HIGH-PRECISION MEASUREMENTS OF CO_2, CH_4 AND H_2O FOR ATMOSPHERIC INVERSION AND EDDY COVARIANCE FLUX BASED ON CAVITY RINGDOWN SPECTROSCOPY

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PICARRO
Reliable by Design

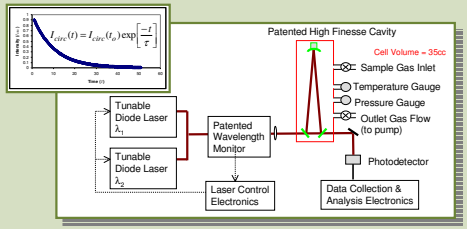
ABSTRACT

Field deployable instrumentation that measures carbon dioxide, methane, and water vapor with both high-accuracy and high-precision would reduce the uncertainty in the determination of terrestrial sources and sinks of these dominant greenhouse gases, resulting in improved predictive models and a deeper understanding of the global carbon cycle.

Existing atmospheric monitors based on non-dispersive infrared sensors have known problems — they are non-linear, sensitive to water vapor concentration, and susceptible to drift. Furthermore, these instruments require extensive modifications and sample conditioning, frequent zero and span calibrations, and significant post processing of the data. Additionally, many cannot easily be calibrated simultaneously from site to site to the level of accuracy required for use in atmospheric inversion studies.

Picarro has developed a line of high-precision carbon dioxide/methane/water vapor analyzers for atmospheric inversion and Eddy Covariance Flux measurements that maintain high linearity, precision, and accuracy over changing environmental conditions, with minimal calibration. The outstanding performance is based on a combination of the unique capabilities of the underlying optical absorption technology, Cavity Ringdown Spectroscopy (CRDS), and engineering designed to maximize the inherent advantages of CRDS including a high-precision wavelength monitor that ensures only the spectral absorption feature of interest is being monitored. Precise temperature and sub-torr pressure control enables excellent accuracy from analyzer to analyzer and low drift over time— important considerations for a network of measurement sites. The extremely compact cell size gives the analyzer fast rise and fall times at very small flow rates translating into significantly reduced calibration gas volumes and enabling a true 10 Hz response. Because the analyzers do not require sample conditioning or frequent calibration and maintain high linearity, precision, and accuracy over changing environmental conditions, these analyzers could significantly improve the accuracy and precision of greenhouse gas measurements while reducing the operating costs of monitoring, enabling higher density deployment.

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 τ.
- 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 does not absorb, the ringdown time is long.

Maximizing the Advantages of CRDS

- Compact, high finesse ring cavity provides ppt sensitivity with high stability
  - 35 ml cavity volume? small enough for very rapid sample exchange with moderate flow while giving a pathlength >12 km
- High precision inline wavelength monitor with femtometer resolution maximizes selectivity resulting in spectral resolution orders of magnitude higher than FT-IR
  - accurate spectral location isolates individual spectral features? high linearity
- Sub-ambient operation enhances selectivity through line narrowing
- Precise temperature and sub-torr pressure stability enhances accuracy and minimizes drift
  - temperature controlled to 1 part in 3000, pressure to 1 part in 500
- Telecom grade DFB lasers and micro-optical components maximize reliability

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Problems with Current Atmospheric Instrumentation

The existing atmospheric measurement instrumentation based on NDIR technology 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

High-precision Carbon Dioxide, Methane and Water Vapor Analyzer

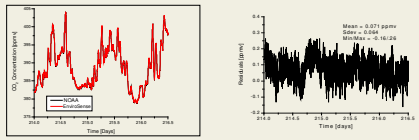
The EnviroSense 3000i is a field-deployable, real-time, ambient gas analyzer that measures atmospheric levels of methane and carbon dioxide with parts-per-billion (ppbv) sensitivity and water vapor with parts-per-million (ppmv) sensitivity while maintaining high linearity, precision, and accuracy over changing environmental conditions with minimal calibration required.

Specifications

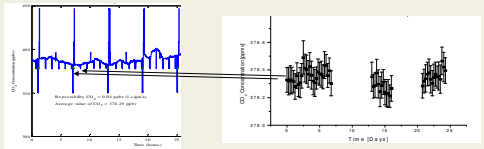
Picarro EnviroSense 3000i

- Precision
  - CO_2: < 200 ppbv in 5 seconds
    < 50 ppbv in 2 minutes
  - CH_4: < 1 ppbv in 5 seconds
  - H_2O: < 100 ppmv in 5 seconds
- Maximum Drift (24 hours/month)
  - CO_2: 150 ppbv / 500 ppbv
  - CH_4: 1 ppbv / 3 ppbv

Comparison With NOAA



- The EnviroSense 2000i analyzer was compared to NOAA's NDIR instrument over the course of a 45 day field trial at NOAA's Boulder tall tower site
  - Over the 45-day field trial, the average difference was 180 ppbv
  - EnviroSense connected to atmospheric gas stream before conditioning
  - While NOAA's NDIR went through periodic calibration (every 5 hours) throughout the trial, the EnviroSense 2000i was calibrated only once

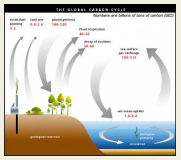


Drift over 25 days < 150 ppbv or 1 part in 2500

An ultra-sensitive, real-time CO_2 and CH_4 analyzer for atmospheric inversion

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.

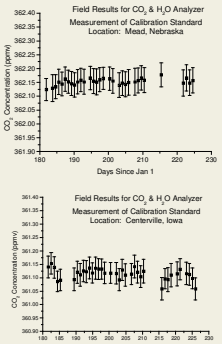


Source: http://www.esd.ornl.gov/iab/iab2-2.htm

High-precision, High-accuracy CO_2 Mixing Ratio Measurements

- The EnviroSense 2000i analyzers 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

Methane, Carbon Dioxide and Water Vapor 10 Hz Flux Analyzer

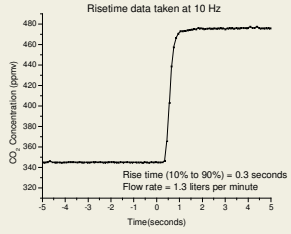
Designed specifically to enable eddy covariance flux measurements of both methane and carbon dioxide, the EnviroSense 3000f provides high precision measurements of methane, carbon dioxide and water vapor simultaneously at 10 Hz in a single, low drift analyzer. The compact cavity design minimizes the sample exchange time enabling a response time of < 0.1 seconds.

- Analyzer utilizes one laser for CO_2, and one laser for CH_4 and H_2O
- Concentration measurements for each species interleaved and reported simultaneously at 10 Hz

Specifications

Picarro EnviroSense 3000f

- Precision
  CO_2: < 500 ppbv at 10 Hz
  CH_4: < 3 ppbv at 10 Hz
  H_2O: < 500 ppmv at 10 Hz



Conclusions

- Field deployable instrumentation that measures carbon dioxide, methane, and water vapor with both high-accuracy and high-precision would reduce the uncertainty in the determination of terrestrial sources and sinks, resulting in improved predictive models and a deeper understanding of the global carbon cycle.
- The EnviroSense high-precision carbon dioxide/methane/water vapor analyzers for atmospheric inversion and Eddy Covariance Flux measurements maintain high linearity, precision, and accuracy over changing environmental conditions, with minimal calibration.
- Performance is based on a combination of the unique capabilities of the underlying optical absorption technology, and engineering designed to maximize the inherent advantages of CRDS including a high-precision wavelength monitor that ensures only the spectral absorption feature of interest is being monitored.
- Precise temperature and sub-torr pressure control enables excellent accuracy from analyzer to analyzer and low drift over time— important considerations for a network of measurement sites.
- The extremely compact cell size gives the analyzer fast rise and fall times at very small flow rates translating into significantly reduced calibration gas volumes and enabling a true 10 Hz response.
- Because the analyzers do not require sample conditioning or frequent calibration and maintain high linearity, precision, and accuracy over changing environmental conditions, these analyzers could significantly improve the accuracy and precision of greenhouse gas measurements while reducing the operating costs of monitoring, enabling higher density deployment.

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Next generation analyzer for high precision monitoring of CO_2,$CH_4$and H_2O