M&C TechGroup NorthAmerica & Argos Scientific

A Public/Private Approach for Technical Evaluation of an Innovative Open-path Hydrogen Sulfide Air Monitoring System

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A Public/Private Approach for Technical Evaluation of an Innovative Open-path Hydrogen Sulfide Air Monitoring System

- 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.

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- 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.

Contents

A Public/Private Approach for Technical Evaluation of an Innovative Open-path Hydrogen Sulfide Air Monitoring System

01 Abstract

02 Project Background: November 2020 to May 2021

03 Project Background: October 2021

04 Study Overview: November to December 2023

05 Study Objectives

06 Summary of Results

01 Abstract

- This abstract presents a summary of a technical evaluation of the Airoptic open-path Tunable Diode Laser (TDL) air monitoring system, conducted to assess its suitability for meeting the performance criteria established by the Bay Area Air Quality Management District (BAAQMD) as part of Regulation 12, Rule 15 (Rule 12-15) for fence-line air monitoring. The rule mandated the installation of open-path fence-line air monitoring systems, including the detection of Hydrogen Sulfide (H_2S) gas, at refineries in the San Francisco Bay Area.

  Initially, the BAAQMD exempted refineries from installing H_2S monitoring equipment due to the lack of commercially available technology meeting the required detection levels. To promote the development of acceptable technology, the BAAQMD encouraged the testing of open-path technologies. To evaluate the suitability of the candidate technology, the operational parameters of the Airoptic open-path TDL system were compared against accepted test methodologies, including the EPA Compendium Method TO-16 and the EPA's Environmental Technology Verification Program's Generic Verification Protocol for Optical Open-Path Monitors.

01 Abstract

- At the request of the Benicia Community Air Monitoring Program (BCAMP), a local community group that advocates for the open and transparent demonstration of the innovative environmental technologies, Argos Scientific, demonstrated the Airoptic system as part of a two-week technology evaluation in December 2023. The evaluation included open-forum demonstrations of the technology with local political officials, the Bay Area Air Quality Management District, oil refineries, the general public and technology vendors. This demonstration marked a new era in the partnership with governmental agencies, environmental groups, and industry to collect, share, and report environmental data.

02 Project Background: November 2020 to May 2021

- In 2015, the Bay Area Air Quality Management District (BAAQMD or Air District) promulgated Rule 12-15 which included the requirement that open-path fenceline air monitoring systems be installed along the perimeters of the refineries in the San Francisco Bay Area (BAAQMD, 2015)
- Included in the 2015 rule was the requirement for continuous fence line monitoring for hydrogen sulfide (H_2S), however BAAQMD concluded at the time that there was no commercially available technology that could detect at the levels to meet the goals of Rule 12-15. Therefore, the refineries were exempted from installing H_2S equipment until it was determined that commercially available technology could meet the monitoring requirements.
- To assist in the evaluation of currently available open path analyzers, one Bay Area refinery sponsored a technology evaluation at one of their fence line air monitoring stations.

02 Project Background: November 2020 to May 2021

Site & System Startup

- 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

02 Project Background: November 2020 to May 2021

California Refinery

02 Project Background: November 2020 to May 2021

California Refinery

02 Project Background: November 2020 to May 2021

California Refinery

02 Project Background: November 2020 to May 2021

California Refinery

TDL Base Unit Installed on Mounting Platform

Retroreflector Mounted on the Reflector Tower

02 Project Background: November 2020 to May 2021

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

03 Project Background: October 2021

- In October 2021, the BAAQMD communicated to the five refineries that the installation of open-path air monitoring systems would be required by January 1, 2023 as part of the Rule 12-15 fence line monitoring requirements.
- As part of this communication, the BAAQMD provided specific performance criteria for the instrumentation. The guidance was further clarified in December 2022.

1. Routine detection limit verification checks and confirmed quantification limits which range from 3 to 25 ppb H_2S, depending on environmental and operational conditions, with an average integrated path detection limit of 15 ppb H_2S.
2. A repeatable detection limit of 25 ppb at a light transmission less than 1%.
3. Demonstrate path average measurement range of 3 to 5000 ppb H_2S with an accuracy of 15% of reading and repeatability of 15% of reading.
4. Perform 3-point calibration checks using sealed gas cells, or equivalent, quarterly at a minimum.

03 Project Background: October 2021

5. Perform bump checks at least monthly at a unique concentration that differs from the calibration checks.
6. Demonstrate real-time validation of TDL data using measurement of another common ambient air component, such as methane, water, or carbon dioxide if present in the spectra.
7. Demonstrate detection limit quantification and verification performed continuously in real-time, reported in near real-time on the refinery fence line monitoring website, and included in the quarterly reports along with the measurement data.
8. Record signal intensity measured in real-time and provided in the quarterly reports.
9. Demonstrate that raw spectral data files can be saved as single files and are made available to the Air District upon request.
10. Provide documentation of quality assurance/quality control metrics and procedures fully documented in the required Air Monitoring Plan (AMP) and integrated Quality Assurance Project Plan (QAPP).
11. The Air District recommends that system operation and performance is based on a standardized method, such as EPA Method TO-16, or a method developed by a credible standardization body, such as ASTM International or the International Organization for Standardization (ISO).

04 Study Overview: November to December 2023

- In November 2023, the Benicia Community Air Monitoring Program (BCAMP) invited technology vendors to demonstrate the technology's compliance with Rule 12-15 at their test facility in Benicia, California.
- Testing of the Airoptic system was performed in an open forum over a two-week time period.
- On the final day of testing, BAAQMD officials, the general public, and representatives from two of the local refineries in the Bay Area were present during the calibration of the system which included validation that the system could detect and quantify H_2S gas concentrations that meet and exceed the BAAQMD Rule 12-15 requirements.

04 Study Overview: November to December 2023

- The Airoptic system was installed at the Benicia Community Air Monitoring Station, where it functioned continuously for several days.
- The analyzer operated with a one-way beam path extending 235 meters for a total optical path length of 470 meters.
- Following its setup, the system began collecting data at one-second intervals, storing raw spectral data for the three primary gases (H_2S, methane and water) under observation.
- The system was tested using NIST traceable gas standards that included both H_2S and methane.
- Comprehensive meteorological data, such as wind speed and direction, were recorded alongside all collected datasets.

04 Study Overview: November to December 2023

Measurement Path

04 Study Overview: November to December 2023

Analyzer Mounting Location

04 Study Overview: November to December 2023

Retro-Reflector Mounting Location

04 Study Overview: November to December 2023

- The system was tested using NIST traceable gas standards that included both H_2S and methane.
- The specific H_2S gas concentrations used in these tests, along with the corresponding dates, are detailed in the table below.

Challenge Dates	Path Average Concentration* (ppb)
11/28, 12/3, 12/5	32.4
11/22	48.1
11/28, 12/3, 12/5	100.3
11/22	160.5
11/28, 12/3, 12/5	321.0
11/22	401.2
11/28, 12/3, 12/5	481.5
11/22	1284.0

* Path average concentration based on NIST traceable calibration gases with 2% measurement error and a 470 meter beam path.

05 Study Objectives

- Objective #1: 10 Sigma Quantification Limits Less than 15 ppb
- Objective #2: Precision & Accuracy Measured at Less Than 15% Across Calibration Range
- Objective #3: Raw Spectral Data Saved
- Objective #4: Real-Time Methane Quantification Stored and Reported
- Objective #5: Real-Time Water Quantification Stored and Reported
- Objective #6: Real-Time Light Signal Tracking
- Objective #7: Detection of H_2S During Study

05 Study Objectives

Objective #1: 10 Sigma Quantification Limits Less than 15 ppb

- Detection limits were evaluated during the system operation to determine if the system could meet the BAAQMD Regulation 12 Rule 15 requirements for H_2S quantification.
- The U.S. Environmental Protection Agency (EPA) defines the Limit of Quantification (LOQ) as follows:

  "The Limit of Quantification (LOQ) is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated operational conditions of the method.“
- The evaluation of LOQ for this test included defining the LOQ as 10 times the measured standard deviation of the data set. In addition, a second check was conducted by inserting a known concentration of a gas near the BAAQMD detection threshold of 25 ppb and evaluation whether the system could meet the BAAQMD’s precision and accuracy measurement requirements of 15%. For this test, a calibration gas with a path-average concentration of 32 ppb was inserted into the beam path and evaluated for precision and accuracy.

05 Study Objectives

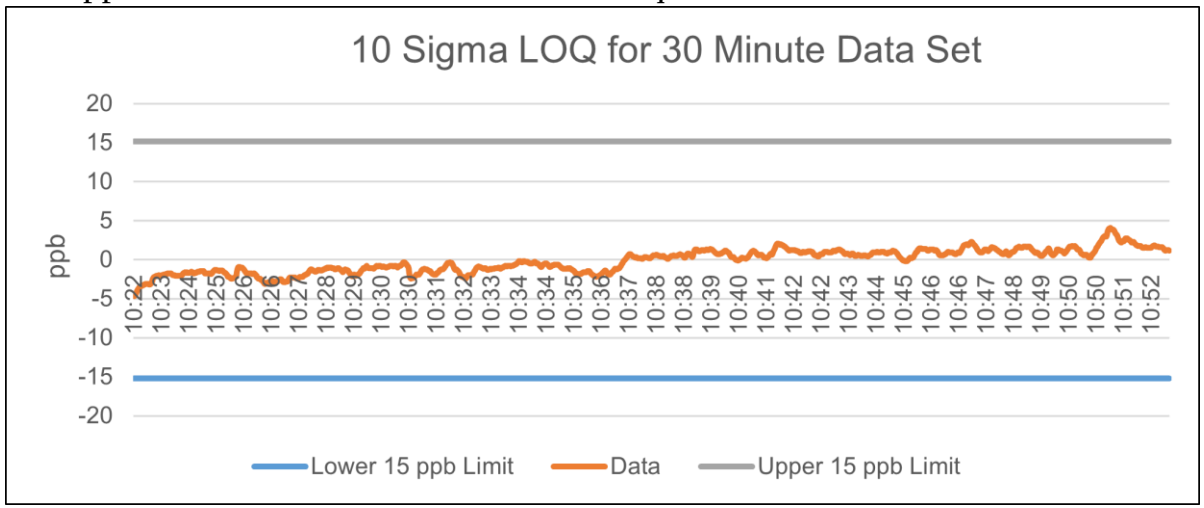
Objective #1: 10 Sigma Quantification Limits Less than 15 ppb

- As the BAAQMD has left the specific definition of LOQ to the equipment supplier, the LOQ for the specific data sets will use both of these approaches for determining the LOQ of the Airoptic system. Specifically, the data will be evaluated as follows:
- LOQ of a Data Set: Using the statistical measurement approach for determining quantification limits, the LOQ for the data set will be defined as 10 times the standard deviation of the data set.
- LOQ of Real-time Data: Using the statistical measurement approach for determining quantification limits, the LOQ for the real-time data will be defined as 10 times the standard deviation of the last 26 data point when no target analyte was detected.
- **It should be emphasized that regardless of the method used to determine the LOQ, it is essential that the limits are verified by inserting concentrations of gases at or near the calculated LOQ and verified as meeting the specific precision and accuracy requirements specified by the BAAQMD for maintaining an accuracy and repeatability of 15% for each reading.**

05 Study Objectives

Objective #1: 10 Sigma Quantification Limits Less than 15 ppb – Data Set

- Data during operational runs when there was no gas present in the beam path.
- Note that because the calibration cell used to challenge the system is permanently mounted inside the analyzer, the data presented includes any noise generated by its presence.
- The LOQ is defined as 10 times the measurement standard deviation. The data set LOQ is based on data collected over a 30-minute period with a total of 1,800 one-second measurements. For that data set, the upper and lower 10 standard deviation quantification limit is calculated to be 15 ppb.

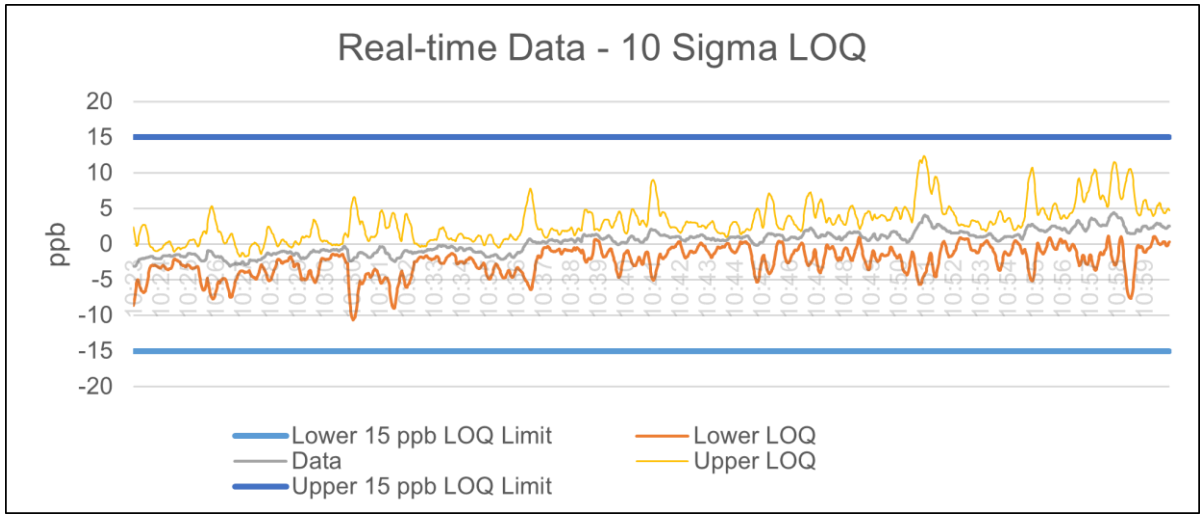


10 Sigma detection limits for data set collected on December 3, 2023

05 Study Objectives

Objective #1: 10 Sigma Quantification Limits Less than 15 ppb – Real Time

- Data during operational runs when there was no gas present in the beam path.
- Note that because the calibration cell used to challenge the system is permanently mounted inside the analyzer, the data presented includes any noise generated by its presence.
- The LOQ is defined as 10 times the measurement standard deviation. The real time LOQ is based on the same data with 10-sigma quantitation limits calculated based on a rolling average concentration based on 26 one-second measurements.



10 Sigma detection limits for data set collected on December 3, 2023

05 Study Objectives

Objective #1: 10 Sigma Quantification Limits Less than 15 ppb – Real Time

- **It should be emphasized that regardless of the method used to determine the LOQ, it is essential that the limits are verified by inserting concentrations of gases at or near the calculated LOQ and verified as meeting the specific precision and accuracy requirements specified by the BAAQMD for maintaining an accuracy and repeatability of 15% for each reading.**

Date	Measured Conc (ppb)	St. Dev.	Expected Conc. (ppb)	Precision (%)	Accuracy (%)	3 Sigma Error
3-Dec	32.8	3.0	32	9.3	2.4	9.1
28-Nov	28.5	1.6	32	5.6	10.8	4.8
27-Nov	34.5	3.6	32	10.3	7.9	10.7

Summary of gas challenges at H_2S concentrations near the 25 ppb quantification threshold

05 Study Objectives

Objective #2: Precision & Accuracy Measured at Less Than 15% Across Calibration Range

- The precision and accuracy of the Airoptic system was evaluated by inserting NIST traceable gases into the beam path and measuring the response of the system.
- These tests were performed on three different dates during the test to evaluate the repeatability of the tests.
- During the test, four gases were inserted into the beam. However, one concentration was excluded from the results as it was determined that the reported concentration of the gas cylinder is different from the actual value.
- This cylinder was tested against four other Airoptic analyzers and in each case, the average measured concentration was significantly different from the cylinder concentration.
- The cylinder will undergo further testing to determine its actual concentration. The measured concentration in Table 4 below is the result after the raw data underwent a baseline correction, and then the calibration curve derived above was applied.

05 Study Objectives

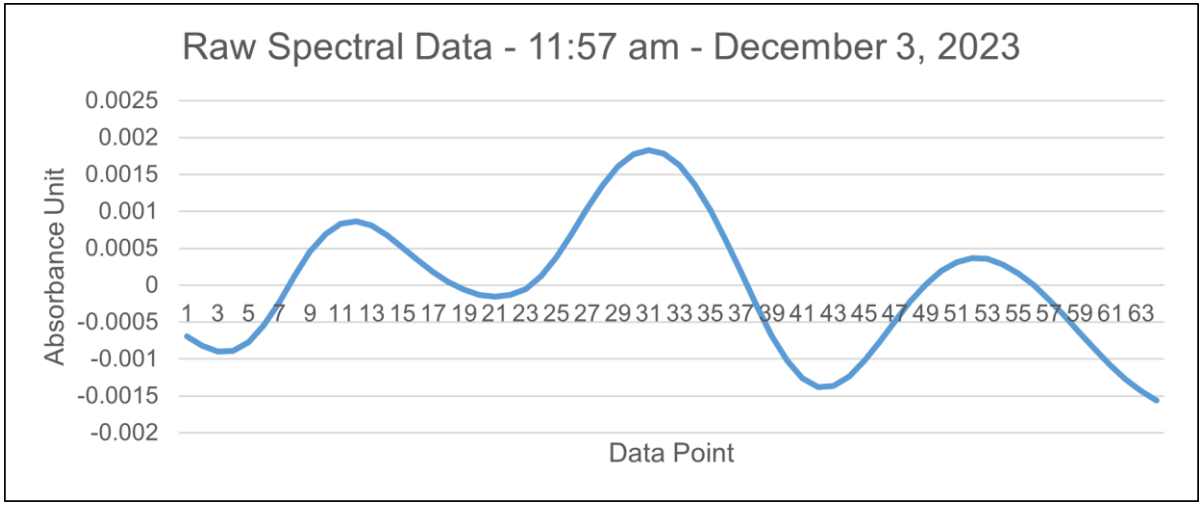
Objective #2: Precision & Accuracy Measured at Less Than 15% Across Calibration Range

Date	Expected Concentration	Measured Concentration (ppb)	Standard Deviation (ppb)	Precision (%)	Accuracy (%)
11/28/2023	0.0	-0.3	0.5	-	-
12/3/2023	0.0	-0.7	0.3	-	-
12/5/2023	0.0	-0.7	0.4	-	-
11/28/2023	33.2	33.2	1.0	2.9	0.1
12/3/2023	33.2	33.2	0.2	0.0	0.8
12/5/2023	33.2	32.1	0.0	0.0	3.3
12/5/2023	33.2	34.8	0.7	1.9	4.9
11/28/2023	102.8	102.5	0.2	0.3	0.5
12/3/2023	102.8	103.4	0.2	0.5	0.8
12/5/2023	102.8	102.8	1.6	1.6	0.0
11/28/2023	493.7	532.1	1.6	0.3	7.8
12/3/2023	493.7	556.7	3.1	0.6	12.8

05 Study Objectives

Objective #3: Raw Spectral Data Saved

- During the study, all raw spectral data associated with the quantification of ambient methane was saved and made available for access in real-time. Below is a sample plot of raw spectral data collected on December 3, 2023.

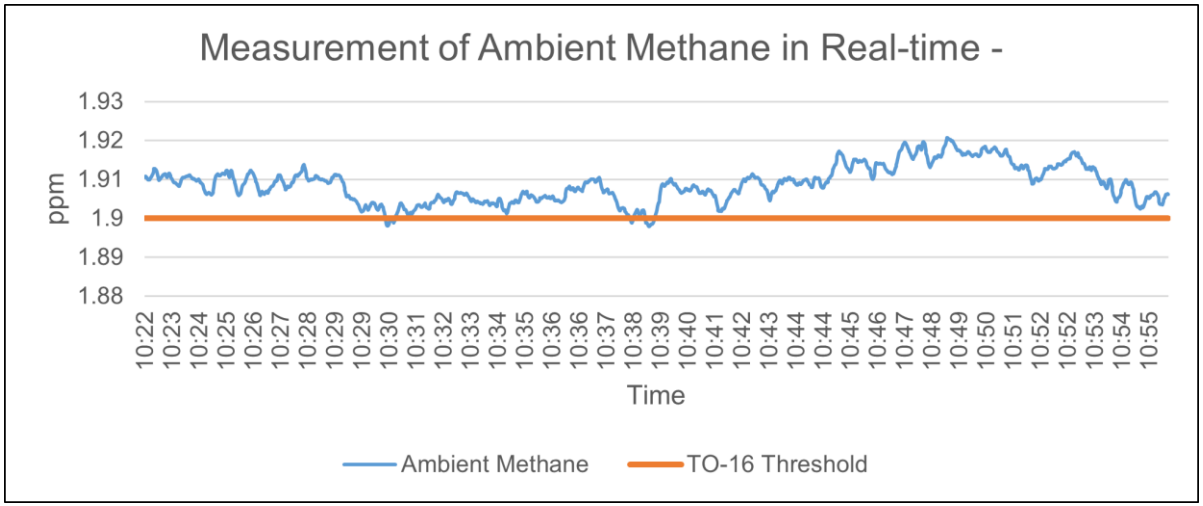


Sample Plot of the Raw Spectral Data Recorded by the System on December 3, 2023

05 Study Objectives

Objective #4: Real-Time Methane Quantification Stored and Reported

- During the study, all raw spectral data associated with the quantification of ambient methane was saved and made available for access in real-time. Below is a sample plot of methane data collected on December 3, 2023.

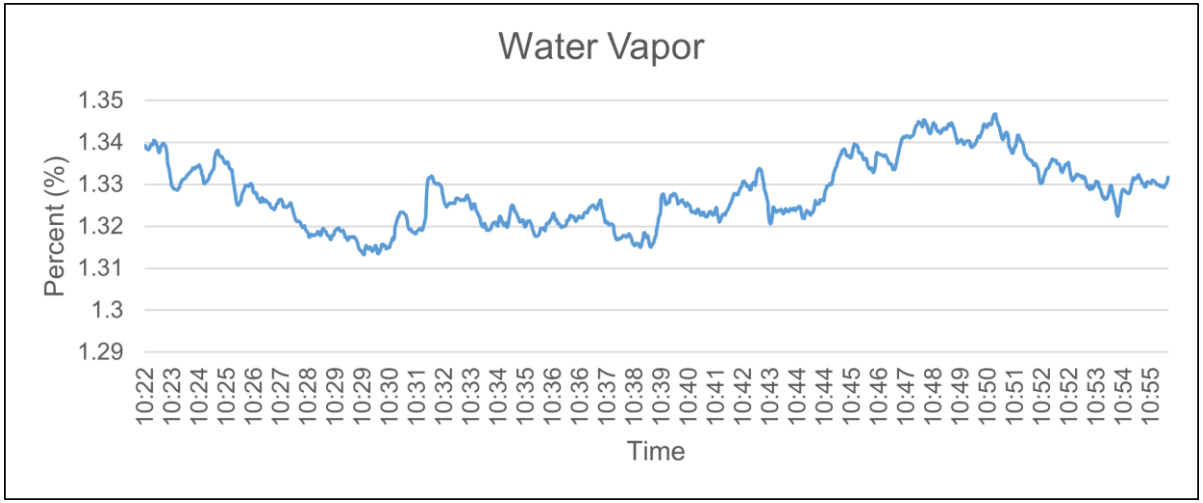


Ambient Methane Data Recorded by the System on December 3, 2023

05 Study Objectives

Objective #5: Real-Time Water Quantification Stored and Reported

- During the study, all raw spectral data associated with the quantification of ambient water was saved and made available for access in real-time. Below is a sample plot of water data collected on December 3, 2023.

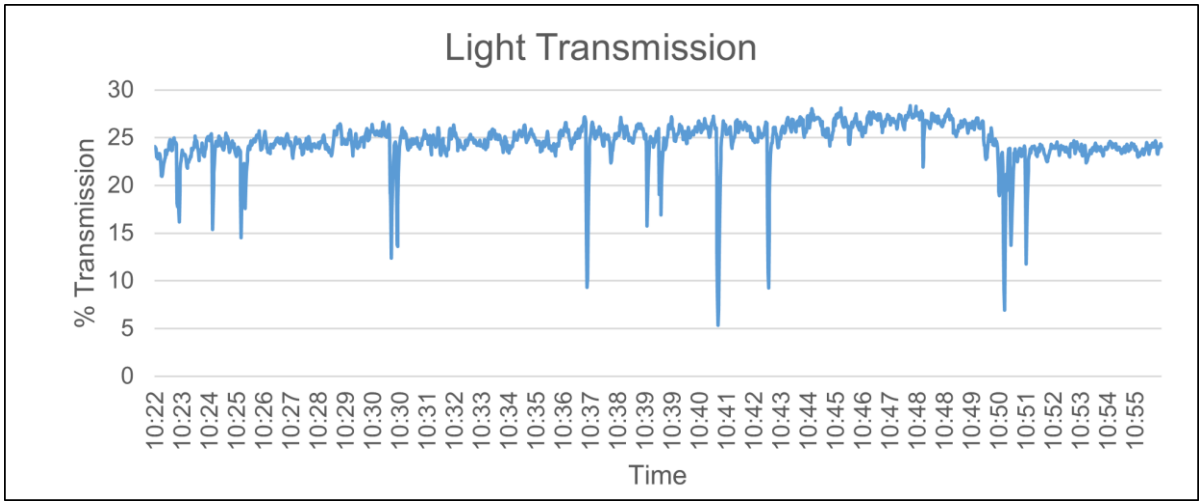


Water Vapor Data Recorded by the System on December 3, 2023

05 Study Objectives

Objective #6: Real-Time Light Signal Tracking

- During the study, all raw spectral data associated with the measured light transmission signal was saved and made available for access in real-time. Below is a sample plot of light signal data collected on December 3, 2023.
- Noted that the sharp drops in light transmission are due to vehicles traveling through the beam path and blocking the light.

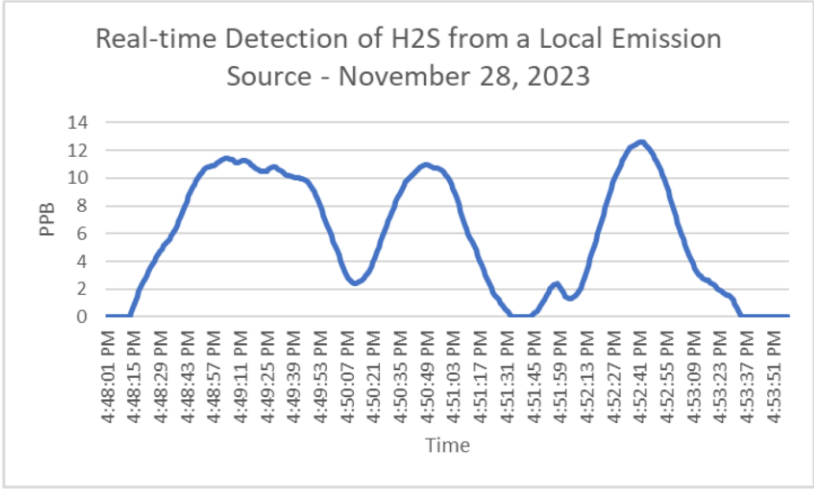


Light Transmission Data Recorded by the System on December 3, 2023

05 Study Objectives

Objective #7: Detection of H_2S During Study

- During the study, specific events were identified as being associated with the detection and quantification of H_2S in the ambient air. During these events, specific data quality indicators associated with H_2S were collected and reported in real-time that indicated the presence of H_2S.
- Evaluating wind direction during the event indicated the most likely source of the H_2S was a nearby oil refinery. Below is a sample plot of H_2S detected during the event.



Detection of H_2S During Study

06 Summary of Results

- The purpose of the study was to demonstrate that the Airoptic open-path H_2S TDL meets all of the regulatory requirements associated with BAAQMD Rule 12-15. The data presented in this study clearly shows the system meets or exceeds all of the requirements.

Evaluation Criteria	Pass/Fail	Study Reference
10 Sigma Quantification Limits Less than 25 ppb	Pass	Objective #1 – Determinations of Quantification Limits
10 Sigma Quantification Limits Average Less than 15 ppb	Pass	Objective #1 – Determinations of Quantification Limits
Real-Time Quantification Limits Less than 25 ppb	Pass	Objective #1 – Determinations of Quantification Limits
Precision Measured at Less Than 15% Across Calibration Range	Pass	Objective #2 Development of a Calibration Curve Objective #3 – Evaluation of Precision and Accuracy Across Concentration Range
Accuracy Measured at Less Than 15% Across Calibration Range	Pass	Objective #2 Development of a Calibration Curve Objective #3 – Evaluation of Precision and Accuracy Across Concentration Range
Raw Spectral Data Saved	Pass	Objective #4 – Saving of Raw Spectral Data
Real-Time Methane Quantification Stored and Reported	Pass	Objective #5 - Real-Time Methane Quantification Stored and Reported
Real-Time Water Quantification Stored and Reported	Pass	Objective #6 - Real-Time Water Quantification Stored and Reported
Real-Time Light Signal Tracking	Pass	Objective #7 - Real-Time Light Signal Stored and Reported
Reference Standard Methods	Pass	Objective #8 – Validation of System Performance Based on Regulatory Guidelines

Special thank you to the Benicia Community Air Monitoring Program (BCAMP) for hosting the technical evaluation and bringing together local political officials, the Bay Area Air Quality Management District, oil refineries, the general public, and technology vendors in an open forum to discuss air quality issues that affect us all.

THANK YOU FOR LISTENING!