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
    - \( \text{H}_2\text{S} \) analysis enables optimization of Lean NOx Traps
    - other non-traditional gas species including \( \text{NH}_3, \text{H}_2\text{CO}, \text{N}_2\text{O}, \text{NO}_2, \text{NO} \)
- Extending the platform to a multispecies analyzer
  - a scaleable architecture
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 CO₂ and CH₄ without interference from H₂O 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 NH₃ at ppt levels to minimize yield loss and prevent haze formation
- Advanced combustion analysis to optimize NOₓ reduction approaches
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$_2$S, NH$_3$ and H$_2$CO 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
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
CRDS is a laser based optical technique

- absolute absorption measurement
- measurements directly related to concentration using the Beer-Lambert Law
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
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
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

Trace measurement of water vapor

- $H_2O$ Mean = 5.0 ppbv
- $H_2O$ Precision = 0.78 ppbv @ 1 sigma
- Measurement Interval = 20 seconds

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
Narrowband Spectroscopy Maximizes Selectivity

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

<table>
<thead>
<tr>
<th>Resolution (cm⁻¹)</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR</td>
<td>0.5</td>
</tr>
<tr>
<td>CRDS</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

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

H₂S - Spectral Region 2
- PNNL reference (1 atm)
- Measured (30 Torr)
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

Hydrogen Sulfide in Diesel Exhaust

- Absorption (cm$^{-1}$)
- Wavelength (μm)
- Losses [ppb/cm]
- WL monitor signal (a.u.)

H$_2$S in 5% CO$_2$
- 2.5 ppm
- 1 ppm
- 500 ppb
- 300 ppb
Specificity → Accuracy Without Interference
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
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$_2$O

Rise and fall times for H$_2$S

- 10%-90% = 1.4 seconds
- 90%-10% = 1.2 seconds

Clean out of water vapor
(Sticky gas species)

- Cleanout time (90% to 10%) = 10 minutes
- Flow Rate = 0.3 liters per minute

zero to 500 ppmv H$_2$S
10%-90% = 1.4 seconds
90%-10% = 1.2 seconds
High Speed Analysis

- Scanning flexibility allows
  - application specific spectral scanning schemes
    - $\text{H}_2\text{S}$ with LDL of 50 ppbv at 1 Hz in exhaust for sulfur balance for LNT optimization
    - $\text{H}_2\text{S}$ with LDL of 2 ppbv (1 min) for ambient monitoring within cabin
    - $\text{NH}_3$ with LDL of 0.2 ppbv in ambient
    - $\text{NH}_3$ with LDL of 10 ppbv at 1 Hz in exhaust
    - $\text{H}_2\text{CO}$ with LDL of $\sim$15 ppbv as MSAT
    - $\text{H}_2\text{CO}$ with LDL of $\sim$ 0.5 -1 ppmv at 1 Hz in exhaust
  - 10 Hz operation for monitoring dynamics and capturing transients
Near – Infrared Molecular Fingerprints

- Each molecule absorbs at a different wavelength or set of wavelengths
- Multi-species operation requires a broadband spectrometer
Picarro’s Multispecies CRDS analyzer—A Scaleable Architecture

- Narrowly tunable (20 cm\(^{-1}\)) distributed feedback (DFB) laser
- Broadband wavemeter with 500 cm\(^{-1}\) bandwidth and 0.0003 cm\(^{-1}\) resolution
- Broadband high finesse mirror coatings with >500 cm\(^{-1}\) bandwidth

Single species:
- Laser control electronics
- Cavity
- Detectors
- wavemeter

Multi-species:
- Laser control electronics
- Optical combiner
- Laser control multiplexer
- # lasers limited only by multiplexing technology and bandwidth of optics
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.
Targeted Gas Species for the application:

- Ammonia (NH₃)
- Hydrogen Sulfide (H₂S)
- Nitrous Oxide (N₂O)
- Methane (CH₄)
- Carbon Dioxide (CO₂)
- Water (H₂O)

<table>
<thead>
<tr>
<th>Species</th>
<th>Precision (5 minutes)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>2 ppbv</td>
<td>1 sigma @ zero</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>1 ppbv</td>
<td>1 sigma @ zero</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>10 ppbv</td>
<td>1 sigma @ zero</td>
</tr>
<tr>
<td>Methane</td>
<td>10 ppbv</td>
<td>1 sigma @ 1 ppmv</td>
</tr>
</tbody>
</table>

**Notes:**
- Precision measurement in 5 minutes.
- Measurement accuracy varies for different species, as indicated by the notes for each species.
Proprietary electronics design enables:
- Measurement of two or more gas species with a single analyzer

**Ammonia Concentration**

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

**Hydrogen Sulfide Concentration**

- 1-sigma (1.0 sec) = 7.5 ppbv

**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
Nitrous Oxide Concentration

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

- Picarro’s ultra-trace gas analyzer is enabling measurement of non-traditional gas species such as H₂S, NH₃ and H₂CO with high sensitivity, at high speed and without interference in a dynamically changing exhaust stream.

- What is your measurement challenge?
  - N₂O, NO₂, NO, HNCO

- Whether your requirements are for a single species or for multiple species—imagine the possibilities …

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