WS-CRDS – A Universal Instrument for Precision Measurement of GHGs

Summary. Picarro WS-CRDS-based analyzers are the first GHG monitoring instruments to combine simple, turnkey operation with sensitivity and precision at the parts per billion level, no interference between gas components, and very low drift. Able to simultaneously measure multiple components directly from real air samples with no special preparation, their unique combination of state-of-the-art performance, high speed (seconds), and rugged simplicity makes WS-CRDS instruments ideal for global/local atmospheric monitoring applications and connected enterprises and specific emissions flux measurements.

Introduction

Global surface temperatures are predicted to increase 1.4°C to 5.8°C over the period from 1990 to 2110, which is a rate of warming unprecedented during the past 10,000 years. In order to limit this global warming and its potential catastrophic consequences, levels of carbon dioxide and other greenhouse gases (GHGs) will have to be regulated and reduced as never before. This creates a huge and diverse monitoring challenge, including the need for regional and global field monitoring networks, and direct monitoring of GHGs at sources (e.g. power plants, landfills) and sinks (e.g. geo-sequestration sites). It also requires ongoing laboratory analysis and climate modeling studies, and R&D efforts targeted at "greener" combustion technologies. This article describes a relatively new type of trace gas analyzer based on WS-CRDS (Wavelength-Scanned Cavity Ring Down Spectroscopy) that is ideal for all these applications, with a combination of speed (up to 10 Hz), precision, sensitivity, dynamic range, specificity, and the ability to simultaneously measure multiple gases (e.g., CO_2, CH_4, and H_2O) with a single compact instrument. In contrast to other GHG monitoring methods, the low drift and fully automated operation of these rugged WS-CRDS instruments means the very same instruments now used in world-leading research labs can be operated in the field by semi-skilled technicians, and also used in unattended monitoring applications with intervals of weeks and even months between re-calibration. This aspect offers numerous practical benefits, including minimizing the cost impact of implementing comprehensive GHG monitoring. This paper explains all the various advantages of WS-CRDS, and discusses some specific current applications and challenging site installations, as well as newly emerging applications.

WS-CRDS Background

Nearly every small molecule (e.g., CO_2, H_2O, CH_4) has a unique near-infrared absorption spectrum consisting of sharp well-resolved lines. So in theory, the concentration of a specific molecular species can be determined simply by accurately measuring the intensity of one or more of these absorption lines from an accurately determined quantity of sampled air or exhaust gas matrix. However, conventional optical instruments, including spectrometers, NDIR (non-dispersive infrared) monitors and even absorption monitors based on TDL (tunable diode lasers) don't have the requisite combination of spectral resolution, sensitivity, large linear dynamic range and low drift that is necessary to use this spectral information to measure GHGs in many real-world applications, particularly those involving remote locations. Fortunately, WS-CRDS has none of these limitations and also provides several other advantages, including speed, simplicity, long-term stability and a small footprint – see figure 1.

Figure 1. Picarro GHG analyzers are compact, rugged and unaffected by harsh operating conditions.

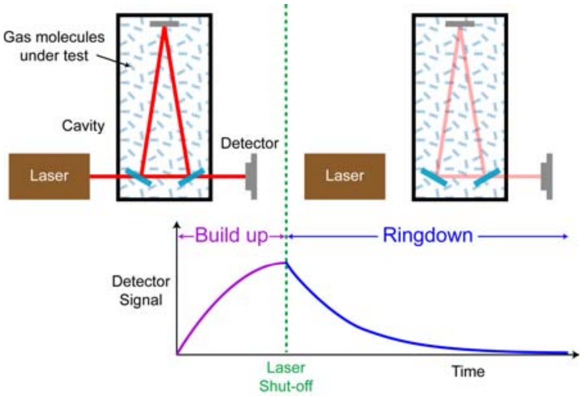

Figure 2. The basic principles of WS-CRDS. Light from a tunable laser is trapped in a three-mirror cavity. When the laser is turned off the ring down time for the light to decay is faster if the cavity contains molecules that absorb at the laser wavelength.

In WS-CRDS, light from a narrow-linewidth, wavelength-tunable laser diode enters the sampling cavity which contains three exceptionally high reflectivity (>99.999%)

mirrors, – see figure 2. This cavity is automatically and precisely temperature and pressure stabilized. When the signal from the detector reaches a steady state condition, the laser is switched off. Because the mirrors do not have 100% reflectivity, the light intensity inside the cavity slowly leaks out and this ring-down (decay) is followed in real-time by a quantitative photodetector. If the cavity contains a gas species that absorbs even weakly, this introduces a second light loss mechanism. This results in a shortened decay time, which forms the basis for a highly quantitative measurement of absorption and hence gas concentration.

The Advantages of WS-CRDS

Sensitivity and Speed

The key to sensitive measurements in any analytical instrument is a high signal-to-noise ratio, through either a high signal and/or low noise. WS-CRDS provides both. Even with a cavity of only 25 cm in length, the average path length that any photon effectively travels within the WS-CRDS cavity can be over 20 kilometers, thus giving rise to much higher signal levels than other optical techniques. And, because WS-CRDS measures decay rates, rather than transmitted (absorbed) intensity, shot noise from fluctuations in the laser intensity or detector response have no effect on the measurement, unlike conventional spectrometers and gas analyzers based on intensity measurements. Thus, instrument noise is inherently very low. Additionally, because the laser wavelength is systematically scanned over the target absorption line during each measurement cycle, the area and peak intensity of the line are very accurately determined. (Up to 10 points are typically measured across each target absorption line). Just as important, the baseline is also continuously scanned at multiple points. The end result is sensitivity in the ppbv range, even pptv for some gases, with up to six orders of magnitude linear dynamic range. The high signal-to-noise of WS-CRDS also enables real-time data acquisition (in contrast to say gas chromatography) and the option of data rates as high as 10 Hz. Indeed the signal-to-noise can be so high for WS-CRDS analyzers that they have even been used to study trace isotopes of water directly from low humidity air samples at an altitude of over 11,000 feet[*] - see figure 3.

Figure 3. A WS-CRDS was recently successfully deployed near the top of Mauna Loa in Hawaii, at an altitude of 11,000 feet (3.4 km).

Specificity

Together with precision wavelength monitoring, the use of wavelength scanning of a narrow-line laser light source also provides the spectral resolution and stability necessary to measure target gas species even in complex gas mixtures. Specifically, by using a patented absolute wavelength monitor, the laser wavelength is always known – to a precision of 2MHz. So the instrument always measures the correct line for the target gas. Moreover, even in the rare case that there are other gas components with near-overlapping lines, the area and height of the measurement line can be accurately determined. (Obviously, this would not be possible with a single-point measurement approach.) This means that WS-CRDS does not require sample preparation or purification, enabling direct sampling of atmospheric air or raw automobile exhaust, as well as captured and/or purified samples.

Absolute Precision - Low Drift

Another key advantage of WS-CRDS is its capability for high absolute precision, i.e. low calibration drift – see Figures 4 and 5. There are several reasons for this. The first is that WS-CRDS measures a decay rate, not an absolute signal intensity. So neither long- or short-term drifts in the laser power, laser power meter, or detector response have any effect on the fixed relationship between the WS-CRDS decay rate and the sample gas concentration. Another factor is the wavelength scanning. This not only supports multiple measurements across the line profile but also measurements at multiple baseline locations, eliminating the need for a "zero gas" reference. The third factor is a function of implementation, namely the stability of the cavity conditions. In Picarro gas

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[*] *Visit www.picarro.com to read how scientists from the University of Colorado and the University of New Mexico have successfully deployed a Picarro precision water isotope analyzer at a remote monitoring station near the top of Mauna Loa, Hawaii.*

analyzers, the WS-CRDS cavity is actively maintained at a fixed temperature and pressure. The pressure is held constant by use of a pressure sensor and feedback loop control over the flow valve – see Figure 6. As a result, Picarro gas analyzers are immune to changes in ambient conditions and deliver such low drift that they can operate for weeks, and even months, between re-calibration These factors make them ideal for unmanned sites in remote GHG monitoring locations or places with limited accessibility, such as a tall industrial exhaust stack.

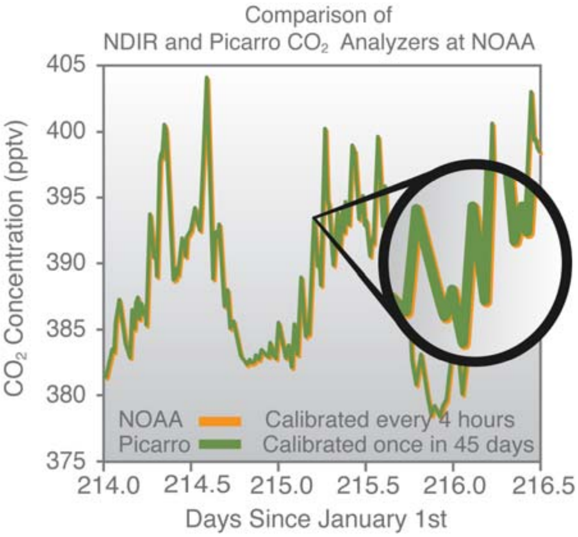

Figure 4. The low drift and absolute precision of a WS-CRDS CO_2 instrument can be seen in this data subset from a 45-day NOAA field trial comparing atmospheric data taken by a Picarro G1200 analyzer with that from NOAA's NDIR analyzer. The Picarro analyzer was calibrated only once over the 45-day period, whereas the NDIR analyzer required calibration every 4 hours. The average difference is < 180 ppbv/day. The Picarro analyzer was able to sample unconditioned gas with an average drift of < 0.8 ppbv/day.

Multiple Gases

Wavelength resolution and species selectivity also means that a single WS-CRDS instrument can be configured to simultaneously and independently monitor multiple trace species, e.g. CO_2, CH_4 and H_2O. In some instances, a single laser is able to scan lines for more than one species. Where the target absorption lines are more widely spaced, two or more laser modules are incorporated in a single instrument as needed.

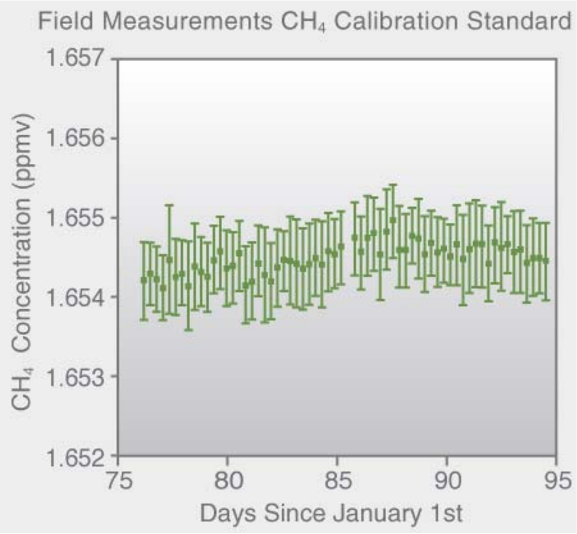

Figure 5. The low drift of a WS-CRDS CH_4 instrument is illustrated by these atmospheric measurements from an 18-day field trial of a Picarro G1202 analyzer at Oregon State University. Without recalibrating, the analyzer performance over 18 days of operation in the field yielded a precision of 0.5 ppbv in 5 seconds and a drift of < 0.8 ppbv (peak to peak) per day.

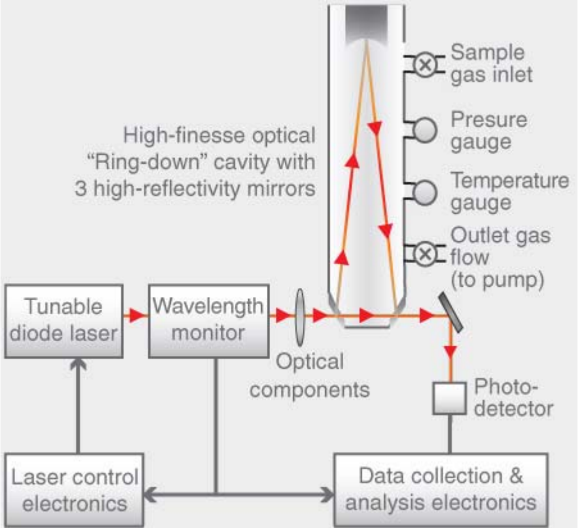

Figure 6. Schematic showing all the major components of a Picarro WS-CRDS analyzer. Active stabilization of the cavity temperature and pressure are key to the instruments' high precision.

Rugged Packaging and Operational Simplicity

For the past decade, Picarro has focused on implementing WS-CRDS in instruments designed and built to maximize these inherent advantages while also delivering operational simplicity. In particular, these gas analyzers were designed from the ground up to be used unattended in the field without user intervention for up to six months, while providing reference laboratory performance. In addition to rugged reliability and low-drift, this also requires software system for simplified operation, data processing and storage, as well as remote access. These instruments are built on a Windows-based platform. They are pre-programmed at the factory to target specific absorption lines and all basic functions such as wavelength scanning and raw decay curve processing are completely automated and transparent to the user. The cavity pressure, temperature and sampling rate are also factory preset. At the simplest level of operation, all the user has to do is tell the instrument to start taking data and select the time interval over which the final data is be averaged. No further training is required. Since the original data set is stored in the instrument, the data "acquisition time," i.e. integration time, can be re-adjusted after the data has been captured.

For remote field operation, each instrument includes a RS-232 serial interface as well as an Ethernet port, and supports an optional cell-phone modem. So any authorized party can receive or access the data continuously or at arbitrary times. This is particularly useful where the instrument is being used to monitor site compliance or where the measurements are to be the basis for tradable commodities such as carbon credits.

Some applications have a need to monitor GHGs at multiple site locations. Picarro analyzers support this need by including software and hardware to control an external valve sequencer. This enables a single instrument to sample gases from multiple lines on demand, lowering the overall cost of measurement.

In order to enable long-term unattended operation in the field as well as mobile (e.g. truck, boat mounted) applications, Picarro WS-CRDS analyzers are also extremely rugged and tolerant of changes in temperature, pressure, and humidity, as well as tolerant of vibrations and shocks. Visit www.picarro.com to see a short video of one these analyzers performing to specification in a small boat bouncing along the Sacramento River delta at 40 knots in driving rain.

For laboratory applications, these GHG analyzers can be operated as stand-alone units. Data can be downloaded through the RS232 interface or Ethernet ports or by using a USB flash memory stick. Or the instrument can be simply integrated into a more complex setup through one of the interfaces.

Limitations of Other Techniques

WS-CRDS analyzers are the first instruments to provide the combination of performance and rugged operation to service virtually all GHG measurement applications. However, there are legacy technologies which can service a subset of these applications.

GC (gas chromatography) has always been the "gold standard" for atmospheric science laboratories, because of its high precision and sensitivity. However, it often requires sample preparation and a supporting vacuum line as well as a skilled technician. It can be automated, but requires very frequent calibration as its sensitivity is prone to drifts. GC is also slow – up to orders magnitude slower than WS-CRDS. These factors mean that it is completely unsuited to remote operation. Remote sites can only be analyzed by a technician performing sample capture, which is costly and time-consuming and does not support continuous monitoring.

NDIR (non-dispersive infrared) uses an optical filter(s) and a broadband light source to measure near infrared absorption of target species. These units are small and portable but have two significant limitations compared to WS-CRDS. First, they don't have the spectral resolution to eliminate signal crosstalk between various gas molecules. So, they cannot be used with mixed gas samples, without preparation/purification. And second, they require very frequent calibration, in part because of their non-linear response, which adds significant cost to their use in terms of technician time and the cost of span and zero gases. They are not suitable for most unattended field applications.

TDL (tunable diode laser) technology uses a laser just like WS-CRDS thereby solving the crosstalk problem that limits NDIR. However, these instruments don't use a resonant cavity so they have a shorter pathlength, i.e. lower sensitivity, than WS-CRDS. In addition, TDL is a traditional intensity-based measurement, so it is affected by laser and detector shot noise, another factor limiting its sensitivity. And since the laser power and detector response drift with time, TDL systems require frequent calibration. Some users have attempted to employ TDLs in an open path configuration, to address the pathlength/sensitivity limitation and also provide a transect measurement over an extended area. These efforts have met with only limited success because the instrument response is affected by temperature and pressure gradients in the open path, over which the operator has no control.

GHG Application Examples

Picarro WS-CRDS gas analyzers are now used in several laboratory applications by leading GHG research institutions, including NOAA National Oceanic and Atmospheric Administration (Boulder, CO) and the Max Planck Institute in Germany. But it is the field applications that really show the full potential of WS-CRDS for GHG applications.

GHG Monitoring at Harsh Locations

Picarro WS-CRDS analyzers have recently been successfully deployed at monitoring stations in the Arctic and at the 14,000 foot summit of Mauna Loa (Hawaii). A particularly challenging location is Lamto, Ivory Coast, because this site is characterized by very high humidity and ambient temperatures that can easily exceed 40°C. The Picarro G1301 is now operating there, providing simultaneous and continuous measurements of both methane (CH_4) and carbon dioxide (CO_2) at a precision of parts per billion. The instrument is located adjacent to a 50 meter tower allowing data to be taken automatically and continuously via a tube terminating at the top of this tower.

The Lamto GHG program is operated by scientists from the CarboAfrica participants, including the CEA (Commissariat a l'Energie Atomique) in France and the University of Cocody in Ivory Coast. The instrument was first evaluated by a CEA team at the Laboratoire des Sciences du Climat et de l'Environnement, located in Saclay, France, for several months before deployment in Africa. CEA Co-Director Philippe Ciais explains, "At CarboAfrica, we are setting up a network of monitoring sites throughout Africa, in response to the critical lack of field GHG data from this continent. We selected this WS-CRDS analyzer for several reasons, including its stable performance over a wide range of temperature and humidity, and its precision, which well exceeds our minimum requirement of 100 ppbv. In addition, it's simple to operate, and importantly for this remote location, the very low drift of the instrument eliminates the need for maintenance or frequent calibration."

Total GHG Flux Measurements

International climate change treaties and local government ordinances are creating a need for total flux measurements for extended sites, ranging from a single landfill to an entire geographic region. An on-going pilot program in the US mid-west illustrates how this can be achieved. This is the Penn State Ring 2 project in support of the NACP (North American Carbon Program) Mid Continent Intensive. Here, the net CO_2 balance emitted from an extended area is made by taking continuous measurements at five sampling towers. These sites are currently equipped with several different types of sensor including a Picarro WS-CRDS CO_2 analyzer. This project is sometimes referred to as the "Iowa Ring" as the area roughly corresponds to the borders of this state - see figure 7.

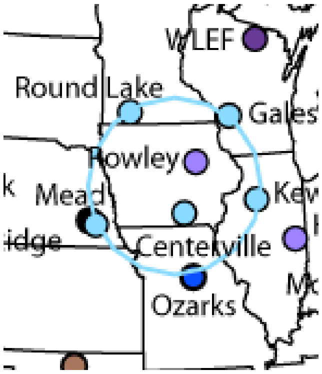

Figure 7. The Penn State Ring 2 project is using WS-CRDS instrumentation and other technologies to measure the entire CO_2 flux of a region roughly spanning the state of Iowa.

By measuring at these key locations around the perimeter and the center of the target area at different tower heights, and by simultaneously measuring wind speed and direction, the net flux within the ring can be determined objectively.

Site Monitoring for Geo-Sequestration Leaks

Geo-sequestration – pumping and permanently trapping liquefied CO_2 deep underground – is likely to play a key role in medium-term overall GHG mitigation strategy. An integral part of this approach will be surface and sub-surface monitoring of these sequestration sites for any CO_2 leaks. In pilot programs, there are already several ways in which any leaks of sequestered material can be detected, including tracer additives, naturally present proxy gases, and direct detection of the carbon dioxide itself, especially using its isotopic signature. WS-CRDS can be used for all of these methods and is the only method suitable for measuring isotopic carbon signature at location in real time.[*]

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[*] *To learn about how WS-CRDS technology is used for stable isotope measurement, visit www.picarro.com to download the whitepaper "Simple, Real-Time Measurement of Stable Isotope Ratios in H_2O and CO_2."*

Tracer additives are chemically stable gases that are added to the sequestered CO_2 specifically to enable leak detection. Several examples, such as acetylene, are ideal candidates for WS-CRDS detection down to the ppbv level. A proxy gas is a species naturally present in the gas being sequestered or naturally found at the site. CH_4 is the most common proxy, because most sequestration sites contain fossil methane, particularly where the site is a former gas/oil well. Direct carbon dioxide detection can be useful, but only in conjunction with other measurements as well as full modeling of existing diurnal and seasonal variations in the local ambient CO_2 levels. Isotope ratios can play a key role here. Sequestered CO_2 will be mainly anthropogenic (fossil fuel) and, especially if derived from coal burning facilities, highly depleted in ^{13}C, resulting in a characteristically low value of the normalized $\delta^{13}C$ ratio - lower than both ambient CO_2 and even the CO_2 causing background variations, generated by local vegetation. So, an instrument that detects both changes in the CO_2 concentration and its $\delta^{13}C$ ratio can yield important information.

One pilot site evaluating WS-CRDS instruments for geo-sequestration applications is the CO_2CRC Otway Project in Victoria, Australia. Specifically, scientists from CSIRO (Commonwealth Scientific and Industrial Research Organisation) are using both a multi-gas CO_2/CH_4 (Picarro G1301) analyzer as well as a isotopic CO_2 analyzer (Picarro G1101-*i*). CSIRO scientist D. Zoe Loh explains, "This trial project is taking magmatic CO_2 from a well drilled during natural gas exploration and pumping it into a commercially exhausted natural gas well nearby. The presence of residual natural gas at both source and sink means the final mole fraction of CH_4 could be as high as 20% making it an excellent natural proxy, hence our interest in an instrument that simultaneously monitors CO_2 and CH_4."

Mobile Landfill Monitoring and Modeling

Landfills are well-known sources of CH_4, and are governed by national and local regulations. Specifically, landfill operators must incorporate a gas trapping system and demonstrate that this eliminates a target percentage of the total CH_4. Current regulations typically mandate compliance verification in the form of periodic checks at random spot locations on the landfill. These spot checks are fraught with potential errors due to changes in wind direction, speed and other ambient factors. Moreover, GHG analyzers measure concentration, when what is really needed is total emitted flux (mass per unit time).

Recently, a tracer method has been proposed and undergone some investigation as a means of measuring total flux. Here a cylinder of C_2H_2 (acetylene) is used to create a localized plume. Models and experiments show that in the far-field, say a distance of 1 km, the spread, and hence dilution, is identical to that from a collection of CH_4 plumes. So by measuring the ratio of the C_2H_2 and CH_4 concentrations, the total flux of CH_4 can be accurately calculated.

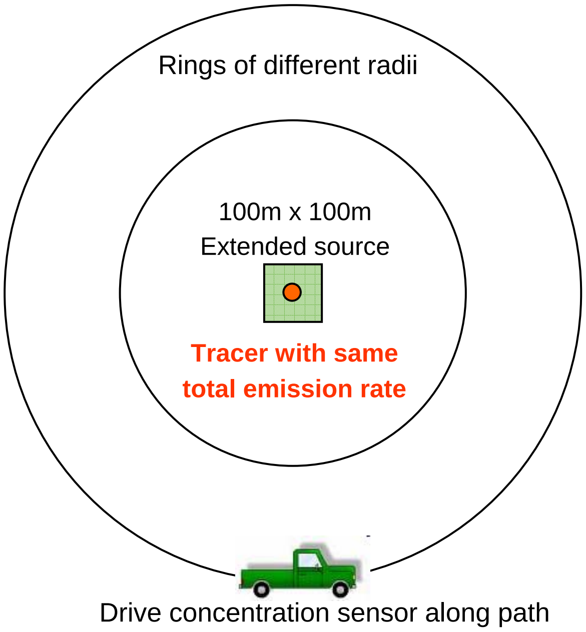

Figure 8. One proposed method to measure the total emitted CH_4 flux from a landfill is to release a known quantity of tracer gas (e.g. C_2H_2) in a single plume and monitor the ratio of the concentration of CH_4 and C_2H_2 tracer along a continuous circumference using a real-time portable analyzer on an electric vehicle.

However, scientists at Picarro have performed simulations that show the spread of the exit plume can be fairly narrow, so that it can pass undetected though a proposed ring of multiple detectors or be under-estimated at best. This drawback can be eliminated by driving a mobile analyzer around the site perimeter while taking continuous measurements – see figure 8[*]. Moreover, a WS-CRDS analyzer is ideal for this since a single instrument can simultaneously measure both C_2H_2 and CH_4, providing the

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[*] *S.M. Tan, E.R. Crosson, and E. Winegar, "Real-time Ambient Monitoring of Fugitive Emissions from Landfills," AWMA Symposium on Air Quality Measurement Methods and Technology, November 2008.*

requisite speed and portability. A prototype has already demonstrated very high precision for C_2H_2: $\sigma = 270$ pptv in 1.1 seconds, and $\sigma = 90$ pptv in 30s. This precision is very advantageous as it minimizes the amount of C_2H_2 that must be released.

Conclusion

Dealing with increased GHG levels and its consequences is arguably the leading socio-economic/political challenge of our age. This massive challenge is being addressed at multiple levels, from the simple point source such as an automobile or power plant, to reducing the total flux from an entire country, and ultimately the planet. It is giving rise to a host of laws and regulations as well a new type of tradable commodity – the carbon credit. WS-CRDS technology is unique in its ability to meet or exceed the performance and reliability issues of virtually all GHG monitoring and research applications that are a consequence of this. The ability to use a single universal GHG accounting tool can simplify the refinement of better climate models, as well as implementation and enforcement of regulations, and bring much needed confidence and objectivity to critical commercial concepts such as carbon credits.

The low drift and absolute precision of a WS-CRDS CO_2 instrument can be seen in this data subset from a 45-day NOAA field trial comparing atmospheric data taken by a Picarro G1200 analyzer with that from NOAA's NDIR analyzer. The Picarro analyzer was calibrated only once over the 45-day period, whereas the NDIR analyzer required calibration every 4 hours. The average difference is < 180 ppbv/day. The Picarro analyzer was able to sample unconditioned gas with an average drift of < 0.8 ppbv/day.