PICARRO

Development of a New N_2O/CO Cavity Ring-Down Spectrometer for Sub-ppb Ambient Gas Monitoring

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Introduction

With a global warming potential of nearly 300, N_2O is a critically important greenhouse gas, contributing about 5 % of the US total GHG emissions. Agriculture soil management practices are the dominant source of anthropogenic N_2O emissions, contributing nearly 75 % of US N_2O emissions. In urban areas, vehicle tailpipe emissions and waste water treatment plants are significant sources of N_2O. We report here a new mid-infrared laser-based cavity ring-down spectrometer (Picarro G5310) that was recently developed to measure sub-ppb ambient concentrations of two key greenhouse gas species, N_2O and CO, simultaneously. It combines a quantum cascade laser with a proprietary 3-mirror optical cavity. The new optical analyzer was set up to monitor N_2O and CO, along with CO_2 and CH_4, in ambient air obtained from a 10 meter tower in Santa Clara, California. Evidence of contributions from traffic and a nearby sewage treatment facility were expected in the measurement data.

Cavity Ring-Down Spectroscopy

Cavity ring-down spectroscopy (CRDS) is a time-based absorption technique employing a high-finesse optical cavity to deliver effect path-lengths in the order of several kilometers. Combined with precise temperature, pressure, and wavelength control, CRDS offers high sensitivity, precision, and low-drift measurements. The G5310 further extends this performance via the use of a quantum cascade laser (QCL) operating in the mid-infrared, a region of the spectrum offering significantly higher sensitivity for nitrous oxide and its than relevant absorption features at shorter wavelengths in the near-infrared.

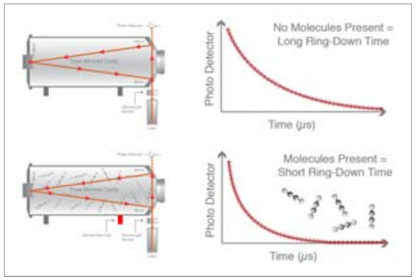


Figure 1. *Analyte concentration derived from time measurement*

Analyzer – Development and Test

A region of the spectrum ~4507 nm offers suitable absorption features associated with N_2O, CO, H_2O, and CO_2. The CO_2 feature allows reporting of CO_2 concentration, however this is based on $^{13}CO_2$. Given the natural abundance of this isotopologue (~1 %), reported CO_2 concentration is subject to variations due to diurnal and annual fluctuations of $^{13}CO_2$:$^{12}CO_2$.

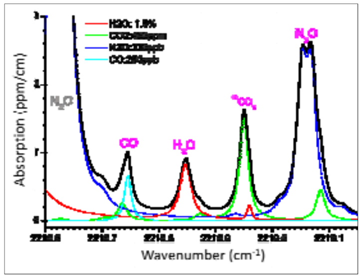


Figure 2. *Spectral region used in development of Picarro G5310.*

Analyzer – Specifications and Test Results

Performance Specifications			
Specification	**N_2O**	**CO**	**H_2O**
Precision (1σ: 5 sec / 5 min)	<0.2 / <0.04 ppb	<0.2 / <0.04 ppb	40 / 6 ppm
Drift (24 hrs)	<0.1 ppb	<0.1 ppb	-
Measurement Range	1-1,500 ppb	1-1,500 ppb	0-3 %
Operating Range	1-10 ppm	1-10 ppm	0-5 %
Measurement Interval	<5 sec	<5 sec	<5 sec

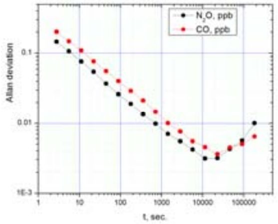


Figure 3. *Allan Deviation for N_2O and CO*

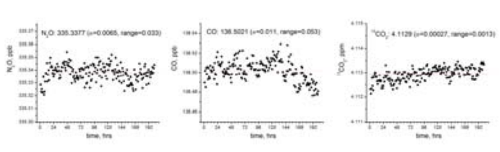
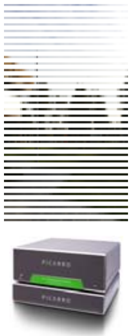


Figure 4. *Long-Term Drift for N_2O, CO, and CO_2*

Experimental Set-up

The experiment was located at the Picarro facility in Santa Clara, California. The G5310 analyzer was connected to a sampling point at a height of approximately 10 meters, with a sample line length of approximately 40 meters. Sample line material was a fluorinated polymer and the air sample was collected at a flow rate of 240 sccm, without drying.

The maps below indicate the location of the Picarro facility. Potentially significant sources of N_2O emissions that were considered likely to influence the measurement data are highlighted. It is also important to note the location relative to major, arterial roadways.



Results and Discussion

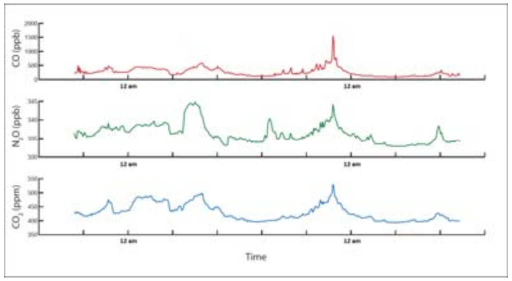


Figure 5. *Time series plot – N_2O, CO, CO_2*

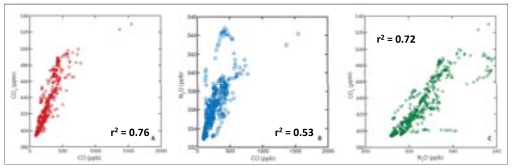


Figure 6. *Correlation plots*

- The G5310 generated high precision data during the 2 day experiment (shown as 5 minute integrated average). There is significant correlation between CO_2, CO and N_2O, suggesting that the variability of the three gases were primarily driven by transit combustion (Figure 5 and Figure 6). The experiment site is close to two highways with heavy rush hour traffic (Figure 7), which was probably the major contributor of the elevated CO and other gases.
- CO >1 ppm may reflect a transient local event, and the CO:CO_2 ratio of these two points (measured in 10 minutes) is above the average trend. With these two points excluded, there is CO_2 (ppm) = 0.1955 x CO (ppb) + 378.9ppm (r^2 = 0.81). The slope is larger than a typical CO_2:CO = 0.13 (Schimdt et al., 2014), probably due to the influence of biological CO_2.
- N_2O concentration occasionally deviated from the general linear trend between N_2O-CO and N_2O-CO_2 (e.g., around Day 2.25-2.35), suggesting local sources of N_2O , probably the wastewater treatment plant, on top of the tailpipe emissions. Further studies are required to understand the locations and types of these sources.

Figure 7. *Google map showing typical local traffic at 6pm of a workday*

Conclusions

Performance test data obtained during development of the G5310 validates the analyzer for long-term background measurements of N_2O and CO. Precision and drift characteristics make the G5310 the ideal choice for measurement network deployment, where frequency of calibration is critical to efficient operations, and long-term measurement precision is vital. In addition, the analyzer has been shown to have the necessary dynamic range to provide essential monitoring capabilities in urban environments. The CO_2 measurement based on $^{13}CO_2$ further extends the range of potential monitoring applications.

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