Robust Hydrogen Sulfide Analyzer for Vehicle Exhaust with a 50ppbv Lower Detection Limit and a 1Hz Data Rate

Ken Sheets[1], Eric Crosson[1], Chris W. Rella[1], Edward Wahl[1]

PICARRO

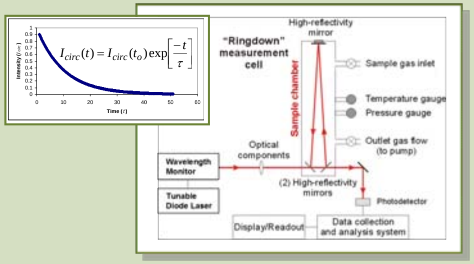
ABSTRACT

Applications ranging from petrochemical process control to semiconductor gas purity to atmospheric monitoring have driven the need for process analyzers with ppb sensitivity and high accuracy. One of the most challenging applications is trace gas measurements in diesel exhaust streams. This application demands fast measurement times (~ 1Hz) due to the rapid speed of engine dynamics. This fast response must also be combined with ultra-high, ppb level sensitivities for many gas species. Finally, the analyzer must provide accurate and reliable measurements with virtually no cross-talk to the other constituents of the complex exhaust stream. Only technologies that can hit all these targets simultaneously bring value to the application

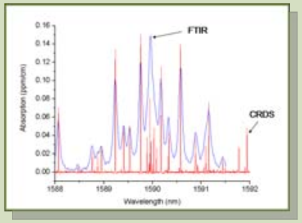
Cavity ringdown spectroscopy (CRDS) is an all-optical technique capable of both high sensitivity and high speed. The technique can be optimized by operating the analyzer cell below atmospheric pressure, where the narrower absorption linewidths permit cleaner isolation of the target absorption line from neighboring background lines. Further improvements to accuracy and precision can be made by adding an in-line precision optical wavemeter that permits absorption lineshape measurements that enhance removal of interfering absorption features.

In this paper we present results obtained with a commercial hydrogen sulfide analyzer that combines the native speed and sensitivity of CRDS with the improved accuracy and reduced cross-talk afforded by an optical wavemeter and sub-atmospheric operation, resulting in best-in-class performance for this gas species and application.

Cavity Ring-Down Spectroscopy



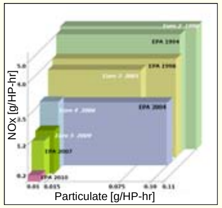
- Light from a semiconductor diode laser is directed into a high finesse optical resonator cavity containing the analyte gas.
- When the optical frequency matches the resonance frequency of the cavity, energy builds up in the cavity.
- When the build-up is complete, the laser is shut off.
- The energy decays from the cavity, 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 is does not absorb, the ringdown time is long.
- The in-line high precision optical wavemeter permits extremely detailed spectral scans that cannot be done using FTIR.



1 Picarro, Inc., 480 Oakmead Parkway, Sunnyvale, CA 94085

Background

- The EPA has mandated an 83% reduction in diesel engine NOx emissions from the 2007 standard by 2010.
- Most diesel engine developers feel they will not be able to meet this requirement by solely tuning the engine . An engine after-treatment system will be required along with an optimized engine design to meet this requirement.
- One of the leading after-treatment approaches is the Lean NOx Trap (LNT). The LNT uses a catalyst to decompose the NOx in the exhaust stream.



- A key challenge with this approach is that the sulfur in the fuel will poison the catalyst and reduce its effectiveness. This requires the catalyst to be periodically regenerated.
- The engine designer needs to have accurate, real-time measurements of the sulfur species in the exhaust to optimize both the engine and after-treatment systems.

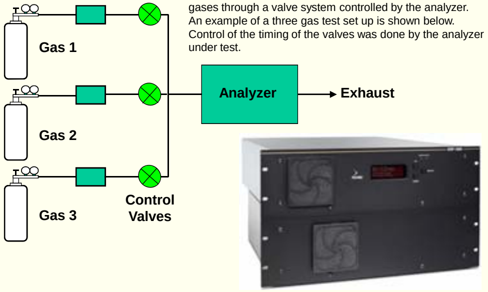
Application Requirements

To meet the needs of this application, the analyzer must have the following capabilities:

- H_2S concentrations free from interference from other gases in the complex, dynamically changing exhaust gas stream.
- Sensitivity or lower detection limit (LDL) of less than 50ppbv
- Measurement rate of 1 Hz to characterize transients and enable correlation with engine dynamics
- A response time (10%-90% rise and fall time) of less than 2 seconds
- A wide dynamic range of 50ppbv to 500ppmv

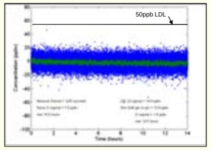
Testing Overview

The analyzer was tested by connecting different sample gases through a valve system controlled by the analyzer. An example of a three gas test set up is shown below. Control of the timing of the valves was done by the analyzer under test.



An ultra-sensitive, real-time hydrogen sulfide analyzer

Lower Detectable Limit



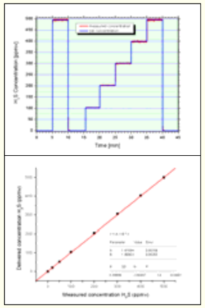
The analyzer was run with zero-air and the resulting data was analyzed to determine the lower detectable limit.

The data on the left shows a lower detectable limit (at 2-sigma) of 14.9 ppbv

Additional tests have shown a lower detectable limit (at 3-sigma) of 7ppbv with a 1 second sample time.

Note that the analyzer has a 1Hz measurement rate enabling the characterization of high speed engine transients.

Linearity / Dynamic Range



To test the linearity and the dynamic range of the analyzer, 6 different concentrations of H2S (from 0ppbv to 500ppmv) were delivered in 5 minute intervals as shown on the left

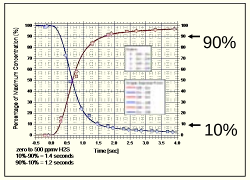
Analysis of the data, gives a linear coefficient of 1.00063. This shows that the analyzer is linear to better than 1 part in 1,500.

Rise / Fall Times

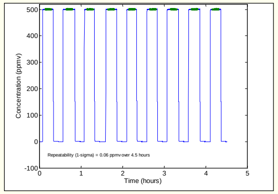
The analyzer was alternately presented with zero-air and H_2S at full span (500ppmv). Data was acquired during these transitions.

The graph at the right shows the resulting data from two rise and two fall transitions.

The data shows that the rise time for the analyzer is 1.4 seconds and the fall time is only 1.2 seconds



Repeatability



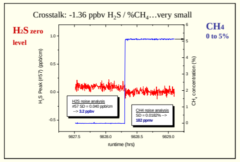
Repeatability at 500ppm = 60ppbv

The analyzer was subjected to alternating zero-air and span gas (500ppmv) to test its repeatability at full span.

The resulting repeatability over 4½ hours was 60ppbv at 500ppm or better than 1 part in 8300.

Superior accuracy and precision without interference

Accurate H_2S Concentrations Without Interference

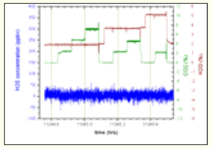


On the left is the result of testing the analyzer with zero-air and either 0% or 5% CH_4 to measure the crosstalk between CH_4 and H_2S.

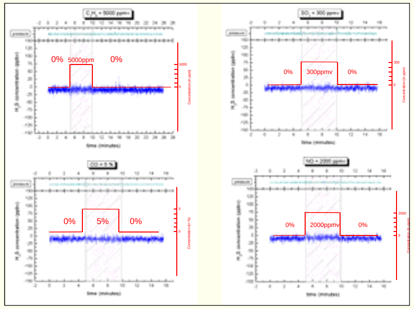
The results show that the crosstalk between CH_4 and H_2S is only 1.36ppbv— significantly less than the lower detectable limit of 50ppbv.

To test for any possible interference from H_2O and CO_2, zero-air was introduced to the analyzer and the H_2O concentration was varied from 2% to 5% while the CO_2 was varied from 0 to 7%.

The resulting data (on right) shows that there was no detectable change in the H_2S measurement during the test.



Additional tests were done with other gases including propane, SO_2, CO and NO. The results, as shown below, indicate that any interference from these gases is significantly below the 50ppbv lower detectable limit of the analyzer.



Conclusions

- Measured performance of Picarro's ESP-1000.H2S analyzer demonstrates it meets or exceeds the requirements of the application:
  - H_2S concentrations free from interference from other gases in the complex, dynamically changing exhaust gas stream.
  - Sensitivity or LDL of less than 50ppbv
  - Measurement rate of 1 Hz to characterize transients and enable correlation with engine dynamics
  - A response time (10%-90% rise/fall time) of less than 2 seconds
  - A wide dynamic range of 50ppbv to 500ppmv

Acknowledgements

- Sze Tan, Hoa Pham, Serguei Koulikov, Bruce Richman, Picarro Research Team

H_2S analyzer enables optimization of engine after-treatment systems