Greenhouse Gas Monitoring made Simple

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Introduction

Among the components which make up the earth's atmosphere, carbon dioxide and methane are particularly important. Unlike any other species, these gases have three special characteristics:

1) Each is a powerful greenhouse gas. That is, each produces positive radiative forcing[1], which tends to warm the surface of the earth.
2) Each exists for a long time in the atmosphere so that fluctuations in concentration are small when compared to average concentration levels.
3) Each has significant anthropogenic contributions.

In addition to water vapor, these gases are key components of earth's natural temperature control system. In fact, the radiative forcing of both of these gases is so powerful that small changes in their concentration have caused measurable increases in the surface temperature of the planet. Quoting from the Intergovernmental Panel on Climate Change (IPCC) 2007 report, "The global average surface temperature…has increased since 1861. Over the 20th century the increase has been 0.6 ± 0.2°C."[2] This increase is due, in large part, to an 85 parts-per-million (ppm) increase in carbon dioxide and a one ppm increase in methane concentration. This increase has resulted in an increase in radiative forcing of 1.94 Wm^{-2} [2]. This change is huge and likely to have resulted in the largest temperature change of any century during the past 1,000 years. The concern about global warming has generated great interest in monitoring greenhouse gases both from an individual researcher as well as a monitoring network prospective.

Monitoring of greenhouses gases - a unique challenge

Atmospheric scientist and environmental regulatory agencies around the world have been monitoring air pollution for many decades. In fact, in the United States there are over 5,000 sites monitoring air pollutants run by federal, state and local agencies. By contrast, there are only about a dozen greenhouse gas monitoring sites in the US. The instrumentation used to monitor atmospheric pollutants is well understood and the community is comfortable with its processes, procedures, and requirements. Without exception, the instrumentation used to monitor trace amounts of each atmospheric pollutant for which the average atmospheric background concentration is known to be at or near zero. For most of these measurements, the purpose is to determine if and when a particular pollutant exceeds a predefined concentration threshold. To achieve this goal, the sensitivity of instrumentation used to measure atmospheric pollutants needs excellent sensitivity but does not require high accuracy; 5-10% of full scale is often sufficient for this task. For example, the six priority pollutants measured by the US Environmental

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[1] Radiative forcing is a measure of the influence a factor has in altering the balance of incoming and outgoing energy in the Earth-atmosphere system, and is an index of the importance of the factor as a potential climate change mechanism. It is expressed in Watts per square meter (Wm^{-2}).

[2] Intergovernmental Panel on Climate Change.

Protection Agency (EPA) are ozone, carbon monoxide, nitrogen oxides, sulfur dioxide, particulate matter, and lead. A list of the average ambient concentration levels as well as the US EPA health protection standards for four of six of these species is shown in Table 1[3]. If one focuses on carbon monoxide, even with a relatively easy-to-achieve 10% accuracy on a 3 ppm measurement, a measurement at or above the 8 ppm standard is 5-sigma away. In other words, the 8 ppm measurement is statistically very relevant.

Table1: A list of ambient concentration levels and protection standards for four of six priority pollutants

Gas Species	**Ambient Concentration (ppm)**	**National Standard (ppm)**
Ozone	0.030-0.050	0.075
Carbon Monoxide	0 - 3	8
Nitrogen Oxide	0.02	0.053
Sulfur Dioxide	0.001 - 0.006	0.140

This is not the case when measuring greenhouse gases such as carbon dioxide and methane. The required accuracy for carbon dioxide is better than 1 part in 3600 or 0.03% and for methane is 0.12% (see Table 2), based upon the inter-laboratory comparability standard stipulated by the World Meteorological Organization (WMO). The reason for this tight accuracy requirement is because researchers need to derive sources and sinks form the spatial and temporal patterns measured. Quantifying these very small changes in greenhouse gas concentrations from year to year are the critical factors required to predict climate change, and to assess the efficacy of policy and support market-based emissions reduction programs.

Table2: Average composition of carbon dioxide and methane in the atmosphere up to an altitude of 25 km.

Gas Species	**Ambient Concentration (ppm)**	**Required Accuracy (ppm)**
Carbon Dioxide	360	0.100
Methane	1.8	0.002

As a result, meeting this high accuracy requirement places extraordinary demands on the atmospheric monitoring community. Using existing quality assurance methods work adequately for the handful of monitoring stations now operating, but is not scalable to larger numbers of monitoring stations. New instruments, data quality assurance procedures, and quality methods will need to be defined and implemented. This is the unique challenge that faces the atmospheric monitoring community as it gears up to implement local, national, and global monitoring networks. Happily, the task of making greenhouse gas measurements and insuring the highest quality data possible has greatly simplified with the introduction of Picarro's cavity ringdown technology.

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[3] http://www.epa.gov/air/urbanair/

Instrument requirements- focus on high accuracy

When monitoring air pollution, virtually all measurement techniques rely on optical methods of one type or another. Many of the manufacturers of these optical analyzers advertise that "their technology" is insensitive to environmental conditions such as changes in ambient temperature. This may or may not be the case. However, regardless of optical technique or matter how stabilized the instrument may be, all require the careful control of the temperature and pressure of the molecules being measured. In addition, in order to measure only the molecules of interest, all optical based techniques require the careful selection and/or control of the wavelengths of light utilized. Lastly, to obtain the highest accuracy possible, the technique used to determine the absorption of light by the molecules of interest must have virtually no systematic effects that lead to optical absorption uncertainties. Four parameters are absolutely necessary to ensure high accuracy measurements of better than 0.1%.

1) Pressure control of the molecules,
2) Temperature control of the molecules,
3) Precise control of the wavelength of light utilized,
4) An optical absorption technique devoid of systematic effects,

Instrument technologists frequently claim that their favorite technology is fundamentally unaffected by modest changes in temperature and pressure. However, they fail to address the affect of temperature and pressure on molecular spectroscopy, and of course, the goal of all quantitative analyzers is to make concentration measurements independent of shifts in molecular physics. Let's take the simple example of molecular temperature and pressure. Small changes in temperature and pressure will change the optical absorption properties of a molecule, which in turn affects a quantitative result. Simply monitoring sample chamber temperature and pressure does not assure that all molecules "see" the same temperature. Any uncontrolled sample chamber is likely to have temperature gradients which could introduce significant errors in concentration readings. Correcting for such gradients is difficult, particularly when ambient temperatures are fluctuating faster than the time required for the sample chamber to come into thermal equilibrium. If this were the case, the monitoring community would have no way of distinguishing between actual changes in greenhouse gas concentrations and gradient effects in the sample chamber. Some manufactures have proposed overcoming their analyzers shortcoming by introducing gas standards into the analyzer. However, greenhouse gas standards are expensive ($1000 per gas cylinder) and even the frequent introduction of such standards (every 6 hours for example) does not insure proper operation of the analyzer between gas standard measurements. In addition, if building out a large scale network, maintaining a large fleet of greenhouse gas standards would be extremely costly and most likely impractical.

A similar case can be made for controlling the wavelength of light. Both absorption filters and lasers can drift in wavelength over time and temperature. Such drifts can lead to systematic errors which are caused by the absorption of light by molecules other than those of interest. This is because ambient air contains lots of different gas species each of which have many hundreds of optical absorption features each at different wavelengths. When a laser or absorption filter drifts there is no way of knowing that some light is not being absorbed by an "interfering" gas species. To remedy this, some instrument manufacturers have proposed spectral correction methods in the belief that the analyzer is measuring the correct spectral feature. However depending on the amount of laser or filter drift, and given the thousands of optical absorption features, these techniques often fail to distinguish the exact spectral region of interest. Once again, in this scenario there is no way for the monitoring community to distinguishing between actual changes in greenhouse gas concentrations and laser or absorption filter drift errors. Similar arguments can be made for the case of the other critical measurement parameters. Only by carefully controlling sample pressure and temperature as well as wavelength and absorption properties can the monitoring community be assured that a given analyzer is accurately measuring the gas species of interest.

The take-away point is that nothing comes for free. Using correction techniques or post-processing methods rather than direct control of critical molecular and optical parameters is highly risky and are likely to lead to erroneous measurements that are difficult if not impossible for the monitoring community to identify.

High Accuracy, Cost Effective Greenhouse Gas Monitor

Picarro has developed an extremely low-drift, high precision greenhouse gas analyzer (Picarro model G1301) able to measure simultaneously the atmospheric levels of methane, carbon dioxide, and water vapor at the parts-per-billion level for global monitoring networks[4]. This analyzer is designed to carefully control the four critical sample, wavelength, and absorption parameters described previously. The analyzer is based on cavity ring-down spectroscopy (CRDS); which is a technique where a gas sample is introduced into a high-finesse optical cavity and the optical absorbance of the sample is determined, thus providing concentration or isotopic ratio measurements of a particular gas species of interest[5]. The components of a basic cavity ring-down spectrometer are a laser, a high finesse optical cavity consisting of three mirrors, and a photo-detector. Operationally, light from a laser is injected into the cavity through one partially reflecting mirror. The light intensity inside the cavity then builds up over time and is monitored through a second partially reflecting mirror using a photo-detector located outside the cavity. The "ring-down" measurement is made by rapidly turning off the laser and measuring the light intensity in the cavity as it decays exponentially with a time constant, τ, that depends on the losses due to the cavity mirrors and the absorption and scattering of the sample being measured. After shutting off the laser, most of the light remains trapped within the cavity for a long period of time, producing an effective path length of tens of kilometers through the sample. Much like a multi-pass cell, this long effective path length gives CRDS its high sensitivity.

It is important to note that CRDS provides an absolute measurement of the optical absorption per unit length (calculated from the ringdown time via the speed of light). Because time measurements can be made using modern electronics with incredible accuracy, it is this characteristic of CRDS which rests at the foundation of its incredible accuracy.

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[4] Appl. Phys. B 92, 403–408 (2008)

[5] K.W. Busch, M.A. Busch, Cavity Ringdown Spectroscopy: An Ultratrace Absorption Measurement Technique, American Chemical Society Symposium Series, Vol. 720 (Oxford University Press, New York, 1999)

The CRDS greenhouse gas analyzer described here utilizes two, high reliability, telecom-grade distributed feedback (DFB) lasers. One laser measures a single carbon dioxide spectral feature at a wavelength of 1603 nm while the other measures methane and water vapor spectral features at 1651 nm wavelength. Light from the DFB lasers are selected using an optical switch and is transported to a highly accurate wavelength monitor via a polarization maintaining optical fiber. The analyzer is designed to simultaneously measure optical absorption using a proprietary traveling wave cavity and the optical frequency at which the absorption occurs using a proprietary wavelength monitor while regulating the temperature and pressure of the ambient air sample continuously flowing through the optical cavity.

Accurate greenhouse gas measurements in humid air

Traditional methods of measuring greenhouse gas inventories in the well-mixed atmosphere have relied upon NDIR (non-dispersive infrared) for carbon dioxide and GC (Gas Chromatography) for methane. Typically, these measurements are performed on dried gas streams for two reasons: a) the concentration measurements for carbon dioxide and methane are only meaningful when extrapolated back to dry-gas conditions – due to the volatility of the water vapor content in the atmosphere and the effect of dilution by water vapor[6].
It has been impractical to make measurements in the wet gas stream because traditional techniques suffer from significant cross-talk between water vapor and carbon dioxide and methane. Furthermore, it is not possible to achieve the overall inter-laboratory comparability standard stipulated by the World Meteorological Organization (WMO) for carbon dioxide (100 ppb) and methane (2 ppb) with these technologies without drying the samples to very low levels, in some cases to a dew point of lower than -60C (0.001 %v). Given the fact that dry-gas measurements are the ultimate goal, it would seem to be appropriate to dry the samples prior to measurement. However, drying air samples to these levels introduces complexity to the sampling system, dramatically increases the surface area and gas fittings in the sampling system, and requires the use of costly consumables that demand the frequent attention of measurement station personnel. It is a significant practical advantage, therefore, to be able to measure dry-gas mixing ratios for carbon dioxide and methane directly in the wet gas stream.

Until the introduction of the Picarro G1301 three species analyzer, greenhouse gas measurements of sufficient accuracy and precision have not been practical in the field. Because this analyzer directly measures the water vapor content of the air stream at the same time as carbon dioxide and methane, the dry gas mixing ratios of these two critically important greenhouse gases can be directly quantified with high precision and high accuracy, even in very humid gas streams.

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[6] The dilution effect is simply the change in mixing ratio of carbon dioxide and methane caused by variability in the humidity. For example, a dry air mass traveling over warm water will accumulate humidity, and this additional water vapor will dilute the concentration of the other gases. Conversely, a humid air mass that becomes drier (as through precipitation) will cause an inverse dilution effect, increasing the conentration of the other gases.

Data quality control

Besides carefully controlling the four critical parameters and being able to accurately measure both wet and dry ambient air, the Picarro G1301 is designed to provide the monitoring community with real-time parameters which help ensure the proper operation of the analyzer. To this end, sample temperature, sample pressure, wavelength targeting, and critical absorption properties of each of the three gas species measured can be continuously monitored even when the analyzer is located in a remote area. Examples of three such parameters are shown in Figure 1. Figure 1(a) shows the amount of water vapor in the sample. Figure 1(b) is carbon dioxide wavelength targeting. Figure 1(c) is the ambient temperature. Figure 1(d) is the sample chamber temperature. Each is shown as a function of time and each parameter can be recorded and stored on the analyzer. These are just a handful of the more than thirty internal processes being continuously monitored by the analyzer.

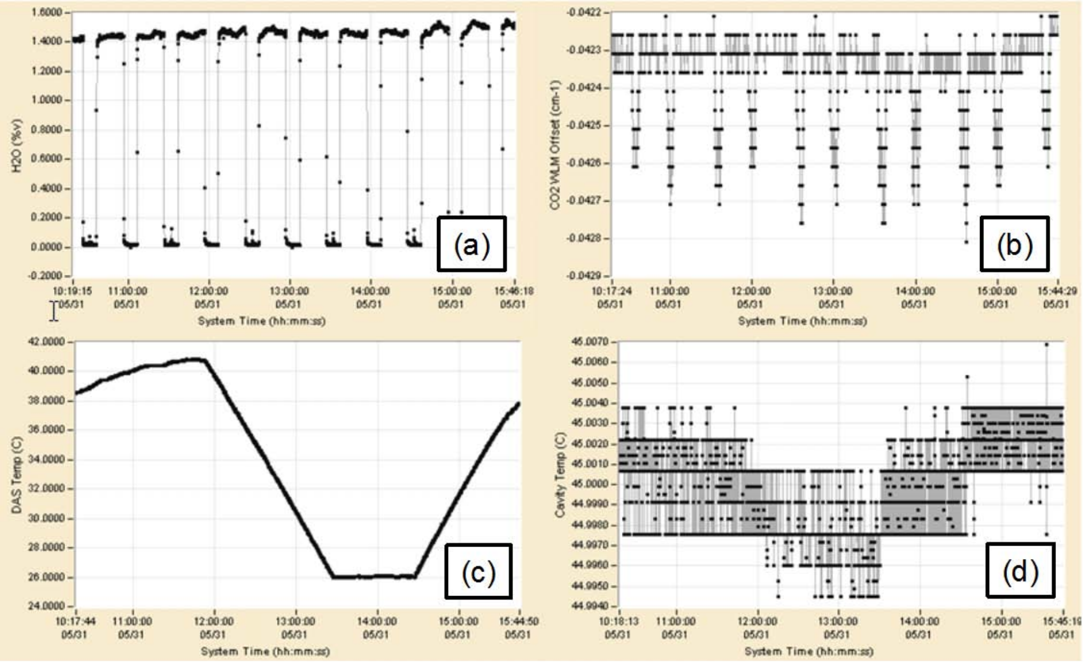

Figure 1. An example of four key parameters which can be used to evaluate the performance of the analyzer in real time. Figure 1(a) shows the amount of water vapor in the sample in percent from 10:17am to 3:45 pm. Figure 1(b) is carbon dioxide wavelength targeting in wavenumbers. Figure 1(c) is shows the ambient temperature in centigrade. Figure 1(d) is the sample chamber temperature in centigrade.

There are clear benefits of using such parameters as a measure of the overall health of the analyzer. Monitoring these parameters not only increases the quality and reliability of concentration data but can also greatly reduce the frequency of introduction of calibration standards, resulting in much lower operational cost. Iif one were to utilize an automated system to continuously monitor a network of Picarro analyzers, one could introduce gas standards only when one or more of the real-time operating parameters exceed pre-defined threshold (as opposed to introducing standards at regular intervals, i.e. every 6 hours). Utilizing this continuous monitoring method would not only help minimized the use of expensive standards but also provide critical parameters which could help when assessing and predicting analyzer performance trends as well as helping to answer analyzer intercomparibility questions.

Picarro G1301: High accuracy, low drift

Five CRDS carbon dioxide and water vapor analyzers were deployed by researchers at Pennsylvania State University as part of the North American Carbon Program's Mid-continental Intensive Regional Study Network of five communications-tower-based atmospheric carbon dioxide measurements located in the upper mid-west, USA. At these sites, atmospheric carbon dioxide and water vapor are continuously monitored. Calibration standards are momentarily measured every 20 hours. All analyzers operated without regular human intervention in conditions where ambient temperatures were not always carefully controlled. An example of measurements of calibration standards using the analyzer located at Mead, Nebraska is given in Figure 2. The analyzer was calibrated before the field installation and no further calibration was performed. The maximum peak-to-peak drift in the analyzer was 0.25 ppmv over the 170 day period shown in Figure 2. When results are fit to a linear function, the drift in the analyzer was determined to be 1.2 ppbv per day. This result can then be used to easily correct the error in analyzer measurements associated with CRDS analyzer drift.

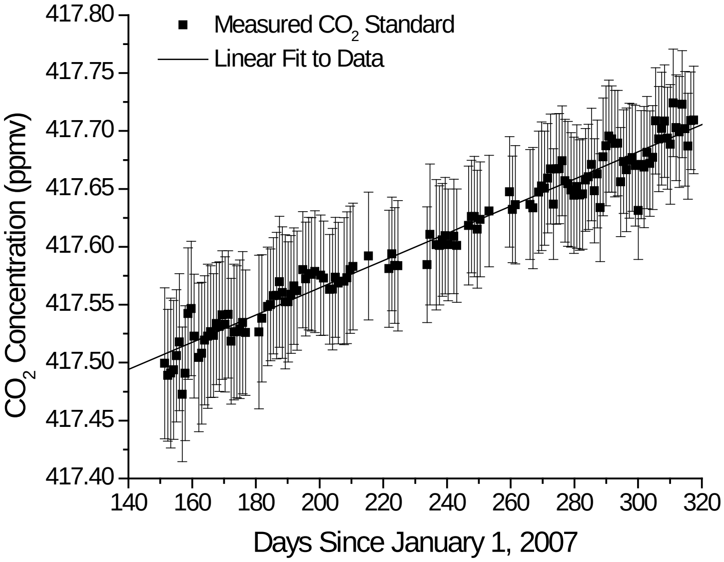

Figure 2. Measurements of a carbon dioxide calibration standard over 170 days at a tall tower in Mead, Nebraska, USA.

Results of round robin test of five analyzers

If any greenhouse gas monitoring network is to be successful, consistency between analyzers is critical. This is particularly true for analyzer-to-analyzer accuracy. Again, as part of Penn State University's Mid-continental Intensive Regional Study, a round robin test was performed in which four NOAA-calibrated standards (gas bottles) tanks were brought to each site where analyzer measurements of each standard were made. The network site separation distances were large, at 125-730 km. Table 3 shows the difference between the carbon dioxide concentrations measured by each analyzer and the known value of each standard. This round robin test was undertaken nine months after the network was deployed and all five analyzers participated. Again, each analyzer was calibrated before field installation and no further calibration was performed. Analysis of the data shows that the largest analyzer difference with any single tank was found to be 0.28 ppm. This translates into a 0.07% difference in accuracy when compared to a typical ambient carbon dioxide concentration of 380 ppm.

Table3: The difference between the measured values and the known value of four NOAA calibrated carbon dioxide gas standards.

Site Location	**Tank 1 error (ppm)**	**Tank 2 error (ppm)**	**Tank 3 error (ppm)**	**Tank 4 error (ppm)**
Kewanee	-0.097	-0.115	-0.049	-0.279
Centerville	-0.155	0.020	-0.158	Unstable
Mead	-0.071	-0.074	0.093	-0.093
Round Lake	-0.047	Not tested	-0.210	Not tested
Galesville	-0.174	-0.162	-0.018	-0.190

Conclusion

One major overall objective when building out a greenhouse gas analyzer network is to help provide information required to predict climate change, and to assess the efficacy of policy and support market-based emissions reduction programs. To be successful will require instrument accuracy of better than 0.03% and 0.12% for carbon dioxide and methane, respectively, over years of operation. Meeting this high accuracy requirement will place extraordinary demands on the atmospheric monitoring community, and on the instrumentation they use.

The Picarro G1301 has been designed from the ground up to focus on the needs of the atmospheric monitoring community. Instrument stability and accuracy continues to be the primary objective, driven by the requirement that the instruments be inexpensively deployed in remote locations, with as few consumables as possible. By combining the incredible precision, accuracy, and simplicity of CRDS technology with smart engineering that insures the gas is measured at a stable pressure and temperature, the G1301 demonstrates accurate measurements of the dry-gas mixing ratios for carbon dioxide and methane that meets or exceeds the demanding requirements of the greenhouse gas monitoring community, even in humid gas streams.