Ultra-Sensitive Measurements of Methane, Carbon Dioxide and Water Vapor for Atmospheric Monitoring

The capability of the EnviroSense 2000i CO₂ atmospheric inversion monitor has been expanded to include simultaneous measurements of carbon dioxide (CO₂), methane (CH₄), and water vapor (H₂O)—now available in the newly released EnviroSense 3000i.

For atmospheric inversion studies, the EnviroSense 3000i produces a precision of better than 0.20 parts-per-million volume (ppmv) for CO₂, 1 parts-per-billion volume (ppbv) for CH₄, and 100 ppmv for H₂O with a total measurement time of five seconds. The EnviroSense 3000i 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 EnviroSense 3000i is based on a combination of the unique capabilities of the underlying technology, Cavity Ringdown Spectroscopy (CRDS), and superior engineering of the ESP-1000 product platform designed to maximize the inherent advantages of CRDS including a patented wavelength monitor, precise temperature and pressure control, and robust digital signal processing to transform raw data into useful information.

**EnviroSense Performance**

Prior to product release, field measurements of CO₂ for atmospheric inversion were made by groups at Penn State, Harvard and NOAA in Boulder, Colorado. At NOAA the EnviroSense analyzer was co-located with an enhanced LI-COR CO₂ inversion monitor. Fig. 1 shows a 45 day period where the EnviroSense analyzer (red trace) and enhanced LI-COR (black 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 EnviroSense analyzer demonstrated a drift of 0.8 ppbv/day. The most exceptional aspect of this result is that the EnviroSense analyzer only received one calibration for CO₂ 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 CO₂ inversion monitor was calibrated every 5 hours in addition to extensive sample conditioning including removal of water vapor from the gas stream and temperature stabilization.

Most recently work has been completed to increase the sampling rate of the EnviroSense 3000i to enable atmospheric flux measurements for both CO₂ and CH₄. Fig. 3 highlights this high speed performance with CO₂ 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.

**Underlying Technology—Cavity Ringdown Spectroscopy**

The underlying technology of the EnviroSense 3000i is Cavity Ringdown Spectroscopy (CRDS). CRDS is an ideal technology for high sensitivity and high precision gas analysis because of three main characteristics. Firstly, 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 CRDS, the ESP-1000 product platform, utilizes a 3-mirror configuration with a finesse that yields a cavity lifetime of ~40 μs, equivalent to an optical path length of ~12 km. The optical and gas flow configuration is shown in Fig. 4 below.
The second distinguishing feature of CRDS is the ability to isolate a single spectral feature. The mode spacing of the ESP-1000 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 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 ESP-1000 provides an interference free hydrogen sulfide concentration measurement in diesel exhaust, a very complex gas stream with a high concentration of interfering species.

The third advantage of 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 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 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 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 CRDS cavity is shown in Fig. 6.

![Figure 6. Light intensity as a function of time in a CRDS system with and without a sample having resonant absorbance. Figure demonstrates how optical loss is rendered into a time measurement in CRDS.](image)

System Design
Development of the EnviroSense 3000i analyzer, and the ESP-1000 product platform on which it is based, has focused on maximizing the inherent strengths of 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 EnviroSense 3000i 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 ringdown rate, or optical loss, as a function of wavelength is handled by a set of custom electronics in the EnviroSense 3000i. 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 – 100 spectral points.

Custom electronics are combined with precise mechanical design to produce analyzer 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 enabling factors for analyzer accuracy, precision and long term stability without human interaction.

Recently the EnviroSense product line has 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 ESP-1000 was designed for reliability—to meet the demanding requirements of industrial process applications. The EnviroSense product line 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 air-monitoring applications.

Summary
EnviroSense 3000i 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. The EnviroSense 3000i maintains high linearity, precision, and accuracy over changing environmental conditions, with minimal calibration. The unique capabilities of the underlying 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 EnviroSense 3000i 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 EnviroSense 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 EnviroSense 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."