White Paper
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Real-time, High Precision Greenhouse Gas Measurements Using a Mid-Infrared Laser-Based Platform

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- GHG
- Greenhouse Gas
- Methane
- CO
- CO_2
- N_2O
- Mid-IR
- Telecom Lasers

We are currently in the final development stages of a mid-infrared laser-based analyzer platform that is capable of monitoring a wide range of species with high precision, accuracy, and selectivity. The core mid-infrared laser technology utilized covers the O-H, N-H, and C-H stretch region between 3-4 microns and the C-O and N-O stretch region between 4-4.6 microns. This platform is designed for use in monitoring key greenhouse gases (GHG) including methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O), in addition to other important "tracer" species such as carbon monoxide (CO). In this paper we will present and discuss data obtained from laboratory testing of early beta units, which demonstrates the sensitivity and accuracy of the platform at sub-ppb levels for CO and CH_4.

Introduction

Real-time, ultra sensitive measurement is required for a wide array of applications, including pollution and GHG monitoring. Traditional approaches such as non-dispersed infrared absorption (NDIR) and Chemiluminescence are slowly being augmented or in some cases replaced with new, laser-based analyzers that are capable of providing real-time ppb-level detection of key atmospheric species. Monitoring of chemical species via their associated fundamental rovibrational bands in the mid-infrared is well established. The requisite selectivity and sensitivity for monitoring greenhouse gases, industrial pollutants, and combustion precursors, intermediates, and products have been demonstrated in numerous studies. Utilizing technology acquired from NovaWave Technologies, we are now developing a new difference frequency generation (DFG) based, mid-infrared laser analyzer platform that is capable of monitoring numerous species with high sensitivity and selectivity (Figure 1). Specifically, the O-H, N-H, and C-H stretch region between 3-4 microns and the C-O and N-O stretch region between 4-4.6 microns is being used to monitor the three primary greenhouse gases; CH_4 CO_2, and N_2O.

Results from pre-market prototypes are shown, with emphasis on CO and CH_4 monitoring. In the case of CH_4, water vapor is simultaneously measured to calculate dry-mole fractions, which is the figure of merit for atmospheric scientists. Analyzer selectivity, precision at the ppb level, and stability is demonstrated.

DFG Laser-Based Mid-Infrared Analyzer

The widespread availability of inexpensive, single frequency near-infrared lasers has led to a number of analyzers that operate in this region. However, the detection of chemical species via near-infrared overtone absorption bands often requires that elaborate, ultra sensitive approaches be used to increase overall system performance, including ultra-long path astigmatic Herriott cells (combined with frequency or wavelength modulation methods), resonant photoacoustic approaches, and optical cavity-based methods such as cavity ring-down spectroscopy (CRDS) and integrated cavity output spectroscopy (ICOS). Although numerous analyzers based on these methods have been demonstrated, and in some cases developed as successful commercial products, the ability to employ these methods can be limited by the need to maintain a pristine environment or the requirement that the vibrational overtone monitored be of sufficient intensity, which is not always possible.

To address this, we are developing a class of analyzers that are capable

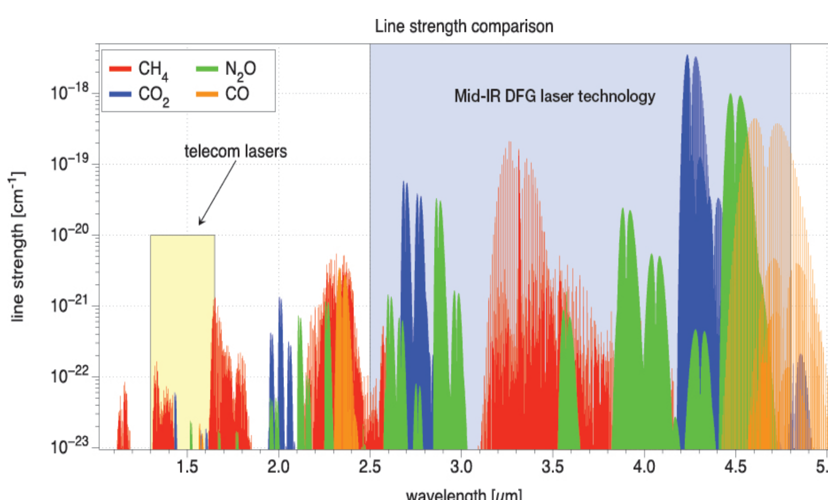


Figure 1: Accessing species via their mid-infrared absorption spectra is desirable, as the associated absorption strength is 10 to 10000 times stronger than in the commonly used near-infrared. In particular, mid-infrared monitoring of greenhouse gases is advantageous as simple, direct absorption approaches can be used to access many species with high specificity, sensitivity and accuracy. Above, spectra of the three primary greenhouses gases is shown in the near-infrared and mid-infrared regions. For CO_2, transitions are approximately 8000 times stronger than those in the near-infrared.

of sensing species via fundamental vibrational bands in the mid-infrared, instead of the more commonly employed near-infrared vibrational overtone bands. As the absorption intensity is typically 10-10,000 times stronger in the mid-infrared compared to that of the near-infrared, simple and robust direct absorption spectroscopy can be used to reliably determine the absolute concentrations or mole fractions of many air quality targets including greenhouse gases. In the case of hydrocarbons, for example, the associated mid-infrared absorption intensities are approximately 100 times stronger on average than those of the near-infrared bands, thereby enabling ppb-level detection limits to be achieved in a remarkably simple, compact and robust analyzer platform.

For CH_4 in particular, monitoring concentrations via the 3-micron band is highly desirable as the associated absorption intensity is nearly 200 times stronger than those of the more commonly used 1.5 micron overtone bands. For gases such as CO_2 and CO, mid-infrared absorption strength is nearly 10,000 times stronger than the associated near-infrared bands. As such, the precision levels associated with cavity-based methods can be achieved without the need for an ultra-high reflectance cavity, which must kept ultra-clean to be effective. In addition to ppt level detection sensitivity, Mid-infrared based approaches could be readily implemented in relatively robust, open-path embodiments, which is difficult or impossible in many cavity-based approaches. Additionally, our unique DFG laser platform leverages telecom commodity lasers, unlike other mid-infrared laser technologies such as QC lasers, which have yet to find parallel, high volume applications. As such, the analyzer can be manufactured with high yield, reproducibility and reliability.

Results

Methane Monitoring

Figure 2 displays a Iris 5500 analyzer that has demonstrated ppt-level detection sensitivity and sub-ppb stability over extended periods of time. The analyzer employs a compact, modular, all-fiber coupled DFG laser as the engine, which is coupled to a small gas cell that is held at a constant temperature and pressure. No cryogens are required for the analyzer, and there are virtually no consumables, a benefit also realized in other laser-based analyzers. Figure 3 shows the analyzer concentration data for a CH_4 calibration gas at approximately

Figure 2: Thermo Scientific IRIS 5500 Mid-IR Laser-Based Methane Analyzer

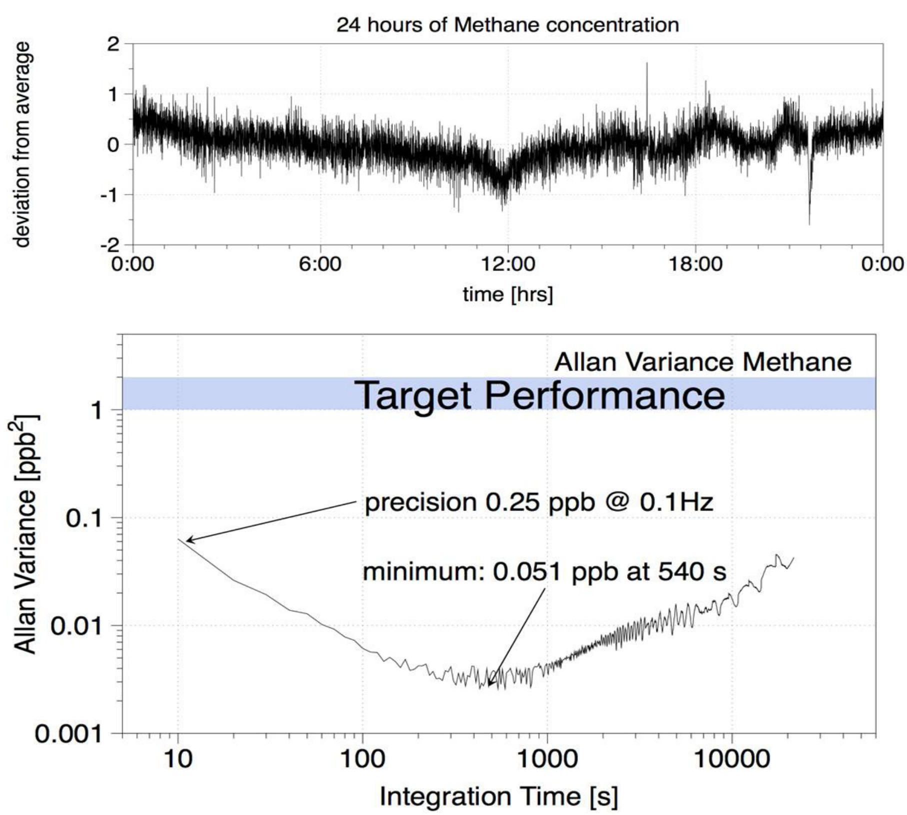
2ppm (ambient level) over a period of 24 hours.. Initial tests of the analyzer indicate a calibration interval of 12-hours for 1-2 ppb level accurate measurements, with the possibility of calibration free operation for single digit ppb level measurements. Also shown in Figure 3 is the Allan Variance, a metric used to quantify precision and stability. Here the first data point indicates a precision level of approximately 250ppt (10 second average/0.1 Hz) and a minimum of about 50ppt with approximately 10 minutes of signal averaging. This level of performance satisfies the WMO guidelines for ambient methane monitoring, and similar results are obtained for the instrument over the full operating temperature range.

Carbon Monoxide Monitoring

The wavelength agility of the mid-infrared laser-based platform enables numerous other important species to be measured, including carbon monoxide and nitrous oxide. A prototype CO analyzer based on the same platform as the CH_4 analyzer but operating at a different wavelength was used to measure ambient CO in the laboratory, which is typically at the 100-200ppb level. Figure 4 shows the result from a CO measurement taken from approximately midnight until 9:30 am. During the night, the air conditioning is off, and air exchange limited, leading to relatively constant CO levels in the building. Shortly after 6 am the air conditioning turned on and outside air was introduced.

The subsequent rapid increase from around 6:45 am until 9 am is attributed to the increased CO emissions from nearby commuter traffic the inset detail shows the typical precision and stability of the analyzer, with sub-ppb precision achieved in a few seconds. For the region around 3 am, the standard deviation is approximately 440ppt for a 10 second measurement This ppb level precision is required for source attribution, as correlations of CO with CO_2

Figure 3: 24 hours time series of Methane concentration and associated Allan Variance. At 10 seconds averaging the precision is 250 ppt, and the minimum Allan Variance is 0.051 ppb at 540 seconds.



measurements can be used to discriminate anthropogenic CO_2 emissions. Figure 5 shows 20-hours of continuous data at 475ppb and the corresponding Allan Variance. At 1 Hz, the precision is 1.8ppb, and drops below the target of 1ppb at 3 second averaging. The minimum of 140ppt is reached after 323 seconds.

Other Applications

The precision levels demonstrated for CH_4 and CO are similar to those obtained for other species at different laser wavelengths. In addition to CH_4, systems for other species such as CO, CO_2, N_2O, and other important gases are under development utilizing this same platform.

An additional application for this platform could be in a dilution CEMS (Continuous Emissions Monitoring System) where the concentration levels are close to the detection limit of traditional analyzers.

The precision, selectivity and generality of the platform should open a number of new applications in addition to air quality and greenhouse gas monitoring.

Conclusion

Trace gas analyzers based on mid-infrared difference frequency generation were demonstrated, showing promising results for the measurement of CH_4 and CO.

- Strong, fundamental absorption bands of trace gases of interest in the mid-infrared permit ultra sensitive detection with simple, robust analyzers.
- Sub-ppb precision at ambient concentrations was demonstrated for CH_4 with 10 second averaging
- Sub-ppb precision at ambient background concentrations was demonstrated for CO with 3 second averaging.
- The generality of the platform will enable the measurement of other ambient GHGs (CO_2 and N_2O) and numerous other species.
- This platform may also be well suited to measure stack gas emissions in a dilution CEMS application.

Figure 4: Time series of carbon monoxide concentration starting at midnight until 9:30 am. The insert shows an expanded view of 6 minutes after 3 am. The precision estimate for this period is 440ppt, given by the standard deviation of the sample (n=36, mean=210 ppb). Time resolution was 10 seconds for this run.

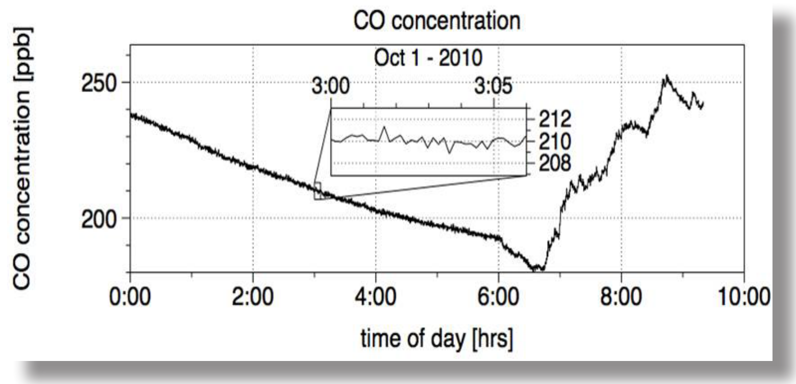
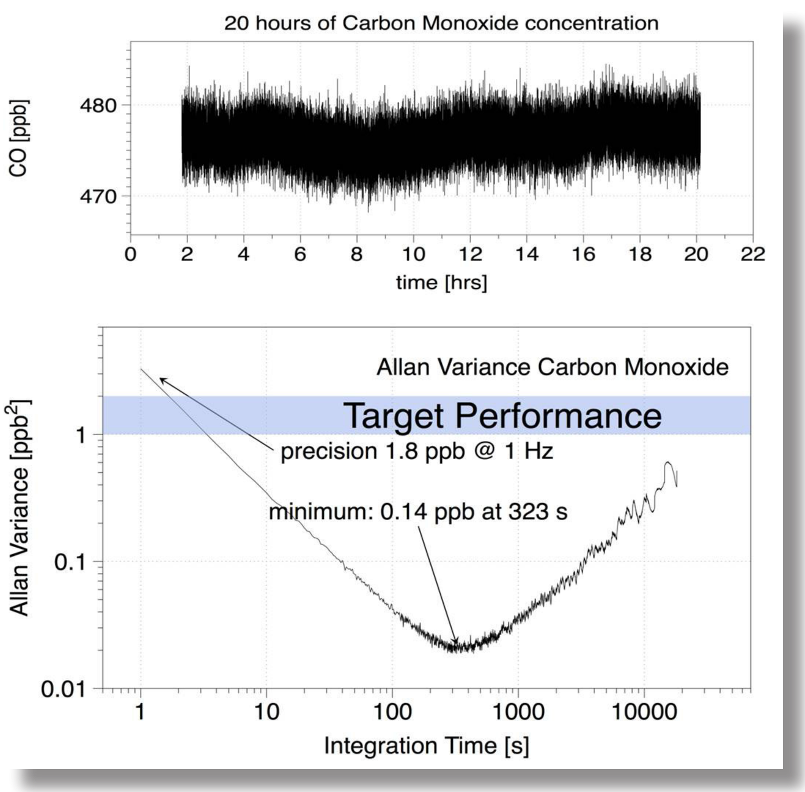


Figure 5: 20-hours time series of Carbon Monoxide concentration and associated Allan Variance. At 1 second averaging the precision is 1.8 ppb, and the minimum Allan Variance is 0.14 ppb at 323 seconds.



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