Enabling Continuous, Field-Based Isotope and Greenhouse Gas Measurements with WS-CRDS-based Analyzers

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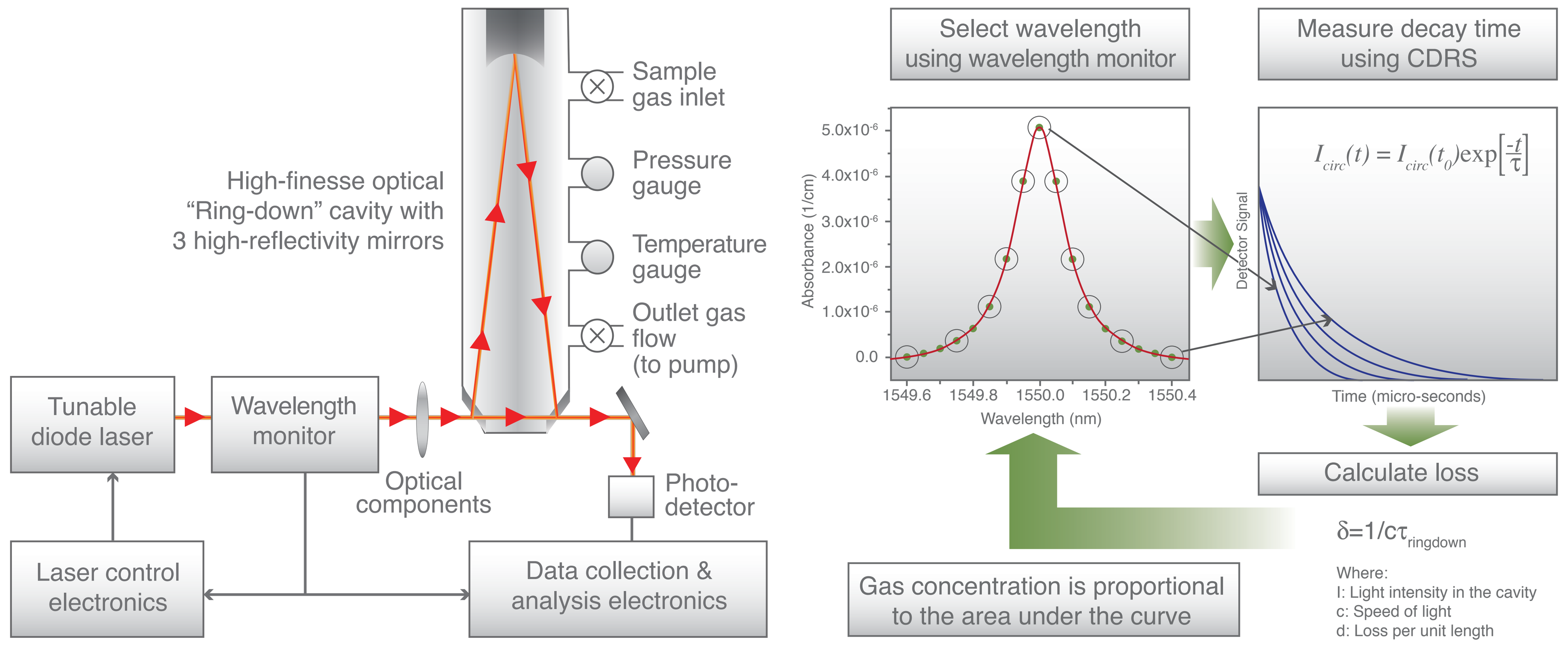
How can a measurement of time be used to quantify concentrations or isotope ratios?



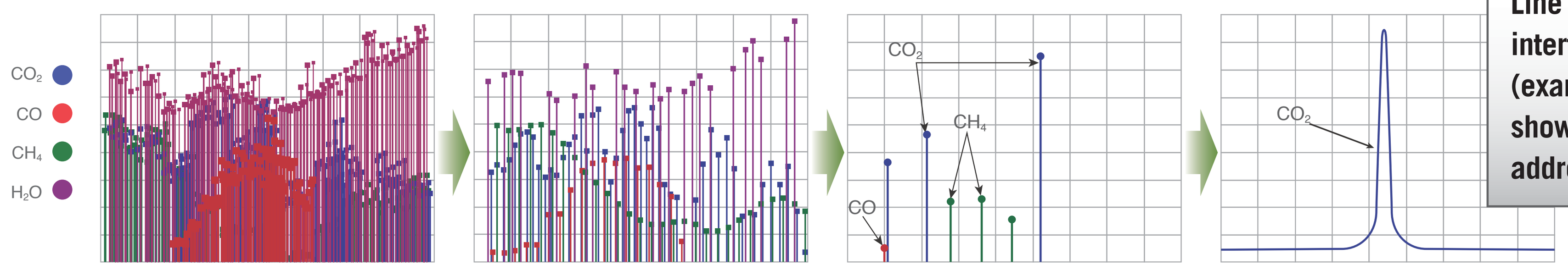
WS-CRDS analyzer schematic

Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS) – How it Works

- Light from a tunable semiconductor diode laser is directed into an optical resonator cavity containing the continuously-flowing analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- Light circulates in the cavity ~100,000 times, traveling >20km The high precision of WS-CRDS comes from this long interaction pathlength providing parts-per-trillion detection levels for some gases.
- The energy decays from the cavity (through a partially-reflective mirror) exponentially in time, or "rings down," with a characteristic decay time. This energy decay is measured, as a function of time, on a photodiode.
- The ring down time measurement is continuously repeated (>100 times per second) at several different well-controlled points in wavelength as the laser is tuned across the molecular signature of the analyte gas.
- WS-CRDS is a measurement of time not of absorbance. When the laser is at a wavelength where the gas in the cavity is strongly absorbing, the ring down time is short; when the wavelength is such that the gas does not absorb, the ring down time is long. WS-CRDS has complete immunity to laser noise since the laser is actually off during the measurement.
- The gas concentration or isotope ratio is determined by a multi-parameter fit to this lineshape (red curve) and is proportional to the area under the curve. The vertical axis is loss (or absorption, measured with cavity ring down); the horizontal axis is wavelength (measured with Picarro Wavelength meter)

Choosing a spectral line

Hundreds of lines for any given species are available for analysis (only need one line per species to measure its concentration). How do we choose which line to use?
Zooming in: choose the strongest possible molecular feature that is as free from interference as possible (example of CO_2 in ambient air).



Line may still have interferences. (example at right shows how WS-CRDS addresses this)

Use multiple lasers and wide-bandwidth optics to allow multi-species operation in a single analyzer.

What are the minimum requirements for high-stability spectroscopic measurements?

Accurate gas and isotope measurements require ***stable*** spectroscopic features.

In a given gas matrix, only two parameters affect the lineshapes of these features:

- **Temperature**
- **Pressure**

Tiny temperature and pressure instabilities cause BIG concentration errors!

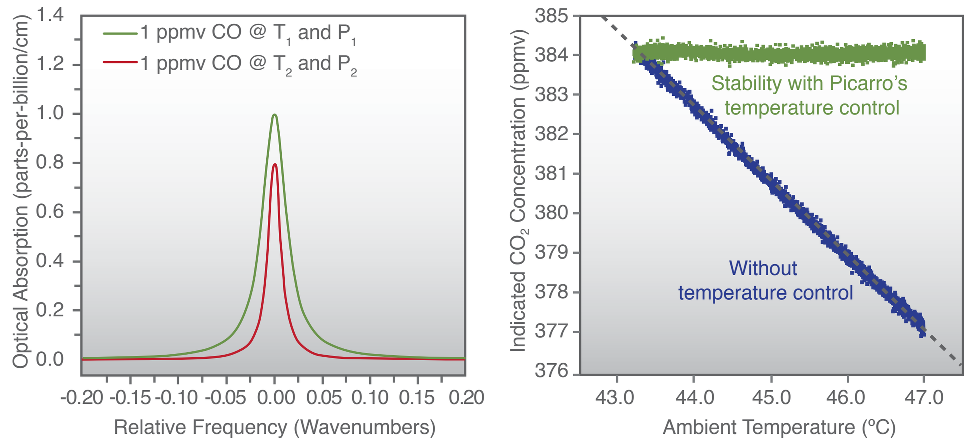
Once the spectroscopic feature is stable, measuring it accurately requires determination of its horizontal axis **(wavelength)** and vertical axis **(absorption)** with high-precision.

- Vertical axis precision given by wavelength monitor
- Horizontal axis precision given by long pathlength and inherent sensitivity of ring down measurement itself

Temperature & Pressure control

In the WS-CRDS analyzer, the temperature and pressure of the gas are also tightly controlled enabling virtually drift and calibration-free measurements over long periods of time.

- Temperature control to better than 1 part in 15,000
- Pressure control to better than 1 part in 1000



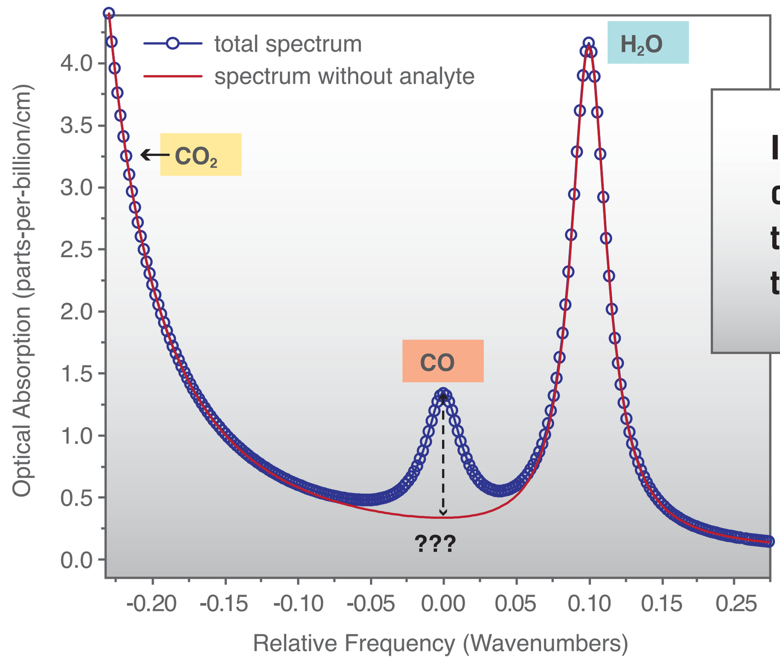
High-accuracy wavelength control – critical to accurate measurements

In an ideal world, there are no nearby interfering lines, so you could just measure the peak and the baseline to find concentration. But in the real world, interfering lines are everywhere

Measuring the peak is easy, but…

How do you measure the baseline under the peak?

In the real world:

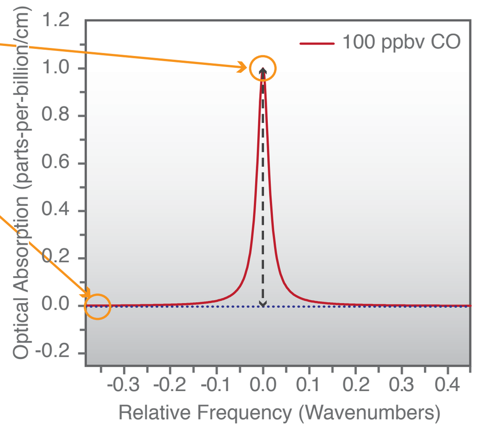


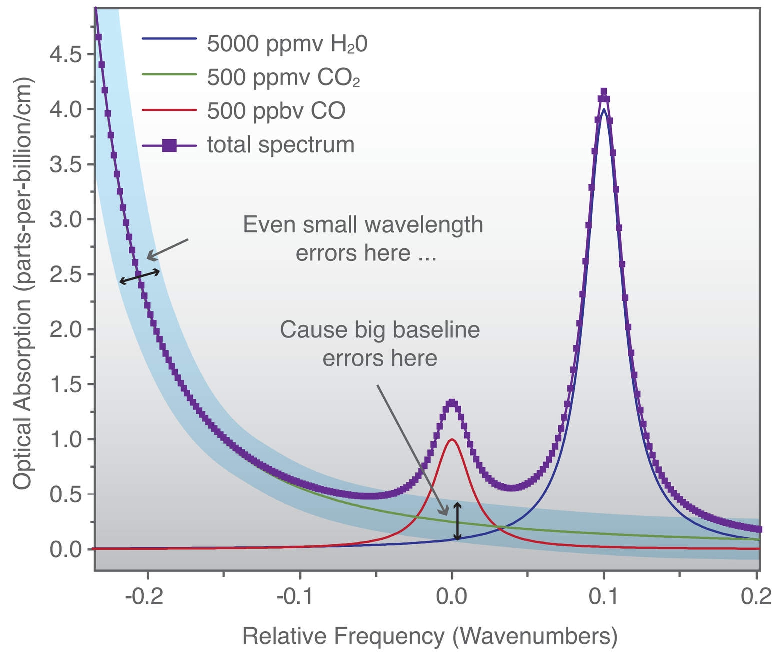
In the real world, you only get to measure the blue circles, not the red line

To measure the baseline under the CO peak, you can't move off resonance, because there is no spot in the spectrum that corresponds to the spectral baseline with ONLY the CO removed (the H_2O and CO_2 are still present). And you can't remove just the CO gas. What do you do?...

In an ideal world:

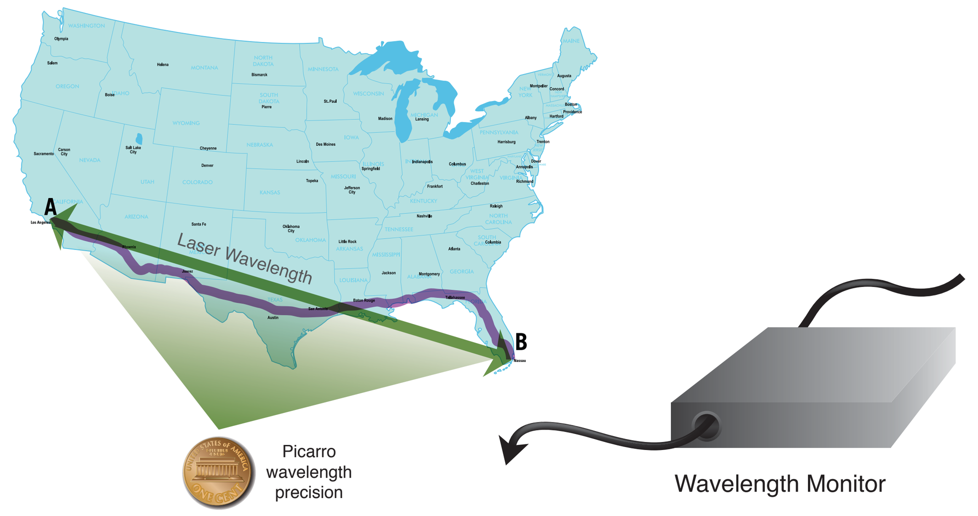
- Measure the peak height here (on-resonance)
- Measure the baseline here (off-resonance) or empty the cavity
- The concentration is proportional to the difference between peak and baseline





Use real-time nonlinear spectral analysis to **quantify** different constituents in the sample. Using the shape of each line, extrapolate the baseline under the analyte peak. ***This process requires a highly accurate wavelength monitor***

The Picarro wavelength monitor: Spectroscopic GPS



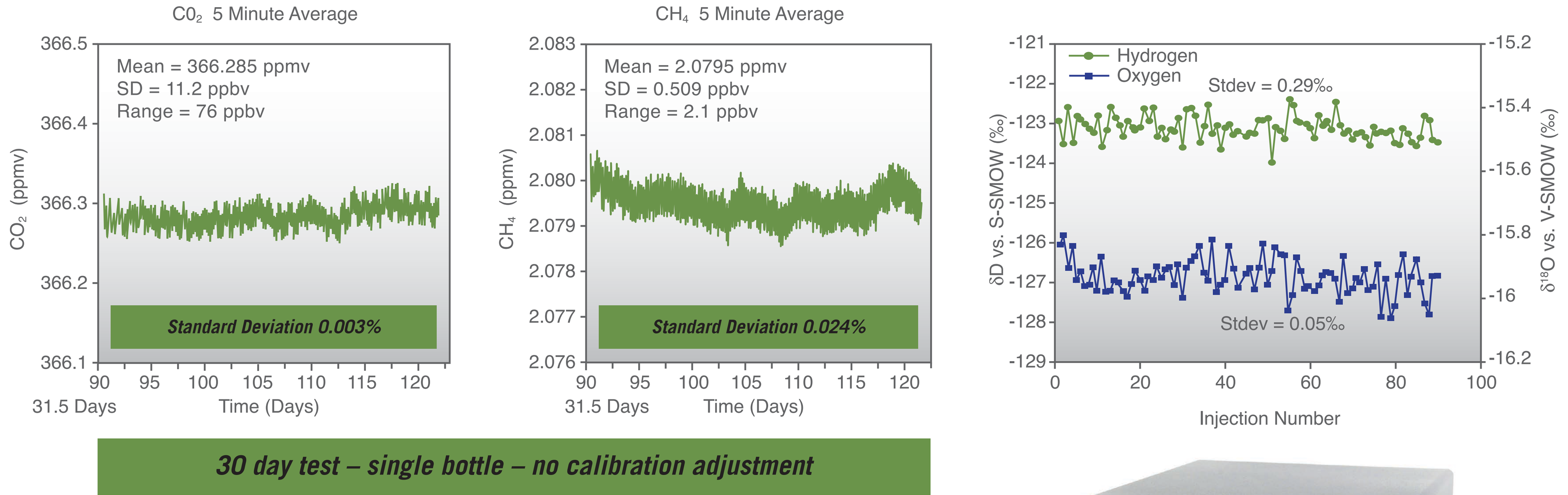
- Proprietary optical sensing technology
- Broadband, fiber-coupled device
- Stabilized to environmental fluctuations
- Precision of 8 femtometers in the near infrared
- 8 femtometers compared to the laser wavelength is like comparing the size of a penny to the width of the US!

A key feature of the WS-CRDS analyzer is the wavelength monitor which allows the wavelength of the laser to be precisely controlled and positioned accurately along the absorption profile of the molecule. This enables fast data acquisition as the entire peak profile does not need to be measured. Further, this wavelength certainty ensures that the system is interrogating the molecule of interest and not a nearby absorption peak of an interfering species.

All instruments undergo field ruggedness testing:

- **MIL-STD810F bench-handling on three axes, 20 drops from 4" height onto a hard surface**
- **0.5g vibration, 15 minutes, 2 axes**
- **Operational temperature cycling, 5°– 45°C**
- **Non-operational hot/cold extreme temperature soaks and start-up testing**
- **>1 week operational burn-in testing**
- **100% performance testing for all key specifications**

High-precision, high-stability data



The precision and long-term stability of these greenhouse gas and isotope measurements is afforded by the temperature, pressure and wavelength control systems of the WS-CRDS analyzers.

Conclusion:

This WS-CRDS technology has been pivotal in developing gas an isotope analyzers capable of being deployed in the field, unattended, for long periods of time, enabling measurements to be done more simply, at lower cost, by a greater number of scientists, moving information-rich, laboratory-quality measurements out of the lab. The combination of this technology and its validation has resulted in highly robust, easy to use instruments that provide highly sensitive and stable data even in challenging environmental conditions. No other gas or isotope analyzer has, to date, been demonstrated to achieve superior precision, accuracy and long-term stability in field conditions without calibration.