The capability of the Picarro $CO_2/CH_4/H_2O$ greenhouse gas analyzer includes simultaneous measurements of carbon dioxide ($CO_2$), methane ($CH_4$), and water vapor ($H_2O$) – all available in a single analyzer.


Picarro G1301 Analyzer

For greenhouse gas atmospheric inversion studies the Picarro G1301 produces a precision of better than 0.05 parts-per-million volume (ppmv) for $CO_2$, 0.07 part-per-billion volume (ppbv) for $CH_4$, and 100 ppmv for $H_2O$. All three species are measured in a total measurement time of five seconds. The Picarro G1301 achieves this high performance with significantly decreased need for calibration compared with traditional instruments and without the need for sample conditioning– removal of water vapor from the sample is not required.

The outstanding performance of the Picarro G1301 is based on a combination of the unique capabilities of the underlying technology, Wavelength-Scanned Cavity Ringdown Spectroscopy (WS-CRDS), and superior engineering of the product platform designed to maximize the inherent advantages of WS-CRDS including a patented wavelength monitor, precise temperature and pressure control, and robust digital signal processing to transform raw data into useful information.

**Analyzer Performance**

Prior to product release, field measurements of $CO_2$ for atmospheric inversion were made by groups at Penn State, Harvard and NOAA in Boulder, Colorado. At NOAA the analyzer was co-located with an enhanced LI-COR $CO_2$ analyzer. Fig. 1 shows a 45-day period where the Picarro analyzer (green trace) and enhanced LI-COR (orange trace) were operated side-by-side at NOAA. The average difference between the outputs from the two analyzers is 180 ppbv (1-σ), and the Picarro analyzer demonstrated a drift of 0.8 ppbv/day. The most exceptional aspect of this result is that the Picarro analyzer only received 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 – including removal of water vapor. In contrast, the enhanced LI-COR $CO_2$ analyzer was calibrated every 5 hours in addition to extensive sample conditioning including removal of water vapor from the gas stream and temperature stabilization.

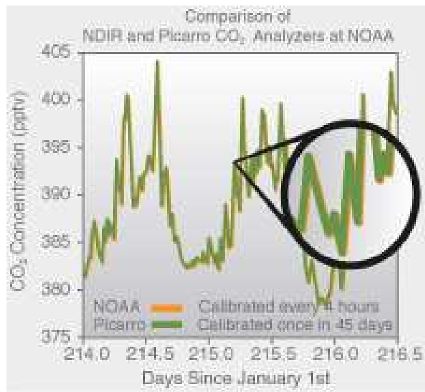


Figure 1. NOAA field trial results from the Picarro Analyzer and enhanced "Gold Standard" Licor $CO_2$ analyzers over a 45-day period. Average difference is 180 ppbv (1-σ) and Analyzer drift 0.8 ppbv/day with the Picarro analyzer sampling unconditioned, un-dried gas.

Continuing development of the Picarro product line has resulted in the ability to make simultaneous atmospheric inversion measurements of $CO_2$ and $CH_4$. Fig. 2. shows methane performance data from a methane in air sample with a nominal concentration of 1 ppmv. Over a 44 hour period of continuous measurement, without additional calibration, the demonstrated precision is 0.7 ppbv (1-σ), for a measurement interval of 1.1 seconds with a drift of 0.6 ppm peak-to-peak.

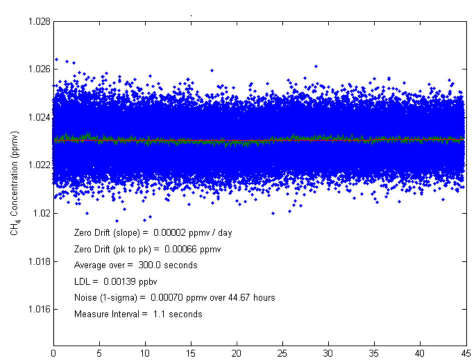


Figure 2. Picarro G1301 measuring methane at 1 ppmv nominal concentration over 44 hours. Precision is 0.7 ppbv and peak-to-peak drift is 0.6 ppm.

Most recently work has been completed to increase the sampling rate of the Picarro analyzers to enable atmospheric flux measurements for both $CO_2$ and $CH_4$ . Fig. 3 highlights this high-speed performance with $CO_2$ concentrations measured at 10 Hz over 15 hours and shows a precision of 100 ppbv (1-σ) and peak-to-peak drift of 92 ppbv.

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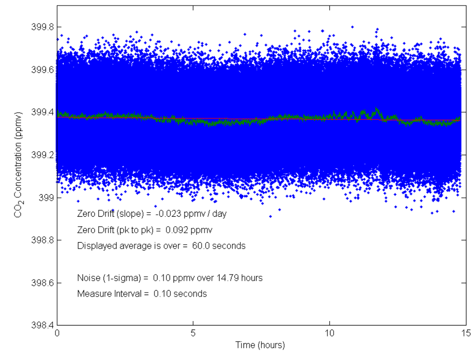


Figure 3. Picarro flux analyzer measuring $CO_2$ concentrations at 10 Hz with a precision of 100 ppbv and drift of 92 ppbv over 15 hours.

**Underlying Technology– Wavelength-Scanned Cavity Ringdown Spectroscopy (WS-CRDS)**

The underlying technology of the Picarro G1301 is WS-CRDS which is an ideal technology for high-sensitivity and high-precision gas analysis because of three main characteristics. First, WS-CRDS provides a very long interaction path length between the sample and optical probe enhancing sensitivity over conventional absorption techniques like Fourier Transform Infrared Spectroscopy (FTIR) and Non-dispersive Infrared Spectroscopy (NDIR). Picarro's implementation of WS-CRDS utilizes a 3-mirror configuration that yields a cavity lifetime of 10's of μs, equivalent to an optical path length of nearly 20km. The optical and gas flow configuration is shown in Fig. 4 below.

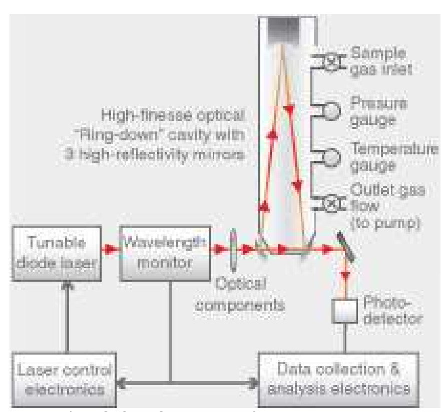


Figure 4. WS-CRDS cavity configuration and sample gas flow in the Picarro G1301.

The second distinguishing feature of WS-CRDS is the ability to isolate a single spectral feature. The mode spacing of the optical cavity results in a resolution of 0.0003 $cm^{-1}$ compared to the resolution of 0.5 $cm^{-1}$ in a typical FTIR – an improvement of ~1000 times. 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 WS-CRDS also simplifies the corrections for any interfering species that do occur, further increasing the sensitivity, accuracy and precision of the analyzer. Fig. 5 shows how the extreme spectral resolution of the analyzer provides an interference-free hydrogen sulfide concentration measurement in diesel exhaust, a very complex gas stream with a high concentration of interfering species.

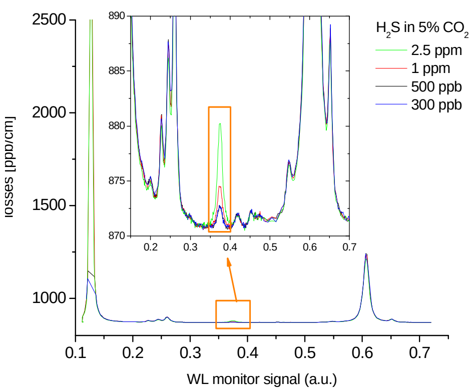


Figure 5. Spectral feature of hydrogen sulfide in diesel exhaust demonstrating how the high spectral resolution provided by WS-CRDS minimizes interference.

The third advantage of WS-CRDS is in the way that optical loss is measured. In conventional optical absorption spectroscopy, light intensity is measured before and after the sample. Loss measurements in WS-CRDS are essentially measurements of time. Light is injected into the cavity until a threshold level is reached at which point the light source is switched off. The essential WS-CRDS measurement consists of determining the decay time of the light. 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. When the wavelength of the injected light is resonant with an absorption feature of a species in the cavity the decay time increases as a linear function of the concentration of the species in the cavity. It is much easier to achieve the time measurement required for WS-CRDS with high precision and accuracy than an absolute or relative determination of light intensity. A profile of the light intensity as a function of time in a WS-CRDS cavity is shown in Fig. 6.

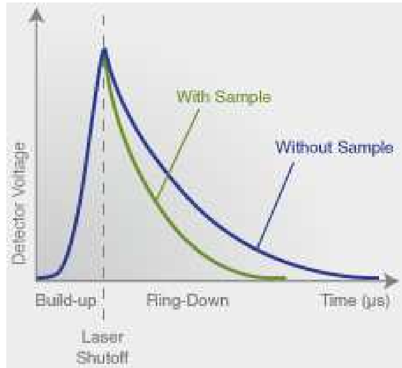


Figure 6. Light intensity as a function of time in a WS-CRDS system with and without a sample having resonant absorbance. Figure demonstrates how optical loss is rendered into a time measurement in WS-CRDS.

**System Design**

Development of the Picarro G1301 analyzer has focused on maximizing the inherent strengths of WS-CRDS – high sensitivity, selectivity, accuracy and precision. System design focused on accurate and reliable wavelength monitoring and control, high speed on-board digital signal processing, temperature and pressure control, and design for reliability.

The Picarro G1301 utilizes a patented, high-precision, inline wavelength monitor that enables the analyzer to set the wavelength precisely, thereby maximizing the selectivity. With this level of control of the wavelength, isolation of individual spectral features is possible enabling accuracy without interference even for complex gas streams, and eliminating one of the key underlying causes of the need for recalibration.

Determination of the ring down rate, or optical loss, as a function of wavelength is handled by a set of custom electronics in the Picarro G1301. At the heart of these custom electronics is a digital signal processing system that gives the analyzer 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 ~6 ms. A typical spectrum consists of ~ 10 to 100 spectral points.

Custom electronics are combined with precise mechanical design to produce analyzer temperature control of better than 1 part in 30,000, and pressure control better than 1 part in 2000. Accurate and reproducible temperature and pressure control are enabling factors for analyzer accuracy, precision and long term stability without human interaction.

Recently the Picarro analyzers have been enhanced to include time stamping of data against NIST standards and allow remote data access. Data can be transferred via either an Ethernet or phone connection.

The analyzer was designed for reliability – to meet the demanding requirements of industrial process applications and brings this high level of reliability to atmospheric monitoring. The high accuracy, excellent precision and low maintenance make it ideally suited to address the demanding requirements of atmospheric and air-monitoring applications.

**Summary**

Picarro G1301 is a field-deployable, real-time, ambient gas monitor that measures atmospheric levels of methane and carbon dioxide with ppbv sensitivity and water vapor with ppmv sensitivity. It maintains high linearity, precision, and accuracy over changing environmental conditions, with minimal calibration. The unique capabilities of the underlying WS-CRDS technology are complemented by a superior analyzer design, including a high-precision wavelength monitor providing immunity to interfering gases, meticulous temperature and pressure control, and robust digital signal processing that transforms raw data into directly useable information.

Deployment in several atmospheric monitoring and meteorological facilities, including Penn State University, has shown that the analyzer requires minimal recalibration and no sample conditioning.

“The Picarro G1301 analyzers are providing invaluable field measurements,” said Ken Davis, Associate Professor of Meteorology at Penn State University. “High-precision and high-accuracy measurements of atmospheric composition, like those acquired by the Picarro Analyzer analyzer, are essential to our ability to observe and understand the earth’s carbon cycle. Picarro has been very responsive to our scientific needs.” “We deployed 5 Picarro units in an experimental observational network in the spring of 2007,” said Scott Richardson, Research Associate at Penn State, “and we have found the stability of the instruments to be truly remarkable. The instruments should significantly simplify the task of obtaining high-quality measurements of atmospheric composition.”