High Performance Analyzers for Fast, Real-time Measurements

15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases, and Related Tracer Measurement Techniques

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Novel Instruments Provide New Opportunities

- **Fast Greenhouse Gas Analyzer**: CH₄, CO₂, H₂O at 10 Hz
- **Fast N₂O/CO Analyzer**: N₂O and CO at 20 Hz
- **Carbon Dioxide Isotope Analyzer**: δ¹³CO₂ and CO₂ at 2 Hz
- **Fast Methane Analyzer**: CH₄ at 20 Hz
- **Water Vapor Isotope Analyzer**: δ¹⁸O, δ²H and H₂O at 2 Hz
- **Liquid Water Isotope Analyzer**: δ¹⁸O, δ²H at 120 samples/day
- **Fast Ammonia Analyzer**: NH₃ at 10 Hz
Novel Instruments Provide New Opportunities
(> 280 instruments on 7 continents)

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Lake Untersee, Antarctica (NASA)
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Measurements on-board UAV (ETH Zurich)
High Resolution Absorption Spectrometry: General Overview

Beer-Lambert-Bouguer Law:
\[
\frac{\Delta I}{I_0} = 1 - \exp(-\alpha L_{\text{eff}})
\]

- \( \frac{\Delta I}{I_0} \) = fractional change in laser intensity
- \( S \) = absorption line strength
- \( \chi \) = mixing ratio (mole fraction)
- \( P \) = total pressure
- \( L_{\text{eff}} \) = effective optical path length
- \( \alpha(\lambda) \) = absorption coefficient, \( S \, P \, \chi \, \phi(\lambda) \)
Absorption Spectrometry

Water Spectrum

- Mid-IR strongly absorbs, but is hardware limited
- Near-IR region is accessible with inexpensive telecom lasers
- Near-IR lasers are robust, reliable, easy to use, inexpensive
Cavity Ringdown Spectroscopy (CRDS)
Invented in 1988 by LGR founder (O’Keefe)

- High reflectivity mirrors, $R$
- High-finesse cavity yields long effective optical path
- Rate of decay ($1/\tau$) depends on absorption $\alpha$
- Sensitivity derived from long optical path
- Independent of laser amplitude fluctuations

$$\tau \sim \frac{L}{1 - R + \alpha}$$
Absorption determined from $\tau(\lambda)$ vs $\lambda$: 

$$\alpha(\lambda) = \frac{1}{c} \left( \frac{1}{\tau(\lambda)} - \frac{1}{\tau_o} \right)$$

- Measurement of $\tau(\lambda)$ + Beer’s Law yields mixing ratio
- Requires good laser spatial-mode quality
- Misalignments decrease sensitivity
- Requires relatively fast electronics
LGR’s Off-Axis ICOS: Cavity-Enhanced Absorption Technique

- Optical cavity provides pathlength enhancement: $L_{\text{eff}} = L / (1-R) = c \tau$
- Typical $R = 99.995\%$, $L_{\text{eff}} = 3$-25 kilometers (or greater)
- Extraordinarily robust - alignment insensitive, telecom-grade components
- Allows for near-IR measurements of overtone and combination bands
- Measurements using mid-IR QC lasers provide extremely high sensitivity
Advantages of Off-Axis ICOS (LGR patent)

- All parameters (absorption, \( L_{\text{eff}} \), \( P \), \( T \)) determined quickly (300-Hz, typical)
- Robust optical alignment \( \rightarrow \) negligible alignment drift, mechanically stable
- Off-axis alignment spatially separates beam paths through cell
  \( \rightarrow \) lengthens time/distance before beam retraces itself
  \( \rightarrow \) eliminates unwanted resonance interference effects
- Off-axis alignment eliminates optical feedback from cavity to laser source
LGR’s Off-Axis ICOS: typical raw data trace

**Transmission Spectrum**
- Measure absorption, baseline, detector offset
- Measured ringdown yields $L_{eff}$
- Measure/control gas flow parameters (T, P)
- Sweep laser wavelength at 100 – 500 Hz

**Measured Etalon Transmission**
- Accurately determines laser tuning rate
- Solid etalon ($\text{SiO}_2$)
- Measure length and temperature
- Converts time to relative laser frequency
Advantages of LGR’s instruments

• Sensitive, precise, accurate: long path, absolute measurement
• Selective: high resolution absorption provides specificity
• Fast: absorption spectra recorded directly in milliseconds
• Simple + robust: proven on 7 continents, aircraft, UAV, ocean
• Convenient: low power, open architecture, flexible
• Economical: prices starting at $30k
High accuracy requires minimizing total uncertainty

\[
\left( \frac{\Delta \chi}{\chi} \right)^2 = \left( \frac{\Delta (I/I_0)}{I/I_0} \right)^2 + \left( \frac{\Delta v_{\text{laser}}}{v_{\text{laser}}} \right)^2 + \left( \frac{\Delta P}{P} \right)^2 + \left( \frac{\Delta S}{S} \right)^2 + \left( \frac{\Delta L_{\text{eff}}}{L_{\text{eff}}} \right)^2
\]
Instrumentation Packaging: Options

rackmount (19” wide, 5U)  benchtop

- Portable rugged package allows field operation
- On-board computer provides real-time data analysis & storage
- 90-150 Watts, 27 kg
- No consumables
- Simple user interface; analog, digital (RS232), Ethernet outputs
- Fully autonomous operation
User Interface: Multiple Real-Time Displays

- Multiple display options: numeric, time chart, raw data/spectra
- Measurements of mixing ratio, gas temperature, pressure
- User-selectable data rate (0.01-20 Hz)
Gas Analyzer Options

- Multiport Injection Unit: automatic sampling from 16 locations

- Manual injection of discrete samples

- Remote monitoring/control

- Dynamic dilution system (quantification of high concentrations)
Fast Greenhouse Gas Analyzer ($\text{CH}_4, \text{CO}_2, \text{H}_2\text{O}$)

Applications include atmospheric monitoring, chamber flux

$[\text{CH}_4] = 2.052 \text{ ppm}$

$[\text{CO}_2] = 536.056 \text{ ppm}$

- $\text{CH}_4, \text{CO}_2, \text{H}_2\text{O}$ reported in ppm $\rightarrow$ mixing ratio
- Measurement cell pressure $\rightarrow$ Torr
- Mirror ringdown time ($\tau$) $\rightarrow$ microseconds
- Cell temperature $\rightarrow$ Celsius
- Current data file name, time
Fast Greenhouse Gas Analyzer: 1-Hz raw data

Precision (1 Hz):
- CH$_4$: 1 ppbv
- CO$_2$: 0.16 ppmv
- H$_2$O: 33 ppmv
Fast Greenhouse Gas Analyzer: Time Response

- Inlet switched from air to "zero air" to determine flow response
- Concentration decays yield time constants sufficient for eddy flux
• CH$_4$ and CO$_2$ in air measured at a 1-Hz sampling rate (10-Hz possible)
• Data and associated Allan plots show stable operation and ability to reliably average over long times to improve precision
Fast Greenhouse Gas Analyzer: Stability

- CH₄ and CO₂ in air measured at a 1-Hz sampling rate (10-Hz possible)
- Data and associated Allan plots show stable operation and ability to reliably average over long times to improve precision.
CO₂ (left) and CH₄ (right) were calibrated on a single-point.
CO₂ error bars indicate NOAA’s anticipated uncertainty of ±0.05 ppm.
CH₄ error bars indicate NOAA’s anticipated uncertainty of ±1 ppb for concentrations near 1.8 ppm and ±2 ppb for values outside this range.
Analyzer accurate to ±0.14 ppm for CO₂ and ±1.25 ppb for CH₄.
CH$_4$ measurements vs ref values

- Measurements agree with ref values to < 0.5% (0.1-25 ppmv)
Accurate CH$_4$ from ambient to 1000 ppmv

- Measurements agree with ref values to better than 1% (up to 1000 ppmv)
- High CH$_4$ levels demonstrated in field (rice, peat, landfills) by many users
- Off-Axis ICOS reports mixing ratios with extremely high optical depth
Fast N$_2$O/CO Analyzer for Flux

- Real-time continuous measurements in air
- Extremely wide dynamic range
- Fast (20 Hz) allows eddy covariance flux
- Low power (150 watts) facilitates field operation
- No sample prep - direct measurements in air
CO Analyzer (previous version; LN$_2$)
On-board measurements in troposphere/stratosphere

- Autonomous measurements of CO at 1 Hz on NASA DC8
- Reference gas cylinder used to verify mirror health
CO measurements in stratosphere (NASA DC-8)

- QC laser probes R(7) transition (v band) at 4602 nm (2173 cm\(^{-1}\))
- Cavity enhanced transmission (top) and absorption (bottom)
• CO reference measurements stable (< 0.5%) over 10 hours
• Reproducibility demonstrated w/o regular calibration
Measured CO during a 10-hour flight

- [CO] reached 24 ppbv (13 km, 41,000 ft)
CO in ambient air during NASA DC8 flight

- Data reported at 1-Hz rate
- Precision: <0.5 ppbv/Hz$^{1/2}$
CO + N$_2$O Analyzer: No cryogenic requirements

- Simultaneous, rapid, accurate measurements of CO and N$_2$O
- Sub-ppb precision in < 1 second
Fast CO + N$_2$O Analyzer: compressed air

- Simultaneous measurements of CO and N$_2$O
- CO precision: < 0.3 ppbv in 1 second
- N$_2$O precision: < 0.3 ppbv in 1 second
Fast CO + N\textsubscript{2}O Analyzer: N\textsubscript{2}O measurements

- Simultaneous measurements of CO and N\textsubscript{2}O
- CO precision: < 0.3 ppbv in 1 second
- N\textsubscript{2}O precision: < 0.3 ppbv in 1 second
Fast CO + N₂O Analyzer: CO measurements

- Simultaneous measurements of CO and N₂O
- CO precision: < 0.3 ppbv in 1 second
- N₂O precision: < 0.3 ppbv in 1 second
Fast CO + N₂O Analyzer: CO Accuracy

- Linear measurements over wide range
- Agree with mixture values (to within uncertainty)
Fast CO + N\textsubscript{2}O Analyzer: N\textsubscript{2}O Accuracy

- Linear measurements over wide range
- Agree with mixture values (to within uncertainty)
Fast CO + N\textsubscript{2}O Analyzer: $\sigma_{N_2O}$ vs. $t$

- Simultaneous CO and N\textsubscript{2}O measurements
- CO precision: 30 pptv in 100 seconds
- N\textsubscript{2}O precision: 30 pptv in 100 seconds
Fast CO + N$_2$O Analyzer: $\sigma_{CO}$ vs. t

- Simultaneous CO and N$_2$O measurements
- CO precision: 30 pptv in 100 seconds
- N$_2$O precision: 30 pptv in 100 seconds
Continuous measurements of \(^{13}\text{CO}_2/^{12}\text{CO}_2\) \(\delta^{13}\text{CO}_2\) and \(\text{CO}_2\)
- Fast (2 Hz) allows eddy covariance flux
- Low power (150 watts) facilitates field operation
- No sample prep - direct measurements in air
- Precise: \(\delta^{13}\text{CO}_2 < 0.2\) per mil (30 seconds)
Deployment: CCIA at ZERT (Carbon Sequestration)

Zero Emissions Research and Technology (ZERT) test site
Bozeman, Montana (July 2009)

Month-long release of CO$_2$ (buried pipe) for testing various schemes of leak detection in carbon sequestering

- Quantify $\delta^{13}$C signature of CO$_2$ release
- Measure $\delta^{13}$C from ambient sources (plant respiration)
- Record spatial profile transverse to pipe
- Record temporal variations at several locations
- Compare co-located measurements with other groups
Arriving to ZERT site in Van
ZERT: 0.2 tons/day release of CO₂

Month-long release of CO₂ (buried pipe) for testing various schemes of leak detection in carbon sequestering
Multi-location continuous $\delta^{13}CO_2$ and CO$_2$ (w/ LLNL)

Pump provides fast flow through all sampling lines

Reference cylinders (360 ppm, 2000 ppm)
Carbon Dioxide Isotope Analyzer w/ Multiport Input Unit

- Inlet manifold
- Carbon Dioxide Isotope Analyzer
- Multiport Input Unit
Setting Up Inlets
Inlets A, C, D, E, F, H, I, J spaced by 0.5 m intervals
Inlets B, G are 30 cm above A, F
Inlet K is located with tower shared by other teams
Inlets L, M are controls located 50 m away
Transverse Grid
Ready to Go
Release Starts 7/15/09 at noon

First signal seen at Port F less than an hour after release!
Time Record of Grid 7/15 to 7/17
Inlet L (control): observation of plant respiration

$\delta^{13}C = -27 \%$ plant signature (Keeling plot for one day)
Inlet L (control): observation of plant respiration

$\delta^{13}\text{C} = -29$‰ plant signature
(Keeling plot over 7 continuous days)
Port F: Hot Spot of ZERT Release

- Some CO$_2$ bursts exceed 2000 ppmv
- Data within instrument range: $\delta^{13}C = -58$‰ (ZERT source)
Control L: Filter Day/Night

Respiration seen at night

Day

Night
High CO$_2$ bursts observed $\delta^{13}$C = -58‰ corresponds to source release
Port D: Mixing of Plant and ZERT Leak

Keeling analysis suggests 2 sources:

- Plant respiration
- ZERT release
Respiration of plants is minimally seen during day; good signature of release.

Little of plume seen, perhaps wind is calm at night.
Port D: Mixing of Plant and Leak

Evidence of both sources seen in Keeling analysis. Clear signatures of both plant respiration and ZERT release.
Deployment of CCIA for Carbon Sequestration

Real-time spatial, temporal measurements of $\delta^{13}C$ and CO$_2$ at ZERT test site

- Ability to record distinct $\delta^{13}C$ signature of CO$_2$ release
- Measures $\delta^{13}C$ from ambient sources (plant respiration)
- Records physical map of release transverse to pipe
- Records temporal variations of release at several locations
- Multi-port system provides real-time spatial and temporal measurements of $\delta^{13}C$ and CO$_2$
Summary:
Novel Instruments Provide New Opportunities

- Fast, accurate, continuous real-time data in the field
- Measurements up to 20 Hz (fluxes)
- Precise, accurate over wide concentration ranges
- Measurements of discrete samples (via syringe)
- Measurements of $\delta^{13}C$, $\delta^2H$, $\delta^{18}O$ at 2 Hz
- Low power requirements
- Prices starting at $30k
Summary:
Novel Instruments Provide New Opportunities

- **Fast Methane Analyzer**: CH$_4$ at 20 Hz
- **Fast Greenhouse Gas Analyzer**: CH$_4$, CO$_2$, H$_2$O at 10 Hz
- **Carbon Dioxide Isotope Analyzer**: $\delta^{13}$CO$_2$ and CO$_2$ at 1 Hz
- **Fast N$_2$O Analyzer**: N$_2$O at 20 Hz
- **Methane Isotope Analyzer**: $\delta^{13}$CH$_4$ and CH$_4$ in real time
- **Water Vapor Isotope Analyzer**: $\delta^{18}$O, $\delta^2$H and H$_2$O at 2 Hz
- **Liquid Water Isotope Analyzer**: $\delta^{18}$O, $\delta^2$H at 120 samples/day
- **Fast Ammonia Analyzer**: NH$_3$ at 10 Hz

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Summary

- Fast, real-time field data w/o frequent calibration
- Measurements up to 20 Hz (eddy fluxes)
- Ultra-precise, accurate over wide concentration ranges
- Measurements of discrete samples (syringe injection)
- Measurements of $\delta^{13}C, \delta^2H, \delta^{18}O$ at 1 Hz