

Ultra-Sensitive Measurements of Methane and Carbon Dioxide Help Scientists Track Atmospheric Greenhouse Gas Concentrations

Human activity, primarily fossil fuel use, is adding roughly 3 ppm/yr of CO₂ to the atmosphere and this increase in atmospheric CO₂ concentrations is driving global climate change. Terrestrial ecosystems act as both natural sources and sinks for atmospheric carbon, as shown in Figure 1, but the mechanisms by which carbon is absorbed from and released into the atmosphere are not well understood. Without the ability to determine the regional sources and sinks of CO₂, it is difficult to predict future atmospheric carbon levels and to understand the effect of these elevated carbon levels on the global and regional climates.

Researchers investigating global climate change need extremely precise and accurate measurements of greenhouse gases (principally CO₂ and CH₄) to develop better models of the carbon cycle. Because the net change in the atmospheric carbon dioxide and methane levels is typically very small (typically a small percentage of their nominal concentration levels), these measurements must be made with extraordinary accuracy, not only over time, but across the network from analyser to analyser, and even from network to network, to ensure that a reliable and complete picture of the carbon cycle is obtained. Existing atmospheric monitors, based on non-dispersive infrared (NDIR) sensors, fall short of the requirements for these measurements in several ways: they have a nonlinear response to the target gas, they have an undesirable cross-sensitivity to water vapour concentration, and they are susceptible to drift over time and temperature.

Substantial sample conditioning and data post-processing are needed to obtain meaningful results, in addition to frequent (hourly) instrument calibration using expensive gas standards at each monitoring site. Many cannot easily be simultaneously calibrated across different geographic measurement sites to the level of accuracy required for use in so-called "atmospheric inversion" studies – a common analytical technique used by the atmospheric monitoring community to examine changes in the atmosphere based on measurements made at only a small number of individual monitoring sites.

In response to this need for better instrumentation, a new gas analyser has been designed, based on a novel technology called Cavity RingDown Spectroscopy (CRDS). The ultra-high accuracy and low drift afforded by all-optical CRDS technology makes it ideally suited to the demands presented by atmospheric inversion studies. CRDS has three distinguishing features which separate it from other optical techniques like NDIR. First, CRDS provides a very long interaction path length between the sample and optical probe, enhancing its sensitivity over conventional absorption techniques like Fourier Transform Infrared Spectroscopy (FTIR) and NDIR. In this implementation of CRDS, the analyser utilises an ultra-high finesse, 3-mirror optical cavity that yields a cavity lifetime of ~40 μs, equivalent to an optical path length of ~12 km.

The second distinguishing feature of CRDS is the way in which the optical loss is measured. In conventional optical absorption spectroscopy, light intensity is measured before and after the sample. In contrast, loss measurements in CRDS are essentially measurements of time, not intensity, and thus are insensitive to fluctuations in the power of the light source.

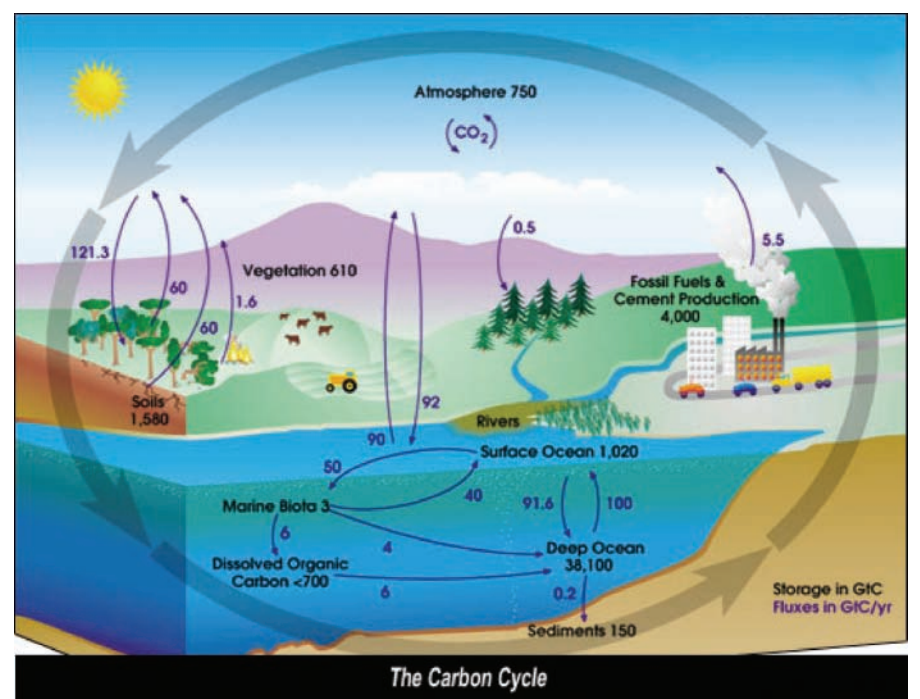


Figure 1. Global carbon cycle.

The third advantageous feature of CRDS is its ability to isolate a single spectral feature. The analyser has a measurement resolution of 0.0001 cm⁻¹ compared to a resolution of ~0.5 cm⁻¹ in a typical FTIR – an improvement of ~5000 times. This is due its ability to operate at an internal gas pressure of 50 to 150 Torr. At this pressure, spectral absorption features are substantially narrower than at atmospheric pressure, and can more easily be resolved from each other. The ability to utilise a single absorption feature ensures that the peak height or area is linearly proportional to the concentration, dramatically increasing the probability that an absorption feature of the species of interest can be isolated from that of any interfering species. The extremely high spectral resolution provided by CRDS also simplifies the corrections necessary for any interfering species that do occur, further increasing the sensitivity, accuracy and precision of the analyser.

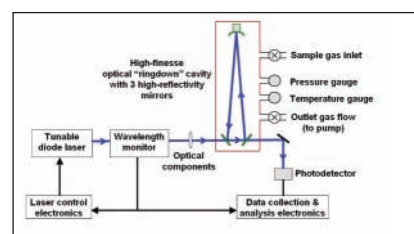


Figure 2. Schematic of CRDS analyser showing optical cavity and sample gas flow.

The essential CRDS measurement consists of determining the decay time of light in an optical cavity filled with the gas stream to be analysed, as shown in Figure 2. Light from a semiconductor diode laser is directed into a high finesse optical resonator cavity containing the 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. The light circulating in the cavity then decays from the cavity, or "rings down," with a characteristic decay time. The ringdown time is measured as a function of laser wavelength – when the gas in the cavity is strongly absorbing, the ringdown time is short; when the gas does not absorb, the ringdown time is long. Said another way, when the wavelength of the injected light does not match an absorption feature of any gas in the cavity, the decay time is dominated by mirror loss. However, when the wavelength of the injected light is resonant with an absorption feature of a species in the cavity, the decay time decreases as the reciprocal of the species concentration. Again, a key advantage of CRDS, particularly with respect to measurement noise, is that a high-quality time measurement is much easier to achieve than a good absolute or relative determination of light intensity. Figure 3 shows a profile of the light intensity as a function of time in a CRDS cavity.

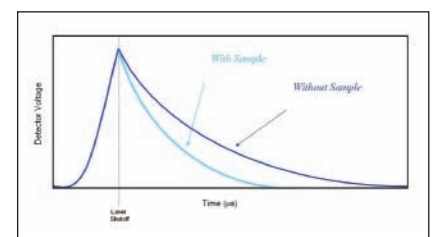


Figure 3. Light intensity as a function of time in a CRDS system with and without a sample having resonant absorbance. This demonstrates how optical loss is rendered into a time measurement in CRDS.

The CRDS technology can be easily adapted to measure a wide variety of gas species, including gases composed of trace

isotopes. Figure 4 shows an example of an isotopic measurement, in which the extremely high spectral resolution of the analyser is evident.

The analyser utilises a high precision, inline wavelength monitor that enables it to set the laser wavelength precisely, thereby maximising the instrument's selectivity. With this level of wavelength control, isolation of individual spectral features is possible, enabling accuracy without intra-species interference even for complex gas streams, and eliminating one of the key underlying causes for most other instruments to require recalibration. The in-line, high-precision optical wavelength monitor enables extremely detailed spectral scans that cannot be done using NDIR.

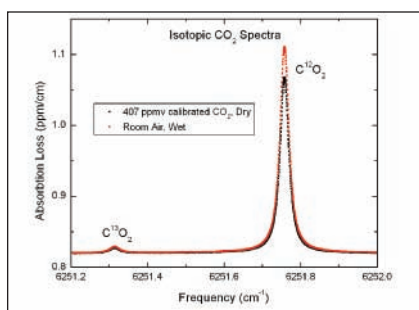


Figure 4. CO₂ spectrum taken by CRDS analyser showing the extremely high measurement resolution (0.0001 cm⁻¹) used in analysers designed to measure isotopic ratios of carbon in CO₂ and CH₄.

The instrument's electronics include a digital signal processing system for determination of the ringdown rate, or optical loss, as a function of wavelength, giving it the speed to measure multiple spectral features, accurately detect multiple species, and provide concentration results at high repetition rates of up to 10 Hz. The data measurement interval is ~6ms and a typical spectrum consists of ~10-100 spectral points.

The analyser maintains temperature control of better than 1 part in 3000, and pressure control better than 1 part in 500. Accurate and reproducible temperature and pressure control are critical factors for analyser accuracy, precision, and long term stability without human interaction.

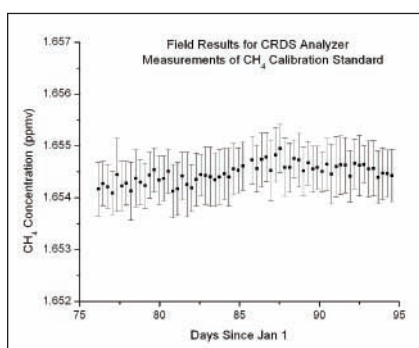


Figure 5. CH₄ calibration gas measurements from a CRDS analyser in the field. CH₄, CO₂ and H₂O are continuously monitored and calibration gases are measured daily. Analyser performance over 18 days of operation in the field: precision = 0.5 ppbv in 5 seconds, drift = 0.8 ppbv (peak to peak) or 0.05% per day.

Field trials were recently carried out in North America at Pennsylvania State University and at the National Oceanic and Atmospheric Administration (NOAA) on this newly-available CRDS analyser, capable of performing high-precision measurements of CO₂ and H₂O. The analyser is designed so that it does not require frequent calibration; it maintains high linearity, precision, and accuracy for many months, over changing environmental conditions, requiring little or no sample preparation. In addition, another recently-developed, CRDS-based analyser, which simultaneously

measures three different molecular species, CO₂, CH₄, and H₂O, has also been evaluated by NOAA. Figure 5 shows results from similar tests at Oregon State University.

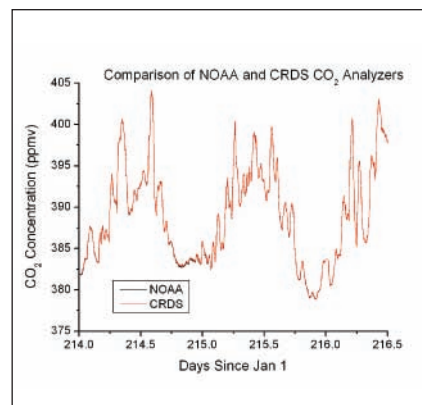


Figure 6. NOAA field trial results from the CRDS analyser and enhanced "gold standard" NDIR-based CO₂ analyser over a 45 day period. Average difference is 180 ppbv (1-σ). The CRDS analyser sampled unconditioned gas and drifted 0.8 ppbv/day.

At NOAA the analyser was co-located with an enhanced NDIR CO₂ inversion monitor. Figure 6 shows a 45-day period where the analyser (red trace) and enhanced NDIR (black trace) were operated side-by-side at NOAA. The average difference between the outputs from the two analysers is 180 ppbv (1-σ), and the analyser demonstrated a drift of 0.8 ppbv/day. This represents a drift of only 0.0002% over one day, and 0.045% over 45 days. The most exceptional aspect of this result is that the analyser received only one calibration for CO₂ and water vapour at the end of the trial, and it was not necessary to condition the gas stream in any way. In contrast, the enhanced NDIR CO₂ inversion monitor was calibrated every five hours, and required extensive sample conditioning including removal of water vapour from the gas stream and temperature stabilisation.

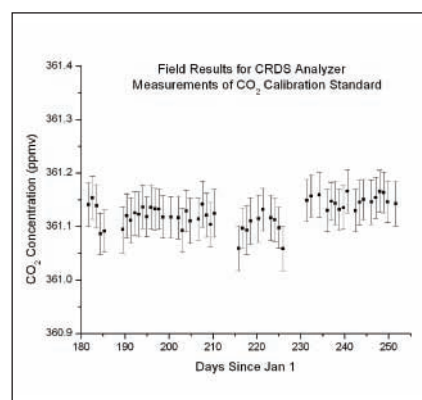


Figure 7. Calibration gas measurements from CRDS analyser located on a measurement tower in Centerville, Iowa. CO₂ and H₂O are continuously monitored and calibration gases are measured every 20 hours.

These CRDS instruments are designed to measure atmospheric CO₂ for atmospheric inversion studies. Five of these analysers were recently deployed as part of the North American Carbon Program's Mid-continental Intensive Regional Study Network, consisting of five communications-tower-based atmospheric CO₂ measurement stations located in the upper Mid-West US. A primary goal of this 18-month project is to increase the density of regional atmospheric CO₂ data. Doing so will enable atmospheric inversion data to provide well-constrained regional ecosystem carbon flux estimates. Additionally, by increasing the density of measurement sites, the correlation between increased data density and resulting increase in accuracy of the inversion-derived flux estimates can be

determined quantitatively using field observations, thus providing guidance to future observational network designs. Figure 7 shows data from one of the tower-based sites.

Field deployment of the CRDS analysers has begun. Results indicate that they meet or exceed the requirements of the atmospheric inversion application, and they do so without the need for sample conditioning. The analysers maintain their calibration for extended periods of time, reducing the need for calibration, dramatically reducing maintenance costs. The field results indicate that the extreme accuracy and stability of the analysers could significantly reduce calibration and maintenance costs and facilitate networked deployment.

For atmospheric inversion studies, the CRDS analyser produces a precision of better than 0.20 parts-per-million volume (ppmv) for CO₂, 1 part-per-billion volume (ppbv) for CH₄, and 100 ppmv for H₂O with a total measurement time of five seconds. Certainly, as this technology gains acceptance within the environmental monitoring community, users will demand higher data rates, increased precision and accuracy beyond current standards, and analysers which measure multiple gas species in addition to those mentioned here. Work on these new analysers is underway as instrument manufacturers continue to anticipate the needs of atmospheric monitoring networks just coming online.

AUTHOR DETAILS

Aaron Van Pelt

Marketing Engineer

Picarro Inc.

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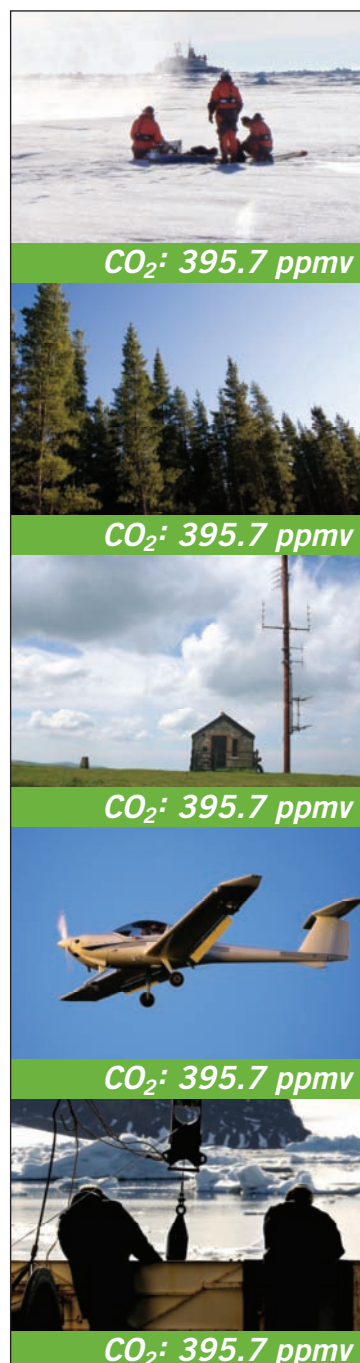
480 Oakmead Pkwy.

Sunnyvale, CA 94085

avanpelt@picarro.com

direct: 408-962-3919

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