P-22: A Compact Cavity Ring-Down Spectroscopy Analyzer for *In Situ* Measurements of CO_2, CH_4, and Water Vapor

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INTRODUCTION

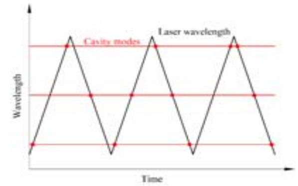
Picarro GasScouter (G4301)

- Measures ***CO_2, CH_4, and H_2O*** concentrations simultaneously in < 3 seconds
- For ***ambient monitoring*** and ***soil flux chamber*** studies
- Proven Cavity Ring-Down Spectroscopy (***CRDS***) technology
- Ultra light : ***25 lbs***
- Ultra low power: ***25 W***

- Built-in interchangeable battery (***8 hr*** life)
- Built-in pump with a ***~1 L/min*** flow
- No wavelength monitor
- No pressure or temperature control

	CO_2	CH_4	H_2O
Raw precision	0.4 ppm	3 ppb	-
Precision (5 min)	0.03 ppm	0.3 ppb	@ ~0% H_2O: 1-σ < 20 ppm @ 1.5% H_2O: 1-σ < 70 ppm
Drift (24 hr, 50 min avg.)	0.75 ppm	0.5 ppb	-
Measurement range	0 – 3 %	0 – 800 ppm	-

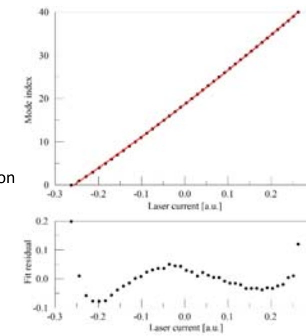
METHODOLOGY



- New method of collecting data – FSR Hopping
- Freely sweep the laser current over full spectral range and collect ring-downs on cavity modes when we get a full injection
- Can only trigger a ring-down even at given resonant points defined by the cavity length, separated by an FSR
- Subtlety is that injection efficiency is <100%, so every time the current is swept over a cavity mode in frequency space there **is not** a guaranteed ring-down event

- Rely on the cavity to give a relative laser current to frequency relationship
- Each cavity mode is separated by 0.0206 cm^{-1}
- Gives a frequency comb that we can relay on that does not change
- Then we can rely on a fit in FSR space to find the absolute frequency that the center of the line is located. This yields a highly accurate and precise frequency reference and scale that we can now fit and accurately integrate to find the concentration of gas contained in the cavity

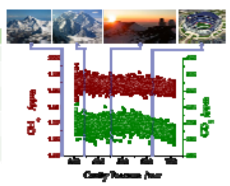
- Figure to the upper-right shows a third order polynomial fit to the laser current to frequency relationship
- This curve changes with ambient temperature and age, and is clearly much higher order than third order; shown by the 20% error in mode assignment at the edges
- This explains why most simple current to frequency relationships do not average for long periods of time, and are highly unstable

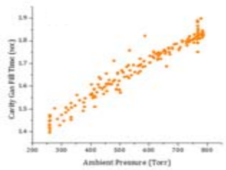


T & P SENSITIVITY COMPENSATION

Pressure sensitivity compensation

	CH_4 ppm
Santa Clara	1.962 ppm
Denver	1.964 ppm
Mauna Kea	1.968 ppm
Mount McKinley	1.970 ppm
Mount Everest	1.972 ppm

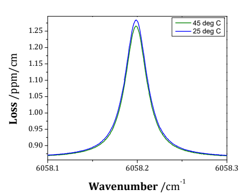




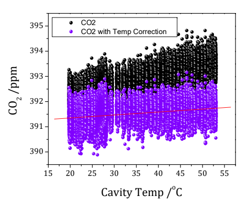
- Pressure has an effect of the measurement in this instrument.
- The pressure changes the optical path length within the cavity, so fluctuations within the cavity move the modes in frequency space, which can lead to smearing in frequency space and thus in loss of the feature adding to the noise of the instrument.

Temperature sensitivity compensation

- Ambient temperature will change the temperature of the gas going into the cavity, and hence the number of moles
- Also changes the statistical probability of molecules being in the particular excited state, tabulated in the Partition function



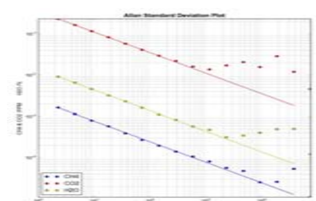
- A spectrogram of a H_2O line at 2 different temperatures
- The line changes because of collisional broadening and the Doppler width



	Performance w/o empirical correction	Performance with Correction
CH_4	0.22 ppb/°C	0.04 ppb/°C
CO_2	35 ppb/°C	10 ppb/°C
H_2O	12 ppm/°C	3 ppb/°C

RESULTS

Analyzer Stability and Drift – Allan Standard Deviation



- With all of these corrections in place, measurements yielded are extremely stable and even to the acceptable ambient monitoring precisions
- Long-term stability of instrument is due to pressure and temperature compensation through models
- Short-term drift is completely negligible allowing for no calibration to be done throughout experiment
- High precisions can be reached for CH_4 and CO_2

- Even though there is no pressure or temperature control, it is the extremely stable frequency axis that allows for these long averaging times
- With this stability it is easy to see that this instrument can be used continuously without calibration for measurements on the 1 ppb accuracy scale. This is extremely applicable to fast enhancements over ambient, including soil fluxes (shown Below) and fugitive emission quantification.

Ambient measurements