M&C TechGroup North America

Innovative Open-path Tunable Diode Laser for Monitoring Hydrogen Sulfide Gas at the Fence Line

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Innovative Open-path Tunable Diode Laser for Monitoring Hydrogen Sulfide Gas at the Fence Line

- M&C TechGroup North America is the leading manufacturer, supplier, and designer of gas phase-sampling equipment and analyzer systems in North America. Providing gas analyzers, sample extraction probes, driers, and integrated systems, M&C has more than 30 years of experience providing analysis components for both regulatory compliance and process-control monitoring applications. M&C's engineered solutions can be found throughout the world in power generation, refinery, chemical, steel, waste incineration, cement glass, and ambient monitoring installations. Led by a team of experienced engineers and field service technicians, M&C provides innovative technical solutions to solve individual application challenges.

AIROPTIC™
REAL TIME GAS ANALYZERS

- M&C TechGroup is the North American distributor of the AIROPTIC™ laser analyzer system and provides optimal solutions for open-path, fence-line and point monitoring extractive measurements for numerous gases, including but not limited to hydrogen sulfide, hydrochloric acid, hydrofluoric acid, ammonia, methane, hydrocarbons, formaldehyde. Airoptic is an ISO 9001:2015 certified company founded in 2010. Airoptic designs and manufactures high-performance, laser-based analyzers for process control and emission monitoring in various applications associated with petrochemical, chemical, and oil and gas drilling industries. The GasEye series models include open-path, in-situ, and extractive analyzers. Airoptic is one of the original pioneers in introducing novel Mid-IR Interband Cascade Laser (ICL) sources for industrial spectrometers.

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- Argos Scientific has been involved in all aspects of fence-line monitoring technology including original manufacturing, installation, maintenance, field service, repair, data collection, management, quality assurance, reporting, and communication. Argos is currently working with various oil refineries, community groups, and local government officials to provide real-time, fence-line air monitoring systems in the San Francisco Bay Area, Los Angeles, Santa Maria, Haifa Israel, and in Cape Town, South Africa. As the technical liaison between the refineries and the community groups, Argos is responsible for maintaining real-time monitoring systems that update a public access website. Argos provides recommendations on the latest sampling methods for ambient air measurement and ensures that all equipment meets quality assurance standards. Argos manufactures its own state-of-the-art UV monitors, and has developed next generation technology (UVQ-G2) that can simultaneously detect BTEX, SO_2, NH_3, and mercury on a real-time basis. The systems are ideal for fence-line monitoring applications where sampling a large area with a single analyzer is desired. These systems have recently been accredited by ISO 17025.

- The Air District aims to create a healthy breathing environment for every Bay Area resident while protecting and improving public health, air quality, and the global climate.

Contents

Innovative Open-path Tunable Diode Laser for Monitoring Hydrogen Sulfide Gas at the Fence Line

01 Abstract

02 Study Objectives

03 Technology Description

04 Site & System Setup

05 Summary of Performance Data

06 Calibration Summary

07 Summary of Results

01 Abstract

- The use of open-path fence-line air monitoring systems are becoming an attractive alternative to traditional point sampling devices for identifying emissions associated large scale pollution sources. However, critical gaps remain in the utility of this approach as gases such as hydrogen sulfide (H_2S) have been difficult to detect employing open-path systems at concentrations measured by other methods. The paper presents the results of an evaluation of a new open-path H_2S air monitoring system that has been tested at the fence-line of an oil refinery in California. The system can be operated at sample path lengths over 1,000 meters, is capable of quantifying H_2S, water, and methane in real-time, records the raw data spectra, and can be calibrated in the field using both sealed and flow-through gas cells.

  A summary of the data collected by the system during a five-month evaluation period of the technology will be discussed, including an evaluation of the system's detection capability, a discussion of advantages of this approach and a summary of the quality assurance/quality control (QA/QC) checks. In addition, a test plan for overall acceptance of the H_2S system will be presented, which incorporates QA/QC indicators associated with EPA Compendium Method TO-16.

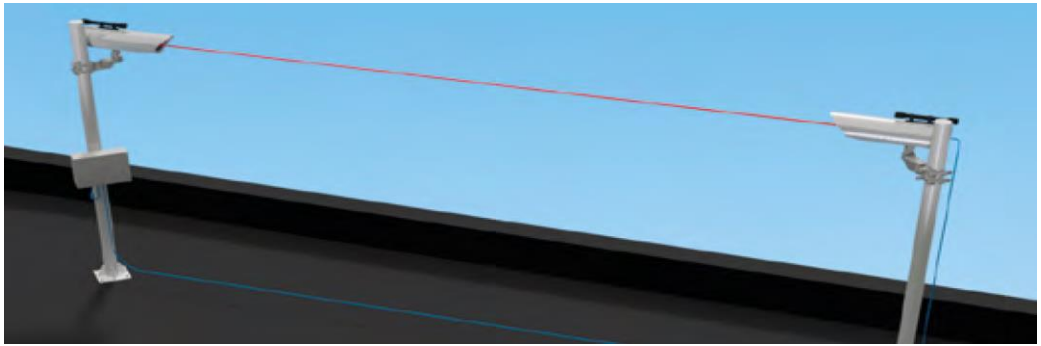
02 Study Objectives

- Determine ability to provide defensible data for use in regulatory compliance applications such as the Bay Area Air Quality Management District (BAAQMD) Rule 12-15 for fence-line air monitoring
  - EPA Compendium Method TO-16 for Fourier Transform Infrared Monitoring of Atmospheric Gases
  - EPA Environmental Technology Verification Program's Verification Protocol for Optical Open-PathMonitors
- Capability for real time data verification
- Ability to perform calibration checks in a timely and safe manner
- Ability to save raw spectral data for independant review
- Collect other metadata to demonstrate operation within normal parameters

02 Study Objectives

Physical Objectives

- System setup for assessment at a real-world, fence-line monitoring site
- One-way sample path greater than 800 meters
- Continuous operation for a minimum of three months
- Ability to perform calibration testing using cylinder gases or sealed calibration gas cells



02 Study Objectives

Data Validation Objectives

- Demonstrate that the data can be independently verified in real-time
  - Validation must be independent of the software used to routinely quantify data
  - Validation must demonstrate how zero, drift and/or interferences, and measurement above the minimum detection limit (MDL) will be verified with expected errors
- Demonstrate how raw spectral data can be saved in real-time and indepentently verified at a later date
- Present the detection limits of the analyzer as measured in path-averaged results (ppb-m)
- Present the detection limits of the analyzer as a function of light transmission signal
- Provide test protocol for testing the precision, accuracy, and linearity of the system

03 Technology Description

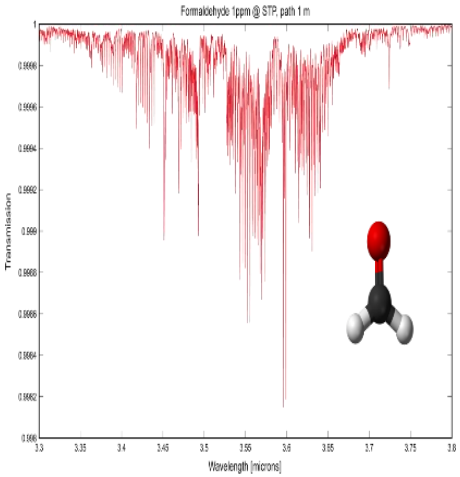
- The Airoptic open-path H_2S tunable diode laser (TDL) monitoring system is a monostatic system that uses mid-infrared laser light to scan across a narrow band of the infrared spectrum where gases such as H_2S, moisture, and methane absorb this light
- The Airoptic system utilizes wavelength modulation technique to enhance signal-to-noise characteristics and reach minimum detectable absorbances in a range of 10^{-6} to 10^{-7} absorbance units
  - This sensitivity yeilds an approximate three orders of magnitude improvement as compared to other optical remote sensing techniques, such as open-path FTIR monitoring techniques

Open Path H_2S TDL Analyzer

Retroreflector

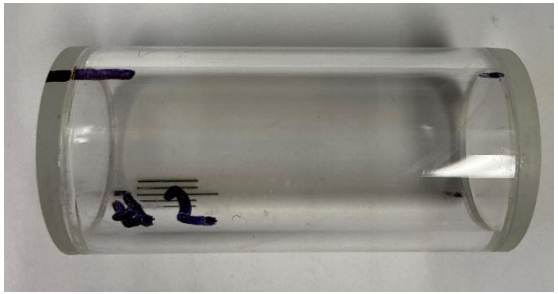
03 Technology Description

- The system monitors and records in real-time the measurement and spectral fingerprint of H_2S, moisture, and methane present in the gas sample and models their absorption of infrared light using a classical least squares analysis routine
  - The analytical models used in the classical least squares routine include exact molecular line-shape functions as well as the laser source characteristics
  - The analytical algorithm automatically corrects for any foreign gas broadening mechanism
- To determine the concentration of H_2S in the gas sample, the software actively subtracts the interfering gases from the sample spectra and then performs an analysis of the H_2S
- The laser frequency is locked into a reference line to assure there is no frequency drift and that the calibration status is maintained



03 Technology Description

- The data output includes the quantified results of all gases in the light spectra, which can be used as real-time performance checks
  - For example, quantified results for methane should be above the natural ambient atmospheric background level of 1.72 ppm
  - Since the system quantifies methane in real time, along with moisture and other interferent gases, the verification of methane above natural ambient levels can be used as a real-time data quality check
- The system uses removable sealed H_2S calibration gas cells to perform calibration checks
  - The sealed cells provide a safe, effective way to determine measurement quality parameters including system precision, accuracy, and linearity



Sealed H_2S Calibration Gas Cell

04 Site & System Setup

- The air monitoring system was installed at a California Refinery within an existing air monitoring station
- The air monitoring station includes several fence-line analyzers including open-path FTIR, UV, and TDL systems
- The one-way sample path was 840 meters (1,680 meters total optical measurement path)
- A field computer collects and stores the raw spectral data and processes the results
- Remote access via Internet connection is available for remote access and data storage
- Data is quantified in real-time with result stored in a text file
- The system can be configured to include real-time evaluation of data quality, alarm threshold, and system operation checks

04 Site & System Setup

California Refinery

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California Refinery

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California Refinery

04 Site & System Setup

California Refinery

Airoptic TDL Base Unit Installed on Mounting Platform

Airoptic Retroreflector Mounted on the Reflector Tower

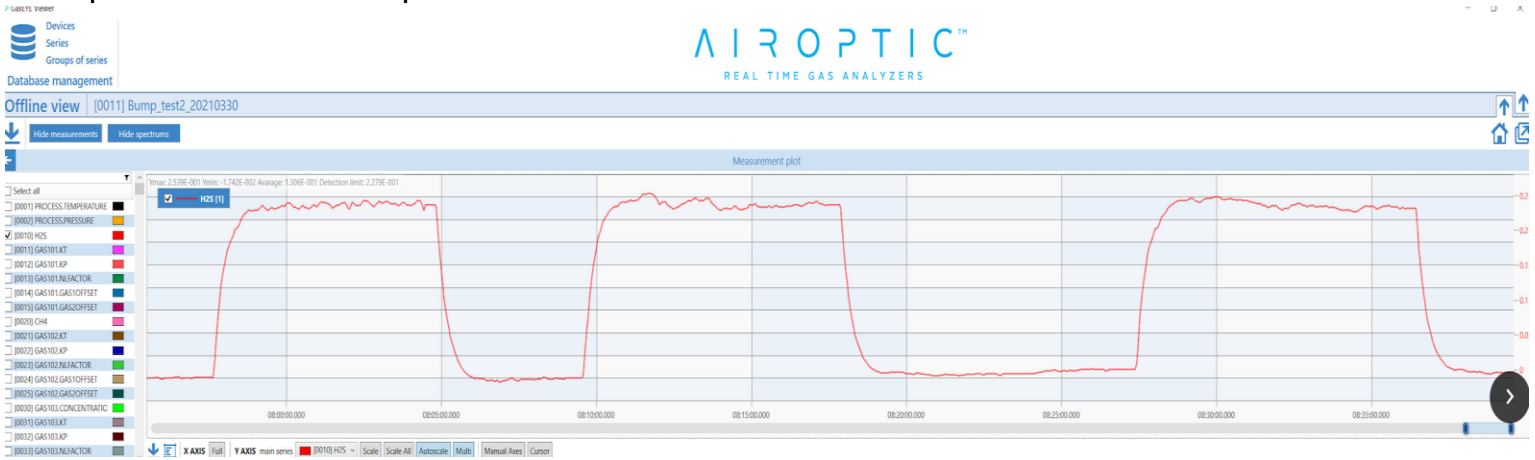
05 Summary of Performance Data

- The system ran continuously for a 6 month period, collecting over 400,000 samples points
- The highest detection limit of 25 ppb was recorded only during periods of extremely low transmission under 1%

Sample Period	November 19, 2020, to May 21, 2021
Sample Frequency	3 seconds to 1 minute
Lowest Observed Detection Limit	3 ppb
Highest Observed Detection Limit	25 ppb
Average Detection Limit	15 ppb
Detection Range	3 ppb to 5000 ppb
Accuracy	2% of readings
Repeatability	1% of reading

06 Calibration Summary

- Calibration checks were performed on the operating system on three independent dates
- A sealed calibration cell with a path-averaged concentration of 250 ppb was inserted into the optical measurement path



Calibration Results from March 30, 2021

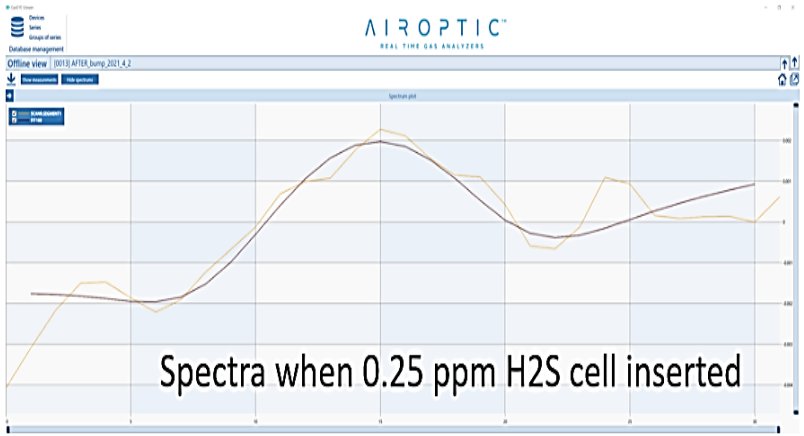
06 Calibration Summary

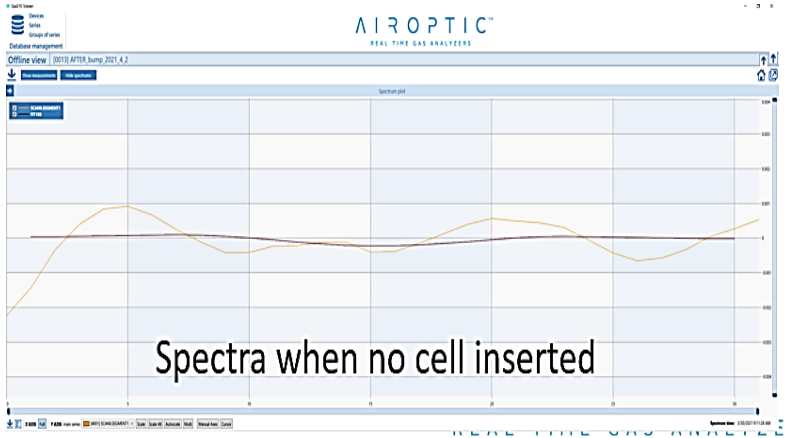
Sample #	Start Time	End Time	Samples	H_2S Conc.	St. Dev.
1	7:58	8:04	120	249.8	3.9
2	8:11	8:17	134	251.7	5.8
3	8:29	8:34	98	250.2	5.6

Calibration Results from March 30, 2021

06 Calibration Summary

- The system response to the presence of H_2S when the sealed calibration cell is inserted into the optical measurement path is clearly seen in the overlay of the reference library spectra against the field measurement spectra
- The spectral response to the presence of H_2S is seen in the absorption peak in the middle of the graphs





07 Summary of Results

- The purpose of the study was to evaluate the performance of the Airoptic open-path H_2S tunable diode laser (TDL) in a real-world installation for suitability of use in regulatory applications
- Operational Results
  - The H_2S TDL system met all operational performance targets
  - The system transmitted and received light at a one-way sample path of 840 meters (1,680 meters total optical measurement path) without requiring any special enhancements to the existing fenceline monitoring platforms
  - The system remained in optical alignment throughtout the 6 month demonstration test period with no major adjustments
  - The system required minimal support from field operations personel
  - The system achieved continual operation throughout the 6 month demonstration test period

07 Summary of Results

- Data Validation Results
  - The system detection limits ranged from 3 ppb to 25 ppb with an average value of 15 ppb throughout the study duration
  - The system saved all of the raw spectra for the H_2S target gas as well as the spectra for all of the spectra for potential interferent gases (including H_2O and CH_4)
  - The system responded to sealed calibration cell gas and produced data that could be independently validated by examining the spectral absorbance features of H_2S in the raw spectral data
  - The system could be challenged in real-time by quantifying the gases that are continually present in the natural background ambient air and comparing them to known thresholds

07 Summary of Results

- Continuing Evaluation
  - Assess the system's detection limits at 80%, 60%, 40% & 20% of full signal transmission. The completed demonstration test optimized optical transmission at 5-8% of transmitted beam intensity. Improvements to the transmitted beam intensity should be easily accomplished by the use of a larger retroreflector. The reported detection limits should be considered a worst-case scenario and only improve with increased transmitted beam intensity
  - Challenge the system with multiple sealed calibration gas cells with lower, varied concentrations of H_2S gas
  - Create calibration cells for methane gas to enhance the data validity of the methane measurement. The quantification of methane in real-time is considered a primary method for documenting the operational performance of open-path air monitoring systems that use infrared light
- **Summary**
  - **The Airoptic open-path H_2S TDL system evaluated at the California Refinery not only met, but exceeded all of the performance checks outlined in the study**

THANK YOU FOR LISTENING!