# A Field-Deployable, High Accuracy Atmospheric Multi-Gas Monitor Based on Cavity Ring-Down Spectroscopy

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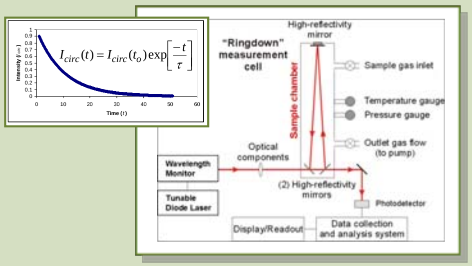
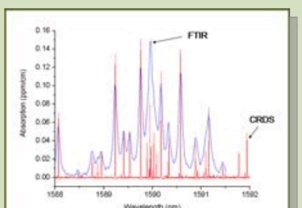
## ABSTRACT

We have developed a field-deployable, real time, ambient gas monitor capable of measuring atmospheric levels of carbon dioxide, methane, hydrogen sulfide, or ammonia with parts-per-billion (ppbv) sensitivity and water vapor with parts-per-million (ppmv) sensitivity. The monitor is based on Cavity Ring-Down technology; which is an all-optical technique capable of parts-per-billion sensitivity and fast 1 Hz or 10 Hz measurement rates in even the most complex gas streams. The high accuracy and excellent precision of this commercially available monitor make it ideally suited to address the demanding requirements of many atmospheric air and emissions continuous monitoring applications. A patented high precision wavelength monitor makes certain that only the spectral absorption feature of interest is being monitored, greatly reducing the analyzer's sensitivity to interfering gas species. As a result, the analyzer maintains high linearity, precision, and accuracy over changing environmental conditions with minimal calibration required. Results from field trials of three different $CO_2$ analyzers at Harvard, Penn State, and the NOAA facility in Boulder CO will be discussed. These results indicate that the analyzers drift less than 500 ppbv per month and have a precision of less than 200 ppbv in a 1.5 second measurement. In addition, test results from $CH_4$, $H_2S$, and $NH_3$ analyzers will also be shown.

## Cavity Ring-Down Spectroscopy




- 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 energy decays from the cavity exponentially in time, or "rings down," with a characteristic decay time $\tau$.
- The ringdown time is measured as a function of laser wavelength. When the gas in the cavity is strongly absorbing, the ringdown time is short; when the gas is does not absorb, the ringdown time is long.
- The in-line high precision optical wavemeter permits acquisition of extremely high-resolution spectral scans that cannot be accomplished using FTIR.

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## Specifications

Picarro EnviroSense 3000i

- Precision
  - $CO_2$: <200 ppbv in 5 seconds
  - $CH_4$: <1 ppbv in 5 seconds
  - $H_2O$: < 100 ppmv in 5 seconds
- Maximum Drift
  - $CO_2$: 500 ppbv / month
  - $CH_4$: 3 ppbv / month

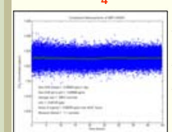
## Problems with Current Atmospheric Instrumentation

The existing atmospheric measurement instrumentation has complications which must be resolved during installation and use

- Device response is non-linear.
- Instruments are sensitive to water vapor concentration.
- Instruments are susceptible to measurement drift.
- Extensive modifications are often required as part of installation.
- Sample conditioning is required before the gas is presented to the instrument.
- Significant post processing is required to obtain meaningful results.
- Instruments require frequent calibration to maintain accuracy.
  - calibration standards are expensive — $1K to $2K for high accuracy

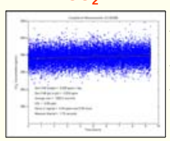
## Measured Precision

**$CH_4$**



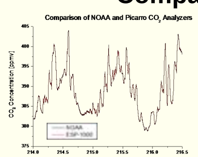
- Zero Drift
  - Slope = 0.02ppbv/day
  - Peak to peak = 0.66ppbv
- Precision
  - 1-sigma = 0.7ppbv
- LDL
  - 1.39pptv

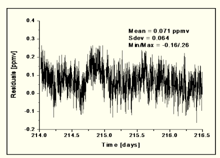
**$CO_2$**



- Zero Drift
  - Slope = 0.03ppmv/day
  - Peak to peak = 0.04ppmv
- Precision
  - 1-sigma = 40ppbv
- LDL
  - 80pptv

## Comparison With NOAA



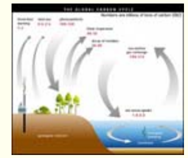




- The EnviroSense 2000i analyzer was compared to NOAA's instrument over the course of the field trial.
- The graphs above are for a two day period. The graph on the left shows the readings from the two instruments overlapping and the graph on the right is the residual between them.
- The average difference between the analyzers was 71 ppbv and the standard deviation was 64 ppbv.
- Over the 45-day course of the field trial, the average difference was 180 ppbv.
- Sources of error include:
  - $CO_2$ concentrations were changing faster than the NOAA instrument can track
  - Water vapor measurement rate not set fast enough
  - Drift in the EnviroSense 2000i clock

**An ultra-sensitive, real-time $CO_2$ and $CH_4$ analyzer**

## Need for High-precision Analyzers

- Human activity, primarily fossil fuel use, is adding roughly 3 ppm/yr of $CO_2$ to the atmosphere.
- Increasing atmospheric $CO_2$ concentrations are changing the climate.
- Globally, terrestrial ecosystems are currently removing about ¼ of the human emissions, but the location of and reasons for this buffer to climatic change are not well under stood.
- Determining regional terrestrial sources and sinks of $CO_2$ is a challenging technical problem.



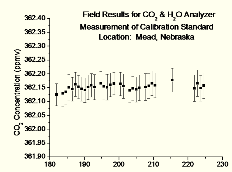
Source: http://www.esd.ornl.gov/iab/iab2-2.htm

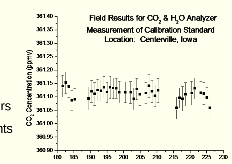
## High-precision, High-accuracy $CO_2$ Mixing Ratio Measurements


- The EnviroSense 2000i instruments are designed to measure atmospheric carbon dioxide 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 of five communications-tower-based atmospheric $CO_2$ measurements located in the upper mid-west, USA. A primary goal of this 18-month project is to increase the density of regional atmospheric $CO_2$ data so that:
  - Atmospheric inversion data can provide well-constrained regional ecosystem carbon flux estimates.
  - The trade off between data density and accuracy of the inversion-derived flux estimates can be determined quantitatively using field observations, thus providing guidance to future observational network designs.

## Long Term Drift in the Field

- $CO_2$ and $H_2O$ are continuously monitored; calibration standards are momentarily measured every 20 hours
- Data shown at right are measurements of calibration standards after installation at Centerville, IA and Mead, NE



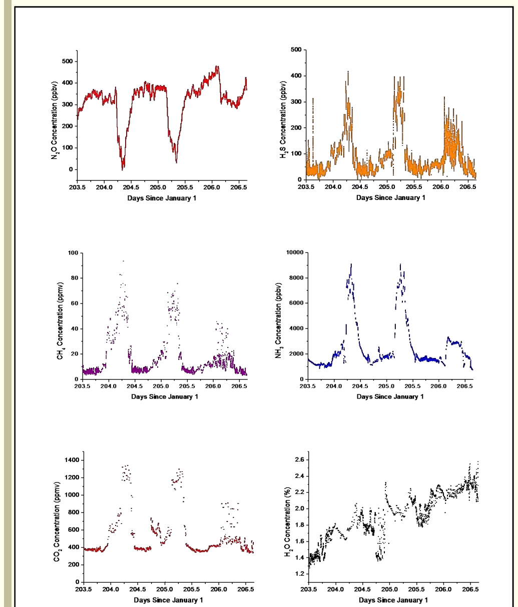




**ppb precision and accuracy without sample conditioning**

## Six-Species Analyzer

Picarro EnviroSense 6000

- Targeted Precision (12 minutes total)
  - $NH_3$: < 1 ppbv
  - $CH_4$: < 1 ppbv
  - $N_2O$: < 10 ppbv
  - $H_2S$: < 2 ppbv
  - $CO_2$: < 500 ppbv
  - $H_2O$: < 500 ppmv




## Conclusions

- Results indicate that the EnviroSense 3000i analyzer meets or exceeds the requirements of the atmospheric inversion application— and does so without the need for sample conditioning
- The EnviroSense 2000i analyzer maintained its calibration for extended periods of time— reducing the need for calibration dramatically reduces the maintenance cost
- Results indicate that the extreme accuracy and stability of the EnviroSense 2000i/3000i analyzers could significantly reduce calibration/maintenance costs and facilitate networked deployment
- A six species analyzer capable of measuring $H_2S$, $CH_4$, $NH_3$, and $N_2O$ at the low parts-per-billion level and $CO_2$ and $H_2O$ at the parts-per-million level has been developed and shown to meet or exceed the targeted sensitivity and precision requirements.

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**Next generation analyzer for monitoring of $CO_2$, $CH_4$, $H_2S$, $NH_3$, $N_2O$ and $H_2O$**