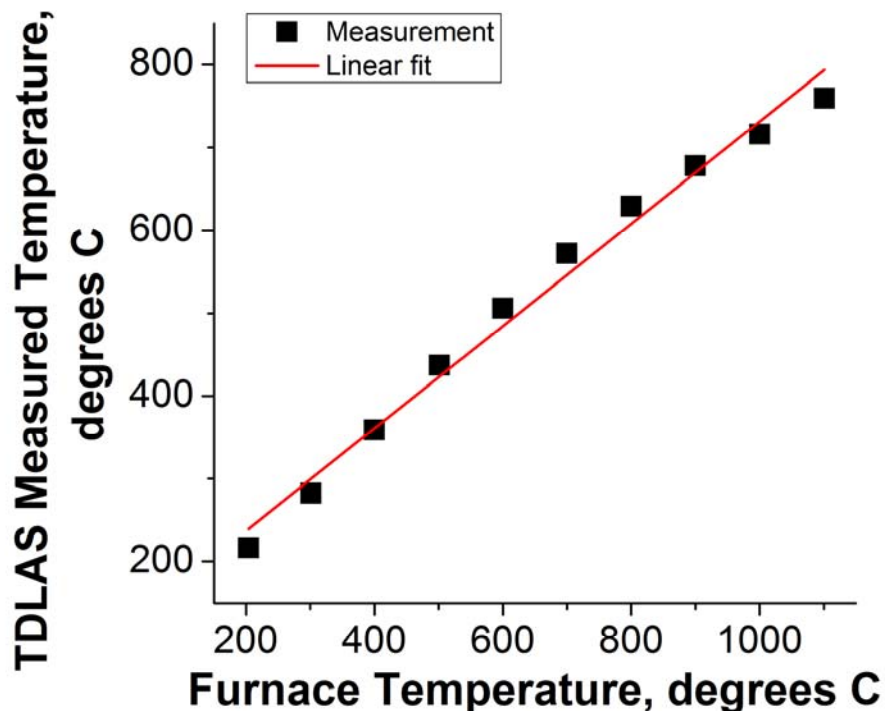
Figure 3.1.4: **The Phase III TDLAS sensor provides an accurate measurement of gas temperature.**

3.2   Off-Axis ICOS Analyzers

In addition to fabricating and testing TDLAS analyzers during this DOE program, LGR also developed extractive Off-Axis ICOS analyzers for industrial applications.   These sensors included an analyzer for syngas production plants, a HF sensor for aluminum smelting facilities, an ammonia in ethylene analyzer for olefin production plants and calibration gas services, and a natural gas sensor for trace contaminant quantification.

3.2.1   Syngas Analyzer

Over the course of this DOE program, Los Gatos Research has developed an Off-Axis ICOS analyzer that can quantify syngas constituents and contaminants. The syngas analyzer was tested to determine its accuracy, linearity, and time response on both major constituents and minor contaminants.   For both carbon dioxide (Figure 3.2.1.1) and methane (Figure 3.2.1.2) the instrument is highly accurate and linear over a wide dynamic range of relevance to syngas applications.
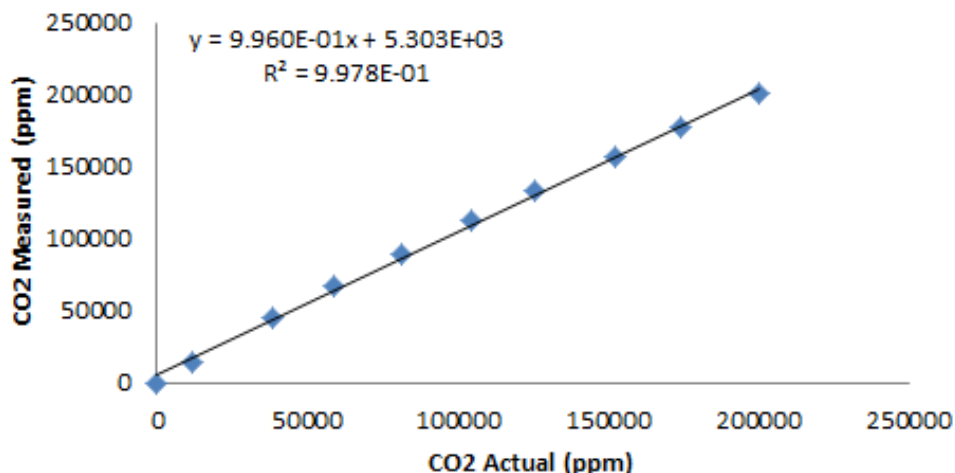
Figure 3.2.1.1: The Off-Axis ICOS instrument is highly accurate and linear from 0 – 25 % CO_2.
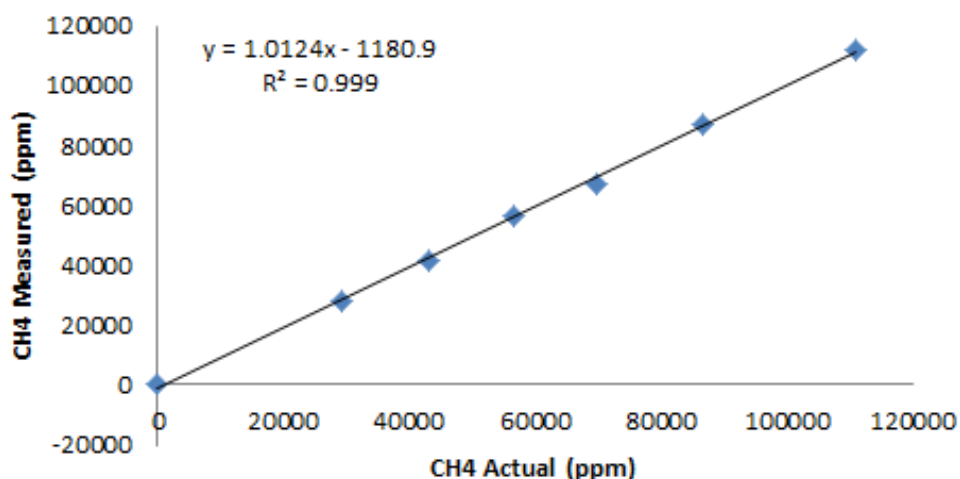

Figure 3.2.1.2: The Off-Axis ICOS instrument is highly accurate and linear from 0 – 12% methane.

Similar results were found for low-level (e.g. ppm level) contaminants.

The time response of the analyzer was determined by rapidly switching instrument inlet between room air and contaminated air. The measured results (Figure 3.2.1.3) show that the instrument can provide a time response (1/e) of 2.36 seconds, sufficient for active reactor control. Note that a faster gas pump can be utilized to achieve response times of up to 10 Hz.
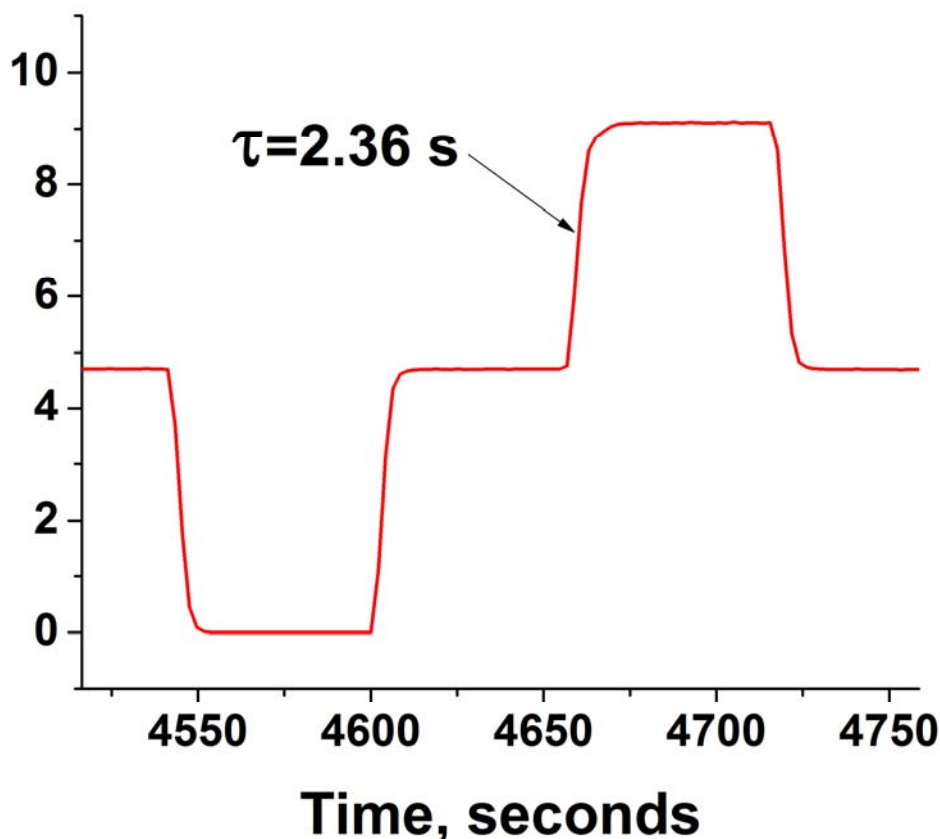
Figure 3.2.1.3: Contaminant level (ppm) versus measurement time shows an analyzer time response (1/e) of 2.36 seconds.

The analyzer was first deployed at the University of Utah's Industrial Combustion and Gasification Research Facility (ICGRF). The University of Utah ICGRF offers a suite of five coal- and natural gas-fired furnaces and two pilot-scale gasifiers capable of operating on a wide variety of fuel feedstocks. The ICGRF is equipped with a comprehensive suite of gas- and liquid-phase analysis capabilities that can be used for comparison with and validation of LGR instrumentation.

In conjunction with another DOE SBIR Phase II Program (Grant #DE-FG02-07ER84672), LGR worked with Professor Kevin Whitty to deploy an extractive analyzer at a biogass reactor in the ICGRF. This instrument was making simultaneous measurements of CO, CO_2, CH_4, H_2S, and other key gases downstream of the syngas generator (through a wet impinger). Some sample measurement results are shown below in Figure 3.2.1.4.

In addition to helping validate the instrument's utility and performance, LGR has gained valuable insight into current instrumentation (e.g. GC, NDIR, electrochemical sensors…) and measurement needs (e.g. H_2, O_2, CH_4 as a proxy for temperature). Finally, Professor Whitty is collaborating with LGR to provide several industrial contacts within the syngas industry.
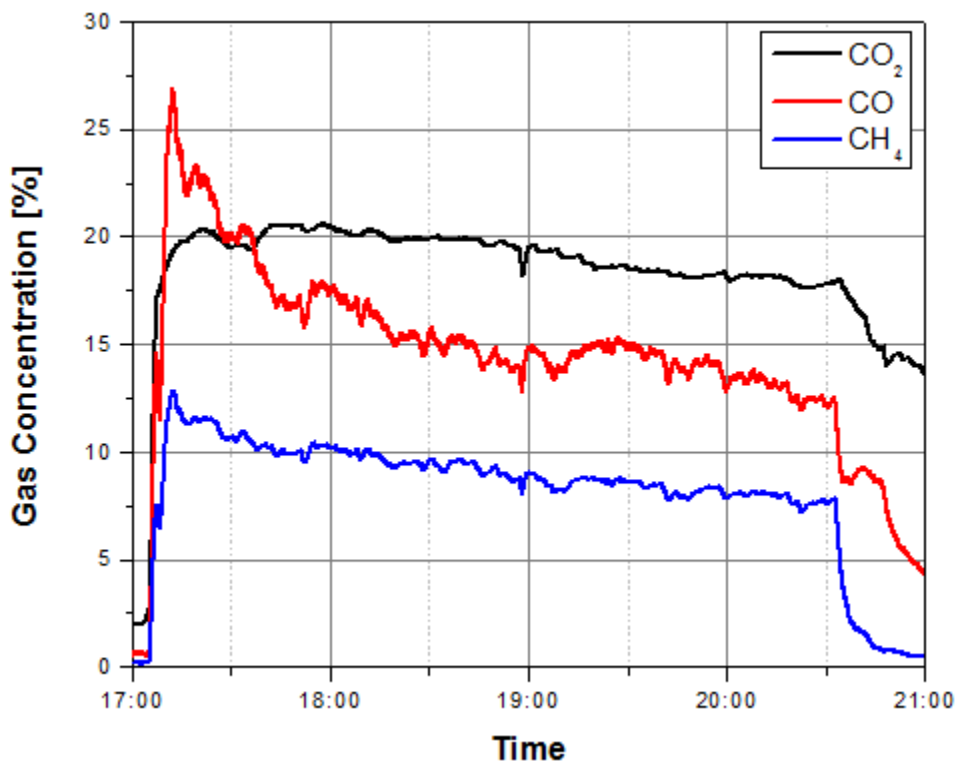
Figure 3.2.1.4: **Preliminary measurements made using an extractive Off-Axis ICOS system that sampled from a syngas generator at the University of Utah's Industrial Combustion and Gasification Research Facility.**

Additionally, the analyzer was deployed at a syngas production facility operated by Coskata, and instrument sales are forthcoming.

3.2.2   HF Analyzer

LGR has further utilized its Off-Axis ICOS technology to develop a HF analyzer. One of the key applications of the analyzer is compliance monitoring of HF in air near industrial sources (e.g. aluminum smelting plants and industrial boilers). One of the key challenges in producing this analyzer involved appropriately coating all of the wetted parts to minimize sample adherence. Prior to applying this coating, the analyzer exhibited a very long response time, taking over 30 minutes to flush to 2 ppb HF (Figure 3.2.2.1).
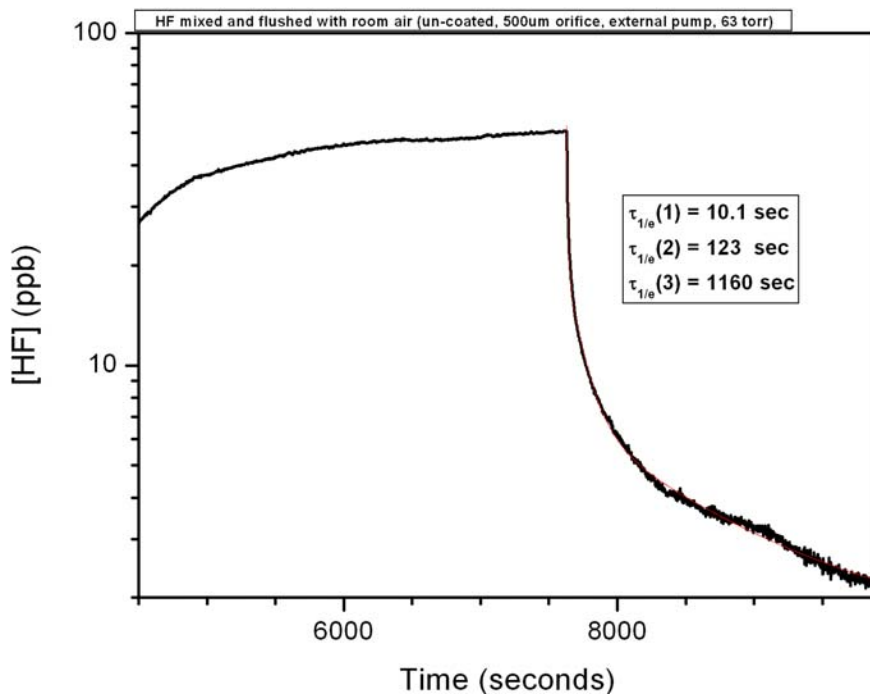
Figure 3.2.2.1:   **Response time of the analyzer prior to applying the appropriate chemical coatings.**

After coating the wetted surfaces, the analyzer was able to detect sub-ppb levels of HF in under 1 minute (Figure 3.2.2.2).
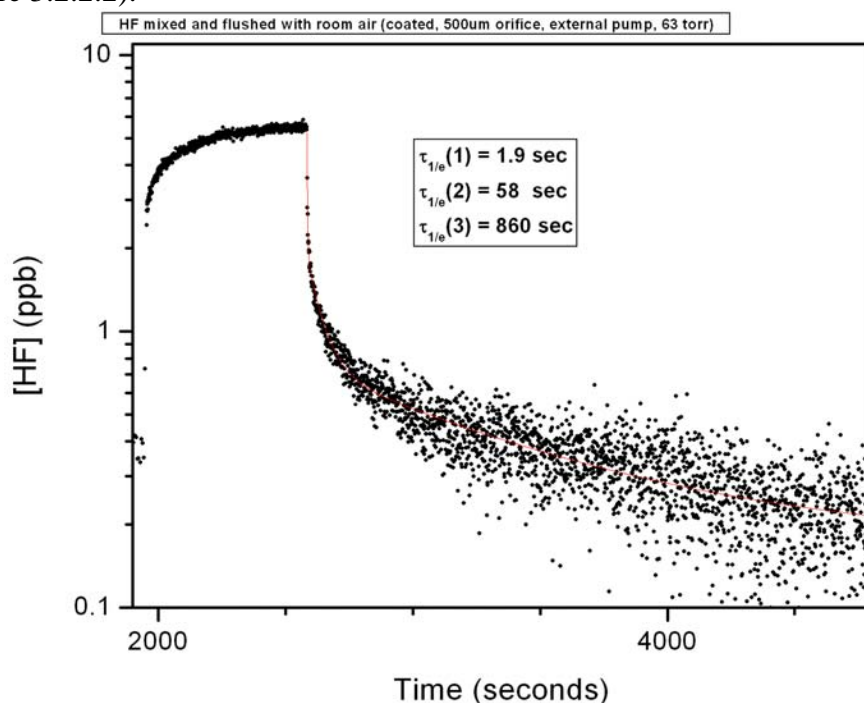

Figure 3.2.2.2:   **Response time of the analyzer prior after applying the appropriate chemical coatings.**

Subsequent to extensive laboratory testing at LGR, the analyzer was deployed with an industrial partner at an aluminum production facility. Ambient air measurements near the facility are shown in Figure 3.2.2.3. The fast time response of the analyzer is evident in the data.
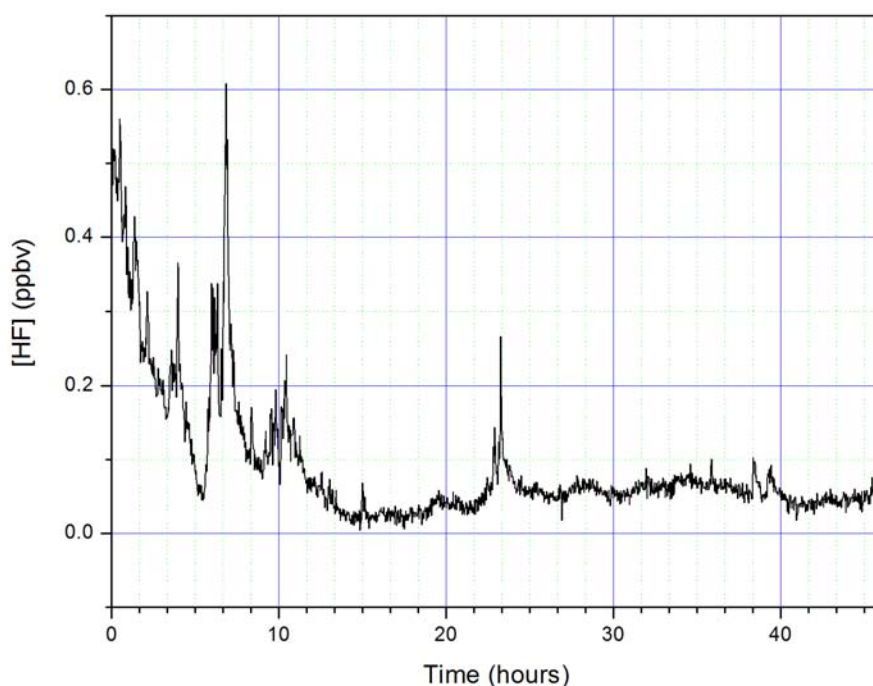
Figure 3.2.2.3:   Ambient air measurements near an aluminum production facility.

3.2.3   Ammonia in Ethylene Analyzer

Olefin manufacturing plants must accurately monitoring ammonia during ethylene manufacturing and end-product verification. Currently, process gas chromatographs are used to measure ammonia; however, they are insufficiently sensitive and fast for real-time process control and high-purity verification. During this DOE program, LGR has extended its Off-Axis ICOS technology to develop an analyzer for trace ammonia quantification in a pure ethylene background.   The sensor utilizes a sophisticated chemometric data analysis routine that includes the basis sets shown in Figure 3.2.3.1.

Note that the analyzer can provide simultaneous measurements of both ammonia and acetylene in ethylene flows. In addition to process control applications, LGR is working with gas manufacturers to quantify calibration standards for conventional gas chromatographs.
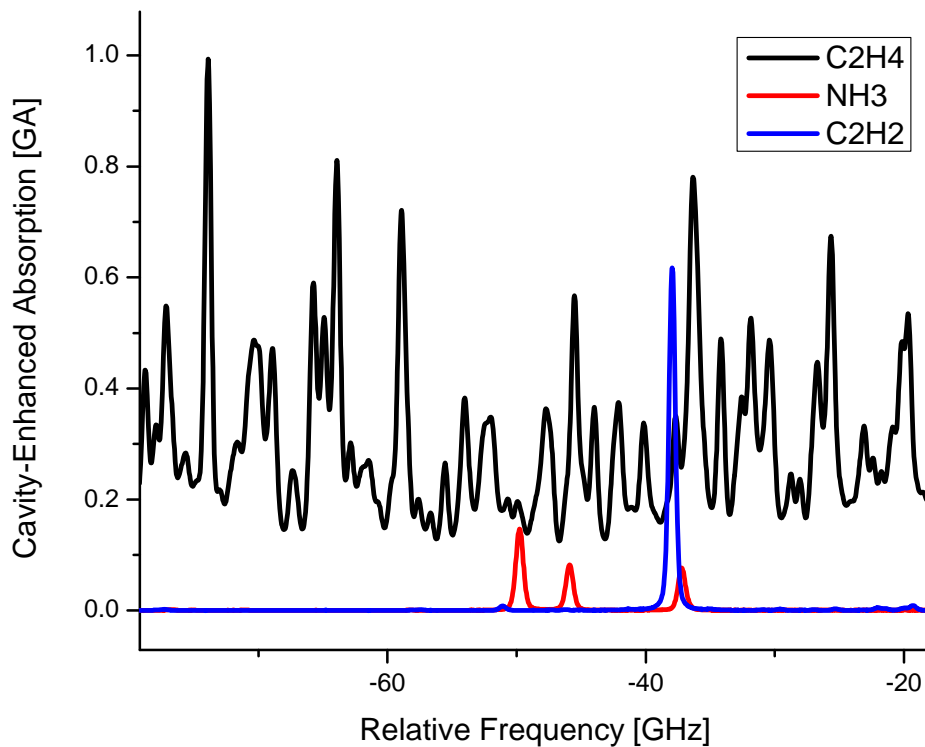
Figure 3.2.3.1:   Basis sets used in the ammonia/ethylene analyzer.

The analyzer was testing on a fixed ammonia/ethylene mixture to determine its analytical precision. The resulting Allan deviation plot is shown in Figure 3.2.3.2 and suggests that the sensor can provide a measurement precision of better than ±3 ppb (1σ) in less than 100 seconds of data averaging.
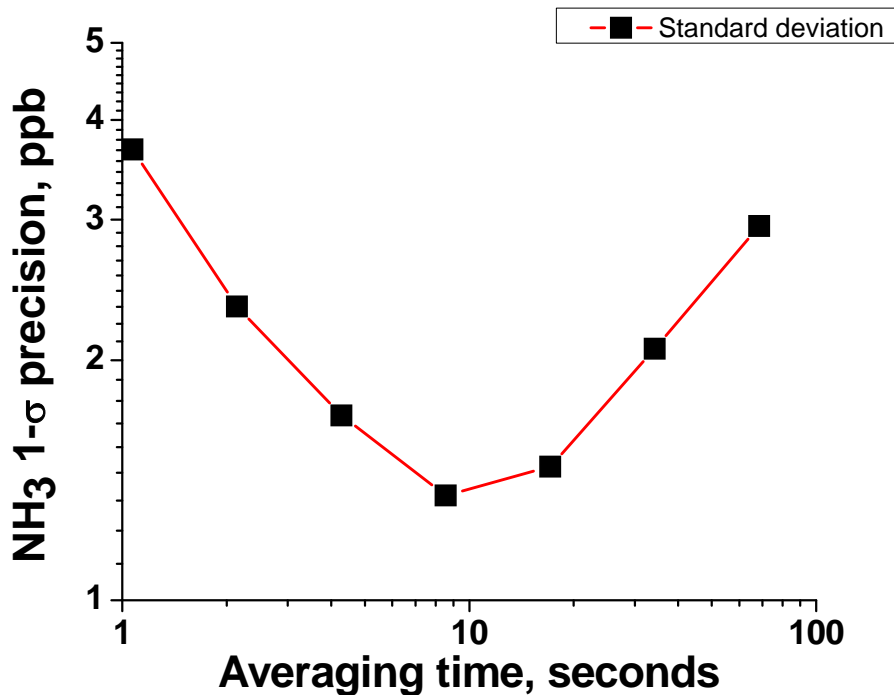

Figure 3.2.3.2:   Measurement precision of the ammonia/ethylene analyzer as a function of measurement time.

3.2.4 Natural Gas Sensor

Natural gas pipelines require multiple analyzers to measure key trace contaminants, including water, carbon dioxide, hydrogen sulfide, and oxygen. With changes in domestic natural gas sources, there is a pressing need for improved analyzers that provide rapid, accurate results over a wide array of gas compositions.

During this program, LGR extended its Off-Axis ICOS technology to measure H_2O, CO_2, H_2S, and O_2 in natural gas. Two analyzers were fabricated (Figure 3.2.4.1). Both analyzers included the provision to control two lasers and thermal control for minimal measurement drift.
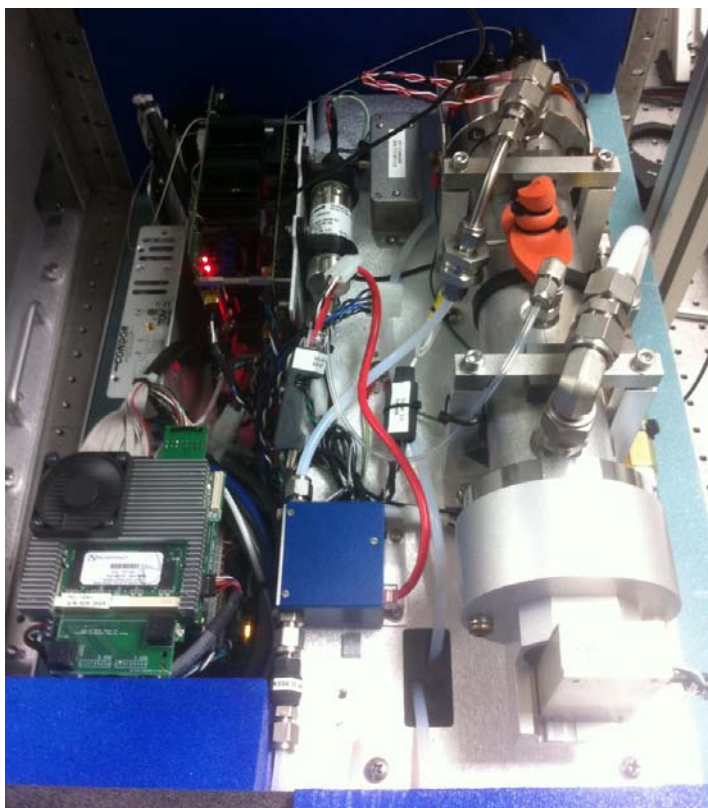

Figure 3.2.4.1:   Off-Axis ICOS analyzer for natural gas contaminant analysis.

The first analyzer had two lasers and operated near 1280 nm and 1400 nm to quantify oxygen and water respectively. The measured basis sets at these two wavelengths are shown in Figure 3.2.4.2 for the target contaminants and methane.
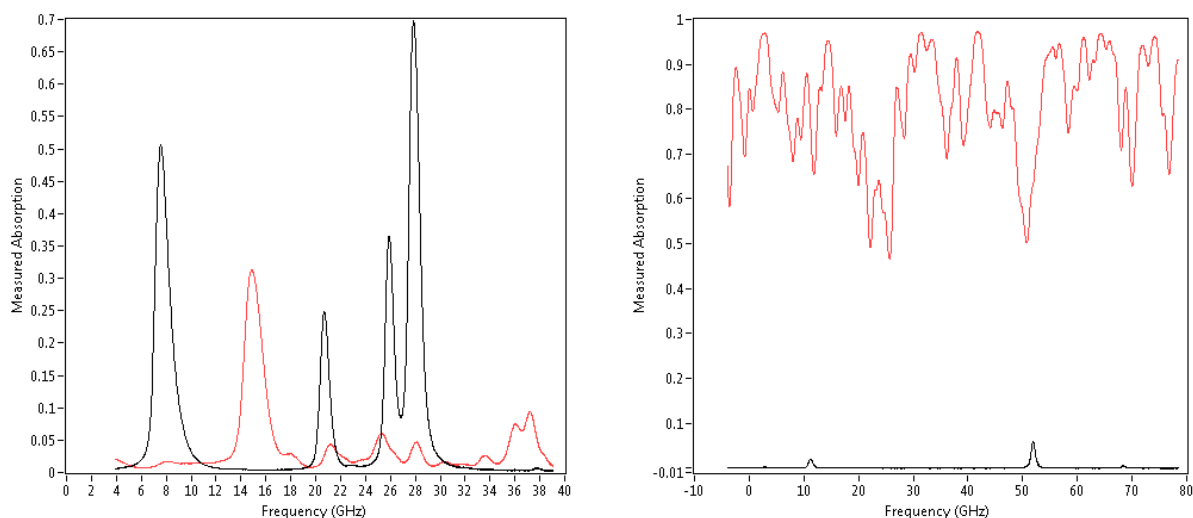
Figure 3.2.4.2: **Basis sets taken at 1280 nm (left) and 1400 nm (right) for the quantification of oxygen and water in natural gas. Methane is shown in red in both panels, and oxygen (left) and water (right) are shown in black.**

Software was developed for the 1280 nm analyzer to fit the measured cavity-enhanced spectra to the basis set functions and determine methane, oxygen, and water concentrations. The spectral fits, shown in Figure 3.2.4.3, demonstrate that the chemometric analysis technique models the observed spectra accurately.
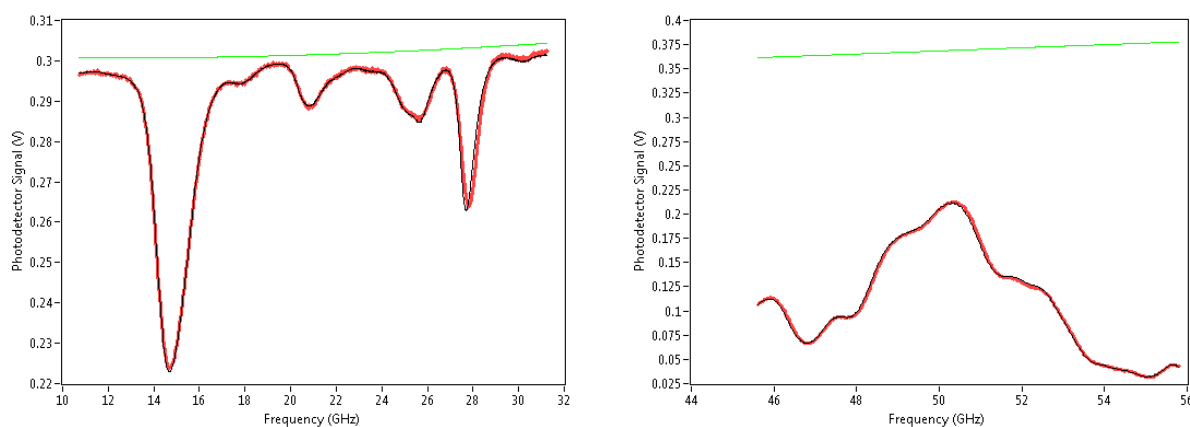

Figure 3.2.4.3: **The measured cavity-enhanced spectra (red) for oxygen/methane (left) and water/methane (right) are fit to the aforementioned basis sets (black). The baseline transmission in the absence of absorption is shown in green.**

Preliminary testing of the 1280 nm analyzer was performed by measuring a constant gas stream consisting of approximately 75 % methane, 5 % oxygen, 20 % nitrogen, and residual (50 ppm) water vapor. The gas stream, which was made by mixing a pure methane tank with ultrapure air, was measured for almost one hour to determine the analyzer short term precision.

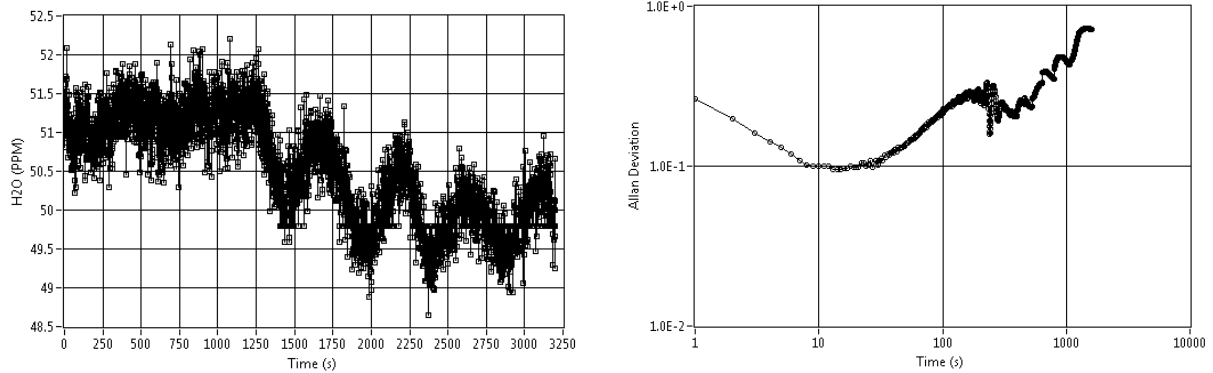The water vapor measurements and resulting Allan deviation plot are shown in Figure 3.2.4.4.

Figure 3.2.4.4: **Water vapor measurements (left) and the associated Allan deviation plot (right) for one hour of natural gas simulant measurements.**

The data suggests that the instrument is capable of measuring water vapor in natural gas to better than ±0.3 ppm (1σ) in 1s, which improves to better than ±0.1 ppm (1σ) in 10s.

Similar data for oxygen is shown in Figure 3.2.4.5, which suggests that the analyzer measures oxygen in natural gas to better than ±100 ppm (1σ) in 1s, which improves to better than ±30 ppm (1σ) in 10s.
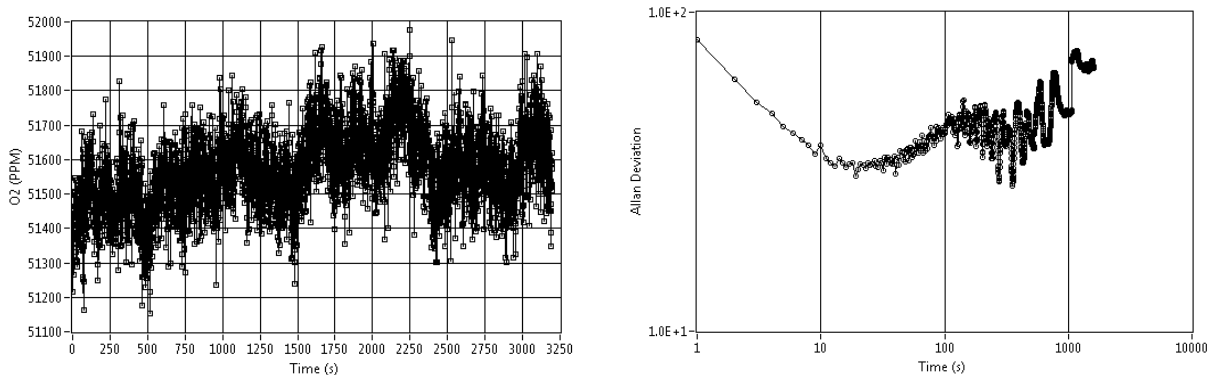

Figure 3.2.4.5: **Oxygen measurements (left) and the associated Allan deviation plot (right) for one hour of natural gas simulant measurements.**

Finally, the instrument also reports methane concentrations as shown in Figure 3.2.4.6. This data suggests that the system measures methane in natural gas to better than ±500 ppm (1σ) in 1s, which improves to better than ±200 ppm (1σ) in 10s.
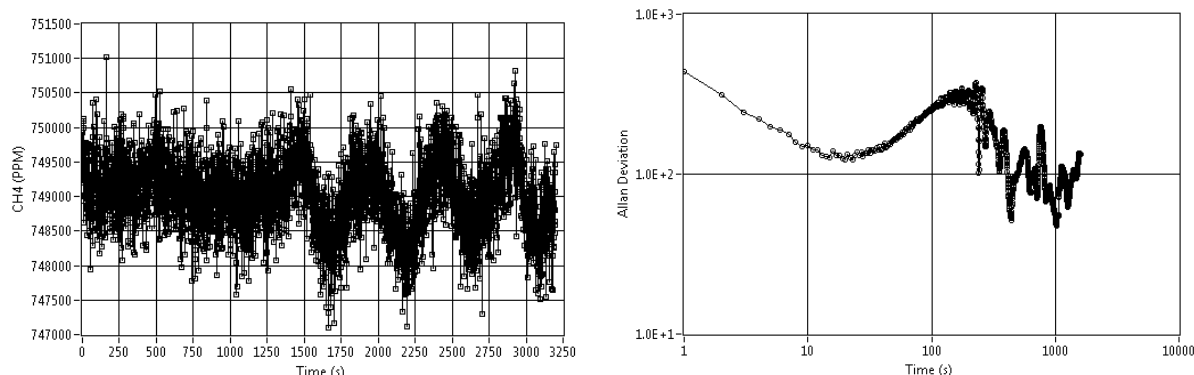
Figure 3.2.4.6: **Methane measurements (left) and the associated Allan deviation plot (right) for one hour of natural gas simulant measurements.**

Note that the aforementioned performance is 1 – 10 times better than existing commercial technology.

One of the most important contaminants in natural gas is hydrogen sulfide (H_2S). Current technology relies primarily on using lead-tape measurements of H_2S. Although these sensors are inexpensive, they require hazardous, expensive consumables, frequent maintenance, and suffer from non-linearity and cross-interference. Very recently, laser technologies have been used to quantify H_2S in natural gas. However, conventional tunable diode laser absorption is insufficiently sensitive and requires extensive sample handling to remove methane and other hydrocarbons from the natural gas stream.

In addition to water and oxygen, Los Gatos Research has successfully extended its Off-Axis ICOS technology to measure H_2S in natural gas. The measured, cavity-enhanced basis sets are shown in Figure 3.2.4.7. Note that hydrogen sulfide is a very weak absorber, but can be readily quantified using Off-Axis ICOS.
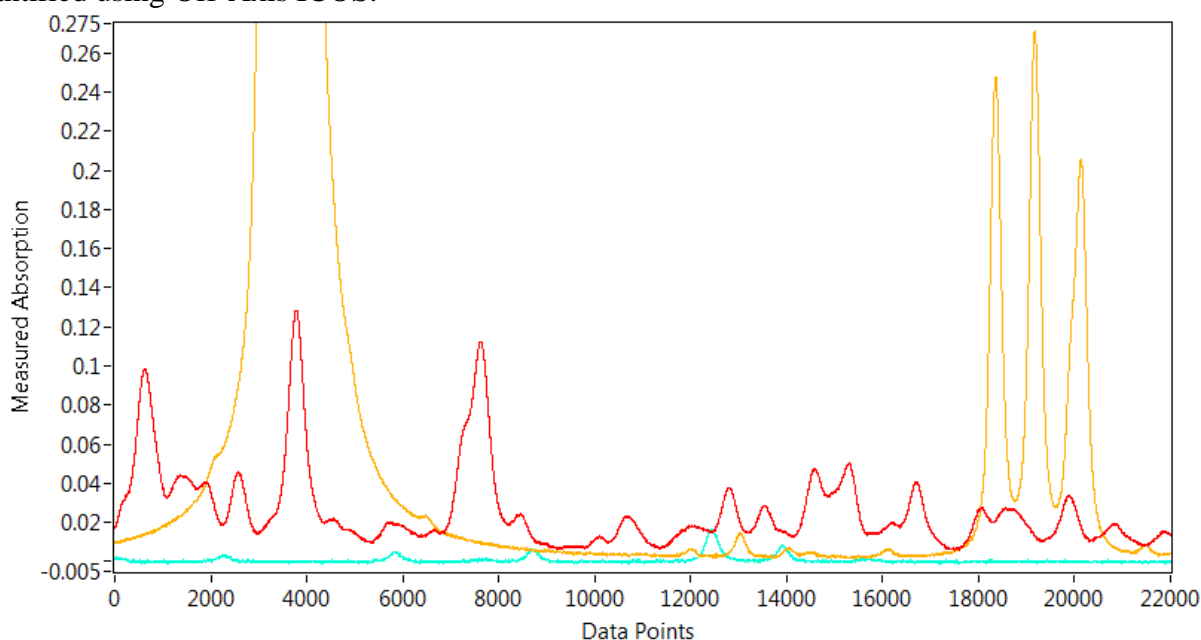

Figure 3.2.4.7: **Basis sets for 10% carbon dioxide (orange trace), 100% methane (red trace), and 10 PPM hydrogen sulfide (blue trace) at 1582 nm**

The hydrogen sulfide measurement precision versus data averaging time (e.g. Allan devation plot) is shown in Figure 3.2.4.8. The data clearly indicates that the analyzer can quantify H_2S to better than 0.2 ppm in 1 second with no sample conditioning, exceeding the capabilities of conventional technologies.
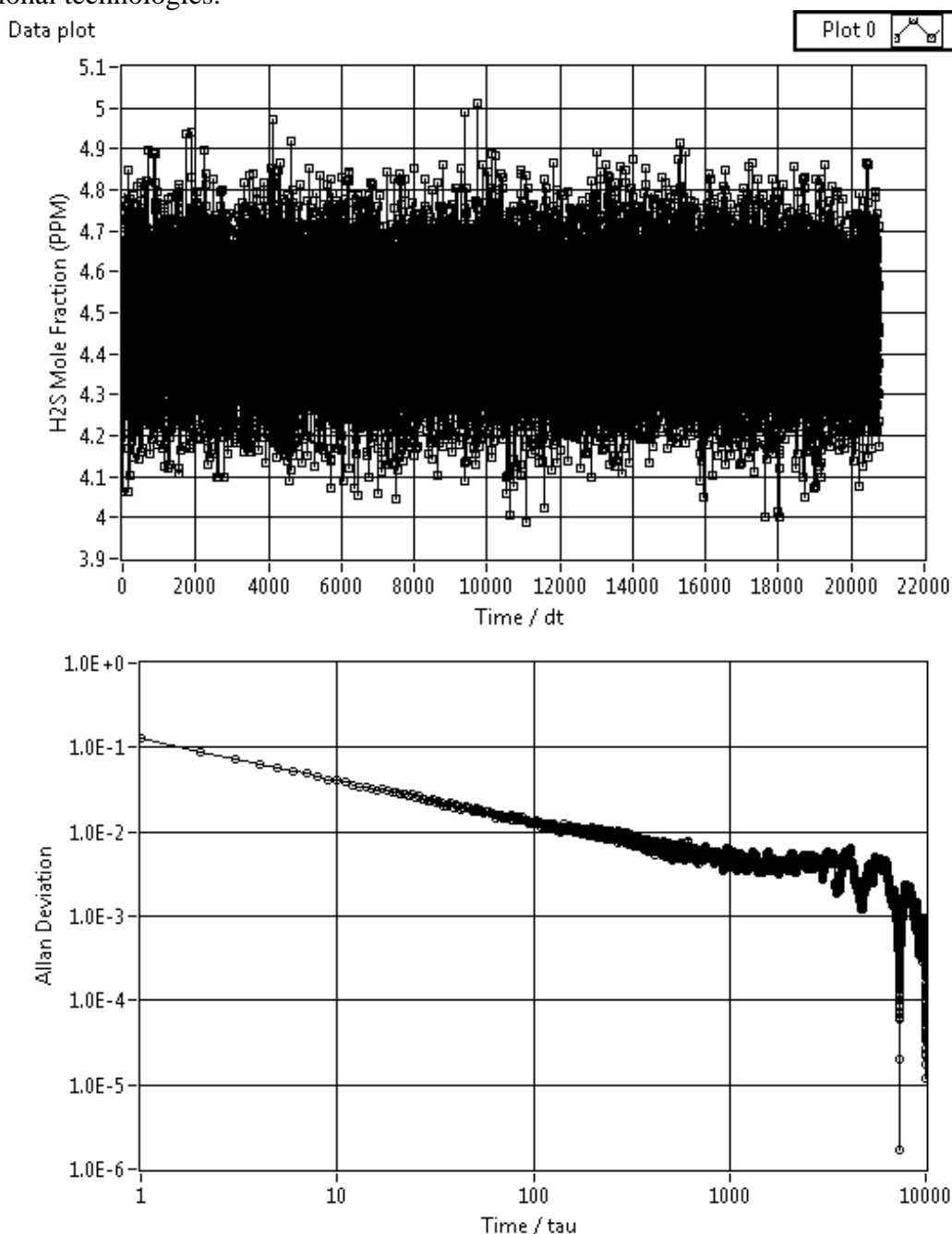

Figure 3.2.4.8:   Raw data (top) and associated Allan deviation plot (bottom) for H_2S in natural gas.

Finally, the linearity of the system was gauged by adding known amounts of H_2S into a natural gas stream. The raw and processed data shown in Figure 3.2.4.9 clearly show that the analyzer is highly linear ($R^2 = 0.9995$) over the typical measurement range of 0 – 6 ppm H_2S.
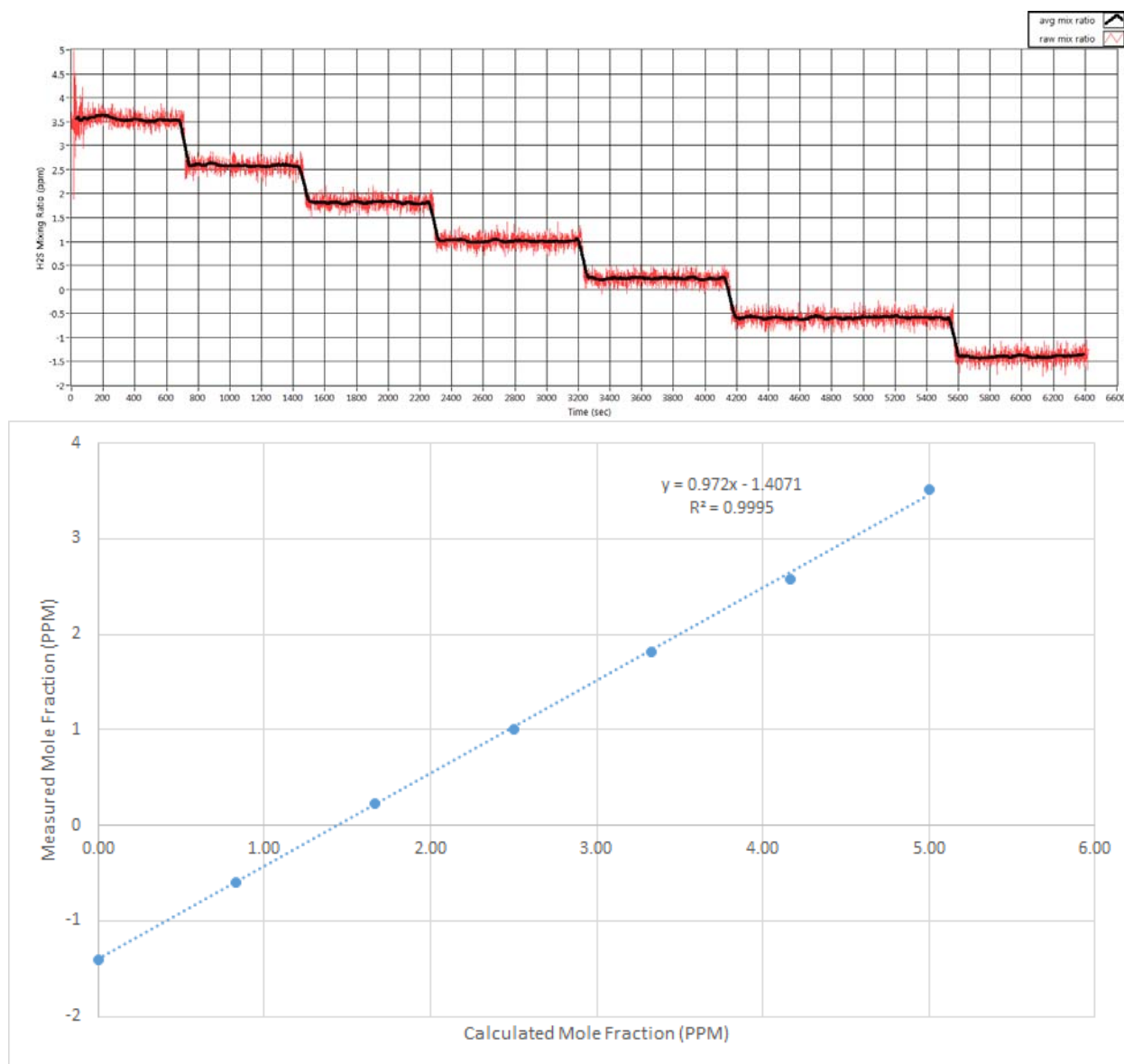
Figure 3.2.4.9: The linearity of the system was empirically determined by adding H_2S to a natural gas stream. The raw (top) and processed (bottom) data show that the sensor is highly linear over the typical H_2S concentration range.

Although less important than H_2S, natural gas providers also need to measure trace carbon dioxide levels. Thus, LGR extended its Off-Axis ICOS technology to address CO_2 as well as H_2S.

As shown above, CO_2 absorbs in the same spectral region as H_2S. Thus, the chemometric algorithm was able to quantify both species simultaneously. The resulting Allan deviation plot for carbon dioxide in natural gas in shown in Figure 3.2.4.10. The data indicates that the Off-Axis ICOS analyzer is capable of quantifying CO_2 to better than 50 ppm in 1 second.
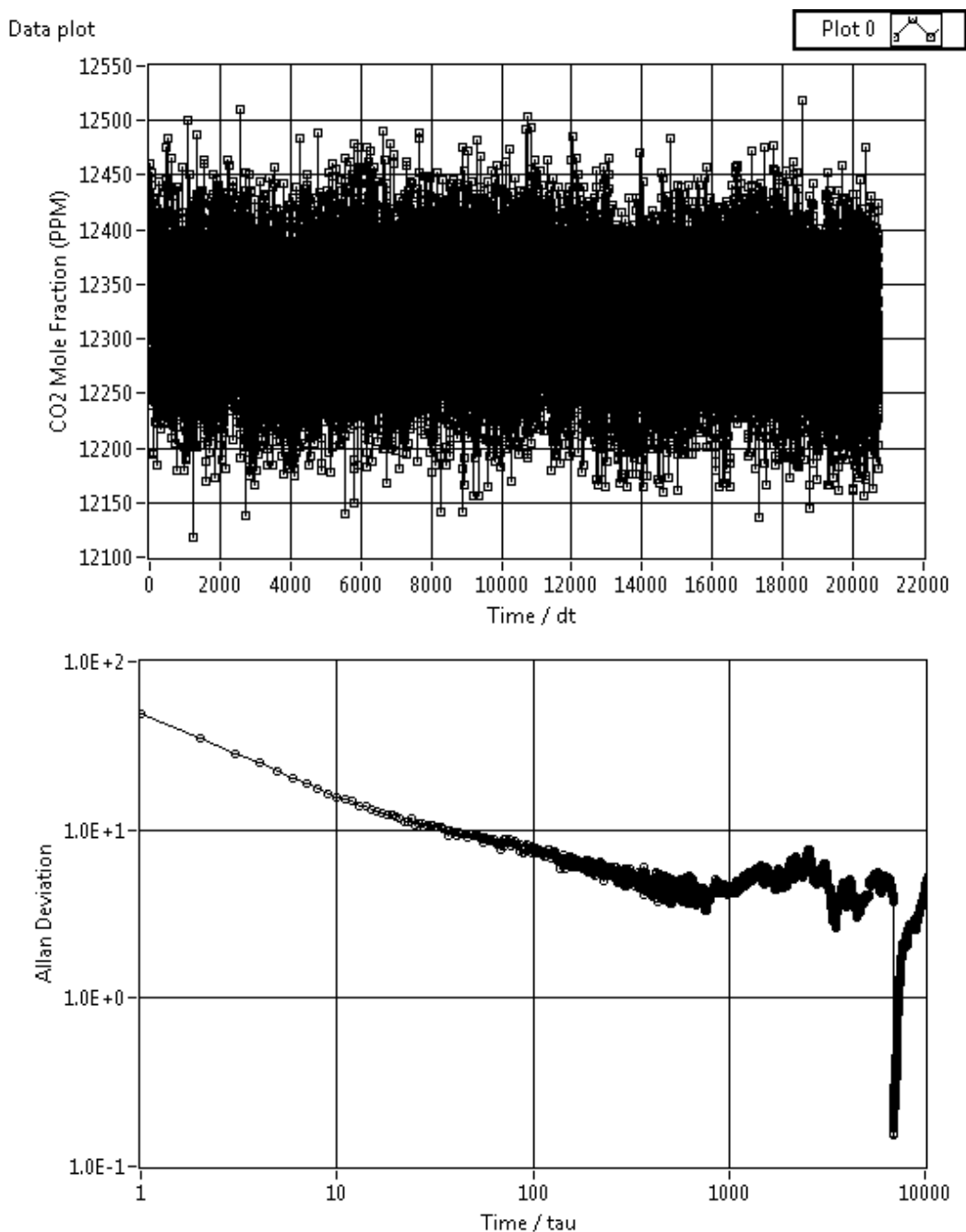
Figure 3.2.4.10: Raw data (top) and associated Allan deviation plot (bottom) for CO_2 in natural gas.

In order to make the sensor more appropriate for industrial deployments, higher measurement pressures were also tested. First, the measurement pressure was increased to 300 torr. New basis sets were acquired (Figure 3.2.4.11).
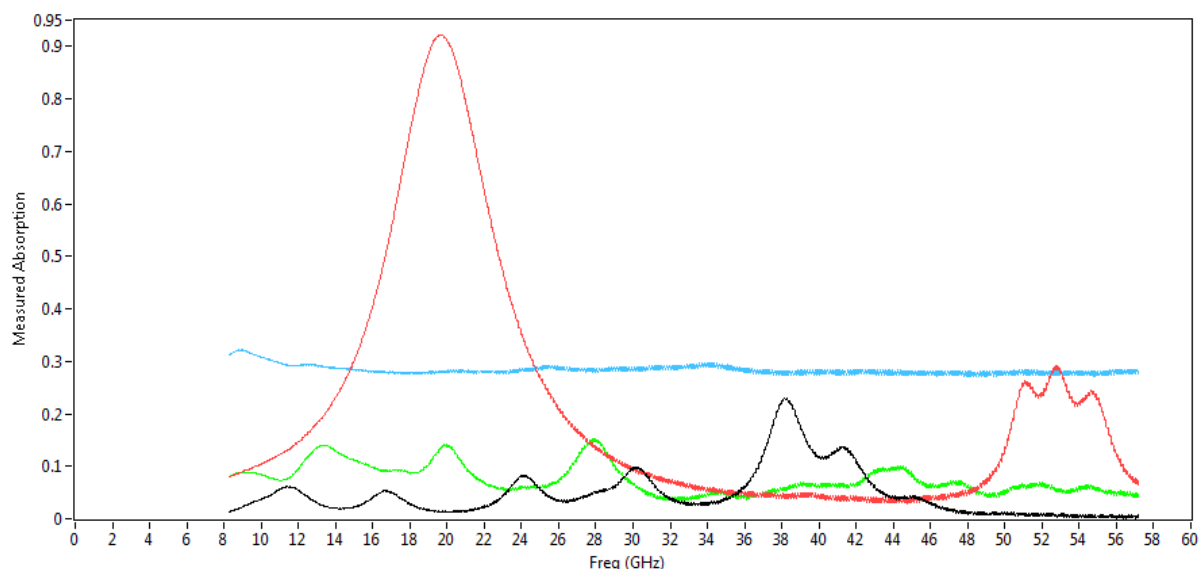
Figure 3.2.4.11: **Basis sets for natural gas (Black: 200ppm H2S - Red: 10% CO2 - Green: 100% CH4 - Blue: 10% Ethane) at 300 torr.**

The chemometric algorithm was then refined to operate at this elevated pressure. A sample measured spectra and fit for hydrogen sulfide in natural gas is shown in Figure 3.2.4.12.
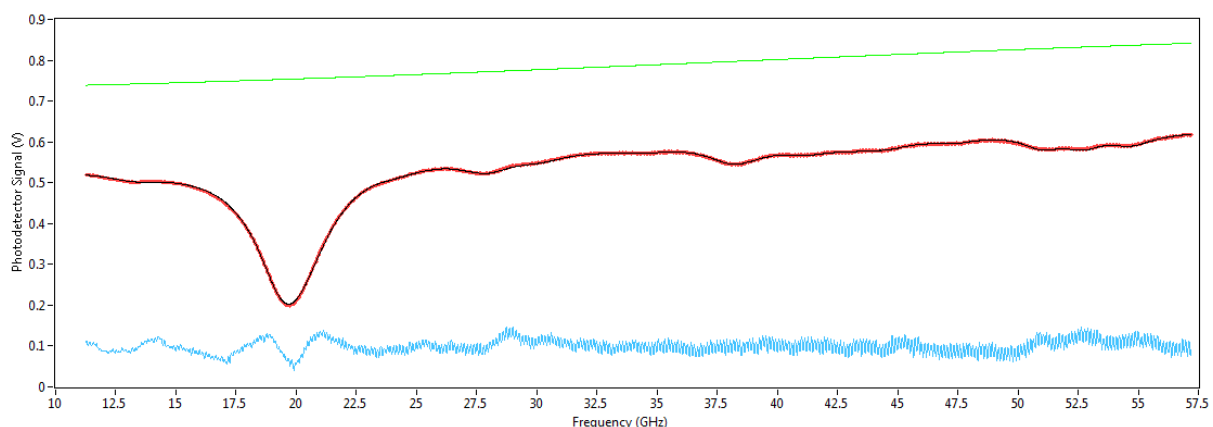

Figure 3.2.4.12: **Measured spectra (black) and fit (red) for a natural gas mixture containing hydrogen sulfide impurities.**

In order to assess the cross-dependencies between the H_2S mole fraction and the other components of the gas mixture, a measurement at constant H_2S mole fraction was performed while switching back and forth between the pure methane cylinder and the natural gas cylinder. In Figure 3.2.4.13, one can see at t = 540 how the reported mole fractions change when switching from pure methane to natural gas. One could expect a steady H_2S value, a sharp increase of CO_2, and a slight decrease of CH_4. However, the instrument shows an increase of the H_2S value. This trend is confirmed at t = 770 when the inlet is switched back to pure methane. This may result from a significant cross-sensitivity between the fitting parameters associated with each gas and suggests that the chemometric algorithm must be further refined.
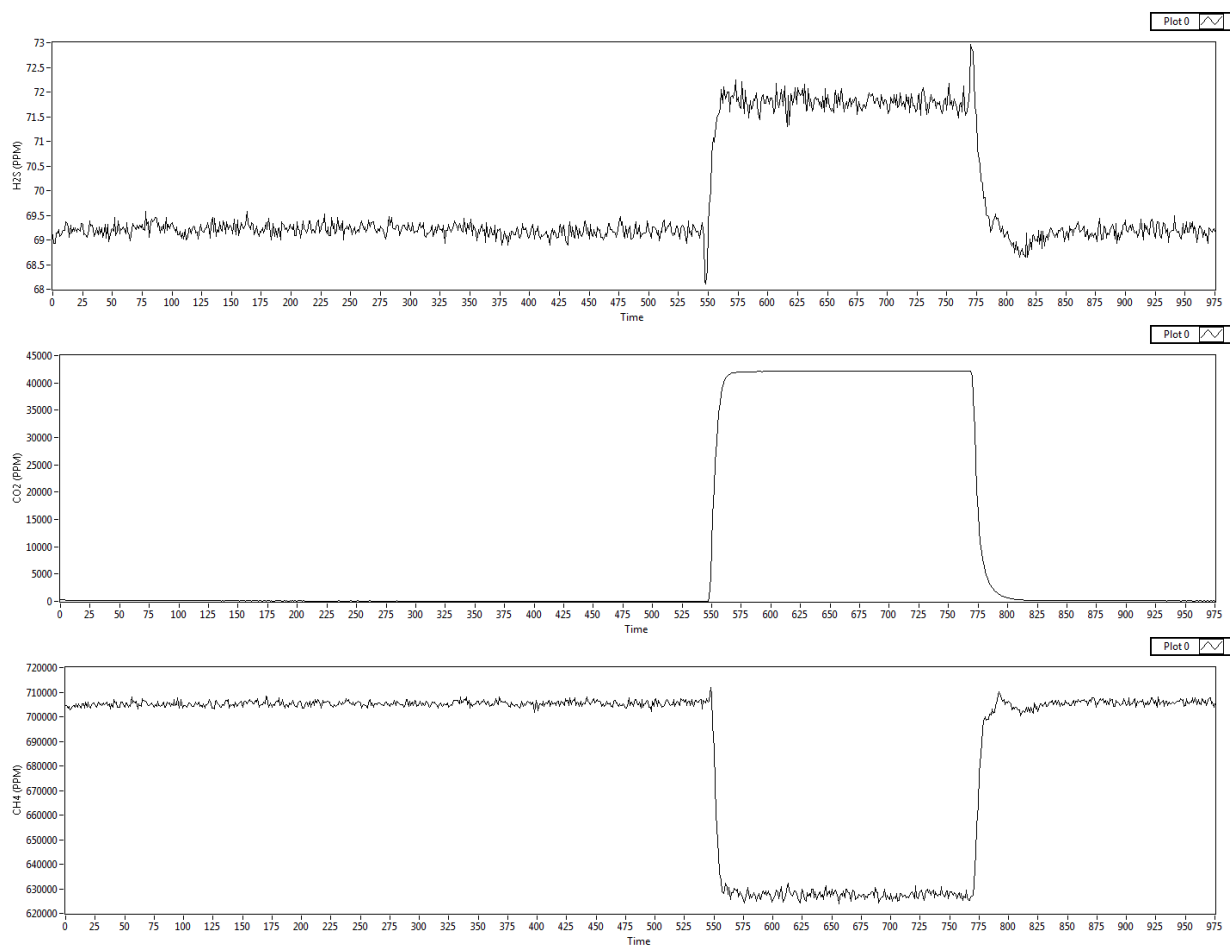
Figure 3.2.4.13: H_2S, CO_2, and CH_4 **Mole fraction vs Time while switching back and forth between pure Methane and Natural Gas Mixture with constant H2S**

Another method of making the instrument more industrially-relevant involved using smaller mirrors (one inch diameter instead of two inch diameter) to reduce the overall costs associated with building the analyzer. The method was tested on H_2S contamination in natural gas and the measurement precision is shown in Figure 3.2.4.14.

As expected, reducing the mirror diameter decreases the measurement precision by a factor of 4. However, the analyzer precision still exceeds other available commercial sensors. Thus, this strategy will most likely be adopted in the LGR commercial product.
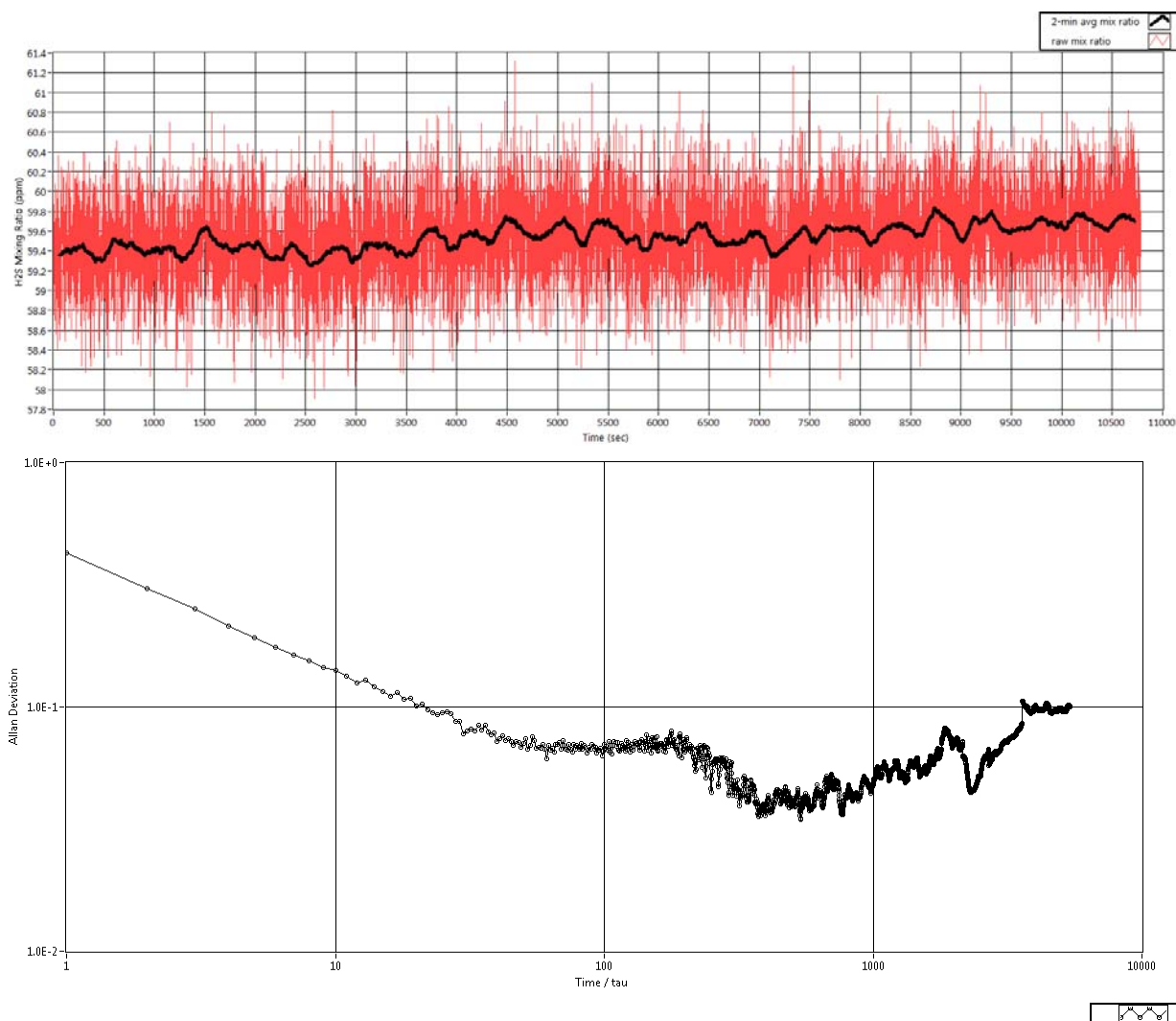
Figure 3.2.4.14:   **Measurement precision for H$_2$S contamination in natural gas taken from an extended measurement of constant composition (top trace). The resulting Allan variance (bottom) shows the measurement precision.**

The final variation of the natural gas analyzer involved using a DFB diode laser operating near 1396 nm to measure water vapor in natural gas. The total pressure was set at 20 torr in order to reduce the background absorption due to methane and ethane. Figure 3.2.4.15 shows that a water line of appropriate strength is present in the center of a methane transparency window near 1396 nm.
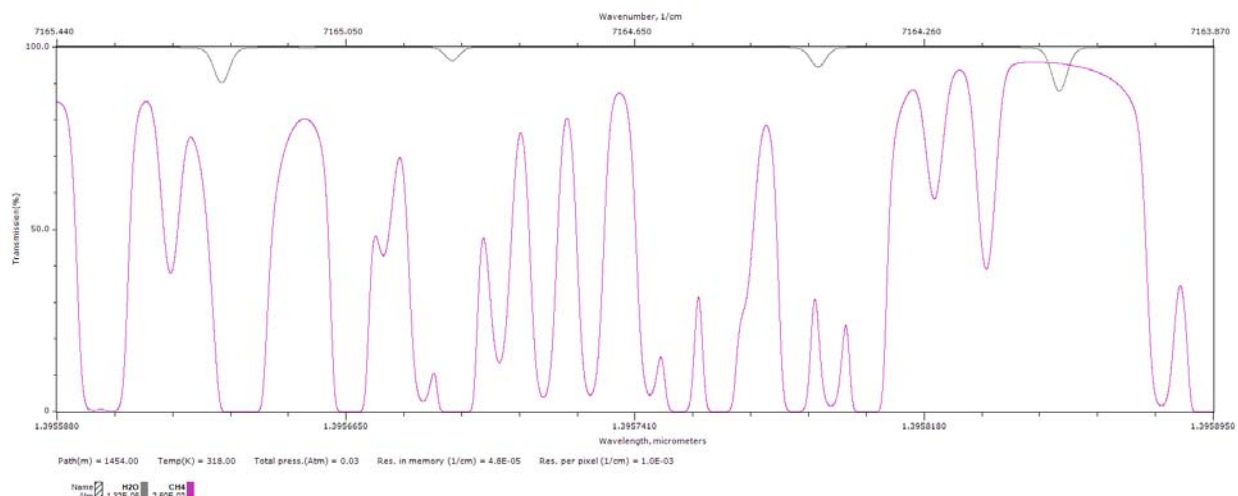
Figure 3.2.4.15: Water absorption feature (black) present in methane transparency window near 1396 nm.

Figure 3.2.4.16 and Figure 3.2.4.17 show the signal acquired while respectively sampling pure methane and ultra-zero air. Water absorption is a significant signal contribution in both spectra and the water line at 69.5 GHz is in a methane absorption dip, as predicted by the simulation (event though the measured methane spectrum differs significantly from the simulated spectrum). This represents a great opportunity to measure water vapor in natural gas over a wide range (sub-ppm to a few thousands of ppm).
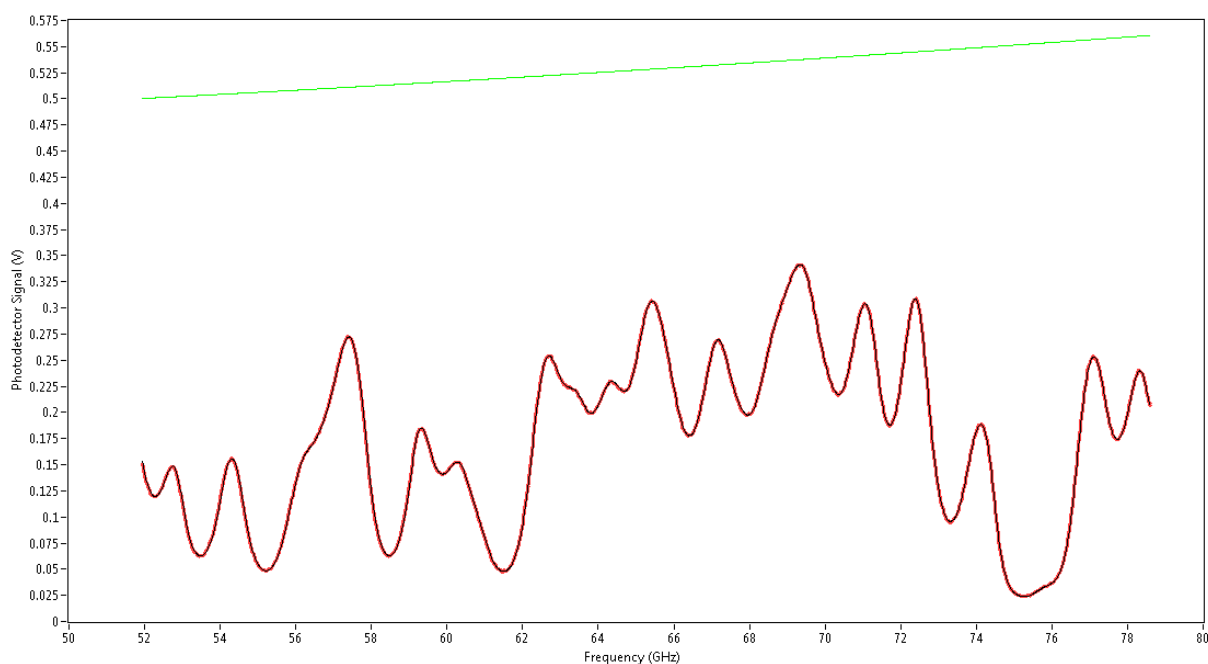

Figure 3.2.4.16: ICOS Spectrum of Pure Methane at 1396 nm and 20 torr Total Pressure
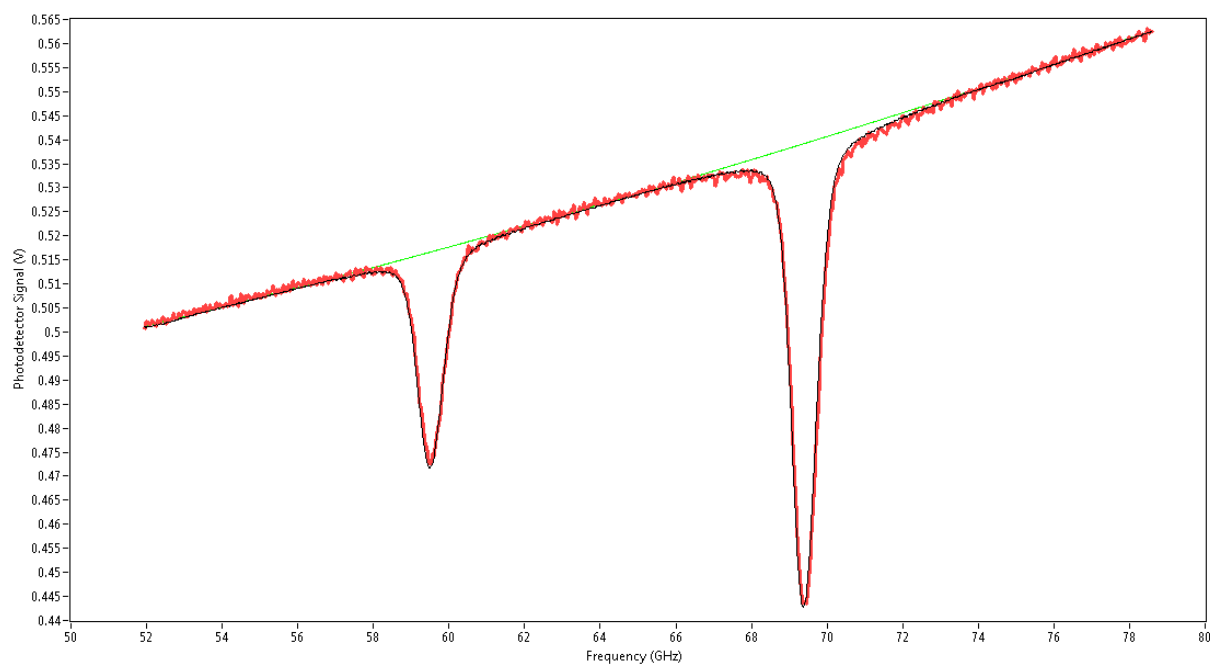
Figure 3.2.4.17:   **ICOS Spectrum of Water Vapor Trace in Ultra Zero Air at 1396 nm and 20 torr Total Pressure**

Figure 3.2.4.18 displays the basis sets used by the chemo-fitter. The water absorbance contribution had to be removed from the methane and ethane basis sets by post processing the acquired spectra.
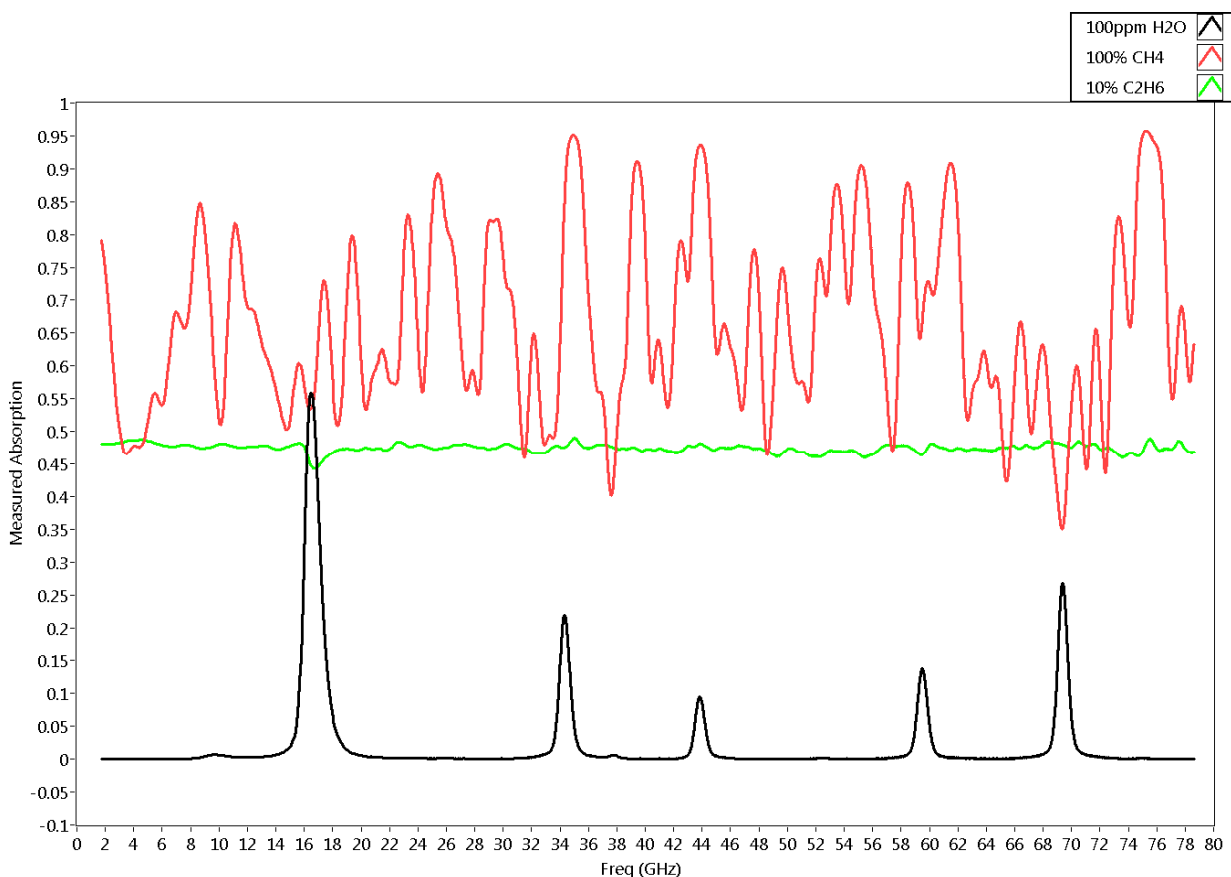
Figure 3.2.4.18: Basis sets used to measure water in natural gas

The water vapor mixing ratio measured by the analyzer was strongly correlated to the temperature in the lab, desorption from the tubing walls being the main water vapor source. This assumption is in good agreement with the fact that the faster the gas flow, the lower the water mixing ratio. The temperature fluctuations in the room made the measurement of a steady water level in methane difficult over several hours. A series of data was acquired over night with the analyzer connected to a methane cylinder with a short and insulated piece of tubing, minimizing the effect of ambient temperature changes on the desorption rate. This led to fairly stable water level on periods as long as 2 hours. The time plot in Figure 3.2.4.19 is a portion of the over-night data series and it starts at a time when the water mole fraction was fairly stable. Figure 3.2.4.20 is the Allan plot derived from the time series data, but it does not accurately indicate the instrument's stability as water mixing ratio fluctuations were occurring upstream. In spite of that, the Allan deviation goes down over the first 200 seconds, it is < 0.1 ppm after 10 seconds and < 0.05 ppm after 1 minute.
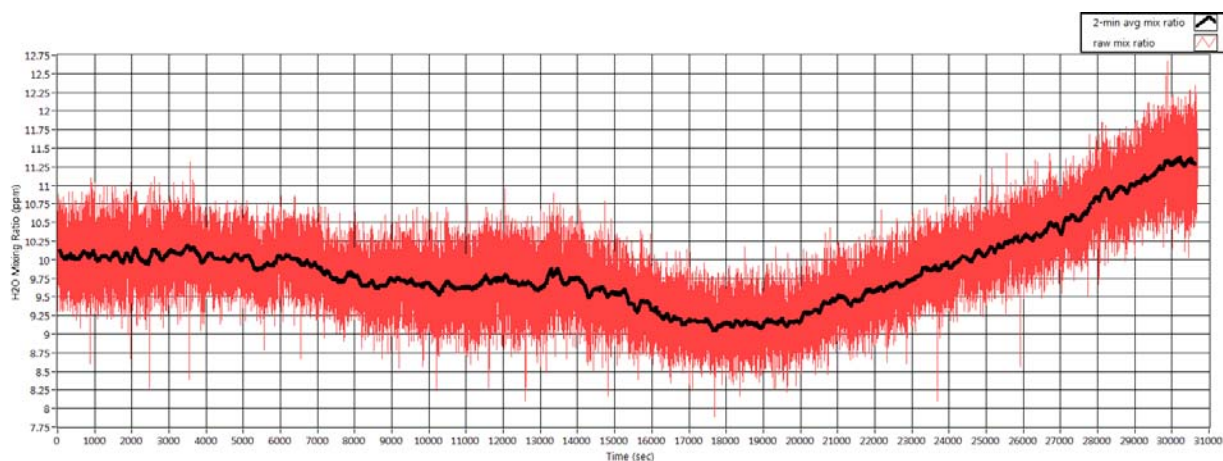
Figure 3.2.4.19: Time series measurement of water vapor in natural gas.
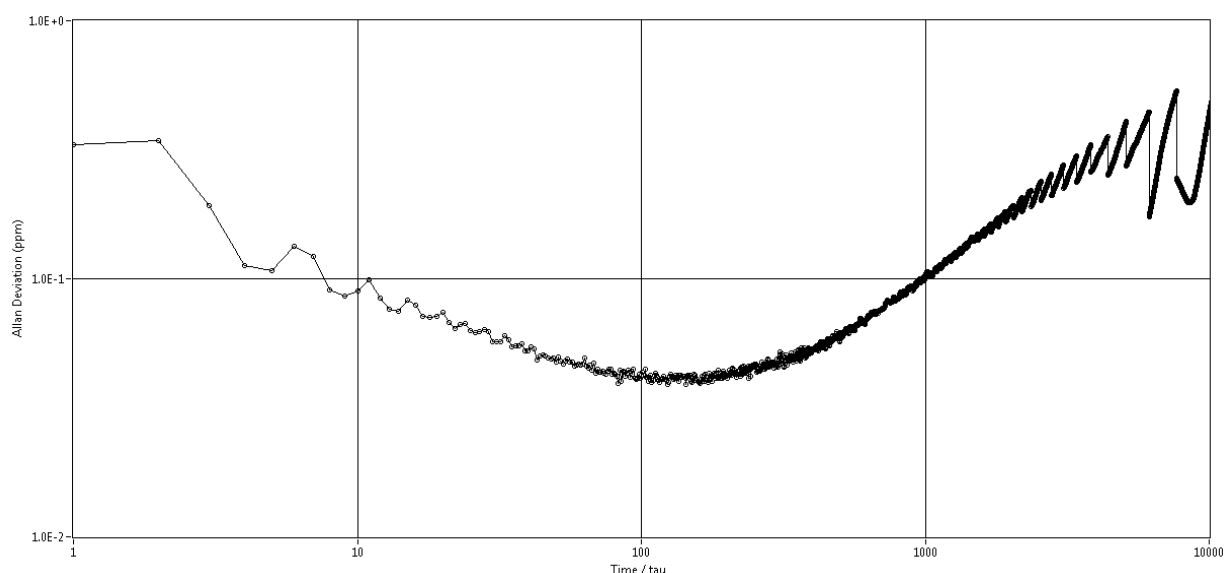

Figure 3.2.4.20: Allan variance resulting from time series presented above.

LGR is now working to commercialize the natural gas analyzer. This process will include cost-engineering and appropriate packaging (e.g. Class 1 Div 1 package). We anticipate initial sales of the natural gas analyzer by late 2014 or early 2015.

4. **Progress and Status:** Include a summary of the activities performed during the reporting period, and identify any overall risks, issues, or concerns related to achievement of energy efficiency performance objectives or goals, tasks, milestones, and schedule. Include results of any go/no-go decisions and status of stage gate metrics to include progress toward achieving the energy efficiency goal or objective, the status of program tracking metrics and risk mitigation plans that address adverse program performance trends. (*If applicable, please provide information for sub-recipient activities in this section as well.*)

N/A

5. **Financial Status:** Provide a summary financial status of the project, identifying any issues with the overall budget, non-federal cost share, and the ability of the project to accomplish its objectives within the approved budget.

The project was completely spent-out according to plan and within the proposed timeline.

6. **Scope issues:** Identify any changes in overall project approach or aims, and reasons for the needed changes. Changes to the objectives and scope require prior approval by the Contracting Officer and need to be communicated to the DOE Project Officer once discovered.

The scope of the project remained unchanged.

7. **Patents:** Identify all patents applied for or resulting from this award.

None.

8. **Publications / Presentations:** Identify all publications and presentations made for industry or government groups resulting from the award during this quarter. Forward supplemental information (e.g., interim reports, photographs, articles, publications, newspaper articles, etc.) to the Project Officer.

LGR has made a series of small presentations and brochures for potential industrial partners. This literature has been made available to the Steel Manufacturers Association (SMA) and the American Iron and Steel Institute (AISI). Test data obtained from the deployment at the ICGRF has been distributed to industrial furnace operators and is being prepared for publication.

Additionally, Dr. Manish Gupta (a key personnel on this project) has written two articles to highlight the application of LGR's Off-Axis ICOS technology for industrial applications:

- M. Gupta, "Cavity Enhanced Laser Absorption Spectrometry for Industrial Applications," *Gases & Instrumentation* (June/August 2012).
- M. Gupta and J. Brian Leen, "Field-Portable Analyzers Based on Cavity-Enhanced Laser Absorption Spectrometry," *American Laboratory* (January 18th, 2013).

These articles are generating considerable interest in the industrial community and LGR has already received substantial interest from many industrial customers.

9. **Commercialization Status:** Identify status of commercialization plan and include activities performed during the reporting period, and identify any issues or concerns related to commercialization.

LGR has released several new products for industrial compliance monitoring, including HF, H_2S, NH_3, and HCl analyzers. Over the course of this Phase III effort, LGR has sold over 12 such industrial analyzers for a total revenue exceeding \$350k. Many of these analyzers will be used for industrial process control to limit pollutant release and optimize catalyst lifetimes. Additional, increasing sales are expected over the next few years.

Additionally, based on the deployment results presented above, LGR has pre-released an extractive analyzer for the simultaneous measurement of CO, CO_2, CH_4, O_2, and H_2O. Initial sales for this unit are expected shortly.

Finally, LGR is working with a large industrial partner to industrialize and deploy the natural gas analyzer. We anticipate initial prototype deployment in 2014 and full commercial release in early 2015.

The additional sales and increased revenue has resulted in LGR hiring 4 additional manufacturing personnel and one additional scientist.

10. **Plans for Next Quarter:** Identify activities to be performed during the next quarter, and specify what accomplishments or goals should be attained.

This DOE project has concluded.