Measuring CO, CH_4, CO_2 & H_2O Simultaneously Using New CRDS Technology to Characterize Urban Plumes & the Well-Mixed Atmosphere

PICARRO

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Abstract

Cavity Ring-Down spectroscopy is becoming a gold standard for atmospheric monitoring. High sensitivity and precision coupled with low drift characteristics ensure optimal operation even in remote field stations or on aircraft and ships. However, current platforms have been limited to two or three species simultaneous observation. Research and development at Picarro have been focused on incorporating the fast optical switching and other technologies required to enable four or more species without compromising the precision and drift that make these instruments valuable to atmospheric scientists.

In addition to carbon dioxide and methane, carbon monoxide is widely recognized as an important tracer gas for characterizing anthropogenic emissions. The ability to take inventory of these three critical gases and quantify their sources and sinks is essential for understanding atmospheric change. We have developed a field-deployable analyzer which can measure all three greenhouse gases plus water simultaneously in a single device, while maintaining high levels of precision. The novel 4-species analyzer is able to measure carbon dioxide (CO_2) concentration to a precision (5 second, one sigma) of 150 parts-per-billion (ppb), methane (CH_4) concentration to a precision of 1 ppb, and carbon monoxide (CO) to a precision of 30 ppb.

Analyzer performance is guaranteed over a wide concentration range to allow precise atmospheric characterization in both well-mixed and urban environments. The ability to measure all four species simultaneously in a single instrument with automatic water correction simplifies data collection and enables precise measurements of the dynamic interplay of anthropogenic and biogenic emissions. The added ability to use the instrument for making measurements in the field, in labs, on manned & unmanned vehicles, including planes and ships, and in remote monitoring stations, greatly increases the quantity and quality of the data which can be obtained by a single researcher. Built-in networking capabilities coupled with guaranteed precision and drift specs enable the analyzer to easily integrate into any global network. Current application work using this instrument include: ground-based urban networks, remote atmospheric monitoring, mobile source identification, and flight-based atmospheric cross-sections.

Cavity Ring-Down Spectroscopy (CRDS)-How it works

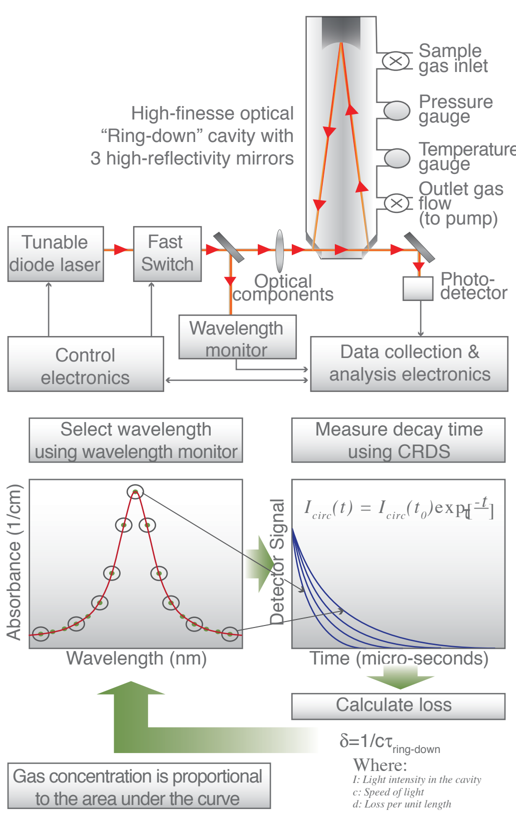

Fig. 1: Diagram of a Cavity Ring-Down Spectroscopy (CRDS) analyzer

1. Light from a tunable semiconductor diode laser is directed into a small (35cc) optical resonator cavity containing the analyte gas
2. When the light build-up in the cavity reaches the required intensity, the laser is shut off
3. Light circulates in the cavity ~100,000 times, traveling ~20 km or more. The high precision of CRDS comes from this incredibly long path length providing part-per-billion detection levels for all four gas species
4. The energy decays from the cavity, through loss mechanisms exponentially in time. This energy decay is measured, as a function of time, on the photodetector and is known as a "ring-down".
   - In an empty cavity, the only loss mechanisms are the mirrors and the ring-down time (the exponential decay time) is relatively long
   - When gas sample species are present, the ro-vibrational modes provide additional loss mechanisms and the ring-down times get relatively shorter, proportional to gas concentration
5. The ring-down time measurement is continuously repeated (~100 times/sec) at several different well-controlled points in wavelength as the laser is tuned across the molecular signature of the analyte gas
6. The ring-down profiles are transformed into an absorption curve with a well-defined lineshape
7. The gas concentration of each species is determined by a multiparameter-fit to the lineshape (shown as a red curve on the left) and are proportional to the area under the curve
8. Picarro's patented wavelength monitor controls the laser position with high-accuracy, ensuring the measurement is independent of potentially interfering gas species
9. Importantly, CRDS is a measurement of time not absorbance and so offers unmatched precision
10. CRDS has complete immunity to laser noise since the laser is shut off during the measurement, thereby offering significantly better sensitivity than other laser techniques

Four Species Measurement from the Ground

Fig 2: Ambient air measurements were made by a Picarro G2401 from the Picarro roof sampling line (Picarro location shown to right as 'A)'. The CO and CO_2 concentration data is shown below show spikes during commuting hours. Wind direction during that time period was West, bringing in air

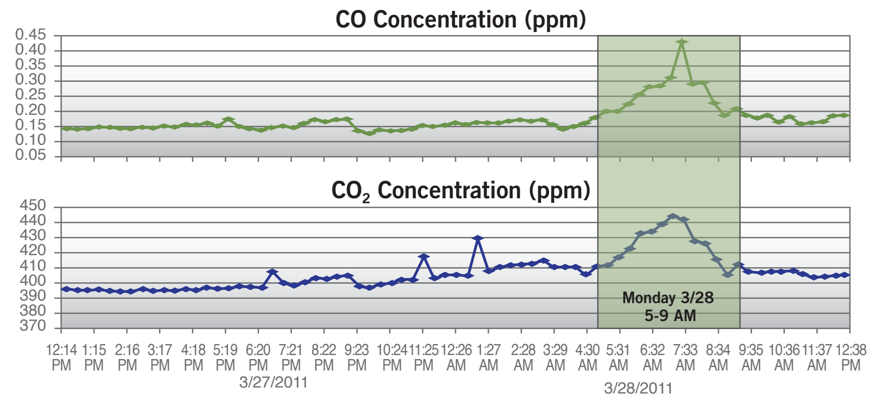

Fig 3: CO and CO_2 concentration data measured from the Picarro roof using G2401.

Instrument Performance Specifications In Dry Air

	CO_2	CO	CH_4	H_2C
Precision 5 sec, 1-σ 5 min, 1-σ	< 150 ppb < 50 ppb	< 30 ppb < 2 ppb	< 1 ppb < 0.7 ppb	< 200 ppm < 50 ppm
Max Drift at STP 24 hrs 1 month *(peak-to peak, 50-min. avg.)*	< 150 ppb < 500 ppb	< 15 ppb < 50 ppb	< 1 ppb < 3 ppb	< 100 ppm + 5 % of reading
Max Uncertainty Using Reference Gas* 1 hr, 2-σ *(peak-to peak, 50-min. avg.)*	< 50 ppb	< 2 ppb	< 1 ppb	n/a

Reference Gas Method

The reference gas method Picarro is currently using is designed to track & correct any CO drift such that the WMO max uncertainty spec is guaranteed to be met. The reference gas does not have to be a standard gas, it just needs to have a known concentration of CO, and could just be compressed air. It is recommended that the reference gas be measured for five minutes every 15 minutes (total of 15 minutes/hour). This is just one potential reference gas scheme that has been tested by Picarro on all four species instruments. Depending on individual analyzer performance, levels of CO being measured , sample humidity, and the research precision requirements, less frequent reference gas measurements may work equally well. Researchers are encouraged to try their own methodology to find what works best for their unique research setting.

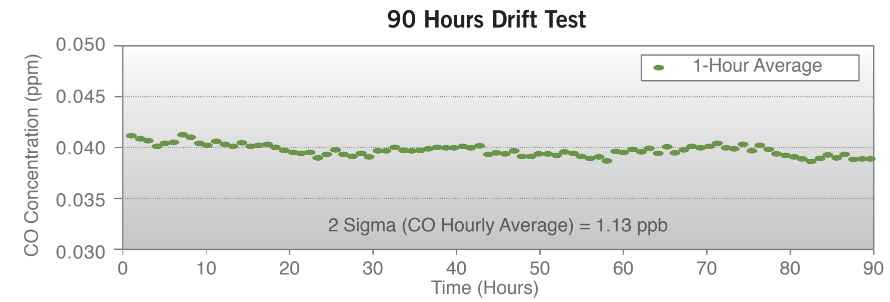

Fig 4: A 90 Hour drift test on the G2401. Hourly averages of CO measurement from a gas bottle are shown. The 5 min reference gas method was used during this period and the correction was applied. The Resulting 2-sigma of the hourly averages was 1.13 ppb for CO. This shows the capability of the instrument to meet the WMO max uncertainty specification.

Flight Simulation Test

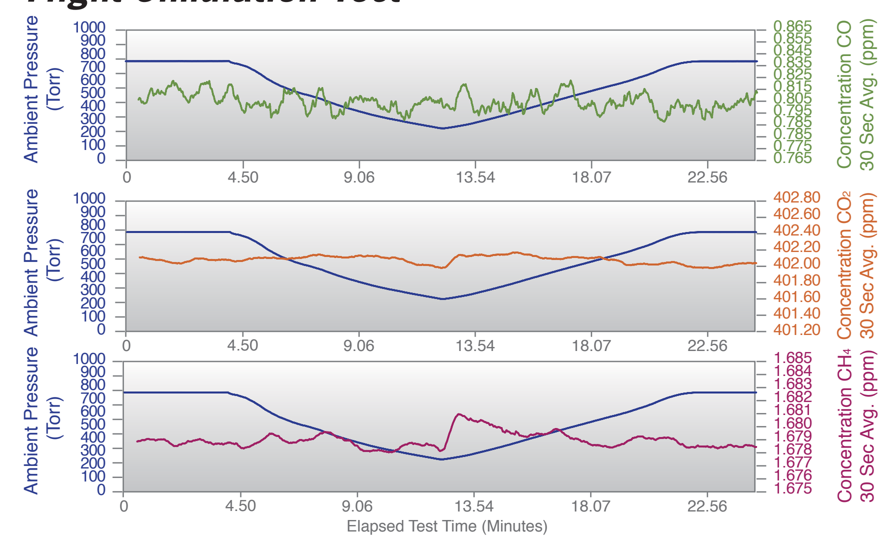

Fig 5: Picarro pressure tests all flight analyzers in a hyperbaric chamber to guarantee performance at altitude. During the test, the chamber pressure cycles between 760 to 250 Torr as the analyzer measures a constant-concentration gas stream delivered at the same pressure as the hyperbaric chamber. Pressure test results for CO, CO_2 and CH_4 of an actual production analyzer are shown.

Flight Performance Specifications

	CO_2	CO	CH_4	H_2C
Precision 30 sec, 1-σ 20 Hz vibration, 1g	< 200 ppb	< 30 ppb	< 2 ppb	< 150 ppm
Max Drift at STP 24 hrs 1 month *(peak-to peak, 50-min. avg.)*	< 200 ppb	< 15 ppb	< 1.5 ppb	< 100 ppm + 5 % of reading
Max Drift with Δ P *(peak-to peak, 30-min. avg.)* Up to 1.4 Torr/sec	< 700 ppb	< 50 ppb	< 7.5 ppb	n/a
Max Drift with Δ T *(peak-to peak, 30-min. avg.)* 15 ºC/Hr for 3 Hrs	< 7.5 ppb / ºC	< 1.5 ppb / ºC	< 0.05 ppb / ºC	n/a