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Cavity Ring-Down Spectroscopy (CRDS): High precision measurements suitable for field, mobile and lab-based work

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University of Bristol, May 7th, 2013

Outline

- Introduction Picarro and CRDS technology
 R. Peters
- Greenhouse Gas analyzers and applications
 R. Winkler
- Stable isotope analyzers and applications R. Winkler
- Mobile solutions using Picarro Investigator R. Peters
- UK DECC network of tall tower measurements
 A. Grant
- Final Question and Answer Period
 All





Company Intro – World Class Ops





Picarro – Who are We?

- Core Technology licensed from Stanford University
- In existence since 1997 began with telecommunications
- Started development of products for optical spectroscopy in 2003
- Today specialize in Cavity Ring-Down Spectroscopy (CRDS)
- Based in Santa Clara, California, with offices in Europe and China
- 95 employees, 30 Ph.Ds, 26 Patents (and counting)
- Over 1500 analyzers in 57 countries

Picarro – Who are We?

Technologists



Transformers



How Green Is Davos?

BY ROMESH RATNESAR | JAN. 28, 2012 7:07 PM UTC | POSTED IN POSTS | 0 COMMENTS

A big slogan around town this year is "Toward A Greener Davos," the name of a WEF initiative aimed at "lowering the amount of pollutants" produced by the forum's 2,600 participants and their entourages. This · • •



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Participators



PG&E, Picarro Hit the Road With **Gas-Sniffing Chevy** Volts



Can mobile gas-sniffing units prevent another pipeline disaster?

JEFF ST. JOHN: JANUARY 30, 2012

Out of all the critical infrastructure that utilities protect, none of it is more critical than natural gas pipelines that can explode and kill people. Pacific Gas & Electric is still reeling from the 2010 pipeline explosion that killed eight people in San Bruno, Calif., one that has led to a massive investigation by state officials and a promise from PG&E to invest billions of dollars in pipeline safety.

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Technology

Optical spectroscopy – molecules in motion

- All molecular bonds are in motion
- Frequency of the motion is dependent on the atoms and bond type
- Specific frequencies of motion relate to specific frequencies of absorption



Optical spectroscopy – absorption spectra



- Beer-Lambert Law $A = \varepsilon lc$
- ε: Bond stretching
 frequency results in
 characteristic optical
 absorption
- *l*: a longer pathlength increases sensitivity (*l* = 20 km in Picarro)
- c: Signal intensity is related to quantity

Cavity Ring-Down Spectroscopy – Hardware

1 – Fire a laser at a wavelength that the molecule does not absorb



Cavity Ring-Down Spectroscopy – Hardware

2 – Fire a laser at a wavelength that the molecule DOES absorb ۲



CRDS: measuring multiple species (the real world)

- Ultra-high sensitivity means that *thousands* of lines for any given species are available for analysis
- Use multiple lasers and wide-bandwidth optics to allow multi-species operation in a single device



Avoiding cross-talk: "ideal world"



ΡΙСΛ R R O

Real world spectroscopy: lines are everywhere



- Measuring the peak is easy, but...
- How do you measure the baseline under the peak?

Picarro wavelength monitor: spectroscopic GPS

- Proprietary optical sensing technology
- Broadband, fiber-coupled device
- Stabilized to environmental fluctuations
- Single shot precision of 8 femtometers in the near infrared





Cavity Ring-Down Spectroscopy – Hardware

ALL spectroscopic techniques are affected by temperature and pressure variations.

Must control the variables that affect the spectroscopic signals:

- Temperature to +/- 0.005 °C
- Pressure to +/- 0.0001 Atm





Cavity Ring-Down Spectroscopy – Hardware

"drop tested according to MIL-STD 810F standard test (4" height, 12 edges (x,y,z axes), 2 drops each edge) and vibration tested (2 axis, 25 Hz, 1gp-p acceleration, 15 minutes each axis) during manufacturing to prove ruggedness in the field"



ΡΙСΛ R R O

Clean and Simple Design







- PC is built-in, pre-installed with Windows and all necessary software, including data integration
- Compact and Plug-and-Play
- Portable Networkable Interfaceable

Inside the box



Cutting-edge technology that is easy to use



Start-up Procedure

- Connect vacuum and inlet tubing
- Connect AC power, keyboard, mouse, monitor
- Turn on Pump
- Press start button
- Get cup of coffee while instrument warms up
- Enjoy your data!

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Suitable for Virtually any Situation



Cavity Ring-Down Spectroscopy - Analytes

Concentration only

- G2103: NH₃
- G2114: H₂O₂
- G2205: HF + H₂O
- G5105: N₂O

Stable Isotopes

- G2131: δ^{13} C in CO₂
- G2132: δ^{13} C in CH₄
- G2201-i: δ^{13} C in CO₂ and CH₄
- G5101-i: δ^{15} N in N₂O
- L2130-i: δD and $\delta^{18}O$ in H_2O
- B2221-i: $\delta D \& \delta^{13}C$ in H₂O & CO₂
- Aurora-CRDS: DIC/DOC & δ^{13} C in CO₂
- Automate-CRDS: DIC/carbonates + iCO₂

- G2203: CH₄ + C₂H₂
- G2204: CH₄ + H₂S
- G2301: CO₂ + CH₄ + H₂O
- G2401: CO₂ + CH₄ + CO + H₂O
- G2508: $N_2O + CO_2 + CH_4 + NH_3 + H_2O$

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{}^{12}\text{CO}_2 + {}^{13}\text{CO}_2
{}^{12}\text{CH}_4 + {}^{13}\text{CH}_4
{}^{12}\text{CO}_2 + {}^{13}\text{CO}_2 + {}^{12}\text{CH}_4 + {}^{13}\text{CH}_4
{}^{14}\text{N}^{14}\text{NO} + {}^{14}\text{N}^{15}\text{NO} + {}^{15}\text{N}^{14}\text{NO}
{}^{1}\text{HO}^{1}\text{H} + {}^{2}\text{HOD} + \text{H}_2{}^{16}\text{O} + \text{H}_2{}^{18}\text{O}
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{}^{1}\text{HO}{}^{1}\text{H} + {}^{2}\text{HOD} + {}^{12}\text{CO}_{2} + {}^{13}\text{CO}_{2}
DIC/DOC & {}^{12}\text{CO}_{2} + {}^{13}\text{CO}_{2}
DIC/Carbonates & {}^{12}\text{CO}_{2} + {}^{13}\text{CO}_{2}
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Markets

Atmospheric Science - GHG



Flux GHG Analyzer Rapid gas exchange Metabolic Process





Isotopic H₂O Source/Fate Water Vapour



Isotopic N₂O Source/Fate Nitrogen Metabolic Process

Ecology



Isotopic H₂O Source/Fate Water



Flux GHG Analyzer Rapid gas exchange Metabolic Process





Isotopic N₂O Source/Fate Nitrogen Metabolic Process



Isotopic CO₂ + CH₄ Source/Fate Carbon Metabolic Process



Food Web, Migration

Hydrology

Agriculture Water Use Efficiency



Glaciology Climate Change





Atmosphere/Metrology Water Vapor





Biology



Animal Metabolism Measure Respired ¹³CO₂



Archaeology ¹³C + D to tell diet



Human Metabolism Double Labelled Water



Animal Migration Measure Feather ¹³C + D



Food Web Measure ¹³C + D PICARRO

Geology



Geological Gas Analysis ¹³CO₂ and ¹³CH₄





Paleo Biosignatures ¹³C + D



Geothermal Fluids Isotopic H₂O Isotopic Carbonates PICARRO



Source Rock Analysis ¹³C + D

Picarro community

A forum for users to ask questions and share experience, knowledge and know-how



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