The Advantages of Cavity Ring-Down Spectroscopy in the Analysis of Diesel Engine Emissions

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Outline

- Applications driving the need for ultra-trace gas analysis
  - requirements for non-traditional emission analysis
- Cavity Ringdown Spectroscopy (CRDS)
  - an all-optical solution for analysis of combustion gases
- Maximizing the advantages of CRDS by design
  - performance and capabilities from a range of applications
    - H_2S analysis enables optimization of Lean NOx Traps
    - other non-traditional gas species including NH_3, H_2CO, N_2O, NO_2, NO
- Extending the platform to a multispecies analyzer
  - a scaleable architecture

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The Need for Ultra-trace Gas Analysis

- researchers investigating global climate change need measurements of greenhouse gases with ppt precision and accuracy to enable better models of the carbon cycle
  - need to measure CO_2 and CH_4 without interference from H_2O and with minimum drift
  - measuring isotopic CO2 ratios in ice core and soil samples
- process control optimization and trace impurities monitoring in petrochemical plants is driving the need for high speed analysis with ppb sensitivity and high molecular selectivity
- move to DUV lithography requires monitoring of airborne molecular contaminants such as NH_3 at ppt levels to minimize yield loss and prevent haze formation
- advanced combustion analysis to optimize NOx reduction approaches

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Requirements for Non-traditional Gas Analysis

- Developers of clean diesel engines and after-treatment systems need advanced combustion analysis to optimize NOx reduction approaches
  - need to measure non-traditional gas species such as H_2S, NH_3 and H_2CO with high sensitivity, at high speed and without interference in a dynamically changing exhaust stream
- Requirements for an ultra-trace combustion gas analyzer—
  - extreme selectivity
  - ppb sensitivity
  - speed from 1 Hz to 10 Hz
  - ppb precision and accuracy
  - reliable
  - easy to use and in some instances, field deployable

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Solution—
Ultra-trace Gas Analyzer Based on CRDS

- **High Sensitivity**, resulting from an extremely long effective pathlength and insensitivity to source fluctuations

- **Excellent Molecular Specificity**, enhanced by a high finesse cavity and narrow line lasers, results in spectral resolution orders of magnitude higher than FT-IR

- **High Linearity**, resulting from ability to distinguish individual absorption features

- **Extremely Low Drift**, enabled by high precision sample temperature and pressure control

- **High Speed**, driven by high speed electronics

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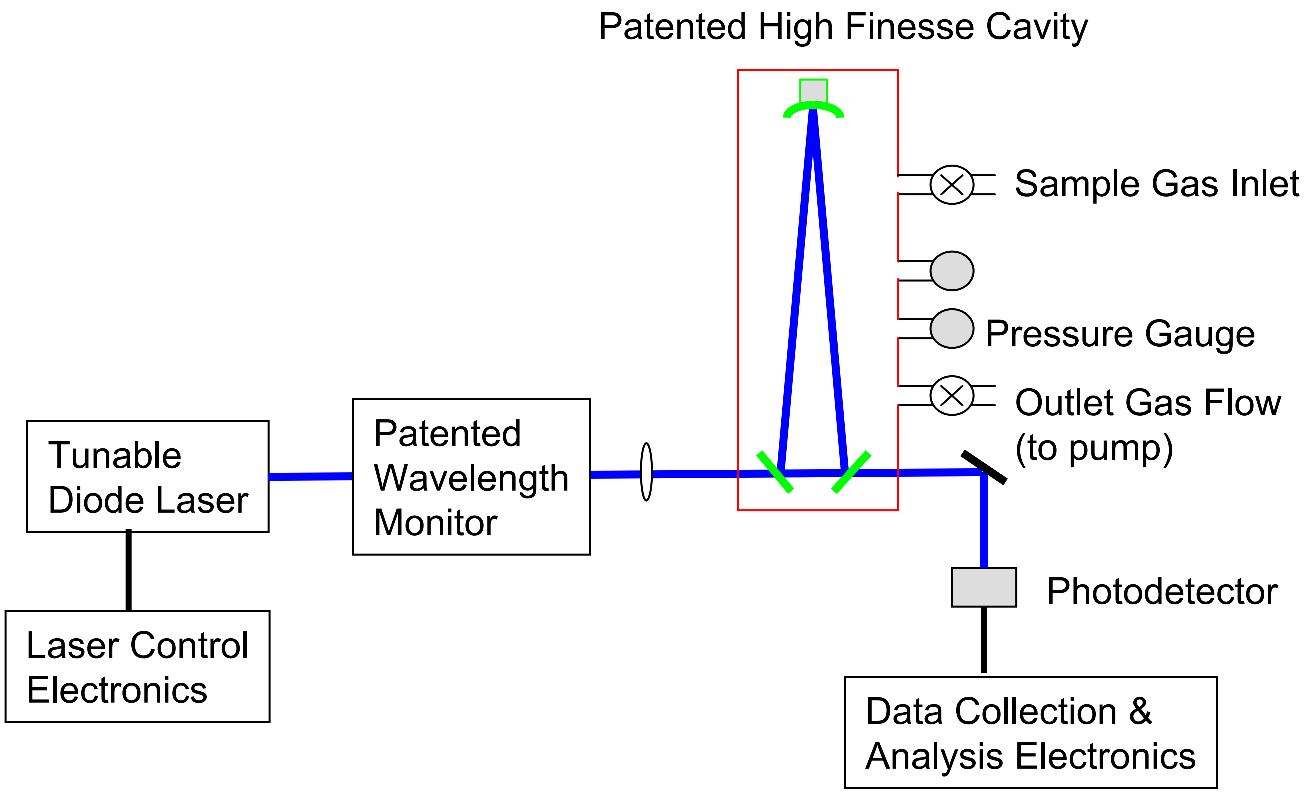
Overview of the Analyzer

- CRDS is a laser based optical technique
  - absolute absorption measurement
  - measurements directly related to concentration using the Beer-Lambert Law



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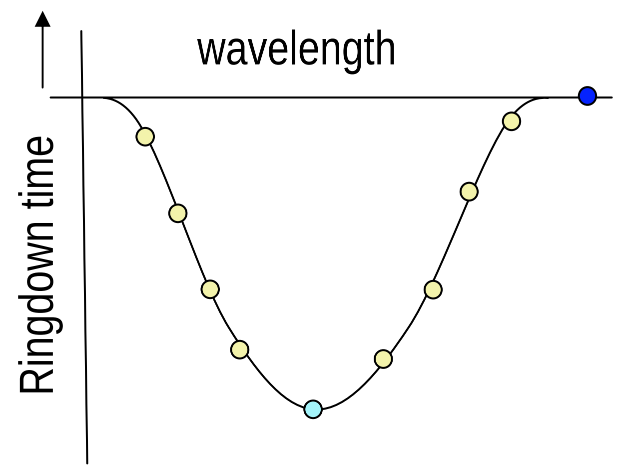
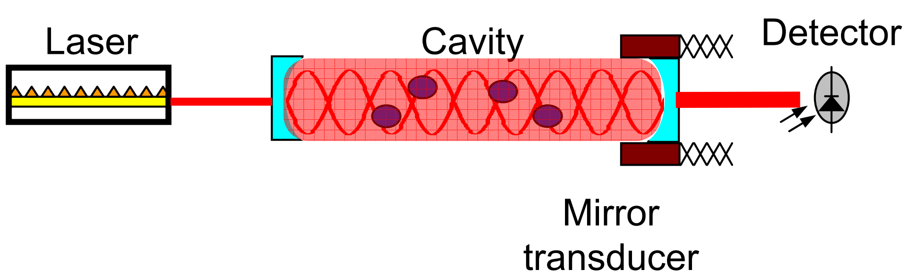
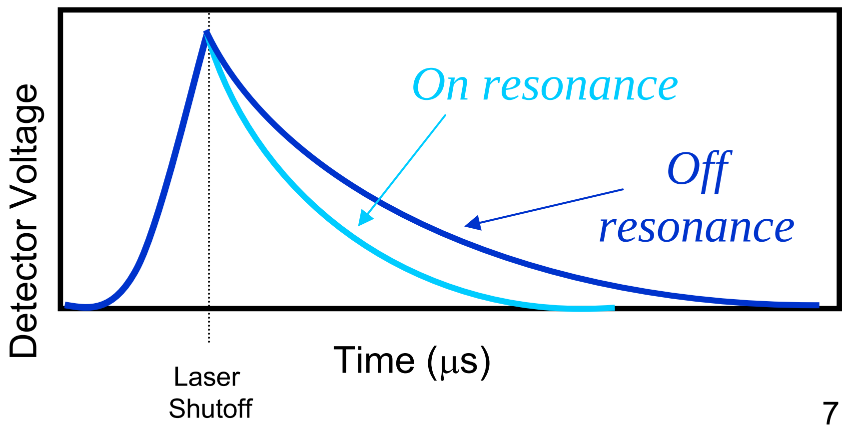
Measurement Process

- The basic measurement algorithm is:
  - tune laser and cavity to desired wavelength
  - inject light into the cavity
  - shut off light when light circulating in the cavity reaches threshold
  - measure decay time of light in cavity
  - change wavelength set point
  - repeat
- Measurement doesn't depend on laser stability







Analyzer Design—
Maximizes 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
- Sub-ambient operation enhances selectivity
  - line narrowing
- High precision inline wavelength monitor maximizes selectivity
  - accurate spectral location isolates individual spectral features
- 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

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Analyzer Design—
Maximizes the Advantages of CRDS, cont'd.

- High speed electronics and spectral analysis enables up to 10 Hz concentration measurement rates
  - kHz spectral data rate
- Scanning flexibility allows for optimization of performance
  - application specific scanning schemes are developed
    - optimize for speed vs. sensitivity
- Telecom grade DFB and micro-optical components maximize reliability

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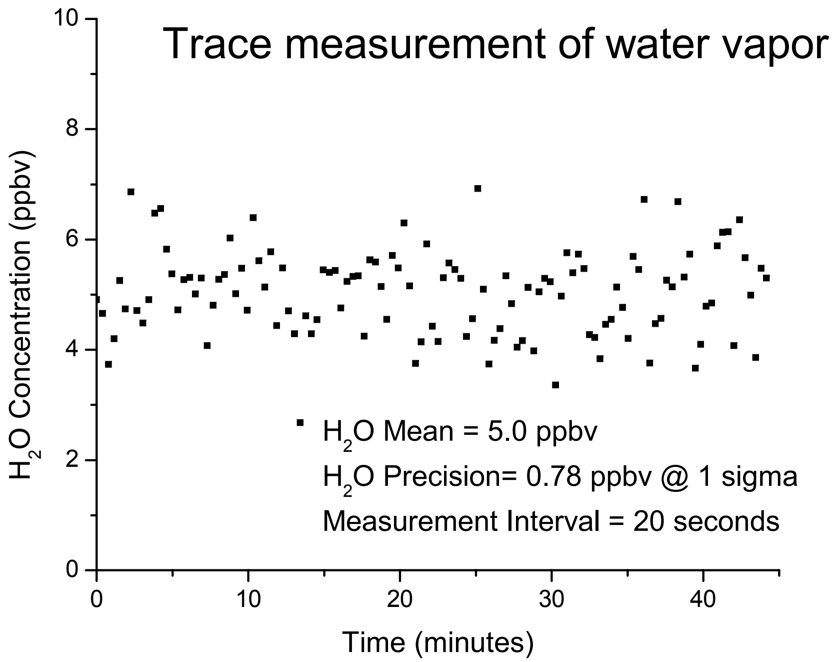
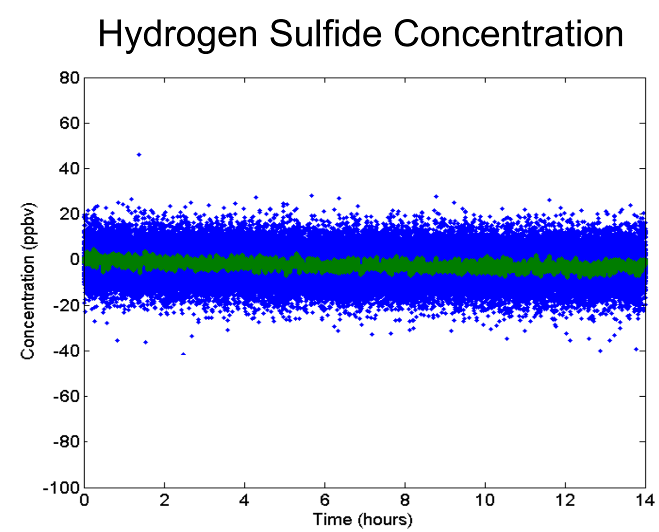
Outstanding Sensitivity

- High finesse cavity with a path length exceeding 12 km results in
  - parts-per-billion sensitivity to a wide variety of gas species
  - sub-ppbv precision in a few seconds
    - – precision 0.78 ppbv for water vapor





- Measurement Interval:
  - Time = 1.0 seconds
- Precision:
  - 1-sigma = 7.5 ppbv in one second
- Zero Drift:
  - Peak to peak = 12.8 ppbv over 14 hours

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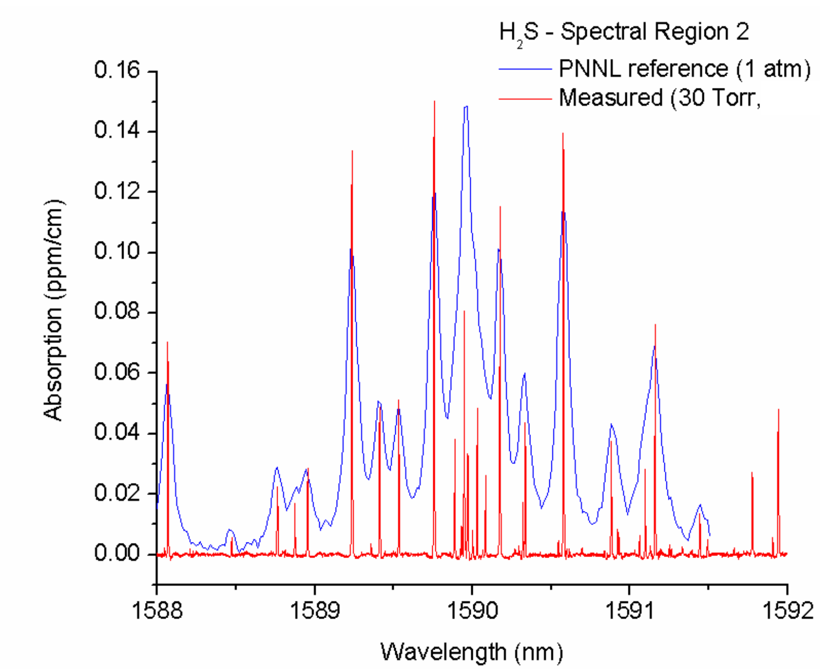
Narrowband Spectroscopy Maximizes Selectivity

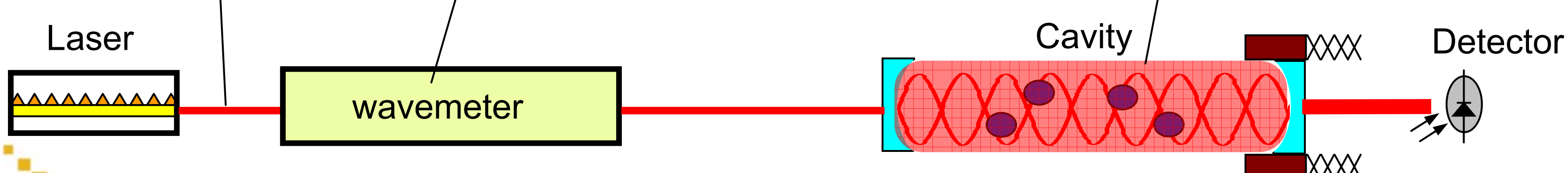


	Resolution (cm^{-1})	Pressure
FTIR	**0.5**	**760 Torr**
CRDS	**0.0003**	**10 to 760 Torr**

Sub-atmospheric pressure operation for narrower absorption features and better contrast with background absorbers

Narrowband laser light source

Proprietary high-precision inline wavemeter for **femtometer resolution** optical wavelength measurements



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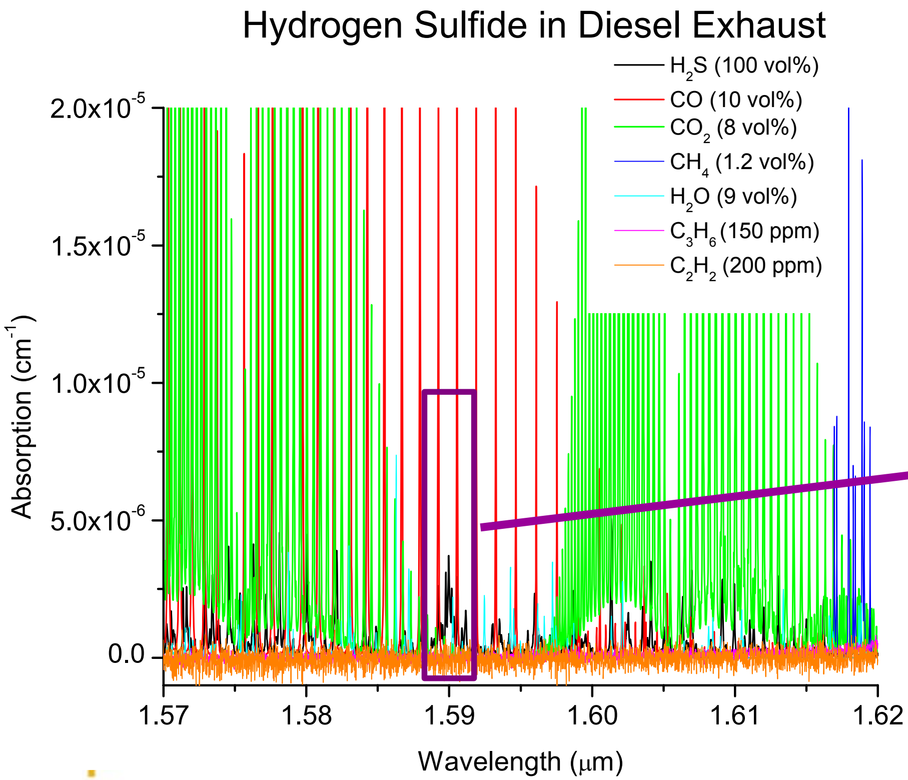
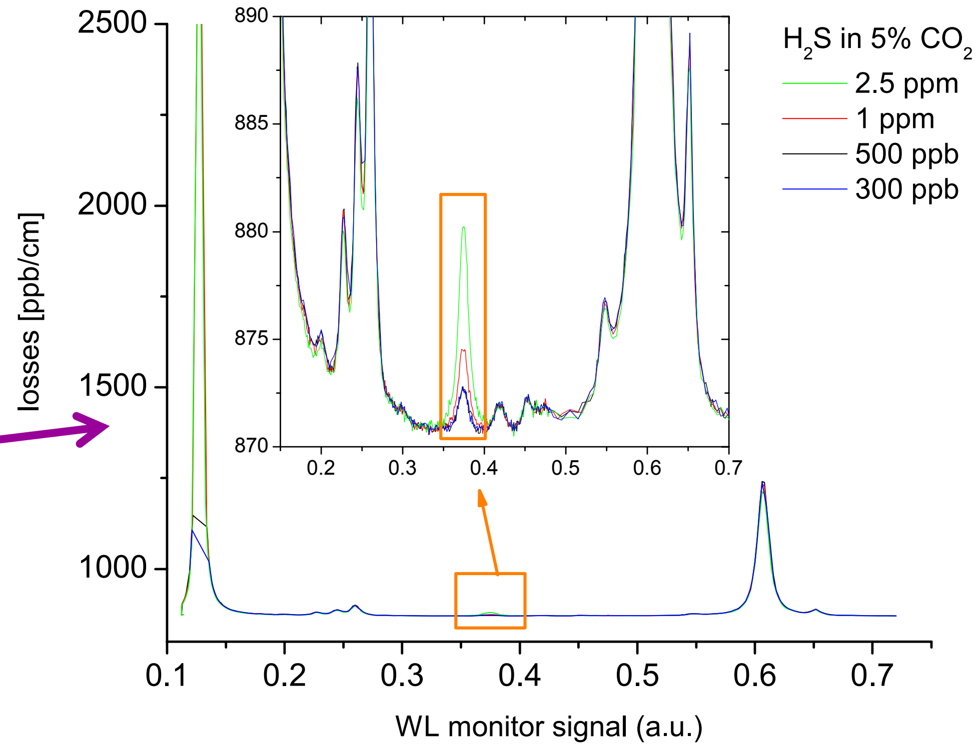
Sensitivity with Selectivity → Specificity

- Proprietary wavelength monitor and narrow linewidth laser provides
  - ability to isolate individual spectral features
  - insensitivity to changes in complex, highly absorbing background gas matrix





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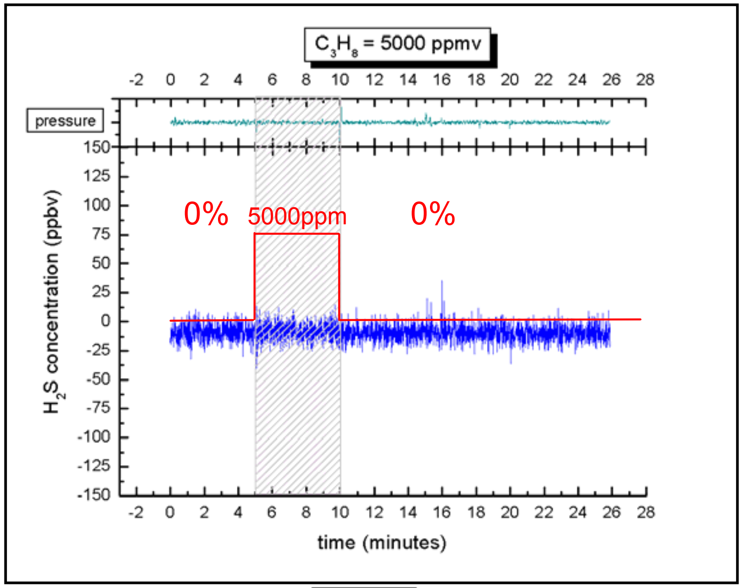
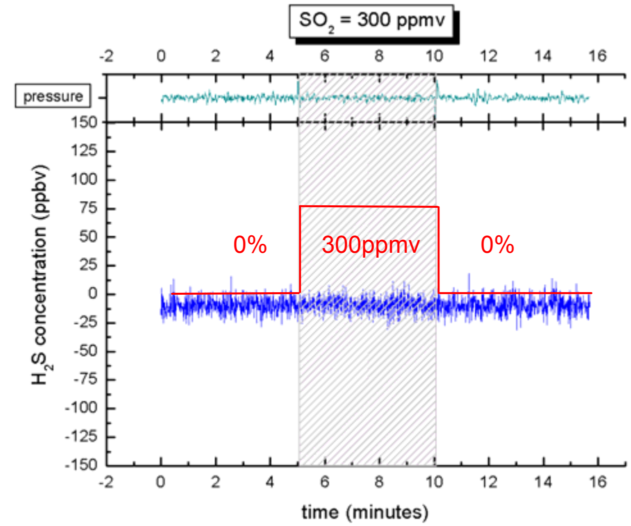
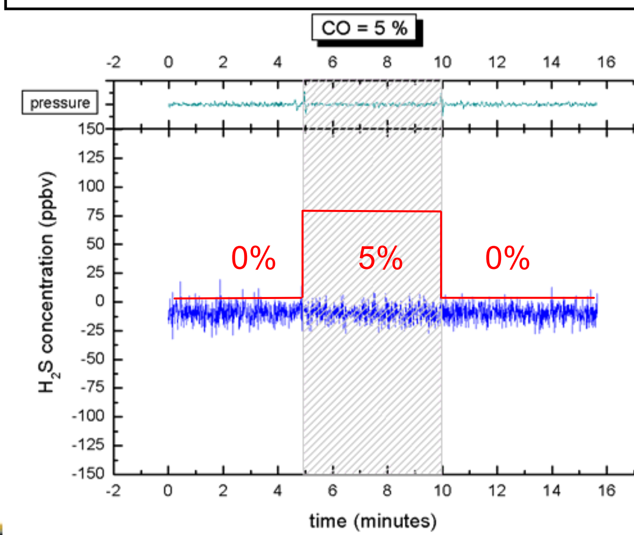
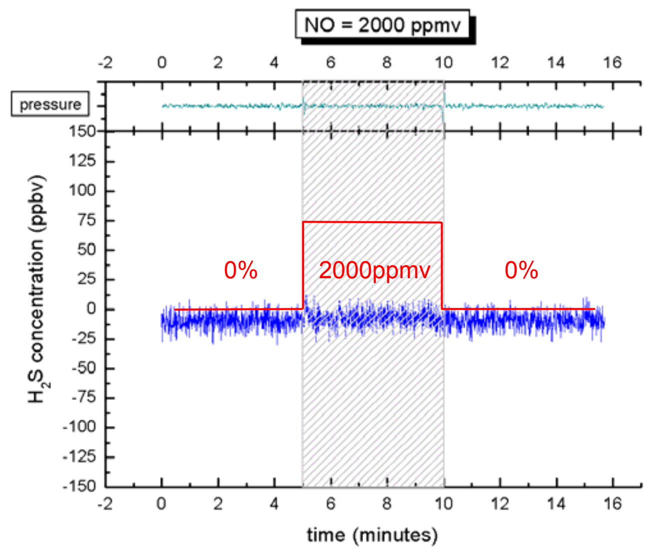
Specificity→ Accuracy Without Interference









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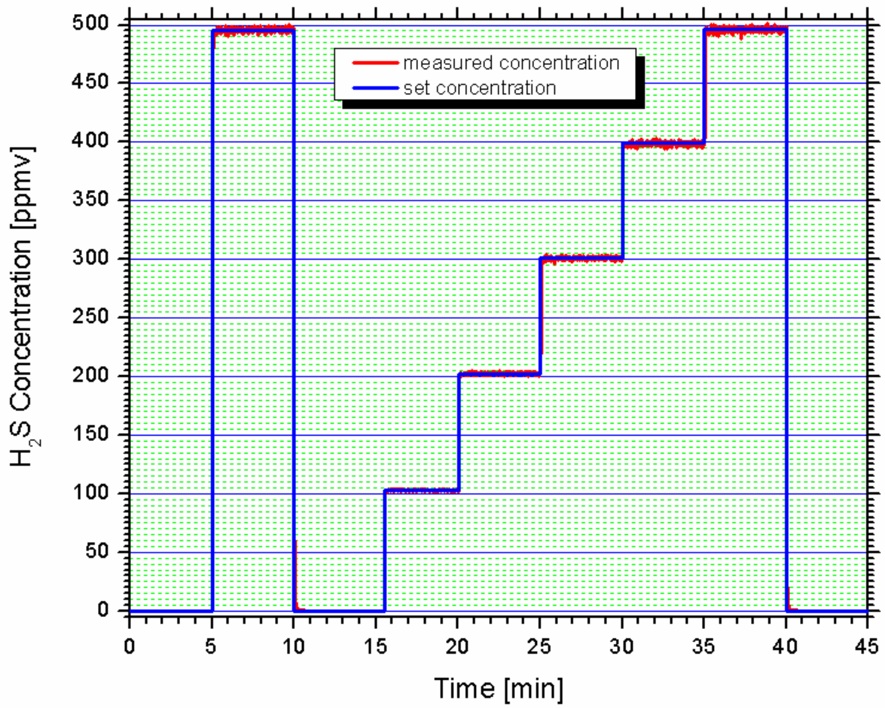
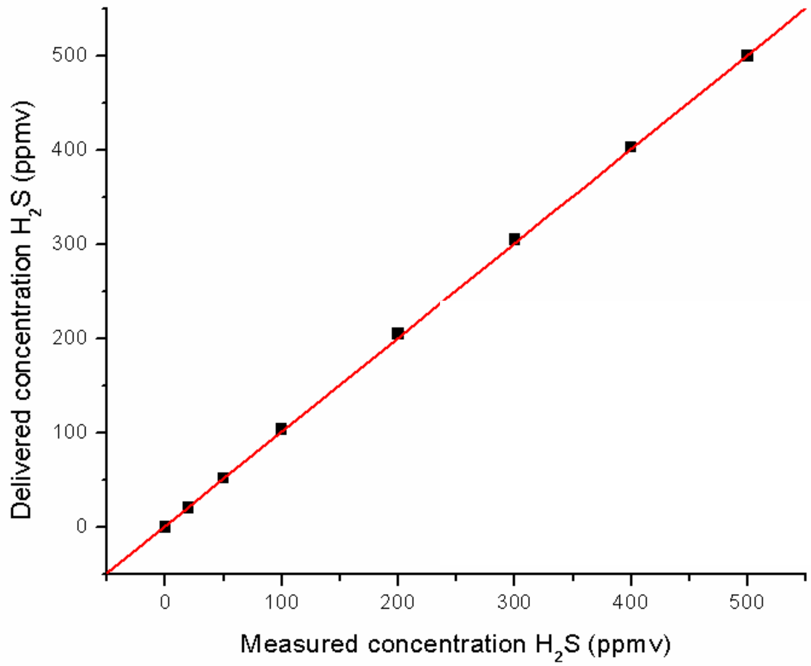
Specificity→ High Linearity

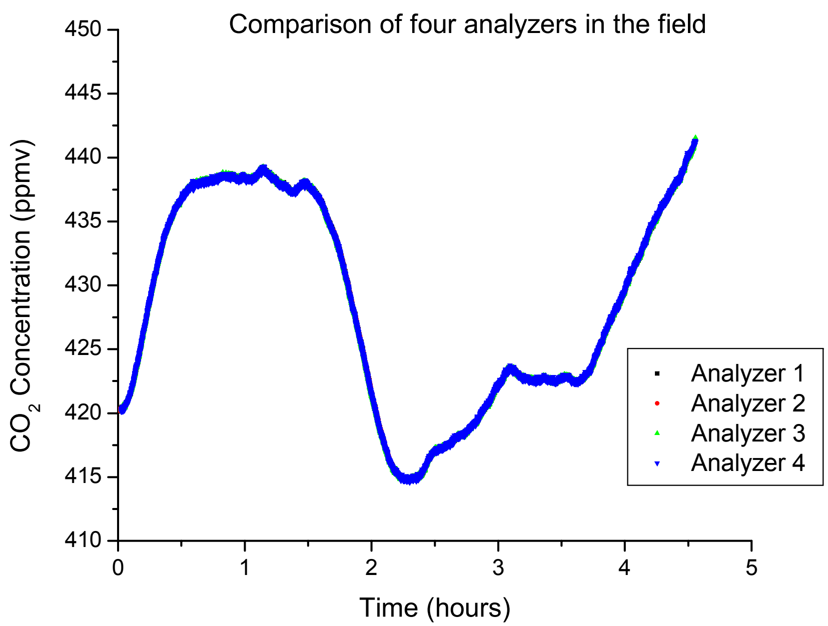


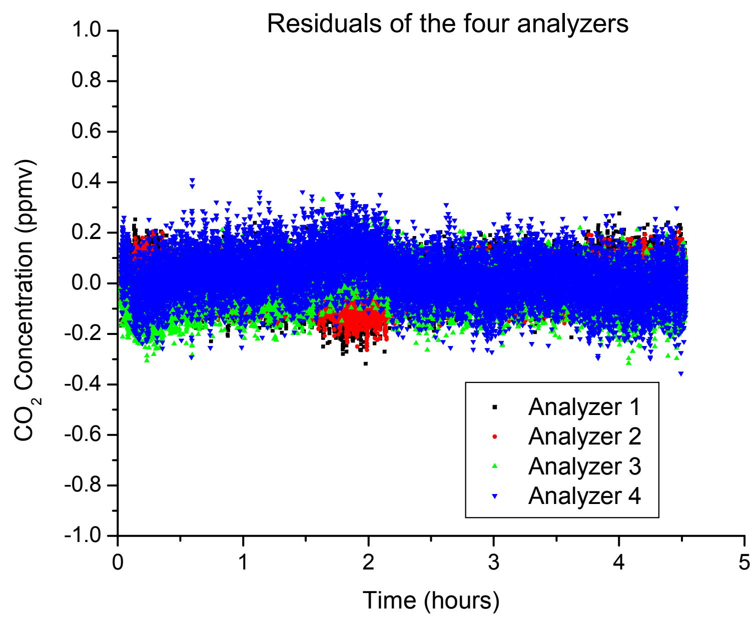


Highly linear across the entire dynamic range

High Accuracy

- precise temperature and sub-torr pressure stability enables
  - excellent accuracy from analyzer to analyzer
  - low drift over time





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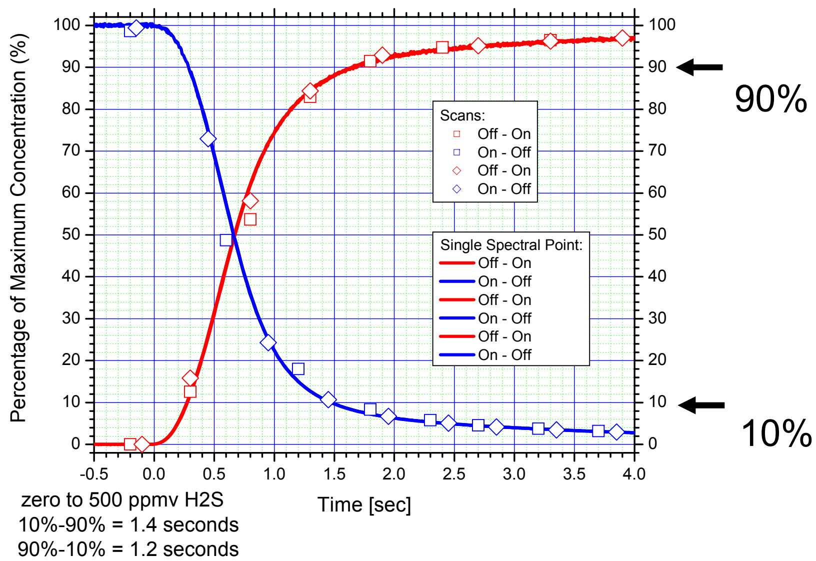
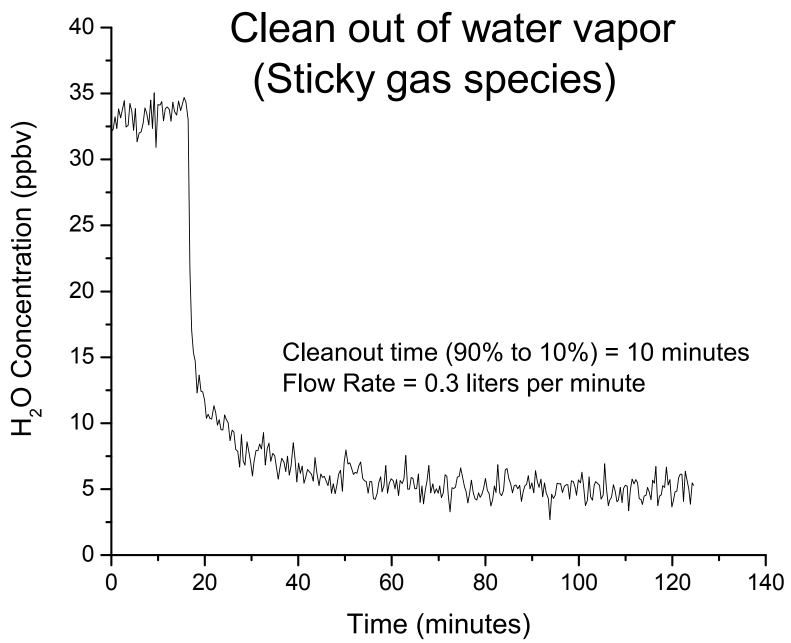
Fast Response

- 0.035 liter sample volume leads to
  - analyzer rise and fall times of ~ a second
  - fast clean out times even for sticky gases like H_2O

Rise and fall times for H_2S





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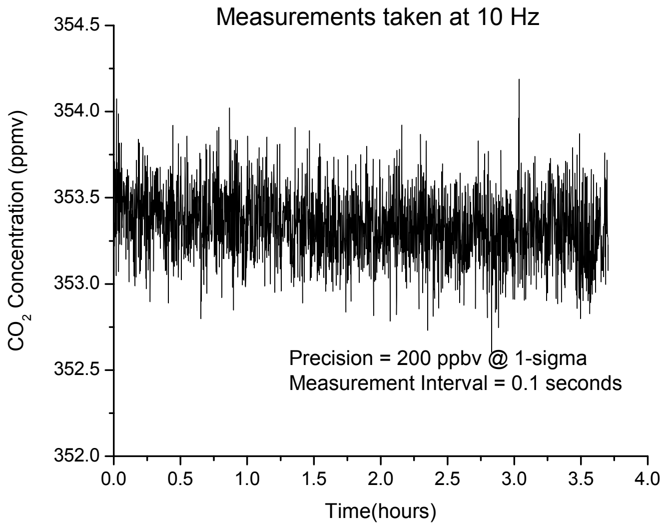
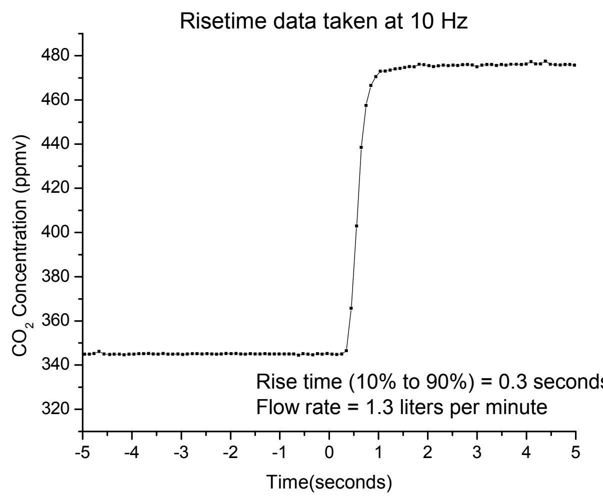
High Speed Analysis

- Scanning flexibility allows
  - application specific spectral scanning schemes
    - H_2S with LDL of 50 ppbv at 1 Hz in exhaust for sulfur balance for LNT optimization
    - H_2S with LDL of 2 ppbv (1 min) for ambient monitoring within cabin
    - NH_3 with LDL of 0.2 ppbv in ambient
    - NH_3 with LDL of 10 ppbv at 1 Hz in exhaust
    - H_2CO with LDL of ~15 ppbv as MSAT
    - H_2CO with LDL of ~ 0.5 -1 ppmv at 1 Hz in exhaust
  - 10 Hz operation for monitoring dynamics and capturing transients





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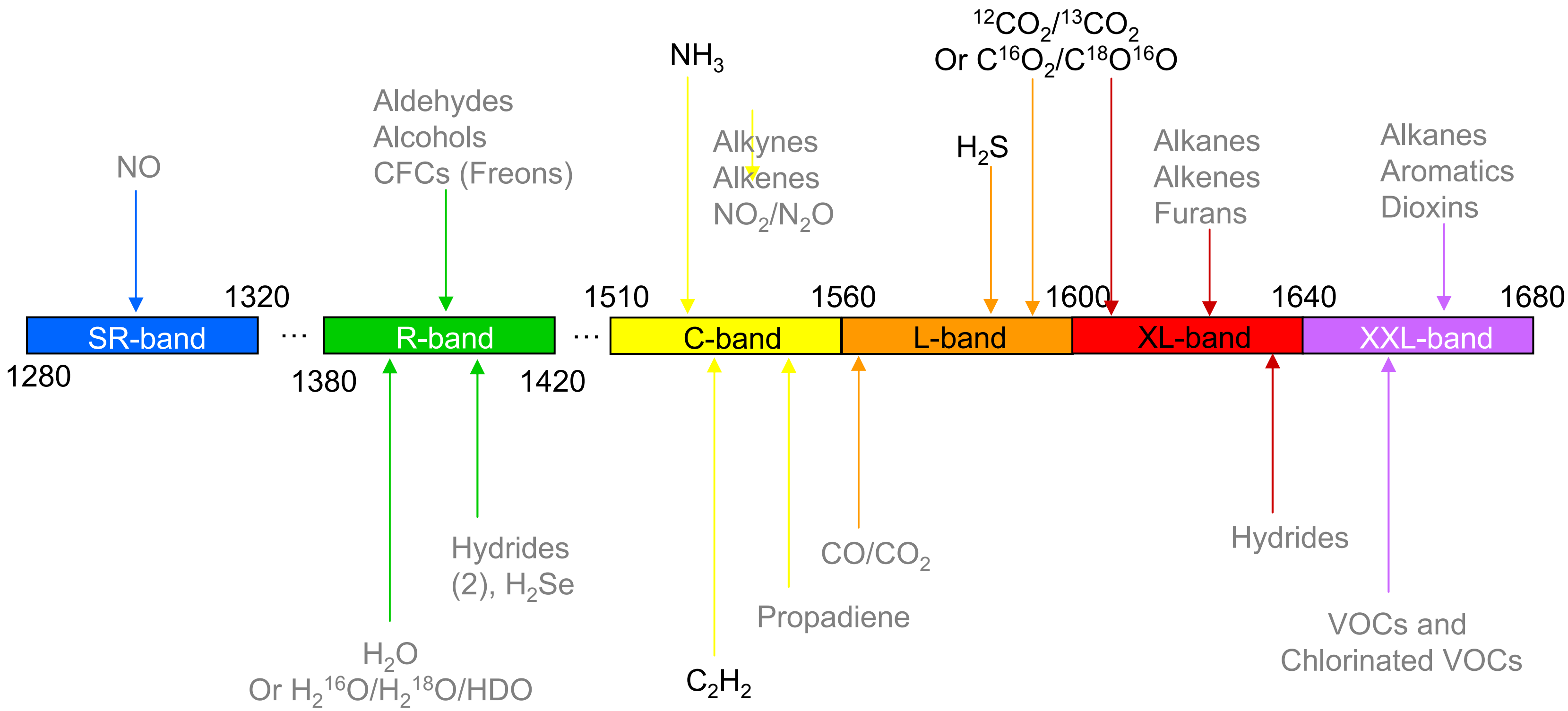
Near – Infrared Molecular Fingerprints



- Each molecule absorbs at a different wavelength or set of wavelengths
- Multi-species operation requires a broadband spectrometer

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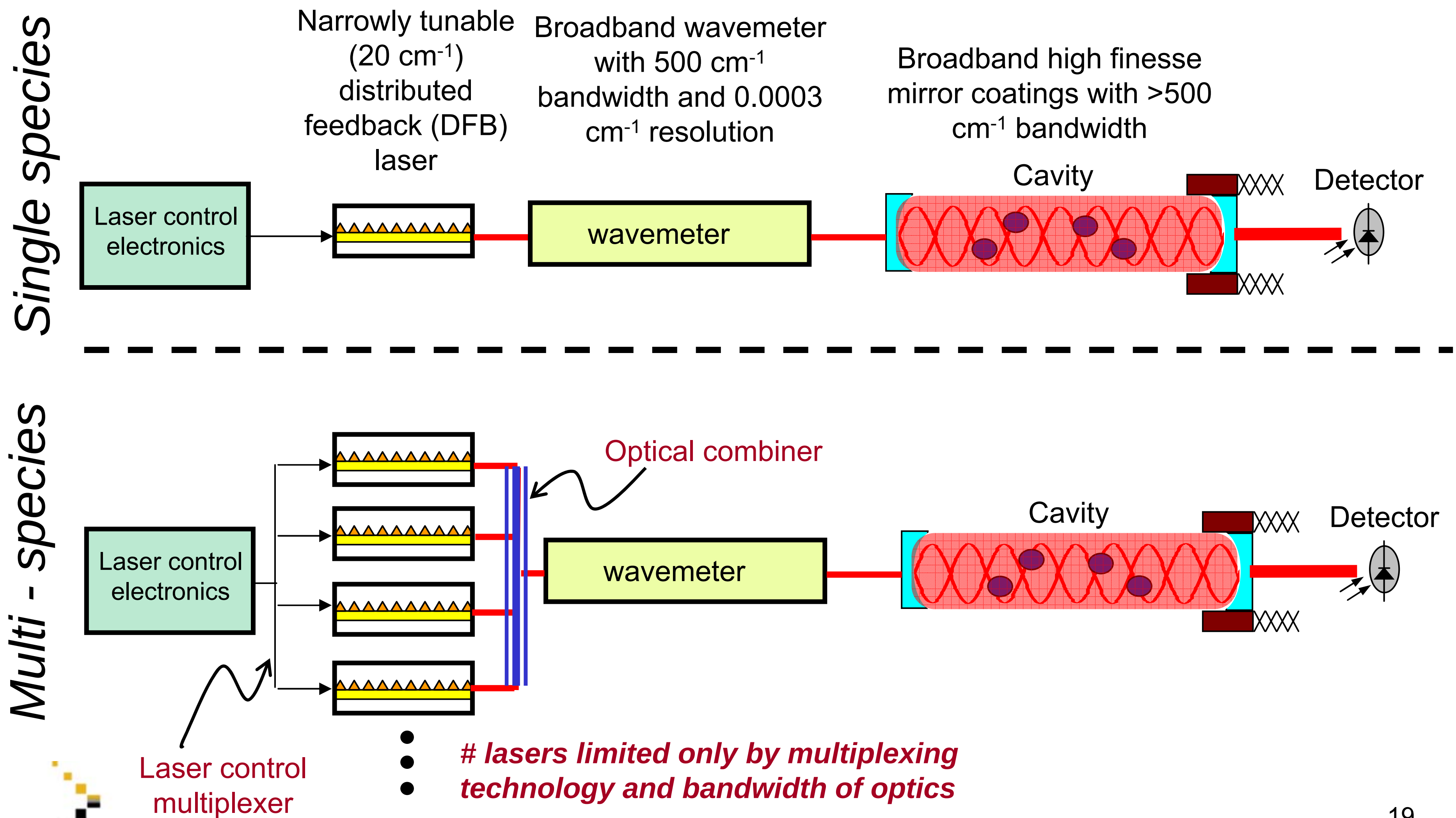
Picarro's Multispecies CRDS analyzer—A Scaleable Architecture

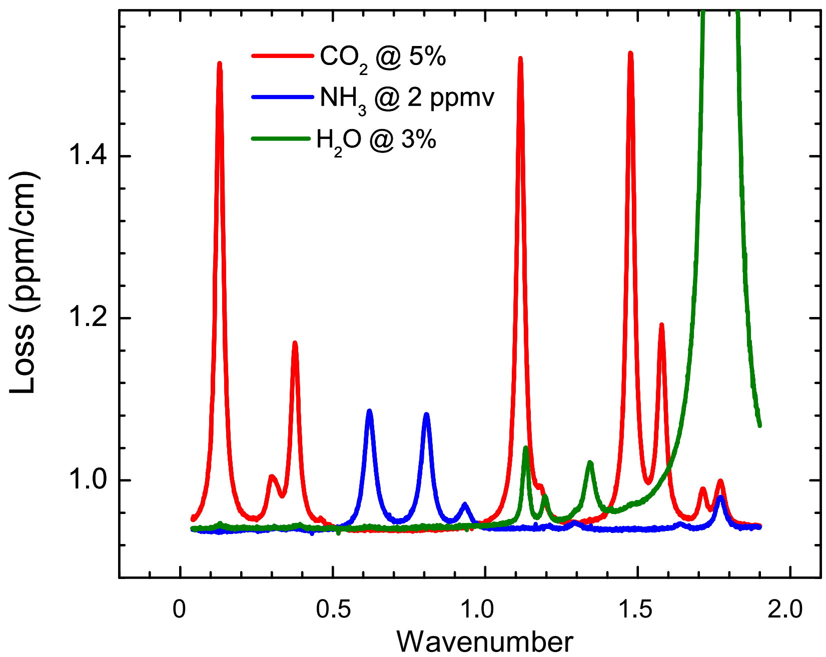


Multispecies CRDS Architecture: Advantages

- Additional species are enabled by adding an additional, reliable telecommunications grade DFB laser
- Same performance characteristics of single species analyzer read directly across to multi-species analyzer, including reliability and ease of use
- Hardware and electronics are reused, minimizing complexity and footprint
- Because all species are measured with the same analyzer cavity, the gas response times and lag times are essentially identical from species to species

A Multispecies Analyzer for Ambient Monitoring—

- Targeted Gas Species for the application:
  - Ammonia (NH_3)
  - Hydrogen Sulfide (H_2S)
  - Nitrous Oxide (N_2O)
  - Methane (CH_4)
  - Carbon Dioxide (CO_2)
  - Water (H_2O)



Species	Precision (5 minutes)	Notes
Ammonia	2 ppbv	1 sigma @ zero
Hydrogen sulfide	1 ppbv	1 sigma @ zero
Nitrous oxide	10 ppbv	1 sigma @ zero
Methane	10 ppbv	1 sigma @ 1 ppmv

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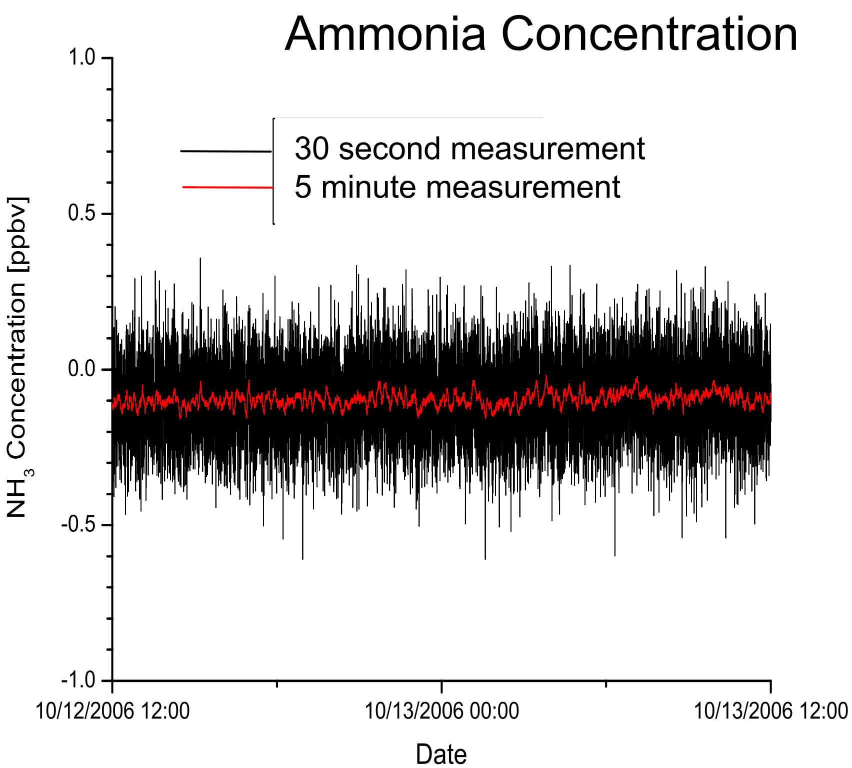
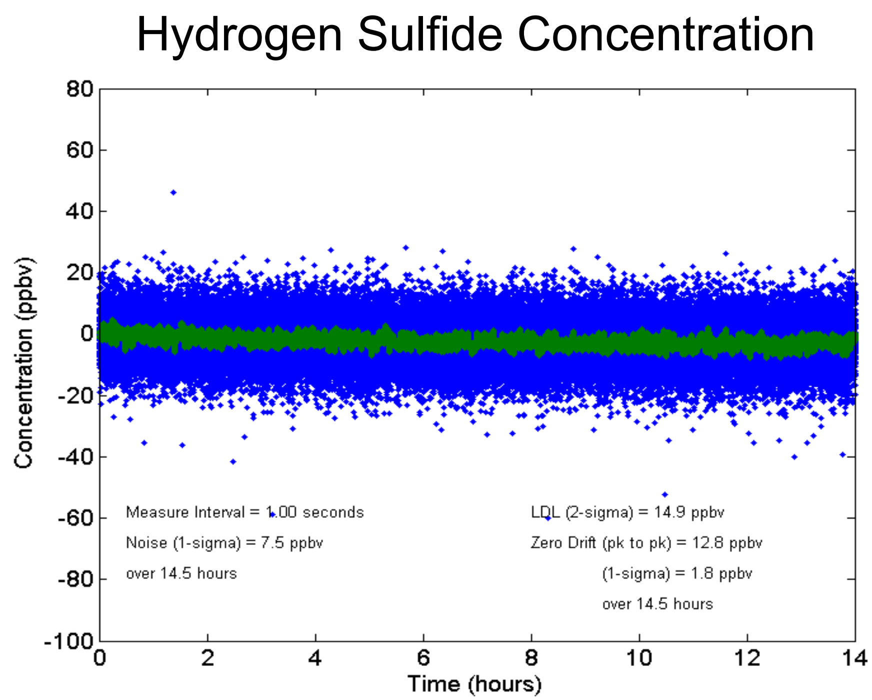
Multispecies Performance

- Proprietary electronics design enables
  - Measurement of two or more gas species with a single analyzer





Ammonia Precision:

- 3- sigma (30 sec) = 0.065 ppbv
- 1- sigma (5 min) = 0.022 ppbv

Hydrogen Sulfide Precision:

- 1-sigma (1.0 sec) = 7.5 ppbv

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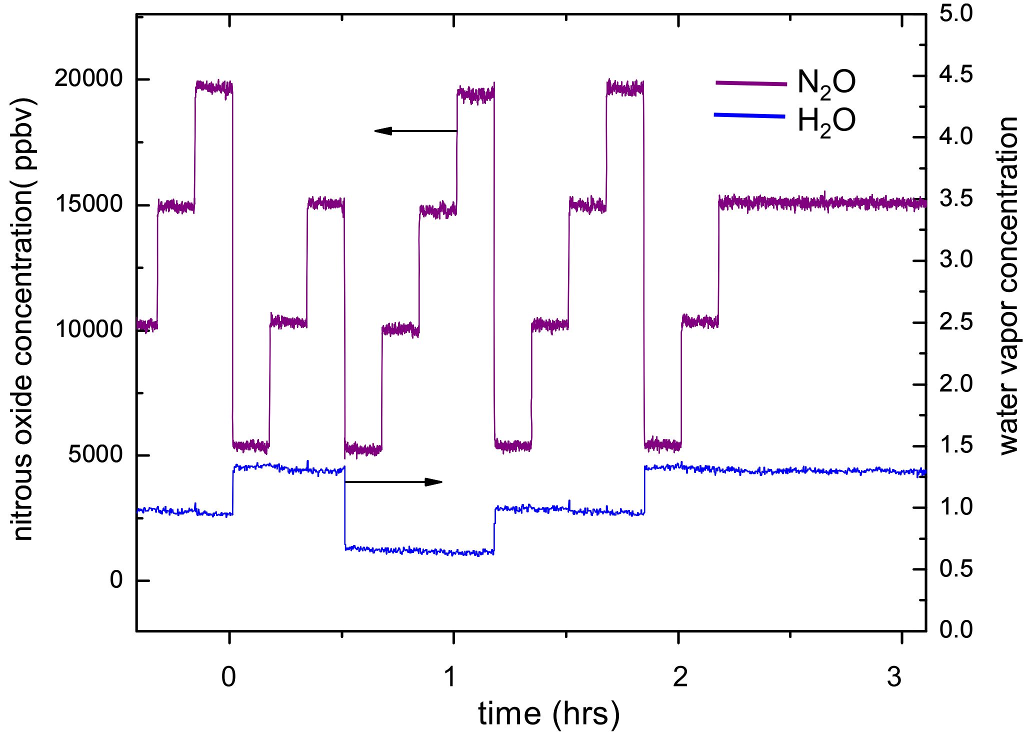
Multispecies Performance, cont'd.

Nitrous Oxide Concentration



- Precision:
  - 1-sigma = 10 ppbv in 5 minutes

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Conclusion

- Picarro's ultra-trace gas analyzer is enabling measurement of non-traditional gas species such as H_2S, NH_3 and H_2CO with high sensitivity, at high speed and without interference in a dynamically changing exhaust stream
- what is your measurement challenge?
  - N_2O, NO_2, NO, HNCO
- whether your requirements are for a single species or for multiple species— imagine the possibilities …
- contact me at
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