Real-Time Atmospheric Monitoring of Stable Isotopes and Trace Greenhouse Gases

Human activity, primarily fossil fuel use, is adding roughly 3 ppm/yr of CO_2 to the atmosphere and this increase in atmospheric CO_2 concentrations is driving global climate change. Terrestrial ecosystems act as both natural sources and sinks for atmospheric carbon, but the mechanisms by which carbon is absorbed from and released into the atmosphere are not well understood. In addition, a recent report of the Intergovernmental Panel on Climate Change, an international assemblage of scientists commissioned by the United Nations to assess the scientific, technical, and socioeconomic information relevant to the understanding of the risk of human-induced climate change, and whose members won the 2007 Nobel Peace Prize, concludes that: "There is new and stronger evidence that most of the warming observed over the last 50 years is attributable to human activities." Without the ability to determine the regional sources and sinks of CO_2, 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 measure-ments of greenhouse gases (principally CO_2 and CH_4, including the stable isotopes of carbon) 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 analyzer to analyzer, 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 measure-ments in several ways: they have a nonlinear response to the target gas, they have an undesirable cross-sensitivity to water vapor 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 analyzers cannot 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 analyzer has been designed, based on a novel technology called Cavity Ring Down 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. 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 analyzer utilizes an ultra-high finesse, 3-mirror optical cavity that yields a ring down time 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 spectro-scopy, 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.

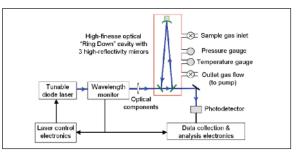The third advantageous feature of CRDS is its ability to

Figure 1. Schematic of CRDS analyzer showing optical cavity and sample gas flow.

isolate a single spectral feature. The analyzer 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 to 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 utilize a single absorption feature ensures that the peak height or area is linearly proportional to the concentration, and dramatically increases 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 analyzer.

The essential CRDS measurement consists of determining the decay time of light in an optical cavity filled with the gas stream to be analyzed, as shown in *Figure 1*. 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 Ring Down time is measured as a function of laser wavelength – when the gas in the cavity is strongly absorbing, the Ring Down time is short; when the gas does not absorb, the Ring Down 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 2* shows a profile of the light intensity as a function of time in a CRDS cavity.

The analyzer utilizes a high precision, inline wavelength monitor that enables it to set the laser wavelength precisely, thereby maximizing 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.

The instrument's electronics include a digital signal processing system for determination of the Ring Down 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 over 10 Hz. The data measurement interval is ~6ms and a typical spectrum consists of ~10-100 spectral points.
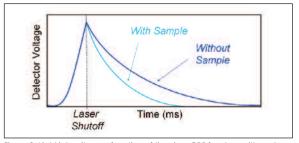

Figure 2. Light intensity as a function of time in a CRDS system with and without a sample having resonant absorbance. This demonstrates how optical loss (or absorption by the gas) is rendered into a time measurement in CRDS.
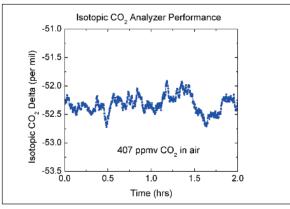
Figure 3. Typical data taken with the isotopic CO_2 analyzer showing 0.15 per mil precision over 2 hours (expressed as $\delta^{13}C$ with a 5-minute measurement interval, measured at a constant CO_2 concentration with a constant isotopic ratio).
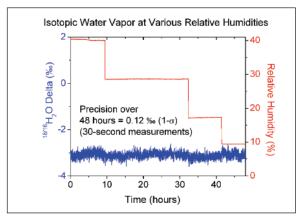

Figure 4. Typical data taken with isotopic water analyzer showing the insensitivity of the isotopic ratio of $^{18/16}O$ (expressed here in units of $\delta^{18}O$) to changes in relative humidity.
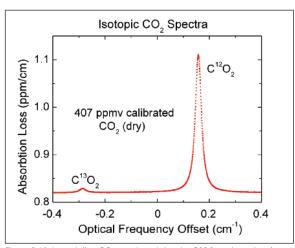

Figure 5. High-resolution CO_2 spectrum taken by CRDS analyzer showing the extremely high measurement resolution (0.0001 cm-1) used in analyzers measuring isotopic ratios of carbon in CO_2.

The analyzer maintains temperature control of better than 1 part in 30,000, and pressure control better than 1 part in 500. Accurate and reproducible temperature and pressure control are critical factors for analyzer accuracy, precision and long term stability without human interaction.

The CRDS technology has easily been adapted to measure a wide variety of gas species, including gases composed of trace isotopes. Scientists have recently begun to use the analyzers to make real-time, continuous measurements of the isotopic ratios in atmospheric gases including CO_2 and water vapor, such as those shown in *Figures 3 and 4*. For example, a measurement of the changing ratios of the two carbon isotopes (^{12}C and ^{13}C) in CO_2 enables the carbon cycle of a given ecosystem to be studied since all plants are somewhat less efficient in absorbing CO_2 containing the heavier isotope (^{13}C). Different plants discriminate to varying degrees on the basis of this isotopic composition in CO_2 and so the sources and sinks of CO_2 can be characterized via such isotopic measurements. Similarly, isotopes of oxygen and hydrogen/deuterium in water are also differentially respired by plants, allowing similar studies to be carried out on the water cycle. *Figures 5 and 6* show examples of the spectra used in these isotopic measurements. The extremely high spectral resolution of the analyzer is evident

– and necessary – enabling it to discriminate between closely-spaced spectral lines arising from different isotopic compositions in the sample gas. Recently, micrometeorological and stable isotope techniques have been combined to study biosphere-atmosphere exchange processes in ecosystems and are increasingly being used to address challenging problems including identification of the primary components of net carbon and water fluxes to help evaluate their response to climate variations and land use change.

Field trials were recently carried out in the US at Pennsylvania State University and at the National Oceanic and Atmospheric Administration (NOAA) on this newly-available CRDS analyzer, capable of performing high-precision measurements of CO_2 and H_2O. The analyzer 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 analyzer, which simultaneously measures three different molecular species, CO_2, CH_4, and H_2O, has also been evaluated by NOAA. *Figure 7* shows results from similar tests at Oregon State University.

At NOAA the analyzer was co-located with an enhanced NDIR CO_2 monitor. The analyzers were operated side-by-side over a 45-day period at NOAA.The average difference between the outputs from the two analyzers was 180 ppbv (1-σ), and the CRDS analyzer 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 analyzer received only one calibration for CO_2 and water vapor over the course of the trial, and it was not necessary to condition the gas stream in any way. In contrast, the enhanced NDIR CO_2 inversion monitor was calibrated every four hours, and required extensive sample conditioning including removal of water vapor from the gas stream and temperature stabilization. The CRDS analyzer demonstrated a precision of better than 50 ppbv for CO_2, and 100 ppmv for H_2O with a total measurement time of 3 seconds.

These CRDS instruments are designed to measure atmospheric CO_2 for atmospheric inversion studies. Five of these analyzers 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 CO_2 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 CO_2 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 8* shows data from one of the tower-based sites.

Field results indicate that the CRDS analyzers meet or exceed the requirements of the atmospheric inversion application, and they do so without the need for sample conditioning. The analyzers maintain their calibration for extended periods of time, reducing the need for calibration and dramatically reducing maintenance costs. The extreme accuracy and stability of the analyzers is certain to facilitate their deployment in networks.
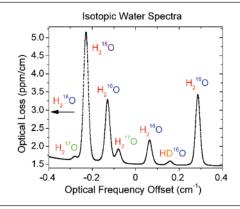

Figure 6. High-resolution spectrum taken by CRDS analyzer measuring isotopic ratios in water. This region of the spectrum contains all of the relevant water isotopologues.
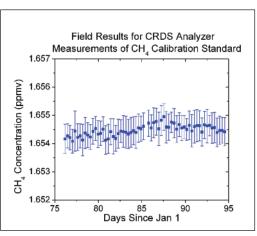

Figure 7. CH_4 calibration gas measurements from a CRDS analyzer in the field. CH_4, CO_2 and H_2O are continuously monitored and calibration gases are measured daily. Analyzer performance over 18 days of operation in the field: precision = 0.5 ppbv in 5 seconds, drift = 0.8 ppbv (peak to peak) or 0.05% per day.
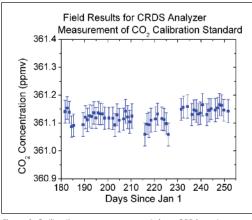

Figure 8. Calibration gas measurements from CRDS analyzer located on a measurement tower in Centerville, Iowa. CO_2 and H_2O are continuously monitored and calibration gases are measured every 20 hours.

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