Air Monitoring Plan for the Phillips 66 Refinery in Rodeo, California

Prepared for
Phillips 66
San Francisco Refinery
Rodeo, CA

Updated: September 5, 2023
Original: July 9, 2021

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Air Monitoring Plan
for the Phillips 66 Refinery in
Rodeo, California

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1. Introduction

1.1 Background

Phillips 66 (P66), Communities for a Better Environment, the Crockett/Rodeo Coalition, the Shoreline Environmental Alliance, and the local community have previously established a Good Neighbor Agreement (GNA) which includes the installation and operation of a fenceline air monitoring system at the Refinery. The fenceline monitoring system that the Refinery operates under the GNA consists of two open-path Fourier Transform Infrared Spectrometers (FTIR), two open-path Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS) systems, two open-path Tunable Diode Laser Absorption Spectroscopy (TDLAS) systems, and six organic gas detectors (OGDs). It also includes one meteorological station to provide wind direction, wind speed, temperature, and relative humidity information. The portions of this fenceline monitoring system that fall under siting, equipment selection, or gas analysis requirements of Rule 12-15 have been integrated into this monitoring plan. However, it should be noted that the requirements of the GNA do not supersede the requirements of Rule 12-15. Similarly, requirements associated with the implementation of Rule 12-15 do not supersede the existing requirements for the operation of the fenceline monitoring system associated with the GNA. As such, P66 will continue to operate the fenceline equipment that is associated with the GNA but that is not required under Rule 12-15, in addition to the equipment which is stipulated by Rule 12-15.

On October 6, 2021, BAAQMD provided updated requirements for refineries to (1) conduct additional H_2S monitoring along refinery fenceline paths, and (2) implement this enhanced monitoring by January 1, 2023. On January 1, 2023, P66 implemented H_2S monitoring. BAAQMD issued updated specifications on December 22, 2022, and P66's response to the updated specifications was submitted on February 10, 2023. This revision addresses feedback from BAAQMD received July 19, 2023.

The remainder of this section gives an overview of the Monitoring Plan and outlines the steps that will be taken to maintain approval of this Monitoring Plan.

1.2 Plan Summary

This section provides an overview of the monitoring plan. Subsequent sections provide additional plan details and associated justifications for the monitoring program design.

Rule 12-15 requires fenceline monitoring of multiple compounds using "open-path technology capable of measuring in the parts-per-billion range regardless of path length" or an alternative measurement technology.[2] The required compounds to be measured include benzene, toluene,

ethylbenzene, xylenes (BTEX), and H$_2$S. In addition, sulfur dioxide (SO$_2$), alkanes, 1,3-butadiene, other organics, and ammonia should be considered for measurements.

BTEX and SO$_2$ are measured by a bistatic UV-DOAS open-path analyzer, with the xenon light source and the detector at opposite ends of the sampling path. Alkanes (as n-hexane) are measured by a monostatic FTIR analyzer, with the light source and detector on the same side of the sampling path and a special mirror at the opposite end called a retro-reflector. H$_2$S is measured by a monostatic TDLAS analyzer. These open-path instruments transmit light across a given path and detect the amount of energy absorption at specific wavelengths to detect and quantify the concentration of target compounds. OGDs monitor the level of explosive compounds in the air, and two of them are included in the 12-15 fenceline monitoring system. A visibility instrument is used to assess low-visibility conditions that cause invalid or missing measurements from open-path analyzers.

The open-path sampling location is shown in **Figure 1** along with OGDs and potential source areas. GPS coordinates, elevations, and instrument inventory are shown in **Table 1**.
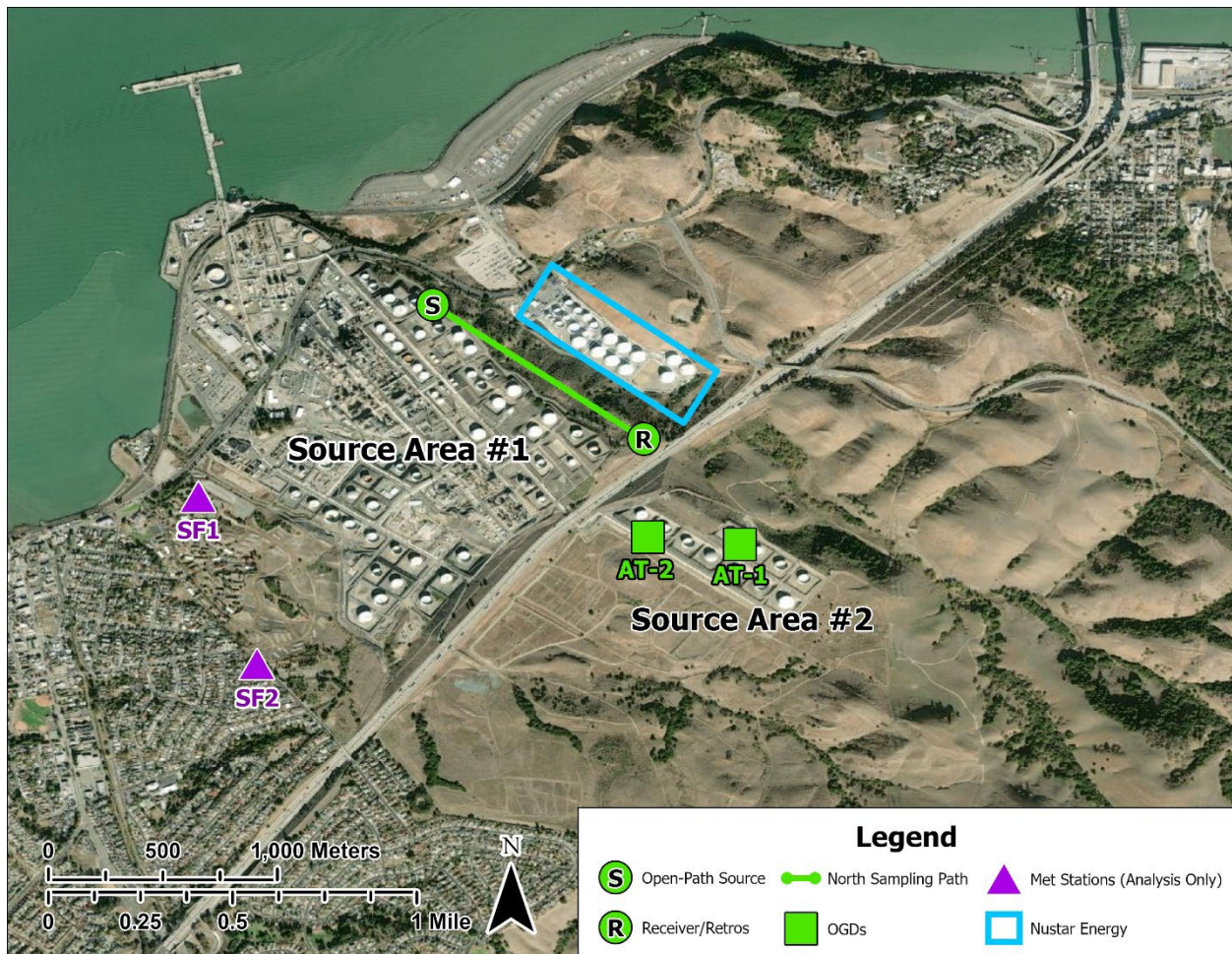

Figure 1. Refinery overview and potential source areas for the P66 Rodeo Refinery.

Table 1. GPS coordinates, elevations, and instrument inventory at each open-path sampling site.

Site	GPS Coordinates	Elevation (ft) above sea level	Equipment
North (Light Source/ Retroreflector)	38° 2'51.3"N, 122°15'7.4"W	200	1 UV-DOAS Emitter 1 FTIR Retroreflector 1 TDL Retroreflector
North (Receiver/Analyzer)	38° 2'32.4"N, 122°14'37.6"W	275	1 Bistatic UV-DOAS Receiver 1 Monostatic FTIR Analyzer 1 Monostatic TDL Analyzer
OGD (AT-1)	38° 2'17.5"N, 122°14'24.0"W	240	1 OGD
OGD (AT-2)	38° 2'18.5"N, 122°14'37.0"W	350	1 OGD

P66 followed guidance presented by the BAAQMD to determine which portions of the fenceline surrounding the Refinery are to be covered by monitoring under Rule 12-15 requirements. Measurements must cover populated areas within one mile of the Refinery fenceline that are likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time, or greater, based on the most representative meteorological measurements for potential Refinery sources likely to emit target compounds. Based on this analysis, the population centers that are less than one mile from the Refinery and lie within this arc are portions of Crockett. No population centers south of the Refinery are subject to fenceline coverage under Rule 12-15 as there is no population in that direction that lies within the arc representing the annual wind rose coverage requirement. Additional details on this analysis are presented in Section 2.2.3.

All instruments are installed and operated following manufacturer specifications, including necessary bump tests, which challenge instruments with known gas concentrations to confirm accurate response. Instruments are operated to meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters. Appropriate completeness criteria are calculated after removing time periods when atmospheric conditions prevented measurement.

Measurements are collected at a time resolution of 5-min. Data from the fenceline monitors are transmitted to a website where the near-real-time results can be viewed by the public. The website also provides a mechanism for public comment, which is monitored by a designated consultant. Data generated by the fenceline monitoring equipment undergo review throughout the measurement and reporting process. Included in this process are automated QA/QC checks that occur before data are reported on the real-time website. Under normal circumstances, a 5-min average measurement appears on the website within 10 minutes of the end of the measurement period. However, the data

uploaded may be impacted by internet traffic. An automated system conducts the quality assurance checks before the data are reported to the website. The website also makes available a rolling 1-hr trend of the 5-min data for each pollutant reported. Final data sets are compiled quarterly and provided to the BAAQMD no later than 60 days after the end of each calendar quarter. Data deliveries are consistent with BAAQMD guidance and additional details are provided in Section 4.6 of the Quality Assurance Project Plan (QAPP). The Refinery will make data available to BAAQMD upon request prior to report submittal.

All data are retained by the facility for a period of five years, consistent with Regulation 12-15-502.

2. Monitoring Plan Design Considerations

This Monitoring Plan was developed in consideration of the following elements:

- Rule 12-15 and related guidance.

- Monitoring objectives, which were established in consideration of Rule 12-15 and related guidance.

- Assessment of potential source areas, target compounds, annual and seasonal meteorology, and overall fenceline monitoring coverage requirements.

- Technical and engineering feasibility related to available monitoring technologies and instrument siting.

- Data management and Quality Assurance/Quality Control (QA/QC) requirements.

Details on each of these elements are provided in the following subsections.

2.1 Key Elements of Rule 12-15 and Guidance

According to the BAAQMD's April 2016 guidelines, the main goals of fenceline monitoring are to:

- "Provide continuous air quality concentration information on a short enough time scale to address changes in fence-line concentrations of compounds associated with refinery operations."

- "Provide data of sufficient accuracy to identify when concentrations of compounds associated with refinery operations are elevated as compared to other monitoring locations throughout the Bay Area."

- "Potentially aid in identifying corrective actions that lowers emissions."

Key considerations provided in the Guidance Document for designing a monitoring plan to address BAAQMD goals are summarized below.

- Conduct "fenceline" measurements of BTEX and H_2S. Consider measuring other compounds, including SO_2, alkanes, 1,3-butadiene, other organics, and ammonia. The term "fenceline" in the guidance refers to a general boundary between refinery property and areas outside the refinery property, not necessarily to an actual fence.

- Conduct measurements in areas where emissions from the refinery could frequently impact populated areas. Specifically, this includes the following:

- "Measurements must cover populated areas within one mile of the refinery fence-line likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time, or greater, based on the most representative meteorological measurements for sources likely to emit the compounds listed above at the refinery."
  - In addition, "Meteorological measurements should also be used and addressed in the Air Monitoring Plan to ensure proper siting of fence-line systems, looking at long-term measurements such as annual average wind rose, but also taking into account more seasonal and recurring short term meteorological events."

- Provide measurements of the compounds at the ppb level or as technology allows.

- Conduct measurements using open-path instruments or an appropriate alternative.

- Provide rationale for the compounds to be measured and not measured.

- Provide rationale for the locations for the measurements.

- Provide rationale for the instruments to be used.

- Collect the measurements every 5 minutes.

- Process the data and display the data in near-real time to a public website.

- Meet data recovery and completeness criteria.

- Develop a QAPP for the measurement program and follow the QAPP.

2.2   Fenceline Coverage

2.2.1   Analysis of Potential Source Areas

Potential Refinery sources were divided into two areas as shown in Figure 1. Source Area #1 includes the Refinery process units and storage tanks, and potential emissions include alkanes, BTEX, SO_2, and H_2S. Open-path systems at the North fenceline will be used to provide measurement coverage at these sources. Source Area #2 includes seasonal storage tanks, and potential emissions only include volatile organic compounds (VOCs). OGDs that can detect VOCs will be used to monitor these sources.

It should also be noted that tanks north of Source Area #1 are owned by NuStar Energy and are not part of the P66 Refinery. Thus, the equipment in that area is not part of this Monitoring Plan as it is not subject to BAAQMD Rule 12-15.

2.2.2   Assessment of Target Compounds

As required by Rule 12-15, P66 considered the measurement of sulfur dioxide (SO$_2$), alkanes, or other organic compound indicators, 1,3-butadiene, and ammonia for inclusion in the Air Monitoring Plan. Alkanes and SO$_2$ are included in the monitoring plan as they have the potential to be present in measurable quantities. 1,3-Butadiene is not included in the fenceline monitoring program because it is not produced as an intermediate or end product at the Refinery and is not present in significant quantities at the Refinery. In addition, ammonia is not included in the fenceline monitoring program as anhydrous ammonia is not used in routine processes at the Refinery. P66 uses open-path FTIR to measure alkanes. These gases are currently being measured at the Refinery and are represented as "total hydrocarbons" on the P66 real-time public website. In addition, SO$_2$ is measured using UV-DOAS and concentrations are reported on the P66 real-time public website. Other specific chemicals requiring monitoring were evaluated from emissions estimates based on available toxic release inventory (TRI) reporting information. Based on this analysis, other gases are already being captured in this monitoring program or did not meet the criteria for monitoring.

2.2.3   Assessment of Annual Meteorology

P66 followed guidance presented by the BAAQMD to determine which portions of the fenceline surrounding the Refinery are to be covered by monitoring under Rule 12-15 requirements. Measurements must cover populated areas within one mile of the Refinery fenceline that are likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time, or greater, based on the most representative meteorological measurements for potential Refinery sources likely to emit target compounds. BAAQMD has provided guidance that this aspect of the analysis should result in an eight-segment wind rose that is used for comparison against the 10% threshold mentioned above.

To perform this analysis, P66 generated eight-segment wind roses composed of sectors that make up 45-degree arcs. The first sector spanned the 0 to 45 degree range (i.e., the arc is centered at 22.5 degrees and extends out 22.5 degrees in each direction). Each additional section was defined by moving 45 degrees from the previous arc's centerline and extending out 22.5 degrees in each direction. P66 generated wind roses using data collected from January 1, 2012, to December 31, 2016, from an on-site meteorological station located at label SF1 in Figure 1. Other Met stations located near the Refinery were considered for this analysis, but SF1 was chosen as the most representative station based on its proximity to the Refinery. To be thorough, P66 analyzed data from the next closest met station (SF2 in Figure 1) and found that the station provided comparable wind data to SF1. Wind direction and speed data collected from the SF1 met station were used to generate various wind roses for the Refinery in accordance with the guidelines discussed above.

These wind roses were used to determine the percentage of time the wind blows in each sector. The annual wind rose showing this information is presented in **Figure 2**.
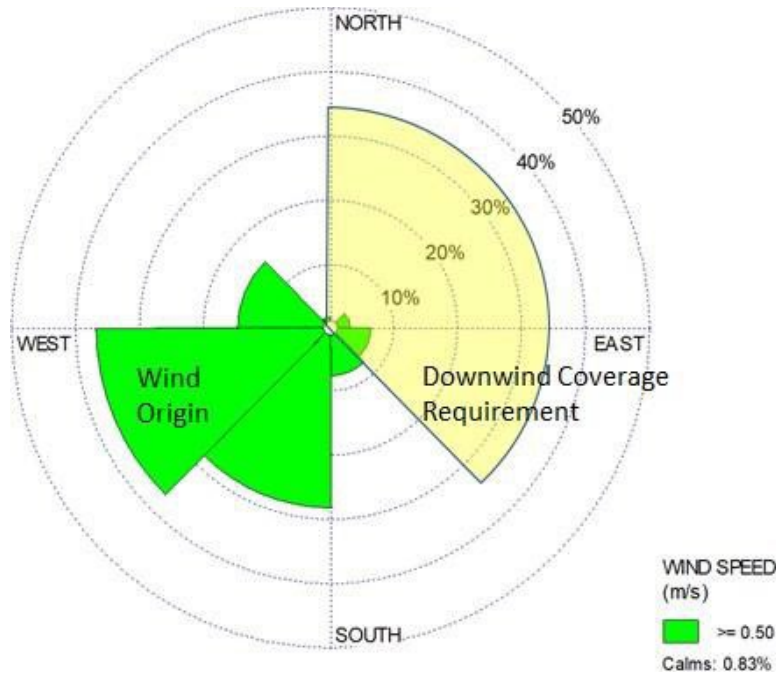
Figure 2. Annual wind rose (SF1 met data analysis from Jan 1, 2012 – Dec. 31, 2016).

Based on this analysis, three sectors have wind blowing at least 10% of the time on an annual basis. Note that the wind rose shows the direction from which wind originates (i.e., the direction the wind is coming from). Thus, the areas that may require monitoring under Rule 12-15 are those with populations that lie in an arc between 0 degrees (due North) and 135 degrees (Southeast) of the Refinery. For clarity, this downwind coverage requirement is shown with yellow shading in Figure 2.

Areas requiring monitoring were then identified by generating an arc for the applicable wind rose sectors and overlaying that arc with the potential emission sources within the Refinery. Using the source as the focus of the arc, a downwind flow map was generated by extending the arc a distance of 1 mile from the origin. **Figures 3 and 4** show the downwind sectors from Source Areas #1 and #2 that meet the annual wind rose requirements for Rule 12-15, as they apply to the populations surrounding the Refinery. The populations that are less than one mile from the Refinery and that lie within this arc constitute portions of Crockett. As seen in **Figure 5**, no population south of the Refinery is subject to fenceline coverage under Rule 12-15 as there is no population in that direction that lies within the arc representing the annual wind rose coverage requirement.

Figure 3. Downwind coverage requirements for source area #1.

Figure 4. Downwind coverage requirements for source area #2.

Figure 5. Downwind coverage requirement for the southernmost potential source.

2.2.4 Assessment of Seasonal Meteorology

In addition to annual wind patterns, a review of seasonal meteorological events was conducted, and results considered in the development of this Air Monitoring Plan. This review of seasonal patterns included analyzing data from January 1, 2012, to December 31, 2016. To determine whether the wind blows in a particular wind rose sector for a significant amount of time on a seasonal basis, a significance threshold of 20% was set for seasonal meteorological events. This threshold is equivalent to an annual significance threshold of 5% of the time for any given wind rose sector because the time basis for a seasonal wind rose is 3 months (as opposed to 12 months for the annual wind rose shown in Figure 2). As the BAAQMD Air Monitoring Guidelines specify a 10% significance threshold on annual basis, P66 considers it conservative to evaluate seasonal wind pattern significance using a threshold equivalent to 5% on an annual basis.

The wind rose data for this seasonal analysis is presented in **Figures 6 through 9**. The results of this analysis reveal that wind patterns in the spring, summer, and fall show the same predominant wind directions as the annual average. While the winds during winter tend to broaden out, they show the same general trend as the annual average with respect to predominant wind direction. In each seasonal wind rose, there are sectors in which the wind blows for a period of time that is above the seasonal significance threshold discussed above. However, in each of those cases, the sector already requires fenceline monitoring equipment coverage, based on the annual wind patterns. Thus, the potential downwind exposure addressed in this plan does not change due to seasonal variation.
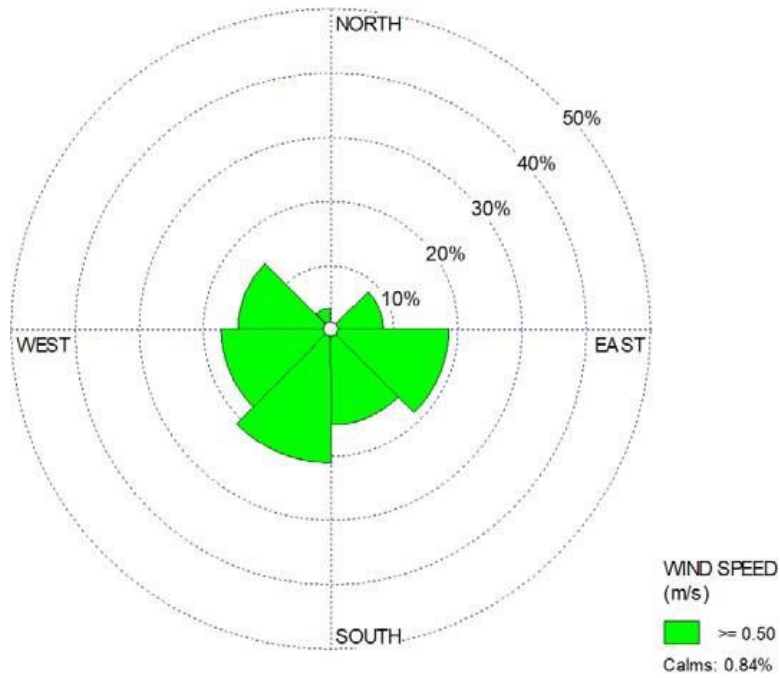
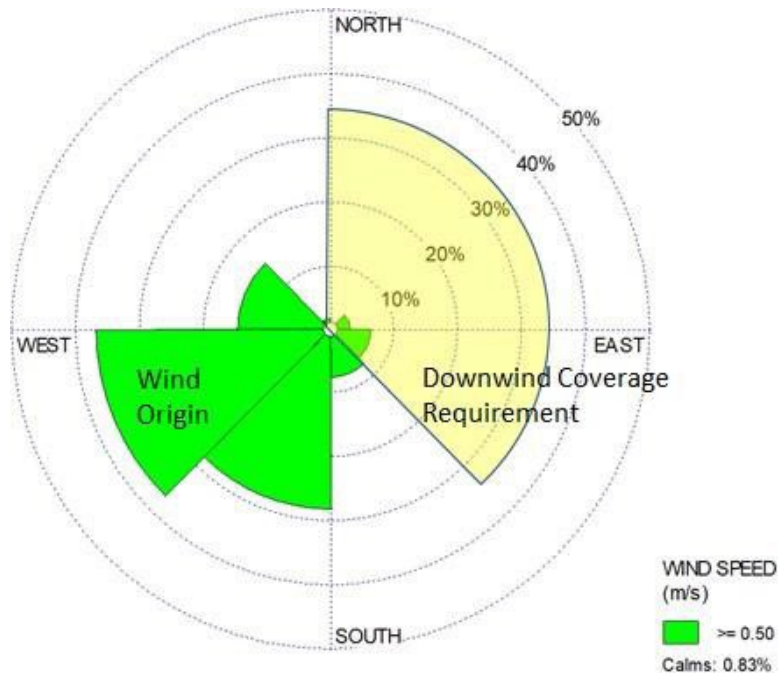**Figure 6.** Wind rose for winter months (Dec, Jan, Feb).
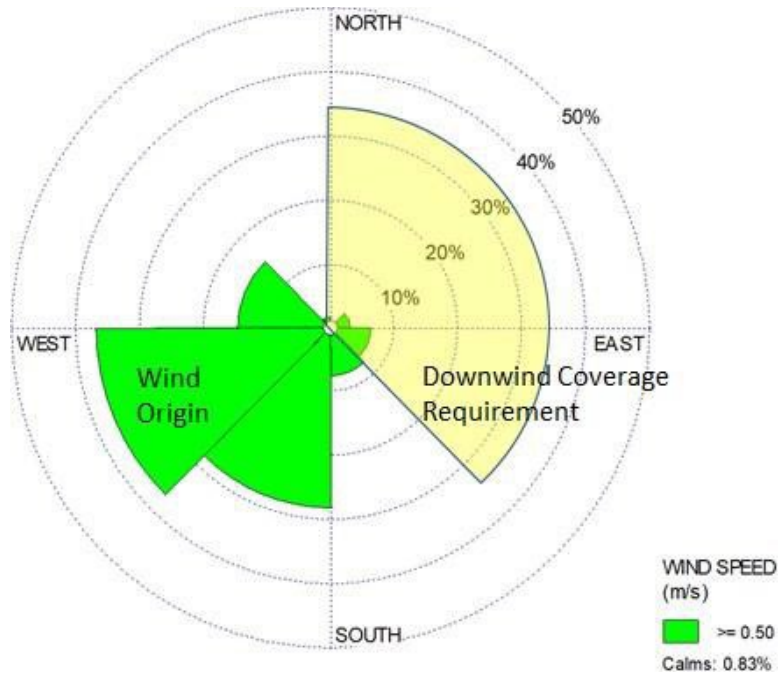

Figure 7. Wind rose for spring months (Mar, Apr, May).

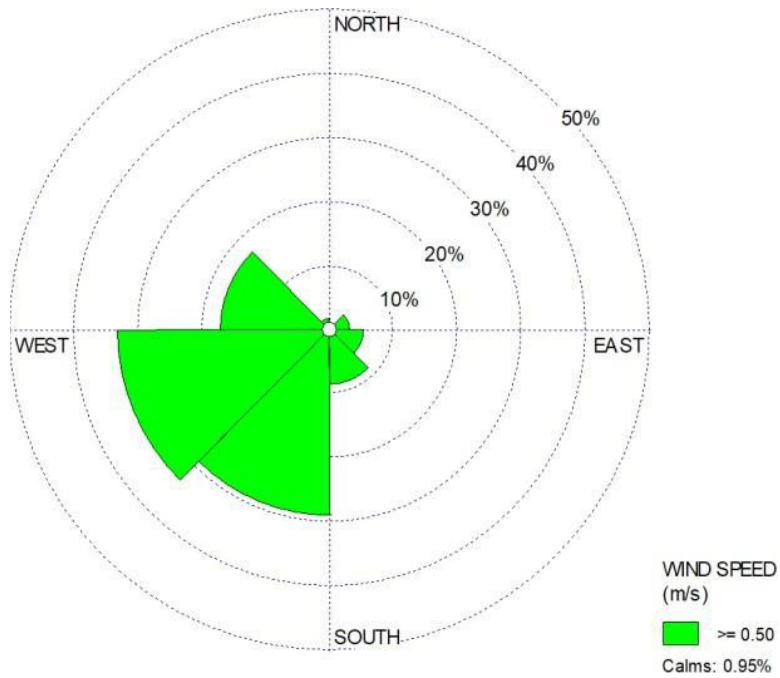**Figure 8.** Wind rose for summer months (Jun, Jul, Aug).

Figure 9. Wind rose for fall months (Sep, Oct, Nov).

2.2.5   Fenceline Monitoring Coverage

Populations downwind of Source Area #1 are covered by the open-path air monitoring equipment on the north fenceline of the Refinery. This air monitoring equipment includes open-path UV-DOAS, TDL, and FTIR analyzers along a path length of approximately 930 meters.

Populations downwind of Source Area #2 are covered by OGDs. Source Area #2 has four regulated storage tanks that are within one mile of approximately 12 houses downwind of the source. The OGDs have the capability of measuring total VOCs on a continuous, real-time basis and satisfy the rule requirement for sample collection time. An additional benefit of the OGD air monitoring technology is that the systems can generally remain in operation during periods of time when the open-path systems may be inoperable due to signal loss from weather conditions.

Every effort has been made to ensure all populations and sources identified as being part of Rule 12-15 are addressed in the Monitoring Plan. However, there are certain areas where locating fenceline equipment is not possible or is not required under Rule 12-15. Note that the siting of existing fenceline equipment was a collaborative effort between the community and the Refinery as part of the GNA for operating the fenceline monitoring program.

The sources located at the north end of the Refinery are covered by the open-path air monitoring equipment that is currently in operation along the north fenceline. A small portion of this fenceline cannot be covered, primarily due to siting issues; this includes a small number of storage tanks west of the fenceline air monitoring equipment that is currently in operation at the Refinery. Extending the path to accommodate the additional storage tanks is not possible due to the terrain and would also degrade the data quality of the fenceline monitoring system by extending the range beyond maximum manufacturer recommended path lengths. The same siting issues are present for point sample technologies, as the terrain is unsuitable for the infrastructure necessary to site a point sampling system. Thus, P66 is operating the maximum possible path lengths within these siting and technological constraints. Additionally, three of the five storage tanks west of the fenceline are exempt from regulation, indicating that few emissions are expected from those tanks.

In the area east of Interstate 80, the seasonal storage tanks are monitored using technologies other than open-path monitoring equipment. This source presents a very low potential risk to population downwind of the source primarily because of 1) the nature of storage tank emissions and operations, 2) the distance between the source and receptors, and 3) the relatively low amount of populated area within one mile of the source.

The emissions plume from liquid storage tanks is typically a broad plume (i.e., as opposed to a narrow plume) that does not carry much buoyancy in the air. This is because storage tank emissions are not released with significant upward velocity, are not high temperature, and many of the organic compounds that exist in these emissions are heavier than air. Considering the nature of storage tank emissions, a release from the tanks in the seasonal storage area would need to be an abnormally large release in order to immediately affect the downwind population. Additionally, the nearest

residence to these storage tanks is nearly one mile away (>0.95 miles) with approximately 12 homes being within 1 mile. This provides a reasonable distance for air emissions dispersion to occur.

Nonetheless, P66 has proposed to include monitoring in the area east of Interstate 80 as part of the monitoring plan under Rule 12-15. This monitoring consists of two organic gas detectors as described previously in this plan. In the event of an abnormal release from one of the tanks located in this area, it is highly likely that emissions from such a release will be detected by an organic gas detector near the tank due to the nature of storage tank emissions. In addition, two organic gas detectors are included in the plan to provide enhanced coverage, as this configuration helps to cover the tanks for a variety of meteorological conditions.

It is also noteworthy that only four storage tanks in the area east of Interstate 80 are regulated and fall within a mile of the nearest downwind residence, and that the OGDs are located immediately adjacent to these tanks. These tanks are the three tanks that are nearest to the westernmost OGD (shown in Figure 1), and the tank located immediately to the southeast of the easternmost OGD. Also, when applying the annual wind rose measurements to this community within a mile of the nearest tank, the wind blows toward this population less than 8% of the time. Finally, note that all regulated storage tanks are included in the refinery tank seal inspection program to monitor the condition of tank seals.

The area that is west of San Pablo Avenue contains no active refinery product processing areas. For this reason, there is no need for air monitoring equipment in this area. Finally, it should be noted that P66 operates fenceline air monitoring equipment similar to the north fenceline monitoring stations along the south side of the Refinery. While the FLM equipment along the south side of the Refinery is not required as part of Rule 12-15, P66 will continue to operate this equipment under the GNA.

2.2.6   Visibility Conditions

Marine and radiation fog is common near Rodeo. Heavy fog may entirely block the signal from an open-path instrument and prevent data collection; however, even light fog can absorb the signal partially and interfere with measurements. The expectation is that measurements are severely impacted when visibility is less than 2.5 miles, as this results in marginal operating conditions for the analyzer (e.g., decreased signal strength or increased integration time). If open-path data are missing or invalid due to low light, and visibility is low, data are flagged as invalid due to low visibility.

2.2.7   Description of Monitoring Equipment

The fenceline air monitoring equipment use beams of light to detect and quantify gases in the air. Different compounds in the air absorb different wavelengths of light. Thus, the general principle of operation of open-path systems is that a beam of light is sent into the open air, and if a gas is present that absorbs light, the system can identify the specific gas by determining which wavelengths

of light were absorbed. Once the gas is identified, the amount of that gas present in the beam path can be determined by how much of each target wavelength was absorbed. A single instrument can send a beam of light out over half a mile, so open-path instruments are very effective in covering large portions of facility fencelines. **Figure 10** illustrates the basic concept of open-path measurements. Note that open-path monitors cannot distinguish between a widely dispersed, low-concentration plume and a narrow, high-concentration plume; they detect average concentrations across the entire distance from transmitter to detectors.
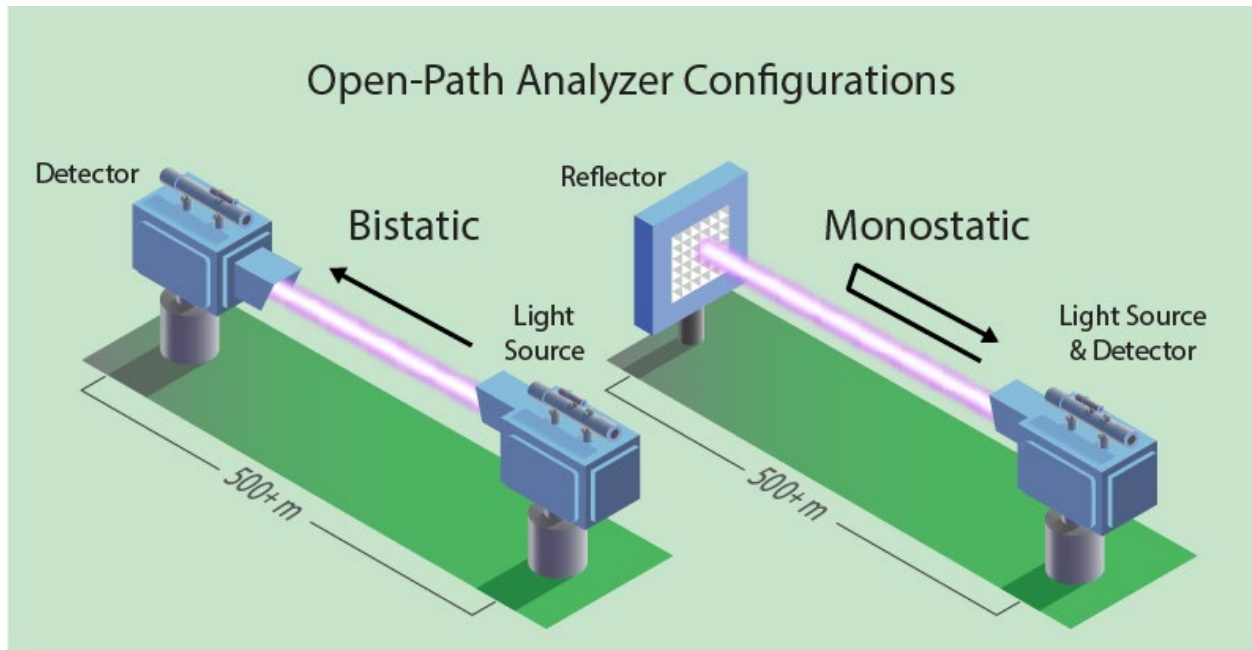
Figure 10. Open-path analyzer basic operating principle. In the monostatic configuration, the light source and the analyzer are in the same enclosure. In a bistatic configuration, the light source and the detector are in separate enclosures and there is no reflector.

BTEX and SO_2 are measured using a bistatic UV-DOAS with a xenon light source. The xenon light is required to measure over the sampling path length of 930 m and to achieve sufficient minimum detection limits (MDL) for BTEX compounds. H_2S is measured using a monostatic TDLAS system, which measures a single absorption line for the target pollutant. A tunable diode laser can emit light over a small range of very specific wavelengths, which allows spectral measurement over a narrow wavelength range. Based on measurements collected at P66, it has been determined that MDLs lower than 25 ppb can be achieved on a routine basis. H_2S is not measured with UV-DOAS because its absorption spectra overlaps with BTEX and generates false positives, and FTIR is not suitable because of poor detection limits and overlap in absorption with other compounds.

Table 2 summarizes the MDL for each target compound by instrument, as provided by instrument manufacturers. The detection limits are for the average species concentration along a path; narrow plumes that only cover a portion of the path would need to have a higher concentration than the

MDL to be detected. Under typical operating conditions, the Unisearch TDL is expected to have an MDL between 3 and 25 ppb at less than 1% transmission. The MDL may be higher than those listed in Table 2 if there is poor atmospheric visibility (e.g., heavy fog, rain, smoke, or dust), the instrument is misaligned, there are hardware problems, or an interferant is present. MDLs at the lower end of the specified range are expected under the opposite conditions.

Table 2. Approximate detection limits for each target compound. Actual detection performance depends on ambient conditions.

Analyzer	Compound	MDL (ppb)
TDLAS[a]	Hydrogen Sulfide (H_2S)	3–25
UV-DOAS (Xenon)	Benzene	10
	Toluene	10
	Ethylbenzene	100
	Xylenes	10
	Sulfur Dioxide (SO_2)	10
FTIR	Alkanes	10
OGDs	Organic Gas (VOCs)	--[b]

[a] Per the December 22, 2022, letter from BAAQMD[1], the level of quantitation (LOQ) is taken to be equivalent to the MDL.
[b] OGDs have a detection range of 0-100% of the lower explosive limit (LEL) of methane, with an accuracy of ±3% between 0-50% LEL and an accuracy of ±5% between 51-100% LEL.

For the Unisearch TDL, a real-time MDL is calculated continuously using the standard deviation of the last seven 5-min average concentration values containing no measurable analyte (as determined by the correlation coefficient). Per the December 22, 2022, letter from BAAQMD[1], the TDL level of quantitation (LOQ) is taken to be equivalent to the MDL, and is calculated as twice the aforementioned standard deviation. The resulting MDL is reported alongside every 5-min average concentration value. Data with real-time MDL values greater than 25 ppb are flagged for additional review and are considered to not meet the performance criteria.

Power, communications, and shelter are required at the light source and detector ends of the sampling path. The retroreflector needs only to be aligned and cleaned regularly for maximum performance. An example of a UV-DOAS analyzer and receiver in a shelter is shown in **Figure 11**, and a retro-reflector is shown in **Figure 12**.

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[1] Bovee, J. "Refinery Fenceline H2S TDL Monitoring System Specifications", Communication to P66 San Francisco Refinery, December 22, 2022.

Figure 11. Example of a UV-DOAS analyzer installation.

Figure 12. Example of a retro-reflector installation.

2.3 Data Management Requirements

2.3.1 Data Recovery

BAAQMD guidance for open-path measurement data recovery is that instrumentation must meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters. Because open-path measurements are affected by atmospheric conditions such as dense fog, invalid data due to low signal strength during low-visibility conditions do not count against completeness requirements. Visibility measurements are made using a forward scattering optical visibility sensor to document the time periods of reduced visibility, as described in Section 2.2.5. Visibility measurements are made at least every 5 minutes to coincide with the open-path measurements.

Other factors that affect data availability include instrument bump test (monthly for a few hours), other maintenance (e.g., replacement of UV bulbs for the UV-DOAS after every 2,000 hours of use, roughly on a quarterly basis), and annual maintenance. Regular maintenance and careful, responsive operation will minimize instrument downtime.

2.3.2   Data Quality Assurance/Quality Control (QA/QC)

A key goal of the QA/QC plan is to ensure high-quality data that are representative and defensible. Clear definitions and procedures for QA/QC are also necessary to inform the public on why some data are missing, flagged as questionable, or invalid. Data review consists of the following types of actions.

An air quality specialist reviews bump test data, instrument field setup, and instrument functionality. Initial bump test data, data processing calculations (i.e., conversion of instrument signal to concentration), data file formats, and data transfer is verified. Throughout operations, the project QA manager ensures that Standard Operating Procedures (SOPs) are being followed, operators are documenting field operations in field data sheets and logbooks, instrument performance checks are being conducted, and instruments are passing the performance checks.

Additional checks focus on internal consistency of the data. Both automatic screening and manual review of data streams is conducted. An air quality specialist performs daily review of data to ensure proper operation of field equipment and provide feedback to the field operators when potential problems are identified. By keeping monitoring equipment operational, higher data completeness can be achieved.

Details of the QA/QC process are provided in Section 3.2.1 and in the QAPP (Appendix A).

3. Routine Operations

Instrument operations, maintenance, and bump tests include daily checks to ensure that data are flowing from all instruments, as well as monthly, quarterly, and annual maintenance activities. Further details are provided in the following sections, which describe routine instrument and data management operations. Full details and documentation are included in the QAPP, which is provided in Appendix A.

3.1   Instrument Operations

3.1.1 UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. Table 3 summarizes typical UV-DOAS maintenance activities as recommended by the manufacturer. Preventive maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms will alert operators to specific issues needing to be addressed.

Table 3. Schedule of maintenance activities and performance indicator checks for the UV-DOAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving check list is maintained).	✓		
Inspect optics on detector and retro-reflector. Clean if necessary.	✓		
Inspect and clean system filters.	✓		
Confirm the alignment to verify there has not been significant physical movement. This is accomplished by noting the integration time and signal strength – both should be less than 250 ms and greater than 90%, respectively.	✓		
Download data older than 12 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	✓		
Inspect all electrical cables for wear. Replace as needed.	✓		
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency. Measure stray light. Realign system if integration time exceeds 250 ms.	✓		
Change out the UV source if the intensity has dropped below acceptable range (service hours >2,000 hours and intensity at 250 nm < 3% with 40 ms dwell time under high visibility conditions).		✓	
Replace ventilation exit and intake filters.		✓	
Clean and inspect optics on detector and retro-reflector.		✓	
Realign system after service. Ensure integration time is less than 250 ms and intensity is greater than 90% under high visibility conditions.		✓	
Check other system performance indicators, if necessary.		✓	
Perform bump test.	✓		
Verify system settings.			✓

3.1.2 TDLAS

The TDLAS has similar maintenance activities to the UV-DOAS. The TDLAS system is also designed to require only modest service and maintenance. Table 4 summarizes TDLAS maintenance activities, as recommended by the manufacturer. Preventative maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed.

Table 4. Schedule of maintenance activities and performance indicator checks for the TDLAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓		
Inspect optics on detector. Clean if necessary.	✓		
Check the alignment to verify there has not been significant physical movement and confirm signal levels. Signal power should be greater than 0.1 mW.	✓		
Download data older than 12 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, or vehicles).	✓		
Inspect all electrical and optical cables for wear. Replace as needed.	✓		
Perform bump test	✓		
Review and test light and signal levels.[a] Signal power should be greater than 0.1 mW.		✓	
Perform a 3-point calibration check		✓	
Verify system settings.			✓

[a] Although signal strength is recorded in real time, it is recommended to consider longer term trends in signal intensity to evaluate the health of the optical components, the effects of cleaning optical components, and the noise characteristics of the spectral data.

3.1.3 FTIR

The FTIR has similar maintenance activities to the UV-DOAS. The FTIR system is also designed to require only modest service and maintenance. Table 5 summarizes FTIR maintenance activities, as recommended by a typical manufacturer. Preventative maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed. Bump tests are performed on site.

Table 5. Schedule of maintenance activities and performance indicator checks for the FTIR.

Activity	Monthly	Quarterly	Annually	18-24 Months	Five Years
Visually inspect the system.	✓				
Inspect optics on detector and retro-reflector; clean if necessary.	✓				
Confirm the alignment to maximize signal intensity.	✓				
Download data older than 6 months from the hard drive, move to a permanent archive, and delete old files from the analyzer.	✓				
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	✓				
Perform bump test.	✓				
Check system performance indicators (an evolving checklist will be maintained).		✓			
Inspect and clean AC system exterior heat sink.		✓			
Review and test light and signal levels. Check average light intensity to establish baseline for IR Source change frequency and retro-reflector wear.			✓		
Replace cryocooler or swap detector module assembly.				✓	
Change out the IR source.					✓

3.1.4 Organic Gas Detectors

The organic gas detectors used here need very little maintenance. On a quarterly basis, the hydrophobic filters should be inspected and cleaned and the response of the OGDs should be tested and/or calibrated using zero and span points. If needed, the OGD can be further disassembled for more extensive cleaning. During gas testing, it is a best practice to confirm end-to-end data transfer from the OGD, through the radio system, to the internal website. The OGD detectors may need more frequent maintenance during times of heavy rain as moisture is a known interferant for the measurement.

3.1.5 Visibility Instruments

For the visibility instruments, monthly maintenance includes inspecting the sensor for dirt, spider webs, birds' nests, or other obstructions. If the sensor is dirty, the glass windows can be cleaned with a glass cleaner. There are no serviceable components in the sensor.

The sensors are calibrated in the field using a manufacturer-specific calibration kit. A calibration kit consists of a blocking plate or block for checking the sensor zero and a scatter plate for checking the sensor span. The calibration fixture is assigned a factory-traceable extinction coefficient (EXCO) used to calculate the expected values during calibrations. Calibrations will be performed every year as specified by a manufacturer.

3.2   Data Management Operations

Raw data management occurs on a real-time, daily, monthly, quarterly, and annual basis. These raw data are not yet intended for the public website. In near-real time, data is transferred from in-field instruments through a data acquisition system (DAS) to a Data Management System (DMS) using a cell modem. Data are also stored onsite on instrument computers in case of cell modem failure. The DMS uses a Microsoft SQL relational database with stored procedures.

The DMS automatically quality-controls data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities are used for continuous examination of data quality. The DMS feeds auto-screened data to the field operations website and notification system to inform and alert project and facility staff. The operations website shows maps and time series plots of BTEX, H_2S, SO_2, and alkanes concentrations, and wind data are also displayed on the maps.

3.2.1 Quality Assurance and Quality Control (QA/QC)

All data values that are not associated with bump tests, other instrument maintenance, or instrument problems are displayed to the public in near-real time. If data are subsequently proven to be invalid, they are removed from the public display.

A non-public field operations website is used for daily graphical review of the data (see example at Figure 13). Common problems include flat signal/constant values, no signal/missing data, extremely noisy signal, rapid changes (spikes or dips), and negative concentrations (see annotated Figure 14 for some examples). An initial review, typically of a one- to two-day running time-series plot of selected parameters for each instrument, allows the analyst to see common problems and verify instruments are operational. If it appears that an instrument is not operating, or the data are missing, the field operator is notified and further investigation and corrective action, if needed, is taken.

Figure 13. Example of non-public field operations website used for daily review of instrument operations.
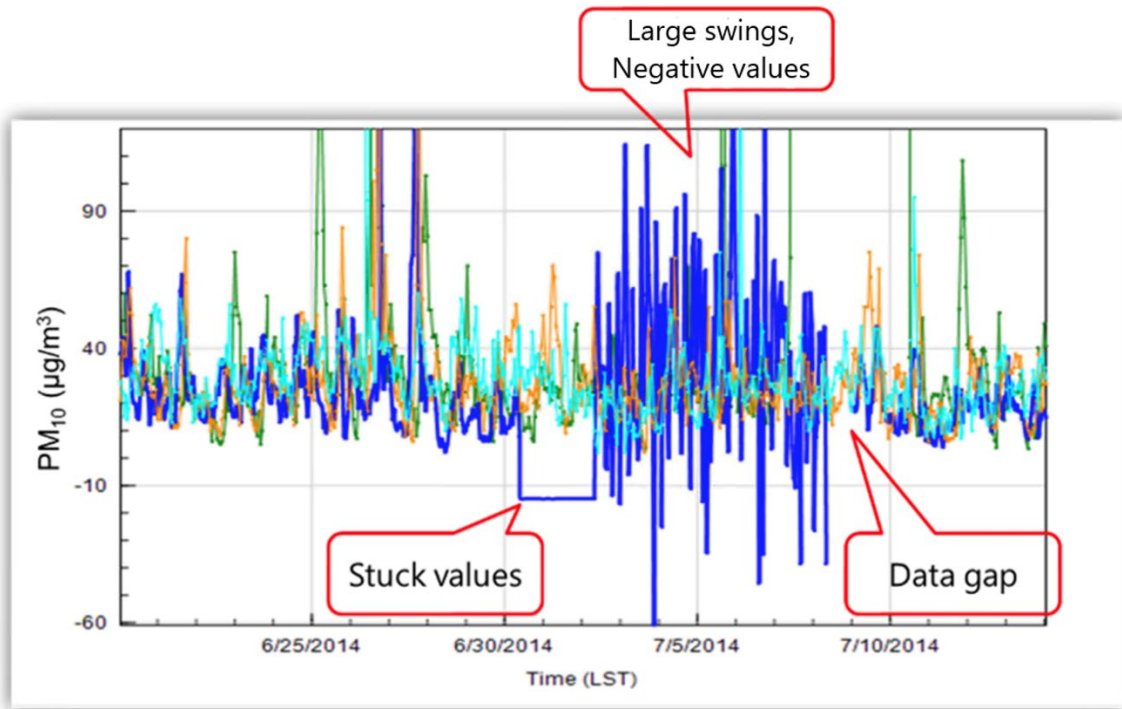
Figure 14. Example of pollutant concentration time series showing stuck values, large swings, negative values, and a data gap. All of these are indicators of instrument issues.

Concentration patterns are reviewed to confirm that they are reasonable with respect to the time of day, season, meteorology, and concentrations are expected and observed at other sites. If anomalies are observed, additional analysis is conducted to determine if there is an instrument malfunction or the data are truly anomalous, but explainable and valid.

Visual review of data is augmented by automated data screening within the DMS upon data ingest. Automated screening checks of data feeds are helpful to focus the analyst's efforts on the data that need the most attention and are used to screen out invalid data for public display. Initial screening checks, along with actions to be taken, are summarized in Table 6. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. All screening criteria (flags and rates of change) are refined during the project based on actual observations. In summary, the DMS auto-screening checks that are used include:

- **Range.** These checks verify that the instrument is not reporting values outside of reasonable minimum and maximum concentrations.

- **Sticking.** If values are repeated for a number of sampling intervals, data are reviewed for validity. Typically, four or more intervals of sticking values are a reasonable time span to indicate that an investigation is needed. Sticking checks are not applied to data below the instrument detection limit.

- **Rate of Change.** Values that change rapidly without reasonable cause are flagged and reviewed.

- **Missing.** If data are missing, data during those time periods is coded as missing. Missing data may indicate a power issue, an instrumentation problem, or a data communication problem. The time period allowed for missing data may be adjusted as the project proceeds to reduce false or excessive alerting. An alert is issued when six 5-minute values (i.e., 30 minutes) are missed.

- **Sensor OP Codes and Alarms.** If the instrument assigns operation (op) codes to data automatically (e.g., for bump tests, internal flow rate checks), the data are reviewed, codes confirmed, and data flags checked.

- **Visibility Impairment.** If signal strength drops below the threshold value and the visibility is less than 2.5 miles, then data from open-path analyzers are flagged as invalid due to weather.

Table 6. Initial screening checks for 5-min data. All valid and suspect data values are displayed to the public in real time. If data are invalid, they are not included in the public display. During data validation, suspect data will be further investigated.

Measurement (units)	Approximate MDL (ppb)[a]	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
Benzene (ppb)	10 ppb. If below, flag as below MDL.	If above 24 ppb, flag data as suspect on the website and investigate validity.	If the same value is observed for four or more intervals, flag data as suspect on the website and investigate validity.	If value changes by more than 12 ppb, flag data as suspect on the website and investigate validity.	If data are missing, code as missing on the website and investigate the cause.	If the sensor indicates malfunction or bump test data, code as appropriate and do not display the data.	If signal strength is below threshold and visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
Toluene (ppb)	10 ppb. If below, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.			
Ethylbenzene (ppb)	100 ppb. If below, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.			
Xylene (ppb)	10 ppb. If below, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.			
SO_2 (ppb)	10 ppb. If below, flag as below MDL.	If above 37.5 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 19 ppb, flag as suspect on the website and investigate validity.			

Measurement (units)	Approximate MDL (ppb)[a]	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
H₂S[b] (ppb)	3-25 ppb. If below, flag as below MDL.	If above 25 ppb, flag data as suspect on the website and investigate validity.	If the same value is observed for four or more intervals, flag data as suspect on the website and investigate validity.	If value changes by more than 25 ppb, flag as suspect on the website and investigate validity.	If data are missing, flag as missing on the website and investigate cause.	If the sensor indicates malfunction or bump test data, code as appropriate and do not display data.	If visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
Alkanes as n-hexane (ppb)	10 ppb. If below, flag as below MDL.	If above 10,000 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 1,000 ppb, flag data as suspect on the website and investigate validity.			
Organic gas (% LEL)	--[c]	If above 100% LEL, flag data as suspect on the website and investigate validity.		If value changes by more than 50% LEL, flag data as suspect on the website and investigate validity.			
Visibility (meters)	If value is less than 0, flag data.	Not applicable		Not applicable			Not applicable

[a]MDL is dependent on atmospheric conditions. Valid data below MDL is evaluated on the basis of correlation coefficient and other operational parameters such as signal strength. If data below the MDL are determined to be valid, but the concentration is below the MDL, it is flagged as below MDL on the public website and in the database.

[b]Per the December 22, 2022, letter from BAAQMD,[2] the level of quantitation (LOQ) is taken to be equivalent to the MDL, and is calculated as twice the standard deviation of a blank sample for the TDL. This LOQ is achievable at less than 1% transmission.

[c]OGDs have a detection range of 0-100% LEL (methane), with an accuracy of ±3% between 0-50% LEL and an accuracy of ±5% between 51-100% LEL.

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[2] Bovee, J. "Refinery Fenceline H₂S TDL Monitoring System Specifications", Communication to P66 San Francisco Refinery, December 22, 2022.

Additional QC checks for the instruments are summarized in **Table 7**. Data that fail checks are flagged in the DMS and brought to the attention of the reviewer by color coding in the graphic summaries. Data are invalidated only if a known reason can be found for the anomaly or automated screening check failure. If the data are anomalous or fail screening, but no reason can be found to invalidate the data, the data are flagged as suspect. Additional analysis may be needed to deem data valid, invalid, or suspect. Common reasons for invalidation include instrument malfunction, power failure, and bump test data that were not identified as such. As the measurements progress, the screening checks are updated and refined. Screening checks are typically specific to the site, instrument, time of day, and season and adjusted over time as more data are collected.

In addition to auto-screening and daily visual checks, data are subjected to more in-depth review on a quarterly basis and when data fail screening. Final data sets are compiled quarterly, and will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter.

On a quarterly basis, validation checks include:

- Looking for statistical anomalies and outliers in the data
- Inspecting several sampling intervals before and after data issues or instrument tests or repairs
- Evaluating monthly summaries of minimum, maximum, and average values
- Ensuring data reasonableness by comparing to remote background concentrations and average urban concentrations
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on observations by site operator
- Ensuring that data are realistically achievable, i.e., not outside the limits of what can be measured by the instrument
- Confirming that bump tests were conducted and were within specifications

These in-depth analyses typically require data that are not available in real time and ensure that final data sets are fully validated.

On a quarterly basis, to ensure all the daily QC tasks are complete, analysts:

- Review any instrument bump test results
- Verify that daily instrument checks were acceptable
- Review manual changes to operations/data, and verify that the changes were logged and appropriately flagged
- Ensure that daily instrument checks have the appropriate QC and OP codes applied

Table 7. Instrument QA/QC checks.

Instrument Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test (accuracy) with benzene and SO_2	Monthly and after major service	±20%[a]
Measurement quality – R^2	Continuous	0.8 to 1.0
Integration time	Continuous	≤250 ms
Signal intensity	Continuous	≥80%[b]
TDLAS		
Bump test[a] accuracy and repeatability (as %CV); H_2S at a concentration between 50 and 100 ppb which differs from 3-point calibration points.	Monthly	±15%
3-point calibration accuracy (as % Error) and precision (as %CV) [a, b, c] The lowest calibration concentration must be in the range of 40 to 60 ppb.	Quarterly	±15% for each calibration point H_2S
5-min LOQ[d]	Continuous	3-25 ppb
H_2S correlation coefficient (r)	Continuous	0.72 to 1.0
Power	Continuous	0.1 mW (corresponds to <1% transmission)
H_2O correlation coefficient (r)	Continuous	≥0.95
FTIR		
Bump test with propane	Monthly	±20%[a]
Signal intensity	Continuous	≥2%[b]
Measurement quality (R^2)	Continuous	0.7 to 1.0
Visibility Sensor		
Accuracy	Annually	±25%

[a] For the TDLAS, accuracy and repeatability specifications from the December 22, 2022, letter from BAAQMD[3] will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions.

[b] NIST TN 1297: Appendix D1. Terminology.

[c] For test concentrations requiring greater than 750 ppm H_2S, safety considerations necessitate certified sealed cells be used. For test concentrations requiring lower than 750 ppm, certified flow-through cells may be used.

[d] Per the December 22, 2022, letter from BAAQMD, the LOQ is taken to be equivalent to the MDL. For the TDLAS, the MDL is calculated as twice the standard deviation of a blank sample.

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[3] Bovee, J. "Refinery Fenceline H2S TDL Monitoring System Specifications", Communication to P66 San Francisco Refinery, December 22, 2022.

Auto-screening checks are discussed in Section 3.2.1. Data flagged through auto-screening are graphically reviewed, and QC flags are updated with daily and quarterly actions (see **Figure 15**). DMS keeps track of data changes in its chain of custody feature—i.e., raw data are preserved as well as all changes.

On a quarterly basis, analysts subject the data to final QC by filling in missing records with null values, and adding OP Codes

- If a record is not created for a particular site/date/time/parameter combination, a null record will be created for data completeness purposes.
- Invalid data will have an OP Code, or in other words, a reason for being invalid.
- Inspect data consistency over three months.
- Review ranges of values for consistency—ranges should remain consistent over months of monitoring.
- Check bump test values for consistency.
- Review quarterly data completeness.

All actions are documented in the DMS, which retains raw data and traceability of all actions that result in the final data. Additional details on the final QC process are provided in the QAPP.

On an annual basis, the performance of the network is assessed by reviewing data completeness by monitoring path, instrument, and species; results of bump tests; reported values in the context of Refinery operations; and data in the context of the meteorology. The results are summarized in an internal technical memorandum and provided to the BAAQMD upon request.
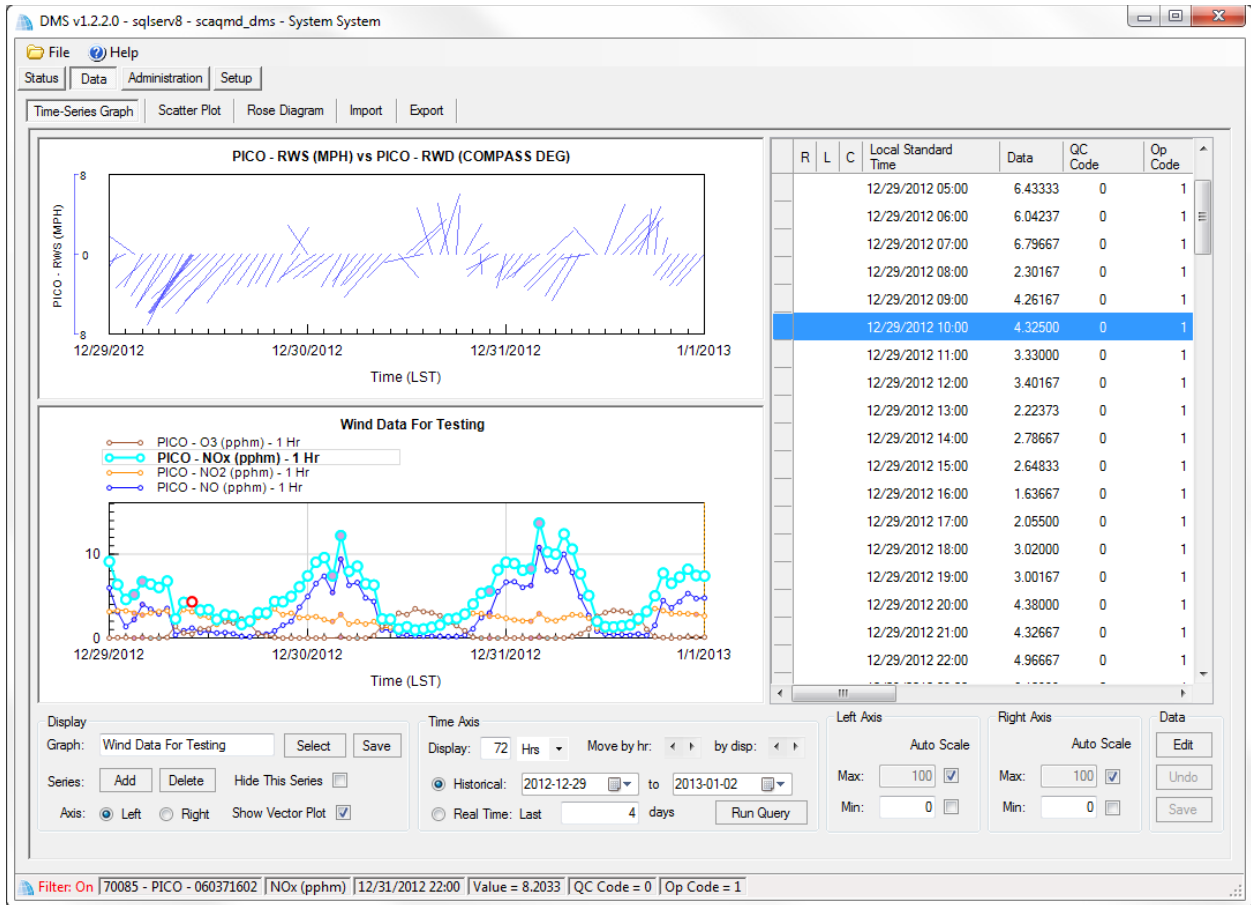
Figure 15. Screenshot of DMS showing winds and pollutant concentrations.

3.2.2 Public Data Availability and Display

Data are screened in real time upon ingest into the DMS, as described in previous sections. Automated procedures are used to ensure that data are properly ingested, stored, processed, and quality-assured, and that products are delivered to a public-facing website in real time, defined here as 10 minutes or less after data collection.

For the public website, key components include visual display of data in real time, context for the public to better understand the concentrations displayed, and a mechanism for feedback on the website.

The preliminary quality controlled data are presented in a time series of benzene, toluene, ethylbenzene, total xylenes, SO_2, H_2S, and alkanes concentrations, and visibility, wind speed, and wind direction. Data are provided as 5-min binned averages. Additionally, for the Unisearch TDL, 5-min MDLs are displayed in real time. Data are color-coded and annotated for quality (valid, invalid, suspect, missing). An example of a public-facing website that allows users to explore data is shown in **Figure 16**.
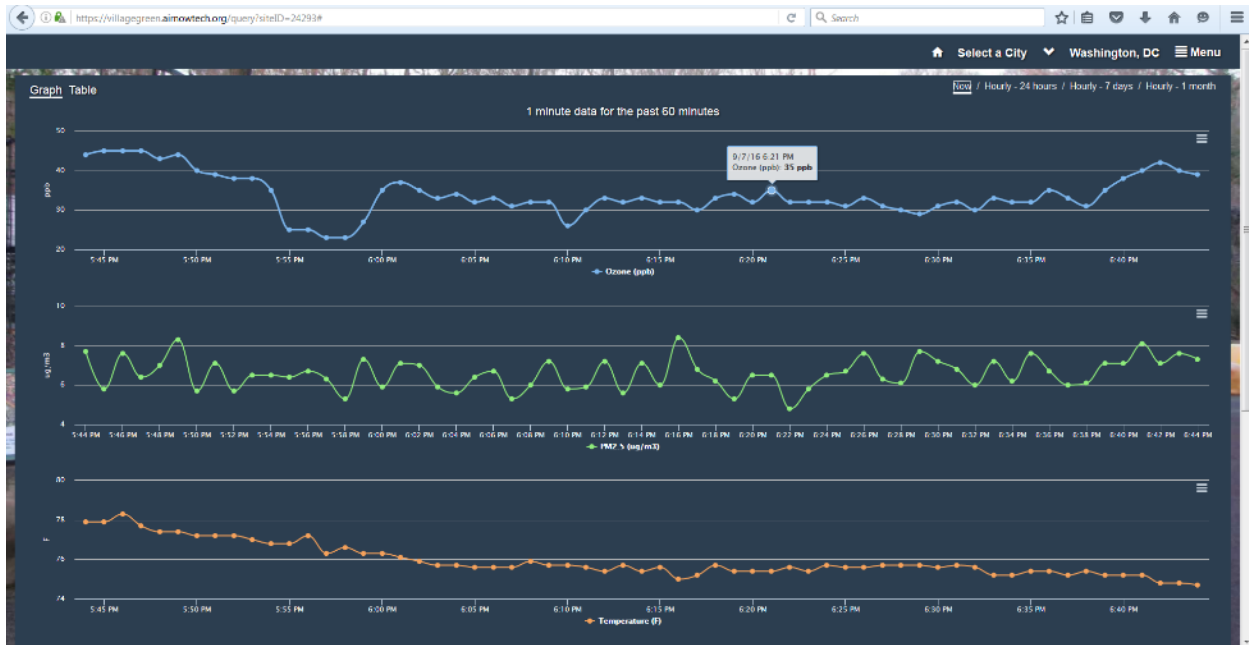
Figure 16. Example of a public-facing web page.

Final data sets are compiled quarterly and will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter. Data deliveries are consistent with BAAQMD guidance and additional details are provided in Section 4.6 of the QAPP. The Refinery will make data available to BAAQMD upon request prior to the report submittal. Raw spectral data files will be saved as single files and made available to the BAAQMD upon request. BAAQMD may make publicly available any of the data routinely submitted in a quarterly report. All data will be retained by the Refinery for a period of five years, consistent with Regulation 12-15-502.

The collected data are high time resolution, spatially variable, and chemically complex. To provide context to this complex data set for the public, the following information is included through a combination of links, graphics, or captions:

- Information about the species measured and the measurement techniques
- Context of what fenceline measurements represent compared to other regional air quality measurements and as outlined by BAAQMD
- Health data provided on the web page is sourced from OEHHA official information
- Discussion of non-Refinery sources that could affect the measured concentrations
- Definitions of abbreviations
- Discussion of data below detection
- Definition of data QC flags and their meaning
- Frequently asked questions (FAQs; *to be developed over time*)
- Quality procedures

Information is written at a public-friendly level. Clarity and thoroughness help to reduce the number of questions that arise.

To facilitate public feedback, a feedback button is provided on the web page. When a user clicks on the button, an email form will pop up for the user to submit comments about the website. The email will be reviewed by Refinery personnel and/or a designated contractor, and archived. Although not all comments need to be addressed, all comments will be made available to BAAQMD upon request. Some of the comments may aid in the creation of FAQs.

4. Document Control

Revision No.	Revision Date	Description
1	7/9/2021	Initial Submission
2	2/10/2023	Amended for new H_2S monitoring requirements with TDL
3	9/5/2023	Revised in response to feedback from BAAQMD received 7/19/2023

Appendix A to the Air Monitoring Plan for the Phillips 66 Refinery in Rodeo, California

Prepared for
Phillips 66
San Francisco Refinery
Rodeo, CA

Updated: September 5, 2023
Original: July 9, 2021

This document contains blank pages to accommodate double-sided printing.

Phillips 66 Rodeo 12-15
Quality Assurance Project Plan

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1. Project Background and Management

1.1 Background

1.1.1 Purpose

Phillips 66 (P66) is conducting air quality monitoring at its refinery in Rodeo, California, in accordance with the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15).[1] The monitoring is following a facility-specific air monitoring plan that is consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.[2] Rule 12-15 requires routine monitoring near the fencelines of all San Francisco bay area refineries for specific air compounds, with data reported to the public. On October 6, 2021, the BAAQMD provided updated requirements for refineries to conduct additional H_2S monitoring along refinery fenceline paths and to implement the enhanced monitoring by January 1, 2023. P66 implemented H_2S monitoring on January 1, 2023. BAAQMD issued updated specifications on December 22, 2022, and P66's response to the updated specifications was submitted on February 10, 2023. This revision addresses items detailed in feedback from BAAQMD on July 19, 2023.

1.1.2 Rationale

Rule 12-15 requires fenceline monitoring of multiple compounds with "open-path technology capable of measuring in the parts-per-billion range regardless of path length," or an alternative measurement technology.[2] P66 is conducting open-path pollutant monitoring and collecting visibility measurements to meet the regulatory requirements.

This document is a quality assurance project plan (QAPP), which documents the measures that the project team will take to ensure that the data collected are of the highest quality.

1.2 Roles and Responsibilities

The project team for this QAPP includes refinery staff, contractors, quality assurance (QA) personnel, field technicians, and website staff members. **Figure 1** shows an organization chart for the project.

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[1] Petroleum Refining Emission Tracking (Rule 12-15; approved by the BAAQMD on April 20, 2016).
[2] Bay Area Air Quality Management BAAQMD (2016) Air monitoring guidelines for petroleum refineries. April. Available at **baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en**.
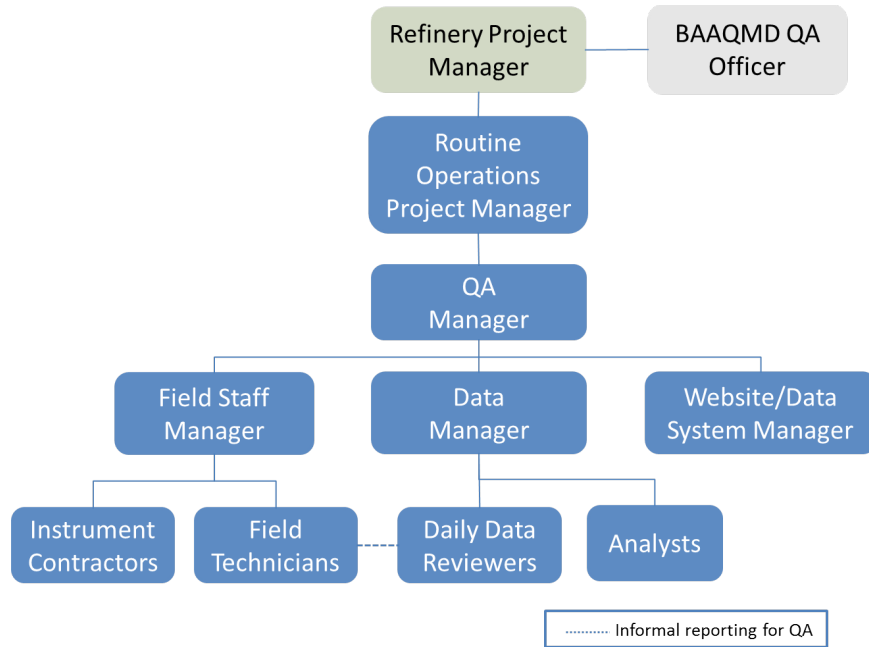
Figure 1. Organizational chart for this project.

The overall project is run by a **Refinery Project Manager** (PM) appointed by P66. The Refinery PM is responsible for overseeing the project and reporting directly to the BAAQMD as the central point of contact.

The **Routine Operations Project Manager** is responsible for overseeing the day-to-day monitoring operations. They report to the Refinery Project Manager.

The **QA Manager** is responsible for ensuring the quality of data collected in this project. The QA Manager (1) oversees daily data review and management; (2) works with the Field Staff Manager to ensure any data issues are promptly addressed by the field technicians; (3) works with the Website/Data System Manager to ensure that data provided to the public are of high quality; and (4) receives validated data from the Data Manager.

The **Field Staff Manager** ensures that Field Technicians and Instrument Contractors are meeting the requirements of the project. The Field Staff Manager coordinates staff coverage and serves as a technical resource for site measurements.

Field Technicians perform necessary instrument maintenance. They ensure that all measurements are collected in accordance with maintenance and audit procedures (see Appendices), standard methods, and regulations, where applicable. Technicians (1) are trained on the operation and maintenance of each instrument; (2) have the necessary and current training required to be on refinery property; and (3) perform the required quality checks on instruments and document all work in site logs.

The **Instrument Contractors** provide technical support for the instruments that are deployed in the field.

The **Data Manager** is responsible for ensuring that daily data review is conducted, data that fail auto-screening are inspected, and data validation follows the proper schedule and procedures. The Data Manager is also responsible for delivering validated data to the QA Manager.

The **Daily Data Reviewers** conduct daily review of the data, data validation, and are supported by Analysts. The Daily Data Reviewers communicate with the Data Manager when issues arise, and may also interact with Field Technicians when they notice an issue that needs to be addressed.

Analysts provide data analysis, including analysis that is used in quarterly reports. Analysts also perform data validation and final quarterly data for generating finalized data to the Data Manager.

The **Website/Data System Manager** is responsible for properly displaying data on the website. The website uses automated alerting to notify the Website/Data System Manager when the real-time data are not available. This manager is responsible for assessing and fixing data communication, as well as other information and technology–related issues concerning the website/data system.

2.   Measurements

2.1   Instrument Selection and Descriptions

The required compounds to be measured are benzene, toluene, ethylbenzene, and xylenes (known together as BTEX), sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and alkanes. These compounds are measured at a 5-min resolution.

BTEX and SO_2 are measured using a bistatic Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS) monitor with a xenon light source. The ultraviolet (UV) light from the xenon source is required to measure over the sampling path length of 930 m and achieve sufficient minimum detection limits (MDL) for BTEX compounds. The analyzer records the intensity of light at discrete wavelengths, and any UV-absorbing gas present in the beam absorbs at a specific wavelength of light. To enable determination of concentration for each compound, Beer's Law is used to convert raw intensity received at the detector to absorbance. Each species of gas has a unique absorbance fingerprint (i.e., peaks in absorbance at different wavelengths are unique to that gas). The analyzer compares regions within the sample absorbance spectra to the same regions within the calibrated reference absorbance spectra using a classic least squares regression analysis. This approach is the same as what was specified in the United States Environmental Protection Agency's (EPA) TO-16 Methodology,[3] although this was not written specifically for UV-DOAS. Closeness of fit is indicated by the correlation coefficient (R^2) derived from the fit of the measured spectra to the reference spectra. The R^2 is provided with each concentration so that potential interference can be detected if present. Selection of analysis regions that are free of absorbance due to other gases within the sample is the primary means of avoiding cross interference. Spectral subtraction is used in cases with overlapping absorbance features. The subtraction technique is proprietary to the instrument manufacturer.

H_2S is measured by a monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) analyzer. A tunable diode laser emits light at a very small range of wavelengths, which allows spectral measurement of an H_2S absorption peak. Because the Unisearch TDLAS operates in a wavelength range that also contains an absorbance feature for water vapor and carbon dioxide (CO_2), the correlation coefficient of these gases can be used as a performance metric. If the water vapor correlation drops below a threshold value, CO_2 correlation is examined. If that also drops below a threshold value, data are flagged as invalid. This logic reflects that water vapor and CO_2 are always present in the atmosphere. The signal strength of the light transmitted through the atmosphere is recorded using a photodiode detector and reported in the data file. Together with an independent visibility measurement, the signal strength can be used to evaluate the impact of atmospheric

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[3] U.S. Environmental Protection Agency (1999) Compendium of methods for the determination of toxic organic compounds in ambient air: compendium method TO-16. Second edition, prepared by the U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH, EPA/625/R-96/010b, January. Available at https://www3.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf.

conditions or misalignment on data quality. Manufacturers report that the TDLAS has H_2S detection limits below 25 parts per billion (ppb) over a 500-meter (m) path length under good atmospheric conditions. The actual MDL depends on atmospheric conditions.

Alkanes are measured (as n-hexane) with a Fourier Transform Infrared (FTIR) spectroscopy analyzer. The FTIR operates similarly to the UV-DOAS analyzer and sends an infrared (IR) light beam through the open air. It is reflected back to the analyzer detector (monostatic configuration) where the absorption due to target gases is determined using Beer's Law. The analyzer uses a classical least squares regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files according to EPA's TO-16 Methodology. The concentration is determined by comparison to known reference spectra. A combination of industry standard methods and proprietary methods are used to mitigate interference from both water vapor and interference gases, including spectral subtraction, path-length adjustments, selecting isolated absorbance peaks for gases of interest, and multi-peak analytics.

Marine and radiation fog is common near Rodeo. Heavy fog, heavy rain, or smoke may block the signal from an open-path instrument and prevent data collection. However, even light fog can partially absorb the signal and interfere with measurements. A visibility sensor indicates when low-visibility conditions impact invalid or missing data from the open-path instruments.

Table 1 summarizes the estimated MDL for each target compound, as provided by instrument manufacturers. The detection limits are for the average compound concentration along a path. This means that a higher concentration than the MDL is needed for the species to be detected when a narrow plume covers only a portion of the path. Under typical operating conditions, the Unisearch TDLAS is expected to have an MDL between 3 and 25 ppb at less than 1% transmission. The MDL may be higher than those listed in Table 1 if there is poor atmospheric visibility (e.g., heavy fog, rain, smoke, or dust), the instrument is misaligned, there are hardware problems, or an interferant is present. MDLs at the lower end of the specified range are expected under the opposite conditions. For the Unisearch TDLAS, data with real-time MDL values greater than 25 ppb will be flagged for additional review and, in the absence of marginal atmospheric operating conditions, considered to not meet the performance criteria.

Table 1. Approximate detection limits for each target compound. Actual performance depends on ambient conditions.

Analyzer	Compound	MDL (ppb)
TDLAS[a]	Hydrogen Sulfide (H$_2$S)	3–25
UV-DOAS (Xenon)	Benzene	10
	Toluene	10
	Ethylbenzene	100
	Xylenes	10
	Sulfur Dioxide (SO$_2$)	10
FTIR	Alkanes	10
OGDs	Organic Gas (VOCs)	--[b]

[a] Per the December 22, 2022, letter from BAAQMD[4], the level of quantitation (LOQ) is taken to be equivalent to the MDL.

[b] OGDs have a detection range of 0-100% LFL with an accuracy of ± 3% in the 0-50% LEL range and an accuracy of ± 5% in the 51-100% LEL range.

2.2   Monitor Siting Rationale

P66 followed guidance presented by BAAQMD to determine which portions of the fenceline surrounding the Refinery are to be covered by monitoring under Rule 12-15 requirements. Measurements must cover populated areas within one mile of the refinery fenceline that are likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time or greater, based on the most representative meteorological measurements for potential refinery sources likely to emit target compounds. Based on this analysis, the populations that are less than one mile from the Refinery and lie within this arc are portions of Crockett. No fenceline south of the Refinery is subject to coverage under Rule 12-15 as there is no population in that direction that lies within the arc representing the annual wind rose coverage requirement. Additional analysis details are presented in the Air Monitoring Plan (AMP).

Organic Gas Detectors (OGDs) monitor the level of explosive compounds in the air, and two of them are included in the 12-15 fenceline monitoring system. A visibility instrument is used to assess low-visibility conditions that cause invalid or missing measurements from open-path analyzers.

The open-path sampling location is shown in **Figure 2** along with organic gas detectors (OGDs) and potential source areas. GPS coordinates, elevations, and instrument inventory are shown in **Table 2**.

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[4] Bovee, J. "Refinery Fenceline H$_2$S TDL Monitoring System Specifications", Communication to P66 San Francisco Refinery, December 22, 2022.

Figure 2. Refinery overview and potential source areas for the P66 Rodeo refinery.

Table 2. GPS coordinates, elevations, and instrument inventory at each open-path sampling site.

Site	GPS Coordinates	Elevation (ft) above sea level	Equipment
North (Light Source/ Retro-reflector)	38° 2'51.3"N, 122°15'7.4"W	200	1 Bistatic UV-DOAS Emitter 1 FTIR Retro-reflector 1 TDLAS Retro-reflector
North (Receiver/Analyzer)	38° 2'32.4"N, 122°14'37.6"W	275	1 Bistatic UV-DOAS Receiver 1 Monostatic FTIR Analyzer 1 Monostatic TDLAS Analyzer
OGD (AT-1)	38° 2'17.5"N, 122°14'24.0"W	240	1 OGD
OGD (AT-2)	38° 2'18.5"N, 122°14'37.0"W	350	1 OGD

2.3   Instrument Operations and Maintenance

Five types of systems are included in this project: UV-DOAS, TDLAS, FTIR, OGDs, and visibility instruments. Additional meteorological data are obtained from an existing meteorological station at the refinery. Quality assurance (QA) is a primary consideration for all operations and maintenance procedures. Scheduled maintenance occurs monthly, quarterly, and/or annually for all instruments. Emergency maintenance occurs as needed when problems are identified during daily data review and auto-screening of real-time data. All actions performed on instruments are recorded in site-specific logbooks.

2.3.1   CEREX UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. Table 3 summarizes typical UV-DOAS maintenance activities as recommended by the manufacturer. These actions help ensure data integrity and maximize uptime, and will be altered as needed. Operational limits used to trigger corrective actions during site visits are further explained in Section 4.4.

Table 3. Schedule of maintenance activities for the UV-DOAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving check list is maintained).	✓		
Inspect optics on analyzer. Clean if necessary.	✓		
Inspect and clean system filters.	✓		
Confirm the alignment to verify there has not been significant physical movement. This is accomplished by noting the integration time and signal strength – both should be less than 250 ms and greater than 90%, respectively.	✓		
Download data older than 12 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	✓		
Inspect all electrical cables for wear. Replace as needed.	✓		
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency. Realign system if integration time exceeds 250 ms.	✓		
Change out the UV source if the intensity has dropped below acceptable range (service hours >2,000 hours and intensity at 250 nm <3% with 40 ms dwell time under high visibility conditions).		✓	
Replace ventilation exit and intake filters.		✓	
Clean and inspect optics on detector.		✓	
Realign system after service. Ensure integration time is less than 250 ms and intensity is greater than 90% under high visibility conditions.		✓	
Check other system performance indicators, if necessary.		✓	
Perform bump test.	✓		
Verify system settings.			✓

2.3.2   Unisearch LasIR TDLAS

Maintenance activities for the TDLAS and the UV-DOAS are similar. The TDLAS system is also designed to require only modest service and maintenance. Table 4 summarizes TDLAS maintenance activities, as recommended by the manufacturer and required by the BAAQMD. Maintenance schedules are altered as needed to optimize system operation and uptime.

Table 4. Schedule of maintenance activities and performance indicators for the TDLAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓		
Inspect optics on detector, clean if necessary.	✓		
Check the alignment to verify there has not been significant physical movement and confirm signal levels. Signal power should be greater than 0.1 mW.	✓		
Download data older than 12 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, or vehicles).	✓		
Inspect all electrical and optical cables for wear. Replace as needed.	✓		
Perform bump test.	✓		
Review and test light and signal levels.[a] Signal power should be greater than 0.1 mW.		✓	
Perform a 3-point calibration check.		✓	
Verify system settings.			✓

[a] Although signal strength is recorded in real time, it is recommended to consider longer term trends in signal intensity to evaluate the health of the optical components, the effects of cleaning optical components, and the noise characteristics of the spectral data.

2.3.3 CEREX FTIR

The FTIR has similar maintenance activities to the UV-DOAS. The FTIR system is also designed to require only modest service and maintenance. Table 5 summarizes FTIR maintenance activities, as recommended by a typical manufacturer. Preventative maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed. Bump tests are performed on site.

Table 5. Schedule of maintenance activities and performance indicator checks for the FTIR.

Activity	Monthly	Quarterly	Annually	18-24 months	Five Years
Visually inspect the system.	✔				
Inspect optics on detector and retro-reflector. Clean if necessary.	✔				
Confirm the alignment to maximize signal intensity.	✔				
Download data older than 6 months from the hard drive, move to a permanent archive, and delete old files from the analyzer.	✔				
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	✔				
Perform bump test.	✔				
Check system performance indicators (an evolving checklist will be maintained).		✔			
Inspect and clean AC system exterior heat sink.		✔			
Review and test light and signal levels. Check average light intensity to establish baseline for IR Source change frequency and retro-reflector wear.			✔		
Replace cryocooler or swap detector module assembly.				✔	
Change out the IR source.					✔

2.3.4 Organic Gas Detectors (OGDs)

The organic gas detectors used here need very little maintenance. On a quarterly basis, the hydrophobic filters should be inspected and cleaned and the response of the OGDs should tested and/or calibrated using zero and span points. If needed, the OGD can be further disassembled for more extensive cleaning. During gas testing, it is best practice to confirm end-to-end data transfer from the OGD, through the radio system to the internal website. The OGD detectors may need more frequent maintenance during periods with heavy rain, as moisture is a known interferant for the measurement.

2.3.5 Visibility Instruments

For the visibility instrument, monthly maintenance includes inspecting the sensor for dirt, spider webs, bird nests, or other obstructions (see Table 6). Obstructions are removed and the glass windows are cleaned with glass cleaner if the sensor is dirty. There are no serviceable components in the sensor. Calibration is performed annually per the instruction manual, and maintenance schedules will be altered as needed.

Table 6. Schedule of maintenance activities for the visibility sensor.

Activity	Monthly	Annually
Visually inspect the system, including all cables.	✓	
Inspect optics on detector and clean if necessary.	✓	
Check calibration. An acceptable % error is less than 25%.		✓

* Calibration checks may be performed less frequently in the future if the measurements prove adequately stable or additional metadata provides assurance that instruments are working properly. Any reduction in the calibration frequency should be approved by BAAQMD.

2.4 Emergency Maintenance Procedures

When a major problem is discovered with the fenceline monitoring system, corrective actions and maintenance procedures are required. The fenceline monitoring system is composed of two major components, field hardware and website software. Separate rotating teams are on-call 24/7 to respond to issues that can be dealt with remotely. Any required field work will occur the next business day. The two teams that are on-call are (1) the Sonoma Technology field operations (ops) team and (2) the Sonoma Technology IT ops team. The Sonoma Technology field ops team is led by the Field Staff Manger and Data Manager, and includes field technicians. The IT ops team is led by the Website/Data System Manager and consists of IS engineers and IT specialists. Sonoma Technology manually checks the website twice daily, and automated checks are enabled. If the automated checks identify a problem, the system will immediately send an alert to the field ops team and/or the IT ops team. This approach helps guarantee that problems are identified and addressed in a timely manner. The on-call teams are required to acknowledge alerts within 30 minutes of their receipt. Refinery personnel will be notified if a solution for issues affecting data availability cannot be resolved. If the system is offline, a maintenance message will be put on the public website at the direction of P66. BAAQMD staff will be notified of monitoring downtime according to BAAQMD Regulation 1-530.[5]

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[5] Area Monitoring Downtime (BAAQMD Rule 1-530), available at http://www.baaqmd.gov/~/media/dotgov/files/rules/reg-1-general-provisions--definitions/documents/rg0100.pdf?la=en.

The rotating field ops team remotely monitors the status of the field sites seven days a week and uses automated checks, such as those listed below, to determine if actions are necessary.

1. Data not reporting
2. Data out of expected range
3. Metadata message indicates a problem with instrument operations

Problems with the analyzers or any associated hardware in the shelters are addressed on the following business day. As soon as a problem is identified, the Sonoma Technology field ops team ensures the proper error message for the affected variables is displayed on the website.

The IT ops team remotely monitors the status of the website and associated equipment using automated system checks (Table 7) to determine actions.

Table 7. Parameters monitored by automated system checks, their monitoring frequency, and threshold for alerting.

Item	Parameter	Monitoring Frequency	Parameter Limit/ Threshold for Alert
Website goes down	HTTP test on the: - Public website - Administrator website DMS API	Every 300 sec	Websites not reachable
DMS systems	- CPU utilization - Memory use - Disk space used	Every 300 sec	- CPU utilization >60% - Memory used >75% - Disk used >75%
Interruption in data flow	- Time since last datum received	Every 30 min	Most recent measurement is behind collection by more than 30 minutes
Test for errors in data processing pipeline	- Process scheduler	Every 300 sec	Pass/Fail

The IT ops team is required to acknowledge alerts within 30 minutes of their receipt. If an issue needs to be escalated for project-specific reasons, the IT ops team will notify the project's primary and secondary point persons at Sonoma Technology. If deemed necessary, Sonoma Technology will notify P66 of any issues affecting data availability on the public website. Any instrument-level outages that occur during the weekend will be dealt with on the next business day, and any issues that occur during weekday nights will be addressed the following business day. In the case of any long-term outage or scheduled maintenance at a specific site, a temporary message will be displayed on the public-facing website to alert the public. BAAQMD personnel will be notified of the outage according to BAAQMD Regulation 1-530. A spare may be installed if there is a long-term problem with a piece of operating equipment.

Corrective action will be taken to ensure that data quality objectives are met. Table 8 lists the types of issues that require corrective actions. This table is not all-inclusive and additional checks may be added as the project progresses. Issues will be identified daily upon review by Daily Data Reviewers, who will work with the field technicians and instrument contractors to resolve issues that need to be addressed on site. Further details on the manual daily data checks are provided in Section 4.3. After all issues have been addressed, a summary of the problems and solutions will be sent to the project manager via email. In the event that an issue is discovered by field or IT personnel that is not included in this list, the issue and corrective actions taken will be documented and the QAPP and relevant SOP will be updated. Updated QAPPs will be submitted to BAAQMD for approval.

Table 8. Potential sampling and data reporting problems and corrective actions.

Item	Problem	Action	Notification	Person Responsible
Erratic data (e.g., data that is not physically possible)	Possible instrument malfunction	Contact Field Staff Manager and Instrument Contractor	Document in logbook, notify Field Staff Manager	Field Technician
Power	Power interruptions	Check line voltage; reset or restart instruments	Document in logbook, notify Field Staff Manager	Field Technician
Data downloading	Data are not transferred to the DMS	Contact Field Staff Manager and Instrument Contractor	Document in logbook, notify Field Staff Manager and Website/Data System Manager	Field Technician
Supplies and consumables	Essential supplies run out	Contact Field Staff Manager	Document in logbook, notify Field Staff Manager	Field Technician
Access to sites	Technician cannot access the sites	Contact Field Staff Manager	Document in logbook, notify Field Staff Manager	Field Technician
Instrument light level	A low light level alert is observed	Contact Instrument Manufacturer; replace bulb	Document in logbook, notify Field Staff Manager	Field Technician/Daily Data Reviewer
Website	Website is down	Contact Website/Data System Manager	Notify Project Manager	Website/Data System Manager
Server	Not working properly	Contact Website/Data System Manager	Notify Project Manager	Website/Data System Manager
Network	Network is down	Contact Website/Data System Manager	Notify Project Manager	Website/Data System Manager

Item	Problem	Action	Notification	Person Responsible
Data flow	Data flow interruption	Contact Website/Data System Manager	Notify Project Manager	Website/Data System Manager
Data flow	Errors in processing	Contact Website/Data System Manager	Notify Project Manager	Website/Data System Manager

3. Quality Objectives and Criteria

3.1 Data and Measurement Quality Objectives

To ensure the success of field measurements, measurement performance or acceptance criteria are established as part of the monitoring design. These criteria specify the data quality needed to minimize decision errors based on the data. Data quality is defined in terms of the degree of precision, accuracy, representativeness, comparability, and completeness needed for the monitoring. Of these five data quality indicators, precision and accuracy are quantitative measures; representativeness and comparability are qualitative; and completeness is a combination of quantitative and qualitative. To ensure appropriate spatial coverage of measurements, a meteorological analysis is discussed in the AMP.

3.2 Data Completeness Objectives

Before consideration of data completeness objectives, it is important to define how data are flagged. In near-real time, data are transferred from infield instruments through a Data Acquisition System (DAS) to a Data Management System (DMS). The DAS consists of a data logger, which calculates 5-min averages, performs initial data quality control (QC) screening and transmits data to a cloud-based DMS. The DMS automatically QCs data, detects outliers and problems, creates alerts, and tracks all data QC activities. As part of the auto-screening process, QC flags are assigned as follows:

    i.   **Valid -** Data are within normal operating parameters.

    ii.   **Invalid -** Data do not meet the QC criteria.

    iii.   **Suspect/Questionable** - Data should be reviewed further.

    iv.   **Missing -** Data have not been received by the DMS for more than 10 minutes.

Automated QC processes for open-path data include assessment of visibility conditions in conjunction with instrument parameters, such as signal strength and/or integration time. This allows automatic screening for invalid data due to weather, as well as for suspect/questionable data due to marginal operating conditions. Data below the MDL are flagged accordingly. The automated data QC process flags any data with poor spectral matches to reference libraries, according to the defined acceptance criteria. These criteria are manually reviewed on a regular basis to ensure thresholds are appropriately defined. The final step of the automated data QC process flags any data with high concentrations (range check), large fluctuations (rate-of-change), or stuck data values (sticking check) as suspect/questionable for additional manual review and verification.

Automated QC processes for point monitors are less complex because their measurement technique is more straightforward. The automated data QC process also flags any data with high concentrations (range check), large fluctuations (rate-of-change), or stuck data values (sticking check) as suspect/questionable for additional manual review and verification.

In addition to the QC flags described above, operational codes (OP) are assigned to provide additional diagnostic information. Table 9 presents an overview of relevant QC/OP codes that are used throughout the QC process, including manual QC.

Table 9. Overview of data quality control (QC) and operational (OP) codes.

Data QC/OP Codes	
Quality Control (QC) Codes	
0	Valid
5	Suspect/Questionable
9	Invalid
Operational (OP) Codes	
0	Valid
17	Below MDL
28	Planned Instrument Maintenance
29	Unplanned Instrument Maintenance
70	Instrument Malfunction
72	Marginal Operating Conditions–Elevated Integration Time
73	Poor Visibility (Weather)
74	Poor Spectral Match
76	Marginal Operating Conditions–Poor Spectral Match
100	Manual Data Review
101	Range Check
102	Rate-of-Change Check
103	Sticking Check

Data completeness is assessed after reviewing the data flags assigned for each 5-min binned average data point. BAAQMD guidance for open-path measurement data recovery is that instrumentation must meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters. Completeness is therefore calculated as follows:

$$Quarterly\ \%\ Completeness = \left(\frac{Count\ of\ hours\ in\ the\ calendar\ quarter\ where\ hourly\ completeness > 75\%}{Count\ of\ all\ hours\ in\ the\ calendar\ quarter}\right) x\ 100$$

Additional data completeness definitions are included below.

- **Possible** – Maximum number of 5-min average concentrations that can be measured in a given hour and logged in the DMS

- **Captured** – Actual number of 5-min average concentrations that were measured in a given hour and logged in the DMS

- **Missing** – Number of 5-min average concentrations not measured or logged in the DMS in a given hour

    Missing = Possible – Captured

- **% Missing** – Percentage of missing 5-min average concentrations in a given hour relative to the possible number 5-min average concentrations

    % Missing = (Missing / Possible) x 100

- **Invalid Total** – Number of invalid 5-min average concentrations measured and logged in the DMS in a given hour

- **% Invalid Total** – Percentage of invalid 5-min average concentrations in a given hour relative to the possible number of 5-min average concentrations

    % Invalid Total = (Invalid Total / Possible) x 100

- **Invalid Environmental** – Number of invalid 5-min average concentrations in a given hour due to adverse atmospheric or environmental conditions

- **Invalid Other** – Number of invalid 5-min average concentrations in a given hour due to anything other than adverse atmospheric or environmental conditions

- **% Invalid Other** – Percentage of invalid 5-min average concentrations in a given hour due to anything other than adverse atmospheric or environmental conditions relative to the possible number of 5-min average concentrations

    % Invalid Other = (Invalid Other / Possible) x 100

- **Expected** – Number of possible 5-min average concentrations in a given hour, adjusted for periods of low visibility during adverse atmospheric or environmental conditions

    Expected = Possible – Invalid Environmental

- **Valid** – Number of valid 5-min average concentrations in a given hour

- **% Valid** – Percentage of valid 5-min average concentrations in a given hour relative to the possible number of 5-min average concentrations

    % Valid = (Valid / Possible) x 100

- **% Hourly Completeness** – Percentage of valid 5-min average concentrations in a given hour relative to the expected number of 5-min average concentrations

  % Hourly Completeness = (Valid / Expected) x 100

3.3 Precision Checks, Bump Tests, and Verification

All measurements outlined here are subjected to precision and accuracy tests. During these tests, a number (N) of replicated 5-min measurements (x_i) of a standard reference material of known magnitude (x_{std}) will be measured. Here, an acceptable number of trials is defined as 7≤N≤15, and a subset of test data will be used for subsequent calculations. The average value of these measurements is calculated as

$$\bar{x} = \frac{\sum_i x_i}{N}$$

and the standard deviation (σ) as:

$$\sigma = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{N-1}}.$$

From these definitions, accuracy (as % error) is defined as:

$$\% \, error = \left| \frac{\bar{x} - x_{std}}{x_{std}} \right| \times 100\%$$

and precision as the coefficient of variation (CV) expressed as a percentage:

$$Precision \equiv \%CV = \frac{\sigma}{\bar{x}} \times 100\%$$

In the field, a bump test is used to verify that the system can detect at or below the target bump test concentration. To confirm high-quality, reliable performance by the UV-DOAS system, bump tests using benzene and SO_2 are performed monthly. For the FTIR analyzer, propane will be used as the test species. The TDLAS will be bump tested with H_2S. The QAPP will be evaluated continuously and will be updated and sent to the BAAQMD for approval if updates are needed before implementation.

For the visibility instrument, sensors are calibrated in the field using a manufacturer-specific calibration kit. A calibration kit consists of a blocking plate or block for checking the sensor zero and a scatter plate for checking the sensor span. The scatter plate is assigned a factory-traceable extinction coefficient (EXCO) that is used to calculate the expected values during calibrations.

For the open-path systems, precision can be measured by evaluating the variance of pollutant concentrations during a period of low-variability, when atmospheric influence on variability is assumed to be minimal. For example, measurements should not be performed in the rain, fog, or when ambient concentrations of analytes/interfering species are changing rapidly (e.g., ozone). On a monthly basis, data are selected during periods with low variability when concentrations are well above the MDL. Bump test data can be used to calculate precision because many of these requirements are also required for successful bump tests.

3.4 Instrument or Standard Certifications

For factory calibrations, a certification of the standard gases used will be requested from the manufacturer. Standards will not be used past their expiration date. Also, the spectral file numbers that are generated during tests will be documented and archived.

4.   Data Management

Data quality criteria are evaluated through (1) automatic data checks conducted by the Data Management System (DMS), and (2) data review by trained analysts (daily data review and periodic, more thorough validation).

4.1   Data Acquisition and Communications

Raw data management occurs on a real-time, daily, monthly, quarterly, and annual basis. These raw data are not yet intended for the public website. In near-real time, data is transferred from in-field instruments through a data acquisition system (DAS) to a DMS using a cell modem. Data are also stored in onsite instrument computers in case of cell modem failure. The DMS uses a Microsoft SQL relational database with stored procedures.

The DMS automatically QCs data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities are used for continuous examination of data quality. The DMS provides auto-screened data to the field operations website and notification system to inform and alert project and facility staff. The field operations website displays maps and time series plots for all compounds and meteorological data.

The automatically QC'd air quality data is displayed on the public website 10 minutes after data collection.

4.2   Automated Data Screening

Automated data screening checks are conducted within the DMS upon data ingest and screen out invalid data for public display. These screening checks help focus the Daily Data Reviewers' efforts on data that need the most attention. Initial screening checks, along with actions to be taken, are summarized in Table 10. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. If, based on a detailed manual review of the data as described in Section 4.3, it is determined that the automated screening criteria are sufficient, they will be left as is. However, if the criteria listed in Table 10 result in erroneous flagging of data, the thresholds will be revised and this QAPP will be updated accordingly. The DMS auto-screening checks include:

- **Range.** These checks verify that the instrument is not reporting values outside of reasonable minimum and maximum concentrations.

- **Sticking.** If values are repeated for a number of sampling intervals, data are reviewed for validity. Typically, four or more intervals of sticking values are a reasonable time span to indicate that investigation is needed. Sticking checks are not applied to data that are below the instrument detection limit.

- **Rate of Change.** Values that change rapidly without reasonable cause are flagged and reviewed.

- **Missing.** If data are missing, data during those time periods are coded as missing. Missing data may indicate a power issue, an instrumentation problem, or a data communication problem. The time period allowed for missing data may be adjusted as the project proceeds to reduce false or excessive alerting. The alerting is set for six missing 5-min values (total time span of 30 minutes).

- **Sensor OP Codes and Alarms.** If the instrument assigns operation (op) codes to data automatically (e.g., for bump tests and internal flow rate checks), the data will be reviewed, codes confirmed, and data flags checked.

- **Visibility Impairment.** If signal strength drops below the threshold value and the visibility is less than 2.5 miles, then open-path analyzer data are flagged as invalid due to weather.

Additional parameters that may be monitored as indicators of data quality include a data quality value for each concentration as reported by the instrument (i.e., correlation between measured and reference spectra), signal strength, and visual review of peaks. These data quality objectives may change if improved objectives are determined during operations. The QAPP will be updated as needed to include the addition or revision of any data quality indicators that are determined to improve data quality (for example, fewer false positives and negatives).

QC flags that are identified through auto-screening are graphically reviewed during daily and quarterly data validation (i.e., not in real time). Review of data flags involves checking the data from the website/database against the raw instrument data. If it is found that data were incorrectly flagged during this process, the analyst may manually change the flag. For example, if calibration data were inadvertently displayed on the public website, the analyst can flag the data as calibration data, resulting in its removal from the public website. The DMS keeps track of data changes in its chain-of-custody feature, which ensures raw data, and all changes are preserved.

Table 10. Initial screening checks for 5-min data. All valid and suspect data values are displayed to the public in real time. If data are invalid, they are not included in the public display. During data validation, suspect data will be further investigated.

Measurement (units)	Approximate MDL (ppb)[a]	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
Benzene (ppb)	10 ppb. If below, flag as below MDL.	If above 24 ppb, flag data as suspect on the website and investigate validity.	If the same value is observed for four or more intervals, flag data as suspect on the website and investigate validity.	If value changes by more than 12 ppb, flag data as suspect on the website and investigate validity.	If data are missing, code as missing on the website and investigate the cause.	If the sensor indicates malfunction or bump test data, code as appropriate and do not display the data.	If signal strength is below threshold and visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
Toluene (ppb)	10 ppb. If below, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.			
Ethylbenzene (ppb)	100 ppb. If below, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.			
Xylene (ppb)	10 ppb. If below, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.			
SO_2 (ppb)	10 ppb. If below, flag as below MDL.	If above 37.5 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 19 ppb, flag as suspect on the website and investigate validity.			

Measurement (units)	Approximate MDL (ppb)[a]	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
H₂S[b] (ppb)	3-25 ppb. If below, flag as below MDL.	If above 25 ppb, flag data as suspect on the website and investigate validity.	If the same value is observed for four or more intervals, flag data as suspect on the website and investigate validity.	If value changes by more than 25 ppb, flag as suspect on the website and investigate validity.	If data are missing, flag as missing on the website and investigate cause.	If the sensor indicates malfunction or bump test data, code as appropriate and do not display data.	If visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
Alkanes as n-hexane (ppb)	10 ppb. If below, flag as below MDL.	If above 10,000 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 1,000 ppb, flag data as suspect on the website and investigate validity.			
Organic gas (% LEL)	--[c]	If above 100% LEL, flag data as suspect on the website and investigate validity.		If value changes by more than 50% LEL, flag data as suspect on the website and investigate validity.			
Visibility (meters)	If value is less than 0, flag data.	Not applicable		Not applicable			Not applicable

[a]MDL is dependent on atmospheric conditions. Valid data below MDL is evaluated on the basis of correlation coefficient and other operational parameters such as signal strength. If data below the MDL are determined to be valid, but the concentration is below the MDL, it is flagged as below MDL on the public website and in the database.
[b]Per the December 22, 2022, letter from BAAQMD,[6] the level of quantitation (LOQ) is taken to be equivalent to the MDL, and is calculated as twice the standard deviation of a blank sample for the TDL. This LOQ is achievable at less than 1% transmission.
[c]OGDs have a detection range of 0-100% LEL (methane), with an accuracy of ±3% between 0-50% LEL and an accuracy of ±5% between 51-100% LEL.

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[6] Bovee, J. "Refinery Fenceline H₂S TDL Monitoring System Specifications", Communication to P66 San Francisco Refinery, December 22, 2022.

4.3 Data Verification

4.3.1 Confirm Daily Operation

Data are reviewed twice daily by a data reviewer to assess instrument operation. This initial review—typically of a one- to two-day time-series plot of selected parameters for each instrument—allows the analyst to see common problems and verify that instruments are operational. If it appears that an instrument is not operating or the data are missing, the Field Technician will be notified, and investigative and corrective actions will be taken if needed.

4.3.2 Assess Data Reasonableness

The data reviewer assesses whether the pollutant concentrations are reasonable with respect to the time of day, season, meteorology, and concentrations expected and observed along other paths. For example, data checks for negative values, stuck values, high rate-of-change, and so on show whether the data are physically reasonable. Other parameters, such as wind direction and correlation with other measurements, may be used to judge the validity of suspect data. Data may not be invalidated based on the source of the pollutant (i.e., offsite). If anomalies are observed, additional analysis will be conducted to determine whether there is an instrument malfunction or if the data are truly anomalous but valid. Data reasonableness is also assessed more thoroughly later during the data validation process. If it is determined during the process of data validation that extended instrument downtime is necessary to address a quality issue, BAAQMD personnel will be notified in accordance with Regulation 1-530.

4.4 Data Validation Approach

On a quarterly schedule, an experienced air quality Analyst validates data by building on the automated screening results. This process starts with an in-depth review of the data that includes statistical tests to ensure the data are valid for the intended end use. The QA Manager evaluates QA and QC procedures and ensures adherence to the methods for meeting data quality objectives. Data validation activities are reviewed and approved by the QA Manager.

Data validation activities include:

- Looking for and investigating any statistical anomalies and outliers in the data.
- Ensuring there are not several continuous 5-min averages of the same number.
- Evaluating monthly summaries of the minimum, maximum, and average values.
- Ensuring the data are not biased by exceptional conditions or events occurring off refinery property.
- Ensuring data reasonableness by comparing the data to remote background concentrations and average urban concentrations.

- Ensuring the data or measurements are realistically achievable and not outside the limits of what can be measured.[7]
- Inspecting several sampling intervals before and after data issues occurred, instrument bump tests were conducted, or repairs were completed to ensure all affected data have been properly flagged.
- Referring to logbooks to see if some values may be unusual or questionable based on observations.
- Assessing instrument metadata (e.g., light intensity, operation codes) to confirm reasonableness.
- Assessing visibility measurements to ensure an adequate signal was obtained to quantify pollutant concentrations.
- Confirming that bump tests or factory calibrations were conducted and results were within specifications.

Data may be invalidated only if it can be traced to a reasonable and verifiable cause. General criteria for suspecting or invalidating data include:

- The monitor appears to have malfunctioned (acting erratic, spiking, or showing other evidence of questionable operation).
- The data are outside of plausible values (indicating a calculation error, averaging error, or instrument malfunction).

Additional QC checks for the instruments are summarized in Table 11. Data that fail checks are flagged in the DMS and brought to the attention of the Daily Data Reviewer in the graphic summaries. Common reasons for invalidation include instrument malfunction, power failure, and bump-test data that were not identified as such. As the measurements progress, the QA Manager updates and refines the screening checks. Screening checks are typically specific to the site, instrument, time of day, and season, and are adjusted over time as more data are collected. The data checks listed in Table 10 are generally robust, but are actively revised if evidence of ineffectiveness is found during daily and quarterly data validation.

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[7] Measurements below the MDL will be flagged in the DMS for review by an analyst.

Table 11. Instrument QA/QC checks.

Instrument Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test accuracy (as % error) with benzene and SO_2	Monthly and after major service	±20%[a]
Measurement quality – R^2	Continuous	0.8 to 1.0
Integration time	Continuous	≤250 ms
Signal intensity	Continuous	≥80%[b]
TDLAS		
Bump test[a] accuracy and repeatability (as %CV); H_2S at a concentration between 50 and 100 ppb which differs from 3-point calibration points.	Monthly	±15%
3-point calibration accuracy (as % error) and precision (as %CV)[a, b, c] The lowest calibration concentration must be in the range of 40 to 60 ppb.	Quarterly	±15% for each calibration point H_2S
5-min LOQ[d]	Continuous	3-25 ppb
H_2S correlation coefficient (r)	Continuous	0.72 to 1.0
Power	Continuous	0.1 mW (corresponds to <1% transmission)
H_2O correlation coefficient (r)	Continuous	≥0.95
FTIR		
Bump test accuracy (as % error) with propane	Monthly	±20%[a]
Signal intensity	Continuous	≥2%[b]
Measurement quality (R^2)	Continuous	0.7 to 1.0
Visibility Sensor		
Accuracy (as % error)	Annually	±25%

[a] For the TDLAS, accuracy and repeatability specifications are from the December 22, 2022, letter from BAAQMD[8] and will be treated as objectives to become requirements once it is proven they can be reliably met under all seasons and atmospheric conditions

[b] NIST TN 1297: Appendix D1. Terminology.

[c] For test concentrations requiring greater than 750 ppm H_2S, safety considerations necessitate certified sealed cells be used. For test concentrations requiring lower than 750 ppm, certified flow-through cells may be used.

[d] Per the December 22, 2022, letter from BAAQMD, the LOQ is taken to be equivalent to the MDL and is calculated as twice the standard deviation of a blank sample for the TDLAS.

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[8] Bovee, J. "Refinery Fenceline H2S TDL Monitoring System Specifications", Communication to P66 San Francisco Refinery, December 22, 2022.

Data are only invalidated if a reason can be found for the anomaly, or in the event of an automated screening check failure. If the data are anomalous or fail screening, but no reason can be found to invalidate the data, the data are flagged. Additional analysis may be needed to deem data valid or invalid. Voided data is flagged as invalid in the database, and a summary of issues leading to invalidated data are documented in the data file.

On a quarterly basis, Analysts ensure all the daily QC tasks are complete by following these steps:

- Reviewing instrument bump test results.
- Verifying that daily instrument checks were acceptable (checks described in Section 4.3).
- Reviewing manual changes to operations/data, and verify that the changes were logged and appropriately flagged.
- Ensuring that instrument checks have the appropriate QC codes applied.

On a quarterly basis, analysts subject the data to a final QC process. This process includes:

- Assigning invalid data a null code (i.e., a reason for being invalid).
- Creating a null record if a record is not created for a particular site/data/time/parameter combination.
- Inspecting data consistency over three months.
- Reviewing ranges of values for consistency (ranges should remain consistent over months of monitoring).
- Checking bump test values for consistency.
- Reviewing quarterly data completeness.

All actions are documented in the DMS, which retains raw data and traceability of all actions that result in the final data.

On an annual basis, the refinery and instrument contractor will review the performance of the network by (1) reviewing the data completeness by monitoring path, instrument, and species; (2) reviewing bump test results; (3) analyzing the reported values in the context of refinery operations; and (4) analyzing the data in a meteorological context. Using analyses similar to those used to support the network design, the contractor will also evaluate the overall performance of the network to ensure it is meeting the project objectives, and prepare an internal technical memorandum summarizing the findings.

4.5   Data Storage and Processing

Redundancy of the DMS data is maintained on a cloud-based system. The data will be stored for a period of five years after sampling. Spectral files for the open-path measurements will be backed up on a separate computer in real time.

4.6   Data Delivery

Final data sets are compiled quarterly and will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter. Outside of the normal quarterly delivery, data will be made available to the BAAQMD within 30 days of a request. Consistent with BAAQMD guidance, quarterly data deliveries will include the following.

- Data for all instrument and parameter combinations in the comma separated value (.csv) data file template provided by BAAQMD. Data will contain:
  - The name of the facility where the equipment is located
  - A unique identification number assigned to each instrument or system
  - A short descriptive name for the instrument associated with the reported unique ID (e.g. TDL, UV-DOAS)
  - The name of the compound being measured
  - The date of measurement, formatted as "yyyy-mm-dd"
  - The hour of the day and the beginning of the 5-min period over which measurements were collected and averaged, reported in Pacific Standard Time (PST) and formatted as "hh:mm" using 24-hr notation
  - The mean 5-min concentration, reported as numeric values for detection events below the LOQ
  - The unit of measure corresponding to the reported mean concentration
  - The averaging period duration (in minutes) for the reported mean concentration
  - The number of values that comprise the reported mean concentration
  - An indicator representing whether the reported mean concentration represents a legitimate air measurement ("Y") or one that has been affected ("N") by an instrument malfunction, adverse environmental conditions, maintenance events, etc.
  - Error codes explaining the reason for invalid or missing data, with multiple codes separated by a semicolon without spaces and the field left blank for valid data
  - The maximum concentration measured during the averaging period, reported in the same units of measure as the mean concentration
  - The required LOQ for the corresponding instrument, reported in the same units of measure as the mean concentration
  - The real-time LOQ for the averaging period, reported in the same units of measure as the mean concentration
  - The average measured light signal for the corresponding averaging period
  - The units of measure for the corresponding light signal

- A record for each 5-min period of the quarter for all instrument and parameter combinations. Records corresponding to missing data will include the facility name, instrument ID, instrument descriptor, parameter, date, time, and error codes with their respective values, and remaining fields will be populated with a value of "NA."

- An assessment of data completeness, as described in Section 3.2.

- A summary of bump tests and calibration checks performed according to the QAPP including the instrument or system, the type of test or check, the start and end date and time of the test or check, and the date and time that the instrument or system resumed normal operations. Potential failed bump tests or calibration checks will be included.

- The results of bump tests and calibration checks performed according to the QAPP, including accuracy and precision. Root cause analysis and a narrative description of maintenance or repairs performed to return the system to proper operations will be included for potential bump tests or calibration checks with accuracy and precision results that are not within the acceptance criteria.

- Data corrections accounting for the effects of gas cells or other equipment on instrument signal.

- Meteorological data and a narrative explanation sufficient to justify where data has been excluded due to adverse atmospheric or environmental conditions.

4.7   Data Flow to Website

4.7.1 Auto-Screening and Alert Review

All data values that are not associated with bump tests, other instrument maintenance, or instrument problems are displayed to the public in near-real time. If data are subsequently proven to be invalid, they are removed from the public display. Data issues identified during the automated QC process triggers communication to the Data Manager to conduct further investigation. The Data Manager and team then decides on the appropriate action to resolve the problem.

Data are screened in real time upon ingest into the DMS, as described in Section 4.2. Automated procedures are used to ensure that data are properly ingested, stored, processed, and quality-assured, and that products are delivered to a public-facing website in real time, defined here as 10 minutes or less after the data are collected.

The preliminary QA/QC'd concentration data are presented in a time series of benzene, toluene, ethylbenzene, xylenes, SO_2, and H_2S. Data are provided as 5-min averages. Data are annotated for quality (valid, invalid, suspect, or missing). Additionally, for the Unisearch TDL, 5-min MDLs will be displayed in real-time.

4.7.2 Data Backfill Process and Schedule

All data, raw and validated, are retained in the DMS. Upon quarterly analysis, data are downloaded from the database, reviewed, flagged, and finalized. After final data is generated, it is backfilled into the database.

5.   Document Control

Revision No.	Revision Date	Description
1	7/9/2021	Initial Submission
2	2/10/2023	Amended for new H_2S monitoring requirements with TDL
3	9/5/2023	Revised in response to feedback from BAAQMD received 7/19/2023

Appendix A. Standard Operating Procedures for the CEREX UV Sentry UV-DOAS

Appendix A

Standard Operating Procedures for the CEREX UV Sentry UV-DOAS

September 5, 2023   STI-7024
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Contents

1. Scope and Application

This SOP covers the use of the CEREX UV Sentry UV-DOAS analyzer in a fenceline monitoring application. This document addresses routine maintenance activities including visual inspections, instrument checks, data management, QA audit testing, and data validation.

2. Introduction and Overview

The CEREX UV Sentry ultraviolet differential absorption spectrometer (UV-DOAS, shown in **Figure 1**) is an instrument that is used to detect BTEX, SO_2, NO_2, and a number of other gases in the ultraviolet (UV) region of the electromagnetic spectrum. The instrument consists of a Xenon light source, several optical elements, including a spectrometer. UV-DOAS instruments may be configured so that the spectrometer and source are in one location (monostatic) or at opposite ends of the path (bistatic). For a monostatic configuration, the light from the light source is collimated with the primary mirror and directed along a path length of about 500 m. At the other end of the path is an array of corner-cube reflectors called retroreflectors that direct the light directly back into the analyzer where the light is dispersed and measured using a spectrometer. The working range of the spectrometer is from about 200 to 400 nm. This document addresses the routine operations and maintenance procedures for the Cerex Monitoring Solutions UV Sentry units. The procedure is intended to guide the field technician in ensuring and verifying that the equipment is performing to expectations. As required, hard copies of this procedure and the associated test forms will be kept on site and a copy of the test form showing the results will be sent to the Refinery Project Manager upon completion of the test procedure.
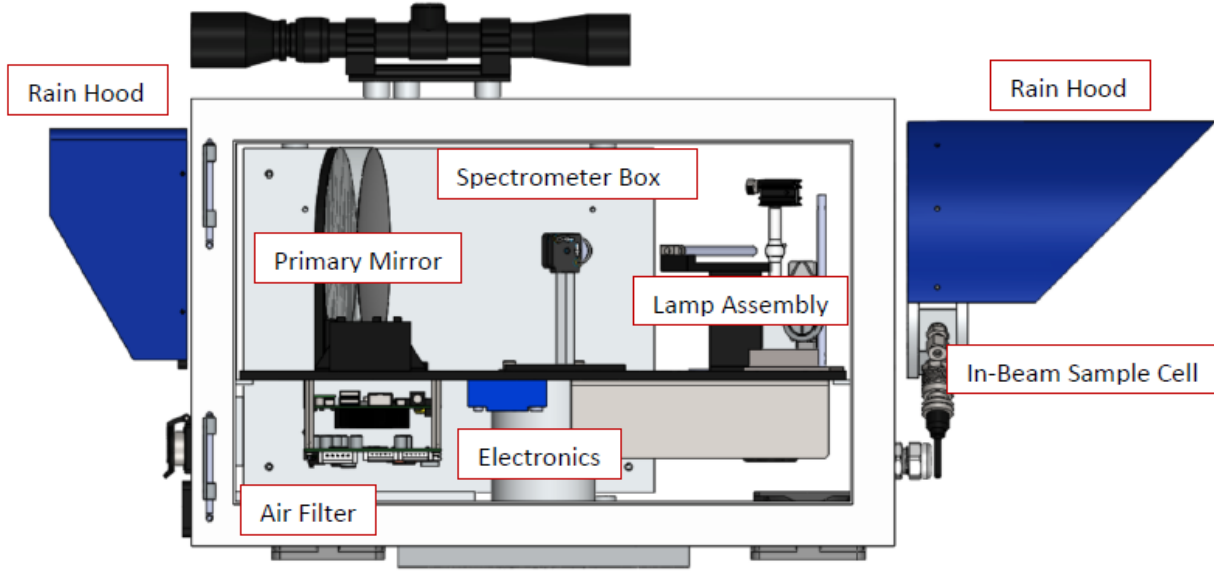
Figure 1. Schematic of the monostatic UV Sentry UV-DOAS analyzer.

The purpose of field maintenance is to ensure that the instrument is operated within specification and for field verification of the factory calibration of the UV Sentry. The QA Test process challenges the instrument using known concentrations of select BTEX reference gases and/or Sulfur Dioxide to verify proper detection and quantification under field conditions.

3. Definitions

Table 1. Definitions of terms and acronyms used in this document.

Term/Acronym	Definition
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes (Xylenes are composed of ortho, meta and para isomers)
Bump Test	Also known as QA Audit; test where gas of a known concentration is introduced to the analyzer to check for response accuracy and precision
CMS	Continuous Monitoring Software
Integration Time	The amount of time the spectrometer detector collects light for (typically 20 to 300 ms)
Intensity	A measure of how much light was collected
PPE	Personal Protective Equipment

Term/Acronym	Definition
QA	Quality Assurance
QC	Quality Control
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
UV-DOAS	Ultraviolet Differential Absorption Spectroscopy

4. Safe Work, Hazard Identification, and Precautions

The following information is intended to provide guidance in ensuring a safe work environment.

Operator Qualifications

Installing, operating, and servicing Cerex UV Sentry analyzers should only be performed by personnel trained in the operation of the system components, familiar with the potential hazards associated with the deployment site, and familiar with the handling of gas delivery and testing equipment.

Work should conform to the manufacturer guidance and site health and safety practices.

The Cerex Monitoring Solutions UV Sentry Series Analyzers are not rated for safe operation in hazardous or explosive environments (not intrinsically safe). Any use in an area that may contain flammable mixtures or highly corrosive vapors requires special preparation to ensure operator safety and safe operation of the equipment.

NOTICE

UV light hazard

Avoid looking directly at light

WARNING – Eye hazard. Risk of eye injury. CEREX UV-DOAS Analyzers contain an ultra-violet light source that may cause eye injury after prolonged exposure. Always wear UVA/B/C eye protection when working on or near the operating equipment.

Procedure Warnings

The procedure contained within this document requires the handling of toxic substances including but not limited to benzene, aromatic hydrocarbons, and sulfur dioxide gas, and it requires the operation of equipment designed for toxic gas containment and dispensation. Improper handling of materials or hardware may result in serious injury, destruction of property, or damage to the UV Sentry. Only qualified individuals should attempt or perform analyzer operation or testing activities.

Safe Operating Precautions

Ensure that a clear escape path is identified.

Standard site personal protective equipment (PPE) is appropriate. If gloves are required for work on optics, nitrile or latex should be used.

NOTICE

Please check off the following steps before conducting maintenance. Doing so reduces the chances of false notifications to the public and clients.

❒ Notify the client and project manager of maintenance tasks.

❒ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.

❒ Confirm that the data is invalidated on the public website before proceeding with maintenance.

❒ When maintenance is complete check the public site <u>for at least 15 min</u> to ensure proper reporting (no missing data, no high values, etc.).

❒ Take out of maintenance mode

❒ Notify the project manager and client when maintenance is complete.

5. Routine Operations

To set the UV-DOAS instrument to acquire data for normal operations, the instrument CMS must be operating and the instrument must be aligned. These actions are detailed in the steps below.

1. Start the CMS software (if not already initiated). You should see a window similar to the one shown below in **Figure 2**.
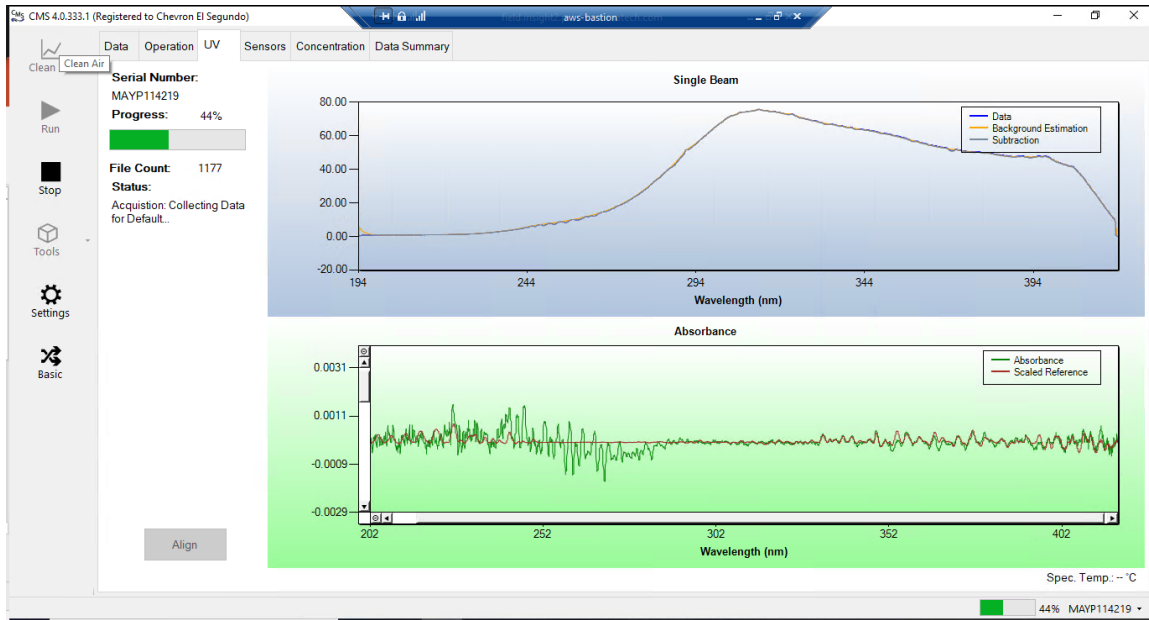
Figure 2. Screenshot showing the **UV** tab of the CMS software. Note that the **Align** button is grayed out because the instrument is in run mode (the **Run** button is also grayed out because the instrument is in run mode).

2.   Under the **UV** tab, left-click on the **Align** button. This action brings up a new screen showing the instantaneous single beam plot (intensity vs wavelength). If the **Align** button is not active, you may need to press **Stop**. The **Align** mode is shown in **Figure 3**.

Figure 3. Screenshot for **Align** mode. The integration time can be entered in the upper right of the screen. In this particular screenshot, the integration time is 38 ms.

3.   Enter an integration time of 25 ms and optimize the signal intensity by adjusting the pan-tilt head of the UV-DOAS unit to adjust the position of the UV beam on the retroreflector.

NOTE: Make sure not to saturate the peak of the spectrum when at 25 ms integration time. An example of a saturated spectrum is shown in **Figure 4**; note that the spectrum is flattened out starting at about 290 nm. Also, ensure there is sufficient intensity at 250 nm compared to the stray light intensity. If there is more than 10% stray light, advanced optical adjustment or bulb change may be necessary. To measure stray light, block the beam from exiting the analyzer with an opaque object (such as a black cloth) and measure the intensity at the wavelength of interest.
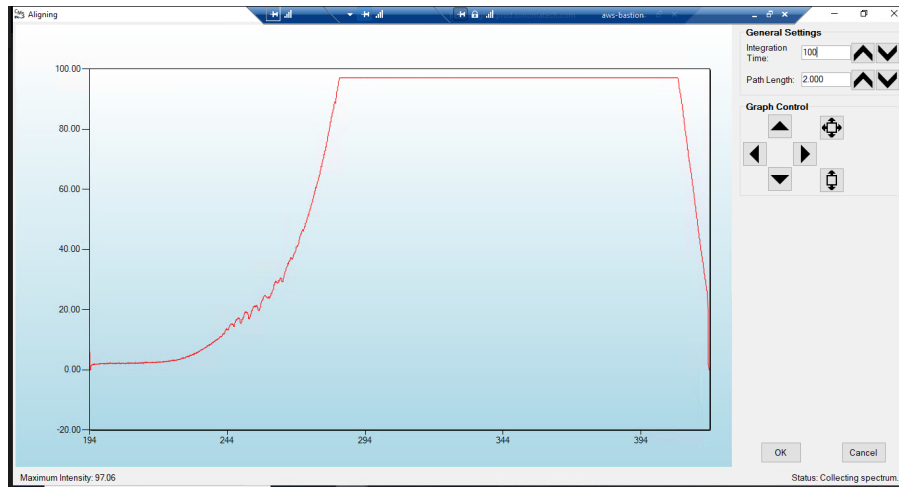
Figure 4. An example of a saturated spectrum when in **Align** mode. Note the "flat top" profile of the spectrum. The spectrum flattens out because the detector has saturated at those wavelengths and cannot quantitatively measure additional light.

4. Once sufficient alignment is obtained, exit the align mode by pressing **Cancel**.

5. Verify settings by left-clicking **Settings**.

Note: If you need to change any setting back to the original configuration, you must go to **File** and **Save** and **Save As Default.** If you change settings, record why they were changed and what they were changed to in the instrument logbook. If settings are changed, they are automatically saved under the directory: C:\Users\CMS-USER\Documents\Cerex\CMS.

- RunTime
    - General
        - Operator Name: **Default** (these will change based on the path and site you are working on)
        - Sitename: **Cerex** (these will change based on the path and site you are working on)
        - Auto Run: `ON`
        - Auto Run Delay (s): **15**
    - File

- File Type: **.CSV**
- Primary Data Logging File: `ON`
  - C:\Users\CMS-USER\Documents\Cerex\Data
- Secondary Data File Logging: `ON`
  - \\OPT1-PC1\VLOData\OPT1_Path1\UVSentry_POC1
    - Note this path will change based on the different computer and path you are working on. This is just a basic file writing path to show you what it should look like.
- Single Data Folder: `OFF`
- Primary Summary File Logging: `ON`
  - C:\Users\CMS-USER\Documents\Cerex\Data
- Secondary Summary File Logging: `ON`
  - \\OPT1-PC1\VLOData\OPT1_Path1\UVSentry_POC1
    - Note this path will change based on the different computer and path you are working on. This is just a basic file writing path to show you what it should look like
- Single Summary File: `OFF`
  - Library
    - Library File: C:\Users\CMS-USER\Documents\Cerex\Library\
  - UI
    - Sort Column: Compound Name
    - Data Summary Chart: `OFF`
    - Concentration Chart: `OFF`
    - Password Protection Settings: `ON`
    - Pump Control: `OFF`
    - Status Control: `OFF`
    - Testing Control: `OFF`
- Analysis
  - General
    - Moving Average Interval: **12**
    - Display Units: **PPM**
  - Concentration
    - Zero Readings on Non-Detect: `OFF`
    - Zero Readings on Negative concentrations: `OFF`
    - Display BDL: `OFF`
    - Quick Analysis MDL Wave length Range: **276 -280 (The range doesn't matter)**
    - Temperature/ Pressure Concentration: `OFF`
  - Filters
    - Absorbance Savitzhy-Golay: `ON`
    - Baseline Correction Savitzky-Golay: `OFF`

- Instruments
  - UV
    - Operation
      - UV: **`ON`**
      - Acquisition Time (s): **30 (this is the "averaging time" of the instrument)**
      - Integration Time (ms): **Always will change if Auto integration is turned on**. This is the amount of time that the instrument will collect light.
      - Path Length (m): **2 (2 for monostatic, 1 for bistatic)**
      - Trigger Mode: **Norma**l
    - Auto Routine
      - Auto Integration: **`ON`** **(the software will determine the integration time)**
      - Intervals (s): **300**
      - Wavenumber Range: **300-310 (This is the range where the intensity will be measured for autointegration determination. This is different on all instruments due to Spectral Background and Intensity Range)**
      - Intensity Range **75-85 (This is the target intensity range for the autointegration routine)**
      - Maximum Integration: **300**
      - Auto Background: **`ON`**
      - Interval (Acquisitions): **5**
      - Wavenumber Range: **266-270**
    - Verification
      - Verification: **`OFF`** **(This inactivates all inputs)**
- Controller
  - General
    - Serial Port: **n/a**
    - Sensor Refresh Interval (s): **15**
  - Sensors
    - **Don't Touch Anything**
  - Alarms
    - **Don't Touch Anything**
- Email
  - General
    - Data Recipient: **Blank**
    - Email Sender: **Blank**
    - Email Periods (s): **60 (doesn't matter the time, we don't use this setting)**
    - Send Data: **`OFF`**
  - SMTP

- Server: **smtp.gmail.com**
- Port: **587**
- Username: **Blank**
- Password: **Blank**
- Timeout (s): **100**
- SSL Authentication: **ON**
- Auxiliary Coms
  - Modbus
    - Modbus: **ON**
    - System Type: **Ethernet**
    - TCP Port: **502**
    - Unit ID: **2**
    - 16-bit unsigned int to: **OFF**

6. After settings are verified and the instrument is aligned, you can place the instrument in run mode.

6. Equipment and Supplies

1. Field notebook

2. Tool kit, especially including: 7/64 hex driver, complete set of combination wrenches, adjustable wrenches, screwdrivers, etc.

3. Cleaning supplies designated to be safe for use on a Cerex UV-DOAS – especially lens paper.

4. All relevant PPE, hardware, and procedural guidance per SOP, Safety Plan, and Safe Work Permit

5. Local or remote network link device (as required).

6. External laptop computer with network interface device to the Sentry unit (as required)

7. Cerex UV Sentry Unit equipped with CMS software

8. Cerex UV-DOAS 8" x 8" x 1" pleated filter

9. Isopropyl Alcohol (≥80%)

10. Distilled water

11. Pressurized sprayers

12. Cerex UV-DOAS UV source bulb

13. Nitrile gloves

14. Cell bump test apparatus (including panels, regulators, valves, meters, etc.)

15. Tubing as required: 1/4" PTFE tubing for gas supply from the bottle to the QA cell

16. Tubing as required: 3/8" PTFE tubing with inline flow indicator from the QA cell to the scrubber

17. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less

18. Gas scrubber appropriate for gas used. Activated carbon may be used for benzene.

19. Reference standard traceable zero compressed air purge gas

20. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher

21. Cerex UV Sentry Unit equipped with CMS software

22. Spare reflector for alignment

7. Maintenance Activities

The following sections outline the routine performance indicator checks and maintenance activities to be carried out for each analyzer and sensor, followed by maintenance forms (see Section 9) used to indicate when the checks are completed and document any corrective actions taken. These activities are also expected, based upon the project plan, to be logged in a site logbook either in hard copy or electronic form and can reference this SOP and associated forms.

The following UV-DOAS maintenance activities and performance checks are recommended by the manufacturer:

- Visually inspect the system.

- Inspect optics on detector and retroreflector; clean if necessary.

- Inspect system filters on the optics and retroreflectors.

- Confirm the alignment to verify there has not been significant physical movement. Note: this is automatically monitored as well.

- Download data from detector hard drive and delete old files to free space, if needed. Ensure data are backed up on external drive.

- Ensure there are no obstructions between the detector and the retroreflector (such as equipment, vegetation, vehicles).

- Change out the UV source.

- Replace ventilation exit and intake filters.

- Clean optics on detector and retroreflector.

- Realign system after service.

- Perform bump test (simulates system-observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit.

- Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency.

- Verify system software settings.

- Deliver previous years data to client and remove from brick and analyzer

7.1 Visual Inspections

1. Ensure that the instrument is running and the data look reasonable.

2. Clean and correct any obvious problems with the system (cobwebs, rodent nests, broken optics, etc.).

3. Inspect all electrical cables for wear; replace as needed.

4. Indicate these visual checks are complete on the form included at the end of this document.

5. Document any changes to the system in the course of these checks in the site logbook.

7.2 Filter Inspection and Replacement

Filters are present on both the instrument and the retroreflector fans. Some DOAS units may have two filters on the analyzer to mitigate salt intrusion and subsequent corrosion. Ensure all system filters are visually inspected and replaced if dirty.

Remove and inspect instrument filters following the procedure described here. Replace if necessary. Ensure fans are running (they should make an audible sound) when the system is turned back on.

NOTICE

The UV Sentry should be powered down prior to changing the filter. When powering down, adhere to the recommended shut-down procedure, which includes properly shutting down all applications, and then shut down the instrument PC.

When the PC has been successfully shut down, remove the power cord from the unit.

The UV Sentry contains a filter which must be changed on a periodic basis. Good airflow through the filter is directly related to the ability of the instrument to properly regulate internal temperature. If

the filter is allowed to become clogged (through lack of maintenance), the system can overheat, and go into thermal shutdown. In extreme cases, damage may occur to the internal electronics.

The main filter is a custom size 8" x 8" x 1" pleated filter, which is stocked at the Cerex factory. If a large number of replacement filters are ordered, the lead time could be several weeks.

7.2.1 Filter Installation Procedure

1. Power down the instrument—you cannot replace the filter with the instrument running. First, close the software and shut down the onboard PC. Next, disconnect the power.

2. The filter is accessible by removing the black plate located beneath the instrument touchscreen. The plate has the words "Filter Access" imprinted on it (**Figure 5**).

3. Use a 7/64 hex driver to remove the six socket-head cap screws that retain the Filter Access Panel.

Figure 5. Location of filter access plate.

4. Once the access plate is removed, the filter can be accessed for removal and replacement. Old filters should be discarded and not re-used. Insert the new filter with the "Airflow" arrow pointing in the "UP" direction (**Figures 6 and 7**).

5. When inserting the new filter, do not force the filter into the slot. If you encounter any unusual resistance, open the side door, and ensure no wires have fallen into the filter slot.

6. When fully inserted, the filter should be flush with the instrument case.

Figure 6. Filter access plate removed and filter partially removed.

Figure 7. Filter completely removed.

7. Re-attach the black filter access panel, using the same driver and six screws.

8. Power up the instrument, make sure CMS software has started, and realign the instrument.

7.3 Light Level Check

For good visibility conditions, signal strength is normally >90% and integration time is normally <50 ms. If it is determined that these values are out of range, re-alignment may be needed.

Check and record signal strength at 250 nm. With an integration time of less than 125 ms, minimum signal intensity at 250 nm should be greater than 5%.

7.3.1 Check for Stray Light

Ensure there is sufficient intensity at 250 nm compared to the stray light intensity. If there is more than 10 - 20% stray light, advanced optical cleaning, replacement, alignment, or bulb change may be necessary. To measure stray light, block the beam from exiting the analyzer with an opaque object (such as a black cloth) and measure the intensity at the wavelength of interest. Calculate stray light by dividing the intensity of the beam while blocked by the intensity of the unblocked beam and multiplying by 100:

$$\%stray\ light = \frac{Intensity\ of\ blocked\ beam\ (\%)}{Intensity\ of\ unblocked\ beam(\%)} \times 100\%$$

Note the result of this stray light calculation in the form at the end of this document.

7.4 Data Management

7.4.1 Archiving and Deleting Older Data

> **Note:** Data older than twelve months should be deleted from the instrument each month to prevent the instrument from filling its 125 GB internal hard drive.

Raw instrument data are stored on the analyzer computer, the site PC, and the hard drive attached to the site PC. Data consists of spectral data containing two columns: one for wavelength and the other for intensity. There are also two types of "summary" files that contain data resulting from the classical least squares analysis of the spectral data as a function of time. These file formats are described in the CMS Software User Manual.[1] Spectral data and summary files are automatically written to the site PC and moved to the external hard drive after a regular interval. Deliver the external hard drive to the client with the frequency indicated in the QAPP.

As noted above, data on the instrument must be deleted at monthly intervals. Details on the proper procedure for deleting data files from the instrument are as follows.

1. Confirm that the data files have been successfully written to the external hard drive attached to a separate PC also located in the instrument shelter.

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[1] CMS Software User Manual Rev 4. CMS Version 4.0.298.1, CEREX Monitoring Solutions, December 5, 2017.

2. Make a note of the amount of available space on the instrument's internal drive on the maintenance form.

3. Locate files older than 12 months on the instrument file directory here: C:\Users\CMS-USER\Documents\Cerex\Data\.

Note: This excludes the Bump Test folder, which should always remain on the instrument computer.

4. Log into the brick PC located in the instrument shelter and locate the data files written from the instrument onto the external hard drive.

5. Confirm all Complete Data Summary files and Simple Data Summary files for the desired month have been transferred over completely to the external hard drive attached to the brick PC.

6. Once you have confirmed that those files have transferred over to the external hard drive, delete those exact Complete Data Summary and Simple Data Summary files from the instrument data folders.

7. For each individual day of single beam folders, ensure that the amount of single beam files are the same on both the external hard drive located on the brick pc and the internal hard of the instrument.

8. If both folder locations match and you have ensured proper file download, you may permanently delete the Single Beam folders from the instrument computer.

9. After all data older than 12 months have been deleted, note how much free space is now available on the instrument's internal drive. If removal of the files does not result in enough free disk space, the disk drive may need to be reindexed (see Section 7.4.2).

7.4.2 Rebuilding the Instruments Indexing Preferences

If deleting data from the instrument does not seem to increase free instrument disk space, you may need to reindex files. To rebuild the index preferences, follow these steps.

1. Under the **Control Panel Menu**, use the search function in the lower left-hand corner of the task bar to search for "Indexing Options".

2. Click on the **Advanced** tab with the shield logo.

3. Click **Rebuild**.

   Note: Once "Rebuild" has been selected, a message saying that it might slow user activity will appear. This will not affect the instruments' ability to perform data collection. On the original indexing option screen, the magnifying glass in the upper right-hand corner will move and the number of items indexed will slowly increase. Take note of the available space on the instrument's internal drive once the indexing has been completed.

7.5 Clean Optics on Detector and Retroreflector

Cleaning the retroreflector is an important part of the maintenance plan. Over time, the retroreflector will collect debris that can alter the performance of the instrument. Caution should be taken as there are electrical fan heaters that are used to keep moisture and particulates from collecting on the retroreflectors.

Optic Cleaning

If light levels are low or visual inspection reveals soiled optics, cleaning optical surfaces with lens paper and solvent can improve light throughput. This applies to the primary mirror, secondary mirror, and quartz windows. In general, if the optic is not dirty, don't clean it, as excessive cleaning of optics can result in scratches and wear over time. If the optic is obviously soiled and is affecting performance, take the following steps. Mirrors with metallic coatings should be treated with extra care because these surfaces are easily damaged on contact.

1. Wear powder-free gloves to avoid transferring skin oils onto the optics.

2. Use compressed air/canned air to remove particles from the surface of the optic. If the optic is sufficiently clean after this step, stop here

3. Use a solvent (isopropyl alcohol or methanol/acetone in a 60/40 ratio) and lens tissue to wipe the optic clean. If using acetone, make sure to use acetone-impenetrable gloves. Wipe slowly from the edges first with a solvent-soaked lens tissue. One technique is to drop solvent on the unfolded lens tissue and drag from one end to the other.

7.5.1 Retroreflector Cleaning

1. Power down any equipment to prevent electrical shock or damage to the system.

2. Use a gentle stream of distilled water, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust built up on the retroreflector.

3. Use a gentle stream of 80% isopropyl alcohol, usually from a weed sprayer or other type of gentle delivery method, to remove any remaining salt or dust built up on the retroreflector.

4. Once the retroreflector has been cleaned and is dry, repower any electrical equipment you powered down and clean any spills you created while cleaning.

7.6 Inspect and Change Out UV Source If Intensity Spectrum Has Dropped Below Acceptable Range

NOTICE

Never power the UV Sentry without a properly installed Xenon UV Source obtained from Cerex.

Powering the system without a UV source may cause an electrical short, which will permanently damage the instrument.

Always remove the Xenon UV Source and secure the analyzer heat sink anode prior to transporting or shipping the UV Sentry.

Failure to remove the Xenon Source and secure the Heat Sink anode prior to transporting or shipping the UV Sentry may cause destruction of the source as well as the anode.

Always check the polarity of the Xenon UV Source for proper installation prior to powering the analyzer.

Installing the UV source with reverse polarity will permanently damage the UV Source and cause immediate failure. The Xenon UV Source is shipped from Cerex with Heat Shrink and labeling over the Anode (+) end of the Source. The UV Source must be installed so the Anode (+) end of the bulb mounts to the Anode Heat Sink. The UV Source will be oriented with the (+) end at the top.

7.6.1 Xenon UV Source Handling

The UV Sentry Xenon Source is shipped from Cerex in a protective plastic enclosure (see **Figure 8**). The (+) Anode end of the UV Source is labeled "UP." The UV Source must be installed with the (+) side UP. Always wear clean powder-free nitrile gloves when handling the UV Source. Oils from hands deposited on the UV Source glass bulb will cause damage in operation. Remove the "UP +" label from the UV Source prior to installation. If the glass bulb is touched with bare hands, clean the glass bulb with isopropyl alcohol or acetone prior to installation.

Figure 8. The ANODE end of the UV Source is marked (+). The CATHODE end of the UV Source is marked (-).

7.6.2 UV Sentry Xenon Source Removal

Prior to shipping or transporting the UV Sentry, remove the Xenon UV Source and secure the anode heat sink assembly.

1. Power off the analyzer and disconnect from power. Allow the analyzer to cool completely.

2. Use the provided key to remove the Source Access Panel (see **Figure 9**).

Figure 9. Opening the source access panel.

3. Wearing clean nitrile gloves, loosen the retaining thumbscrew on the Anode Heatsink at the top of the UV Source (see **Figure 10**).
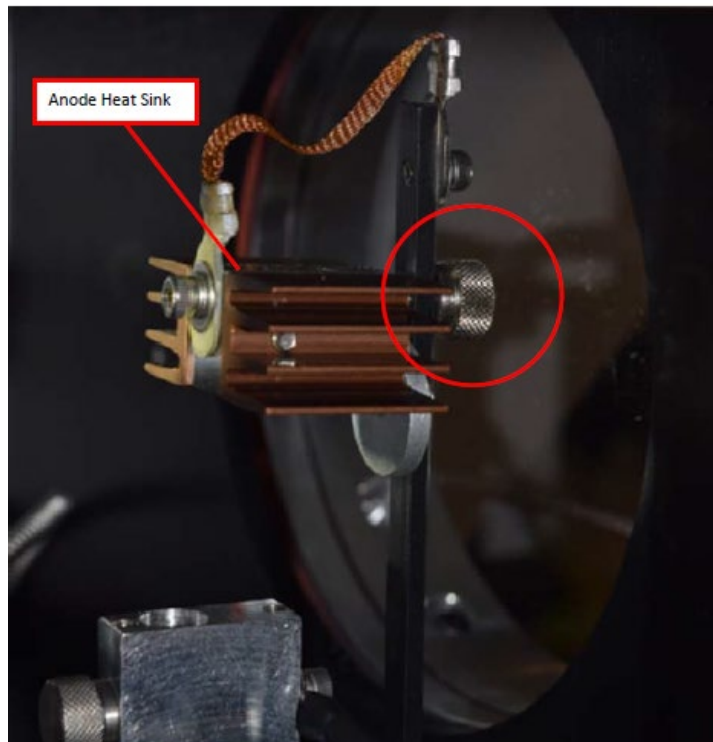
Figure 10. Anode heatsink at the top of the UV source.

4. Lift the Anode Heat Sink off the top of the UV Source. It is connected to the post by a cable. Gently let the heat sink dangle.

5. Loosen the retaining thumbscrew on the Cathode block at the bottom of the source (**Figure 11**).
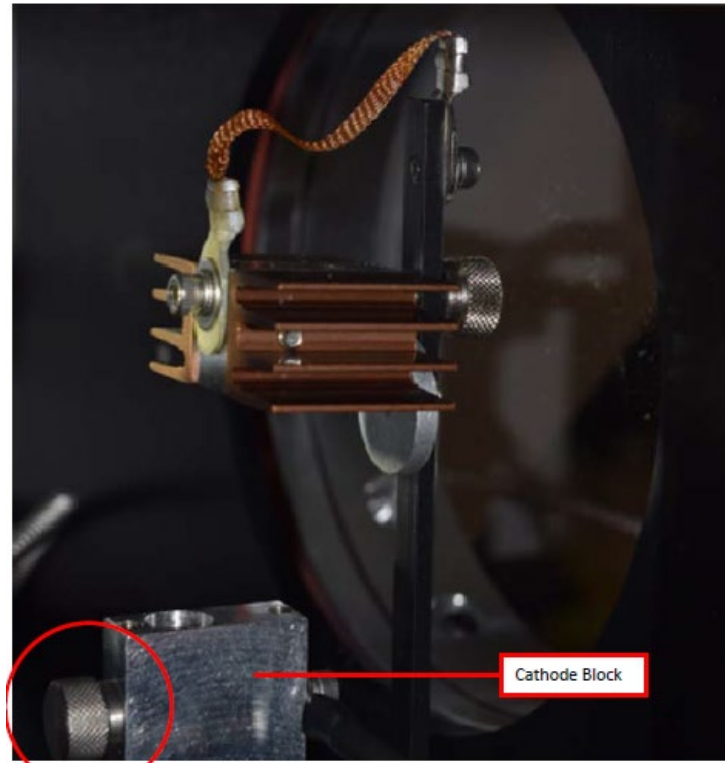
Figure 11. Loosen the thumbscrew on the Cathode block at the bottom of the UV source.

6. Lift the source lamp straight up and out of the mount.

7.6.3 UV Sentry Xenon UV Source Installation

1. Insert the Cathode (-) end of the Xenon UV Source into the Cathode Block (see **Figure 12**). The Cathode end of the UV Source is marked with (-).
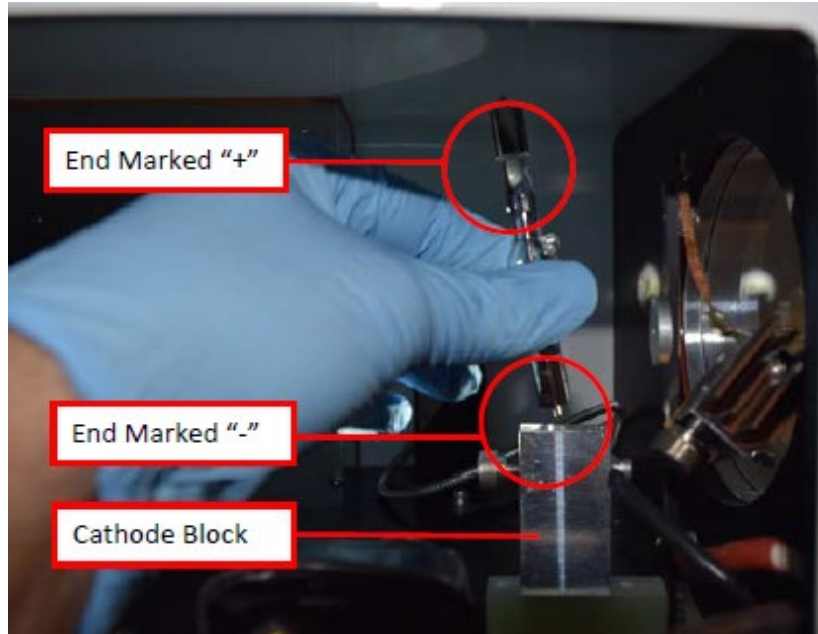
Figure 12. Inserting the Xenon UV Source into the Cathode block.

2. Rotate the UV Source so the nipple on the glass envelope faces the aluminum disc on the mounting post.

3. Tighten the Cathode block thumbscrew gently. Gently pull up on the Xenon UV Source to verify the thumbscrew has made contact with the nipple on the UV Source cathode.

4. Slide the Anode Heat Sink (+) over the top of the UV Source Anode. The Anode end of the UV Source is marked (+). Gently tighten the Anode Heat Sink thumbscrew to secure. Gently pull up on the heat sink to ensure the thumbscrew has made contact with the nipple on the UV Source anode.

5. Reinstall the Source Access Panel prior to powering on the analyzer.

6. Confirm signal strength through remote desktop connection before leaving path.

7.6.4 Secondary Optic Alignment

If there is lower intensity than what was previously observed after the UV Source been replaced, an internal alignment of the secondary optic might be required. This should only be performed by a technician who has been properly trained to perform internal alignments.

Note: Proper PPE must be worn (glasses, sunblock) while performing a secondary alignment to prevent over-exposure to high intensity UV light from the UV Source within the instrument. Also, use an opaque object (such as cardboard or paper) to block as much of the light from the bulb as possible while still maintaining a view of the secondary mirror and fiber (if required).

1. Stop CMS and navigate to the **Alignment** menu.

2. Properly align the instrument at 20 to 25 ms integration time, as shown in **Figure 3**. Make a note of the intensity at 254 nm and the overall shape of the UV signal return.

3. Open the side of the instrument to gain access to the secondary optic.

4. Ensure alignment achieves maximum signal return and is fully aligned to the retroreflector. This is achieved by maximizing signal intensity in align mode at an 8 ms integration time. If signal cannot be confirmed in align mode, this can be done visually by maximizing the visual return brightness on the retroreflector either by looking through the telescope or by placing your head next to the instrument and observing the returned reflection from the retroreflector.

5. If the entire spectrum is visible in the alignment menu, take note of the deep UV intensity at 254 nm. If the instrument is over saturation, as seen in **Figure 4**, take note of the wavelength at which the oversaturation starts.

6. Once the instrument is aligned, take care not to bump the instrument.

7. Adjust the first secondary mirror mount thumb screw to maximize the overall intensity.

8. Move on to the second mirror mount thumb screw and repeat the same process of adjustment to maximize the signal return.

9. In an iterative process, continue to adjust the optical mount screws to maximize intensity, one at a time, until no further gain in signal intensity is achieved.

Note: Only adjust the two thumb screws of the secondary optic.

10. Set the integration time back to 20-25 ms and make sure the instrument is able to achieve a proper UV spectrum, as shown in Figure 3**.** If you are not able to achieve the proper UV spectrum, repeat steps 6-8.

11. Take note of the overall shape of the UV intensity and adjust secondary mirror to maximize intensity at 254 nm**.**

12. Close the access door of the instrument enclosure. Observe if having the access door closed changed the internal alignment.

13. Return the instrument to its normal operation and observe the first few scans to ensure the UV spectra are acquired.

7.7 Perform Bump Test

7.7.1 Apparatus Setup

Audits of open-path analyzers require high concentration (~100 ppm) calibration gases. Standard refinery personal protective equipment (PPE) should be worn at all times, including safety glasses. This procedure requires the use of pressurized gas cylinders; training on proper handling of

pressurized systems is required. The operator-supplied Standard Operating Procedure (SOP), approved by the End User and in compliance with End User's Health and Safety Plan, is also required.

Verify the system is set up (minus the instrument connections) as depicted in **Figure 13**.
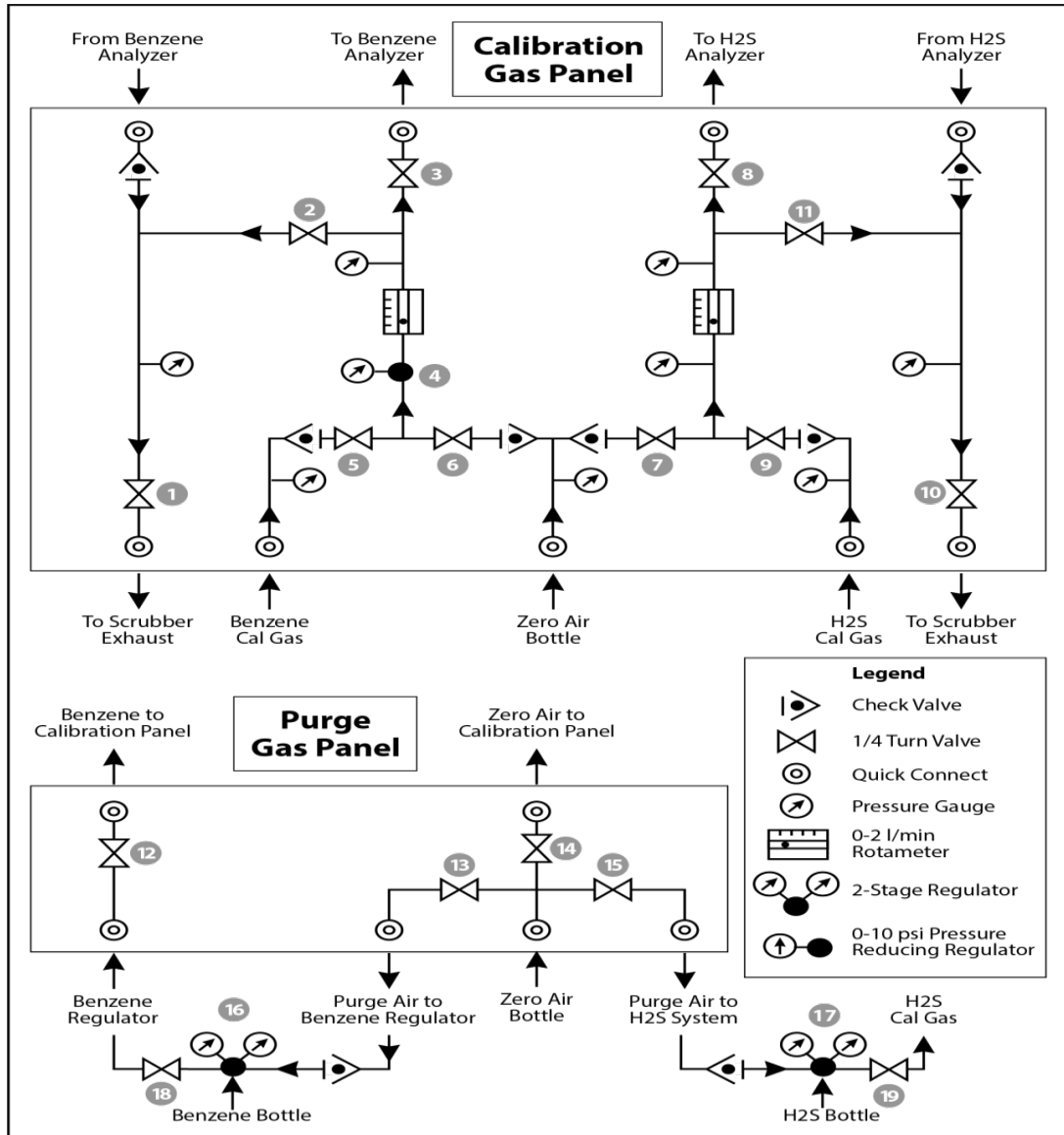

Figure 13. Diagram of the calibration gas panel (top) and purge gas panel (bottom) used for gas delivery.

7.7.2 Prepare CMS for Gas Testing

Note: There is a summary of system settings in Section 5 that can help you when you are changing any setting in the Cerex UV-DOAS instrument.

7.7.3 Configure CMS for Test (This may be concurrent with Gas Purge System setup)

1. The analyzer should be powered and running for **at least 30 minutes**.

2. Stop CMS data collection by pressing the **STOP** button.

7.7.4 Configure Test Files

1. Click **Advanced** on the left side of the CMS software window; password is *advanced*.

2. Under **Advanced** -> **Settings** -> **Runtime -> File**, note the current file path so that it can be restored at the end of the test.

3. Under **Advanced** -> **Settings** -> **Runtime -> File**, turn off **Secondary Logging**.

4. Change the primary file logging paths (both of them) to: C:\Users\CMS-USER\Documents\Cerex\Data\bumptest. Then select **File** and select **Save**.

7.7.5 Leak Check

1. Ensure all the tubing from the purging panel is connected to the calibration panel in the mobile van. Ensure gas cylinders are connected to the purge panel as depicted in Figure 13. Then attach the calibration panel to the analyzer connection in the analyzer shelter.

2. Connect the PTFE tubing containing the activated carbon scrubber to the analyzer exhaust.

3. Close all valves on the calibration and purging panel.

4. Verify that the regulators on the zero air and benzene cylinders are completely closed (all the way to the LEFT!!) to prevent any pressure buildup at the regulator.

5. Open high-pressure valves on both the benzene and zero air bottles.

6. Open valve (14) and slowly open the regulator on the zero air cylinder to a pressure of 5-10 psi, observed on the calibration panel zero gas pressure gauge. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

7. Open valve (12) and slowly open the regulator on the benzene cylinder to a pressure of 5-10 psi on the pressure gauge on the benzene calibration gas channel of the panel. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

8. Open the bypass valve (2).

9. Open zero air valve (6) and slowly open the regulator to a final pressure of about 2 psi (as read on cell and exhaust pressure gauges). **DO NOT pressurize above 3 psi**.

10. Now pressurize cell: slowly open the valve going to the cell (valve 3) and close the bypass valve (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, just open the bypass valve (2) to relieve the pressure on the cell. Wait until the same pressure is reached on the pressure gauge of the exhaust side of the calibration panel.

11. Close the zero air valve (6) going to the benzene regulator on the panel so the system is now fully closed off to external pressure.

12. Watch the system for a minimum of 5 minutes to ensure there is no pressure drop and the system is leak free.

13. Open the leak check valve (1) to release the pressure from the system, and then close all the valves on both panels.

14. Record leak check.

15. Click the **ALIGN** button at the bottom left of the plot display.

16. Adjust the alignment until the signal intensity is optimized.

    a. **Target intensity is 70 – 90%.**

    b. **Target integration time is between 20 ms and 25 ms.**

17. **Record** the intensity and integration time.

7.7.6 Bump Test

This procedure was written assuming that the benzene and zero (purge) air side of the calibration panel has been pressurized according to the procedure above. At this point it is prudent to set up the instrument to start taking test measurements according to the UV-DOAS test procedure.

Background Measurement Using Zero (Purge) Gas

1. Close the secondary pressure regulator (4) on the panel by turning all the way to the left.

2. Open the leak check (1) and bypass valve (2)

3. Open Zero Air Valve (6)

4. Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

5. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, just open the bypass valve (2) to relieve the pressure on the cell. Wait until the desired flow rate has stayed the same and the pressure on the entire system has not increased.

6. Press **RUN** to start background acquisitions

7. Flow compressed zero air purge gas at total flow of 1 L/min for 10 30-second acquisitions.

8. Monitor until a stable zero reading is reached and then allow the analyzer to run until an acceptable background is reached.

9. Close the zero gas valve (6).

10. Close all valves.

11. Close the secondary pressure regulator (4) on the panel.

7.7.7 Span Test

1. Open the leak check (1) and bypass valve (2).

2. Open the benzene valve (5).

3. Adjust the flow of benzene going through the bypass and scrubber until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves (1) and (2)) is typically less than 1 psi.

4. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, just open the bypass valve (2) to relieve the pressure on the cell. Ensure the desired flow rate has stayed the same and adjust as needed.

5. Wait 5 minutes to fill and condition lines and cell.

6. After 5 minutes of Check Gas flow, press **Start** in CMS.

7. Collect Check Gas data.

    a. Observe the concentration reported on the **DATA** tab.

    b. After the concentration becomes stable, allow the analyzer **to run until 7 - 15 stable measurements are made.**

    c. **Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).**

7.7.8 Completion of Test and Purge of Benzene Regulator

1. Close the benzene cylinder. You will see benzene pressure increase and/or fluctuate as the pressure on the bottle regulator drops. This is normal - be patient and wait for the benzene pressure to zero out.

2. When pressure on cylinder and panel read zero, open the benzene purge valve (13)

3. **Verify that the target gas(es) concentration has returned to 0 ppm** with non-detect R2.

NOTE If not, ambient background target gas concentration has changed during the procedure; testing may need to be repeated to verify results.

4. Once zero reading is indicated on the UV-DOAS, close all valves.

5. Close the zero air cylinder and allow for all the pressure to be released from the system.

6. Close all valves and ensure there is zero pressure on the system.

7. Disconnect tubing to the analyzer and activated carbon scrubber.

7.7.9 Restore Normal Operation

1. **Restore** Normal Operation.

    Note: When restoring normal operation, you will change the file writing path in the settings menu back to the normal file writing path (this is slightly different for each unit, so make a note when first setting up the instrument for the QA test). Once you restart CMS, you will see the file number located on the UV main menu of CMS. If the file count restarts and starts at file 1, you have the incorrect file writing path because it is starting a new folder for the entire day. Also, once you restart CMS, look at the single beam graph also located on the CMS UV main menu to ensure a good alignment and intensity in the lower UV wavelengths.

2. **STOP** CMS.

3. Click **Advanced** on the left side of the CMS software window; password is *advanced*.

4. Under **Advanced** -> **Settings** -> **Runtime** -> **File**, turn On **Secondary Logging**. Change both of the primary file logging paths to: C:\Users\CMS-USER\Documents\Cerex\Data. Then select **File** and click **Save**.

5. Check the system alignment as previously described.

6. Press **RUN** to begin monitoring.

7.7.10 Test Suspension

In the event of a leak or plant alarm requiring suspension of work, the process should be safely suspended.

1. If a plant or site alarm sounds during the validation, stop the test immediately as follows.

2. Close the reference gas bottle valve completely.

3. Allow the system to flow purge gas to the scrubber/vent.

7.7.11 Data Evaluation, Reporting and Corrective Action

During these tests, a number (N) of replicated measurements (x_i) of a standard reference material of known magnitude (x_{std}) will be measured. Here, an acceptable number of trials will be defined as 7≤N≤15. The average value of these measurements is calculated as

$$\bar{x} = \frac{\sum_i x_i}{N} \tag{1}$$

and the sample standard deviation (σ) as:

$$\sigma = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{N-1}}. \tag{2}$$

From these definitions, % error is defined as:

$$\% \ error = \left| \frac{\bar{x} - x_{std}}{x_{std}} \right| \times 100\% \tag{3}$$

and precision as the coefficient of variation expressed as a percentage (% CV):

$$Precision \equiv \% \ CV = \frac{\sigma}{\bar{x}} \times 100\% \tag{4}$$

1. Concentration

   a. Average the concentration of 15 consecutive stable measurements.

   b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

      Note: To calculate the certified value that will be seen on the Cerex UV-DOAS from the actual certified instrument calibration gas concentration, you multiply the certified gas concentration by the calibration cell length (0.047 meters) and divide that answer by the path length set in the instrument software. For most Cerex instruments in operation by Sonoma Technology, the path length is set to 2 meters for monostatic instruments and 1 meter for bistatic instruments.

2. Calculate the Limits of Detection and Quantitation.

   a. Calculate the mean (average), sample standard deviation, and % error (sometimes also referred to as % difference) of the selected results.

   b. Report the Detection Limit as three times the standard deviation.

   c. Report the Quantitation Limit as five times the standard deviation.

3. Compile all configuration files, spectra files, and log files into a single folder.

   a. The folder should be named "CUS LOC QATest UV# YearMonDy" where CUS is a three-letter designator for the customer and LOC is a three-letter designator for the facility location.

The QAPP contains the acceptance criteria and warning levels to be used for the test.

Note:
- **If the test produces an error or precision greater than the warning level**: corrective action should be taken so that the precision and error are below the warning levels.

- **If the test produces an error or precision greater than the acceptance criteria**: corrective action should be taken so that the precision and error are below the warning levels. Equipment will not be placed into service (taken out of "maintenance mode") until it meets all measurement criteria.

If the measurements do not meet the data quality objectives listed in the QAPP, repeat the

procedure without adjustment. If the instrument still fails to meet the QA criteria, retest the following day with no adjustment. If these repeated tests continue to fail, initiate corrective actions such as:

- Reviewing data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features.

- Consulting with the project technical lead to identify abnormal changes to the background

- Check wavelength calibration

- Checking for large changes in stray light since the last test and adjusting calibration factors as necessary

- Reviewing gas testing apparatus for leaks or other similar problems

- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

In the event of a failed test after following all steps outlined above, inform the Sonoma Technology Project Manager and Quality Assurance Manager who will review the instrument performance parameters in the list above.

If all parameters indicate that the instrument was performing properly since the last test, data since the last test will be flagged as suspect. If an issue with the instrument is identified, data since the date and time of the instrument issue will be flagged as invalid. All data flagging will be performed by Data Analysts in consultation with the Quality Assurance Manager.

8. Data Validation and Quality Control

Data for the fenceline monitoring network appears on both public and internal sites. The internal website allows for detailed quality control and flagging of the data. Data are checked daily and finalized quarterly as outlined in the QAPP. This section outlines how to perform daily and quarterly data validation.

8.1 Daily Checks

Both the public website and the admin website need to be checked twice daily (for example, before 10 AM and 10 PM).

1. Ensure that the site is operating properly by pointing your browser to the public website.

2. View the data display on the public website. Take note of any outages by selecting **All Compounds**" from the pollutant dropdown menu.

3. View the time series graphs for each compound by selecting each compound in the pollutant dropdown menu. Verify that pollutant concentrations are reasonable by using the guidance in Table 2. Notify the field operations team if anything seems erroneous.

Table 2. Parameters measured with the UV-DOAS and typical observations.

Parameter	Observational Notes
Visibility	~30 miles is the maximum measured by the sensor. Values are typically less than 30 miles due to smog and fog.
Integration Time	Should generally be <250 ms. Report values stuck at 300 ms to PM and fieldopsalerts. Should be anticorrelated with visibility for fog events.
Winds	Typically there is a sea breeze during the day, land breeze at night. Winds are stronger near the coast at met west.
Benzene	Typically below MDL (~1 ppb) – note any high values above REL or immediately visible on the public website (this is a toxic compound
Toluene	Typically below MDL (~1 ppb) – note any high values above REL.
Ethylbenzene	Typically below MDL (~1 ppb) – note any high values above REL.
o-xylene	Typically below MDL (~1 ppb)– note any high values above REL.
m-xylene	Typically below MDL (~1 ppb) – note any high values above REL.
p-xylene	Typically below MDL (~1 ppb) – note any high values above REL.
SO_2	0 to 100 ppb, usually zero. Refineries are a local source – note any high values above REL.
NO_2	Typically 0 to 200 ppb. Values typically peak at night; sunlight destroys it, traffic and combustion produce it. Some instruments may not detect NO_2 if they are saturated.

8.2 Quarterly Validation

Quarterly validation activities involve looking at the data over a longer time period (3 months) than the daily checks (typically a time range of a few days).

1. Plot time series and look for statistical anomalies. If problems are found they may be flagged using the DMS.

2. Review any instrument bump test results.

3. Verify that daily instrument checks were acceptable.

4. Review manual changes to operations/data, and verify that the changes were logged and appropriately flagged; ensure that logged information is complete and understandable.

5. Ensure that instrument checks have the appropriate (Quality Control) QC codes applied.

6. Assign invalid data a Null Code, providing a reason for data being invalid.

7. If a record is not created for a particular site/date/time/parameter combination, create a null record for data completeness.

8. Inspect data consistency.

9. Review collected data ranges for consistency – ranges should remain within expected values over months of monitoring.

10. Check bump test values for completeness; ensure they meet acceptance criteria.

11. Review quarterly data completeness.

9. Maintenance Forms

Path:_____

Technician:_____

Date:_____

Instructions: complete checks described below and enter data or initial next to each one once complete. Make note of any corrective action.

❒ Notify the client and project manager of maintenance tasks.

❒ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.

❒ Confirm that the data is invalidated on the public website before proceeding with maintenance.

❒ When maintenance is complete check the public site <u>for at least 15 min</u> to ensure proper reporting (no missing data, no high values, etc.).

❒ Take out of maintenance mode

❒ Notify the project manager and client when maintenance is complete.

Upon completion sign and date:_____

Checklist of maintenance activities and performance indicator checks for the UV-DOAS.

Table 3. Maintenance activities and performance indicator checks for the UV-DOAS.

Activity / Check	Completed (Y/N)
Visually inspect the system.	
Inspect optics on detector and retroreflector; clean if necessary.	
Inspect system filters on the optics and retroreflectors.	
Confirm the alignment to verify there has not been significant physical movement. Note: this is automatically monitored as well.	
Download data from detector hard drive and delete old files to free space, if needed. Ensure data are backed up on external drive.	
Ensure there are no obstructions between the detector and the retroreflector (such as equipment, vegetation, vehicles).	
Change out the UV source.[a]	
Replace ventilation exit and intake filters.	
Clean optics on detector and retroreflector.	
Realign system after service.	
Perform bump test (simulates system-observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit.	
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency.	
Verify system software settings.	
Deliver previous years data to client and remove from brick and analyzer	

[a] UV bulbs will be changed depending on deep UV performance.

Corrective Actions for UV-DOAS:

UV Sentry Fenceline Detection System

DATE: _____   Location: _____

Test Technician 1:_____ 2:_____

Physical one-way path length_____ m   Instrument Configuration (mono/bistatic)_____

Sentry Alignment and Light Levels

Integration time   _____   Target 20-24 ms
300 nm Intensity   _____   Target 80-120%
254 nm Intensity   _____   Target >5%
Blocked Beam Intensity at 254 nm _____
% Stray Light   _____

Gas Purge System

Flow purge gas   Start Time _____

Prepare CMS

Path length in the CMS Configuration (typically 1 m for monostatic and 2 m for
bistatic)_____ m

Configure Test Files

Site File (i.e., QA Audit UV# YearMoDy)   _____
Baseline Check   _____ init

Reference Gas

Concentration   _____ ppm
Source   _____
Date   _____
Cylinder Pressure   _____

NOTES:

QA Audit Record - UV Sentry Detection System - Page 2

Purge Flow Conditions

    Start Time   _____

    Purge Gas flow   _____ L/min

    NOTES: Around 1 LPM

Check Gas Test

    Initial Gas flow   _____ L/min

                                          Around 1 LPM

    Start Time   _____

    Collect Check Gas Data Start Time   _____

    Data Record:

TIME	PPM	R2
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

    Verify Client   _____ Init

    Stop Time   _____ Init

    Open the **PURGE** gas   Time   _____

    Reference Concentration   _____ ppm

    Average Concentration   _____ ppm

    % error   _____ %

    Std Deviation   _____ ppm

    % CV   _____ ppm

Restore Normal Operation

    Restore running data file   _____ Init

    Press **RUN** to begin monitoring.   _____ Init

Appendix B. Standard Operating Procedures for the CEREX AirSentry FTIR

Appendix B

Standard Operating Procedures for the CEREX AirSentry FTIR

September 5, 2023   STI-7036

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Contents

1. Scope and Application

This SOP covers the use of the CEREX AirSentry FTIR analyzer in a fenceline monitoring application. This document addresses routine maintenance activities including visual inspections, instrument checks, data management, QA audit testing, and data validation.

2. Introduction and Overview

The Cerex AirSentry FTIR monitoring system utilizes Infrared light for gas detection. The system works by first generating IR radiation from an extremely hot Globar source. The light from the source is directed down the open path using a Cassegrain long-path telescope. When the light reaches the opposite end of the path it is reflected using a retroreflector array back to the telescope which then receives the light and sends it to the detector. The Infrared detection system is based on a Michelson Interferometer with a cooled Mercury Cadmium Telluride (MCT) or Deuterated TriGlycine Sulfate (DTGS) detector. A schematic of the Cerex AirSentry FTIR monitoring system is shown in **Figure 1.**
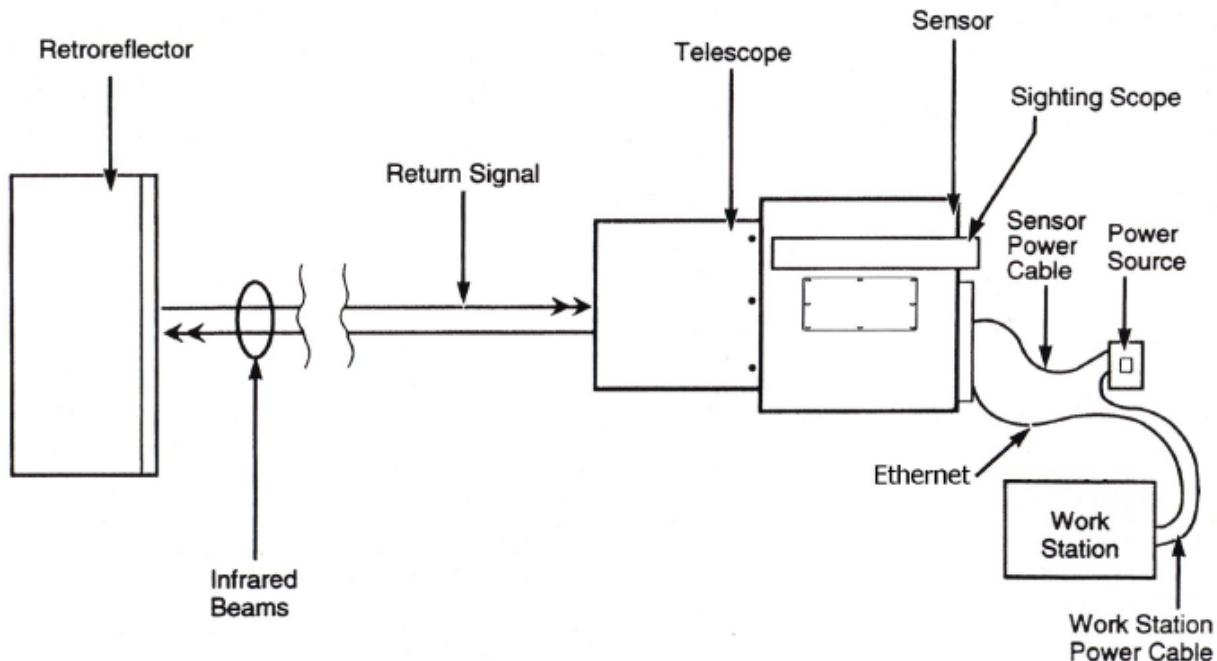
Figure 1. Schematic of the instrument.

The Michelson Interferometer includes the IR source and an optical assembly that includes both stationary and moving mirrors. While the light path defined by the stationary mirror is of fixed length, the light path defined by the moving mirror varies. The Interferometer creates an interference pattern by combining the light from the stationary and moving mirror, thus cancelling different wavelengths of the IR spectrum at different times during each scan of the moving mirror. Once the IR beam returns from the sample volume defined by the path of the IR beam in the air, it is focused onto a cooled MCT or DTGS detector, which converts the incident IR wavelengths into electrical currents at high speed. The MCT detector synchronized with the interferometer continuously scans the full range of the IR spectrum. The IR spectrum, or single beam, is produced by measuring the electrical currents at each given scan and applying a Fourier Transform to produce a graph of signal intensity versus wavelength.

The raw data goes through several transformations in the software. The final step occurs when the software compares the peaks produced in the field data, against quantitative library references of the target gases being analyzed. This allows identification and quantification of each specific gas. Since the calibration is inherent in the library references stored on the PC, there is no requirement for the AirSentry FTIR to undergo "calibration." There is no need to perform a recalibration on a periodic basis. However, as calibration verification is often a requirement in many applications, Cerex provides the (optional) provision to conduct a verification of the system.

3. Definitions

Table 1. List of definitions.

Term/Acronym	Definition
Beer's Law	A mathematical relationship that relates the attenuation of light to the concentration of a substance/material.
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes (Xylenes are composed of ortho, meta, and para isomers)
Bump Test	Also known as QA Audit, this is a test where gas of a known concentration is introduced to the analyzer to check for response accuracy (as %error) and precision.
CMS	Continuous Monitoring Software
Cryocooler	A device used to achieve cryogenic (very low) temperatures. A Stirling engine is commonly used to cool the FTIR detector.
FTIR	Fourier Transform Infrared Spectrometer/Spectroscopy
Infrared	Light that has wavelengths of 700 nm to 1 mm, or 14,000 to 10 cm^{-1}.
Interferometer	Device that uses the interference of light to measure the light "spectrum".
Intensity	A measure of how much light was collected.
MCT detector	A semiconductor detector made of mercury, cadmium, and telluride.
PC	Personal Computer
PPE	Personal Protective Equipment
QA	Quality Assurance
Retroreflector	A special array of "corner cube" mirrors that reflect light directly back to the source location. For FTIR, these are made using gold thin-film coatings.
Spectral Resolution	The ability of a measurement to resolve features in a spectrum. It is the smallest difference in wavelengths (or wavenumbers) that can be distinguished.
Spectroscopy	A technique that uses the absorption of light to detect and quantify the amount and properties of atoms and molecules.
Wavenumber	A common unit = 1/wavelength. It is the "spatial frequency" of the wave. This unit is commonly used in IR spectroscopy.

4. Safe Work and Hazard Identification

The following information should be noted when preparing work plans and permits for safe work practices.

Safe Operating Precautions

1. Ensure that a clear escape path is identified.

2. Standard site PPE is appropriate. If gloves are required, nitrile or latex should be used.

Operator Qualifications

Installing, operating, and servicing Cerex AirSentry FTIR analyzers should only be performed by personnel trained in the operation of the system components and familiar with the handling of gas delivery and testing equipment. This includes troubleshooting, cleaning, replacement of parts, IR light source installation, etc. Operator should be fully trained and experienced in the use of compressed gas cylinders, 1 and 2 stage regulators used in conjunction with the cylinders, flow controllers, and tubing connections. Operator should be experienced with the parameters of flow and pressure, and how these relate to compressed gas and its use with calibrating gas analysis equipment.

Safe Work and Hazardous Environment Operation

Work should conform with manufacturer guidance and site health and safety practices.

The Cerex Monitoring Solutions AirSentry Series Analyzers are not rated for safe operation in hazardous or explosive environments. Any use in an area that may contain flammable mixtures or highly corrosive vapors requires special preparation to ensure operator safety and safe operation of the equipment.

CAUTION – Laser Radiation. Risk of eye injury with prolonged direct exposure. CEREX FTIR Analyzers contain a Class 3B invisible laser radiation when the interferometer cover is removed. Do not remove the interferometer cover. Eye protection is recommended when working near the IR source.

Procedure Warnings

This QA Test procedure requires the handling of a pressurized isobutylene. Improper handling of materials or hardware may result in serious injury, destruction of property, or damage to the AirSentry FTIR. Only qualified individuals should attempt or perform analyzer quality assurance test activities. Cerex assumes no liability for the use or misuse of this guidance document, or for operator-performed QA Tests, Calibration, or Gas Handling activities. No claims are made by Cerex as to the compliance of this procedure with any regulations or engineering best practices. The operator is solely responsible for the safety of personnel and property.

NOTICE

Please check off the following steps before conducting maintenance. Doing so reduces the chance of false notifications to the public and clients.

❒ Notify the client and project manager of maintenance tasks.

❒ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.

❒ Confirm that the data is invalidated on the public website before proceeding with maintenance.

❒ When maintenance is complete check the public site <u>for at least 15 min</u> to ensure proper reporting (no missing data, no high values, etc.).

❒ Take out of maintenance mode.

❒ Notify the project manager and client when maintenance is complete.

5. Routine Operations

To set the FTIR instrument to acquire data for normal operations, the instrument CMS must be operating and the instrument must be aligned. These actions are detailed in the steps below.

1. Start the CMS software (if not already initiated). You should see a window similar to the one shown in **Figure 2**.
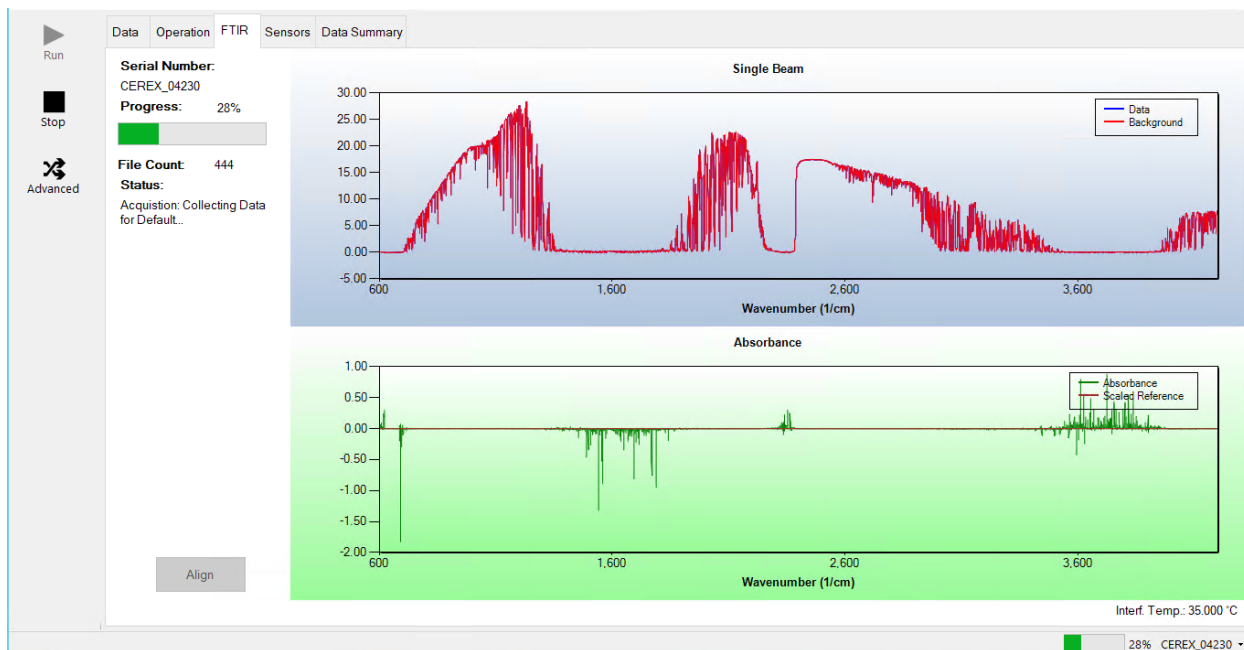
Figure 2. Screenshot showing the FTIR tab of the CMS software. Note that the Align and Run buttons are grayed out because the instrument is in run mode.

2. Under the **FTIR** tab, left-click on the **Align** button. This action brings up a new screen showing the instantaneous single beam plot (intensity versus wavelength). If the **Align** button is not active, you may need to press **Stop**. The **Align** mode is shown in **Figure 3**.
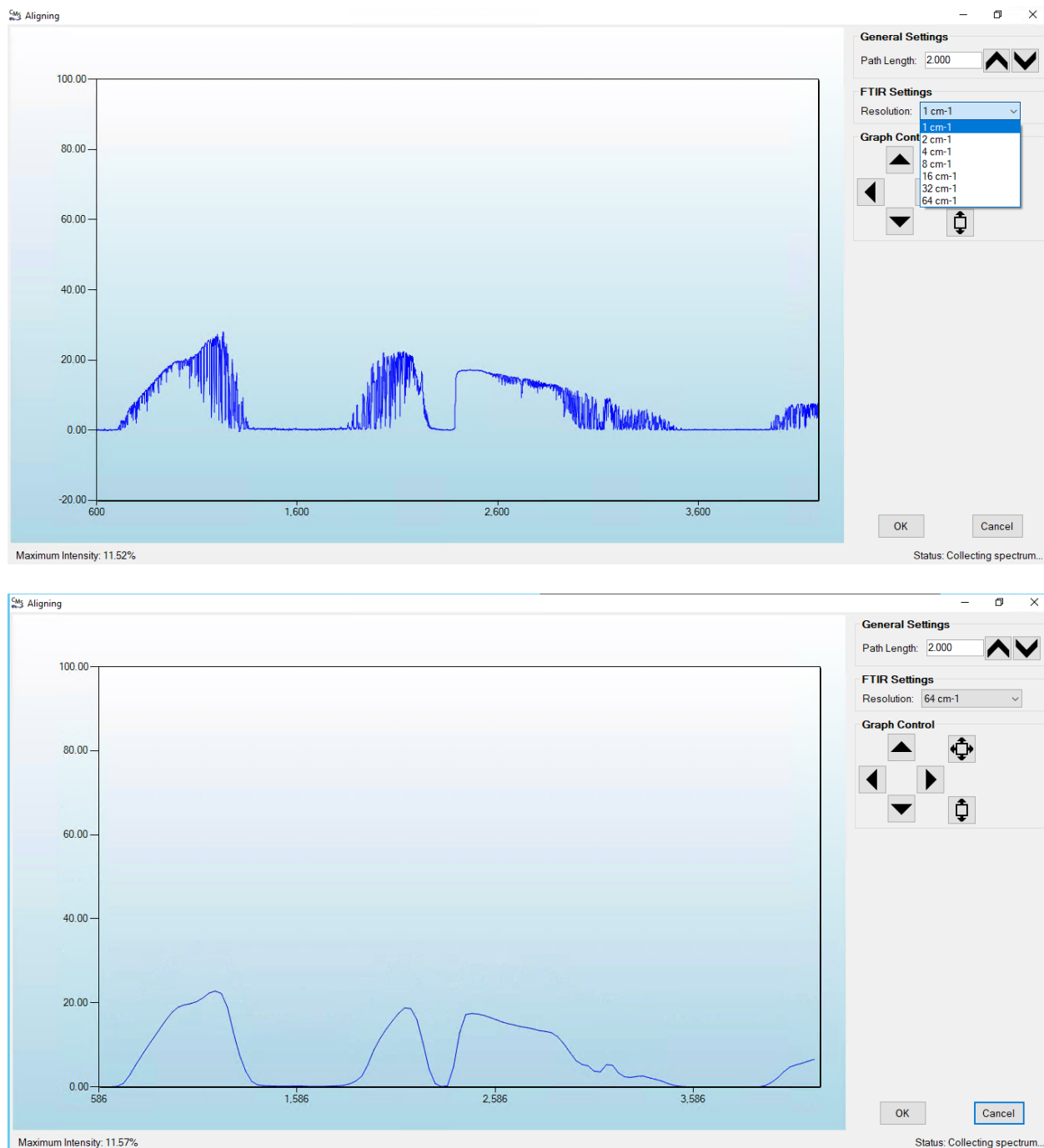
Figure 3. Screenshots of Align mode. The spectral resolution can be selected from the dropdown menu. In these particular screenshots, resolutions of 1 cm^{-1} (top) and 64 cm^{-1} (bottom) are selected.

3. Select a spectral resolution of 64 cm^{-1} and optimize the signal intensity by adjusting the pan-tilt head of the FTIR unit to adjust the position of the IR beam on the retroreflector.

4. Once sufficient alignment is obtained, exit the align mode by pressing **Cancel**.

5. Verify settings by left-clicking **Settings**.

Note: If you need to change any setting back to the original configuration, you must go to **File** and **Save**, then **Save As Default.** If you change settings, record why they were changed and what they were changed to in the instrument logbook. If settings are changed, they are automatically saved under the directory: C:\Users\CMS-USER\Documents\Cerex\CMS.

- RunTime
    - General
        - Operator Name: **Default** (these will change based on the path and site you are working on)
        - Sitename: **Cerex** (these will change based on the path and site you are working on)
        - Auto Run: **ON** (ON means the instrument will turn on automatically if the computer is running)
        - Auto Run Delay (s): **15** (time delay for CMS autostart)
    - File
        - File Type: **.CSV**
        - Primary Data Logging File: **ON**
            - C:\Users\CMS-USER\Documents\Cerex\Data (file path will vary by facility)
        - Secondary Data File Logging: **ON**

            - \\XXX\XXX\... (file path will vary by facility)
                - Note this path will change based on the computer and path you are working on. This is just a basic file writing path to show you what it should look like.
        - Single Data Folder: **OFF**
        - Primary Summary File Logging: **ON**
            - C:\Users\CMS-USER\Documents\Cerex\Data
        - Secondary Summary File Logging: **ON**
            - \\OPT1-PC1\VLOData\OPT1_Path1\UVSentry_POC1
                - Note this path will change based on the computer and path you are working on. This is just a basic file writing path to show you what it should look like.
        - Single Summary File: **OFF**
    - Library
        - Library File: C:\Users\CMS-USER\Documents\Cerex\Library\
    - UI
        - Sort Column: Compound Name
        - Data Summary Chart: **OFF**
        - Concentration Chart: **OFF**

- Password Protection Settings: **ON**
- Pump Control: **OFF**
- Status Control: **OFF**
- Testing Control: **OFF**

- Analysis
  - General
    - Moving Average Interval: **12**
    - Display Units: **PPM**
  - Concentration
    - Zero Readings on Non-Detect: **OFF** (zeros reading below threshold % match
    - Zero Readings on Negative concentrations: **OFF** (zeros reading less than zero)
    - Display BDL: **OFF**
    - Quick Analysis MDL Wave length Range: **276 -280** (not typically used)
    - Temperature/ Pressure Concentration: **OFF**
  - Filters
    - Absorbance Savitzky-Golay: **OFF**
    - Baseline Correction Savitzky-Golay: **OFF**
  - Background
    - Auto Background: **ON** (typically ON for fenceline monitoring projects reporting concentration above background)
    - Interval (Acquisitions): **5** (How far back the routine will search for a background)
    - Depth: **4**

- Instruments
  - FTIR
    - Operational;
      - FTIR: **ON** (sets instrument type)
      - Averages/Co-adds: **28** (how many spectra will be averaged together)
      - Path Length (m): **2** (2 for monostatic units)
      - Resolution: **1 cm-1** (spectral resolution)
    - Verification
      - Verification: **OFF** **(This inactivates all inputs)**
- Controller
  - General
    - Serial Port: **n/a**
    - Sensor Refresh Interval (s): **10**
  - Sensors
    - **Don't Touch Anything**
  - Alarms
    - **Don't Touch Anything**

- Email
  - General
    - Data Recipient: **Blank**
    - Email Sender: **Blank**
    - Email Period(s): **60 (doesn't matter the time we don't use this setting)**
    - Send Data: OFF
  - SMTP
    - Server: **smtp.gmail.com**
    - Port: **587**
    - Username: **Blank**
    - Password: **Blank**
    - Timeout (s): **100**
    - SSL Authentication: **ON**
- Auxiliary Coms
  - Modbus (these settings are specific to the data acquisition software used)
    - Modbus: ON
    - System Type: **Ethernet**
    - TCP Port: **502**
    - Unit ID: **2**
    - 16-bit unsigned int to: ON (does not greatly affect data)

6. After settings are verified and the instrument is aligned, you can place the instrument in run mode.

6. Equipment and Supplies

1. Field notebook

2. Tool kit, especially including: 7/64 hex driver, complete set of combination wrenches, adjustable wrenches, screwdrivers, etc.

3. Cleaning supplies designated to be safe for use on a Cerex FTIR

4. All relevant PPE, hardware, and procedural guidance per SOP, Safety Plan, and Safe Work Permit

5. Local or remote network link device (as required)

6. External laptop computer with network interface device to the Sentry unit (as required)

7. Cerex FTIR Sentry Unit equipped with CMS software

8. Isopropyl Alcohol (≥80%)

9. Distilled water

10. Pressurized sprayers

11. Powder-free nitrile gloves

12. Cell bump test apparatus (including panels, regulators, valves, meters, etc.)

13. Tubing as required: 1/4" metal jacketed PTFE tubing for gas supply from the bottle to the QA cell

14. Tubing as required: 3/8" metal jacketed PTFE tubing with inline flow indicator from the QA cell to the scrubber

15. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less

16. Gas scrubber appropriate for gas used. Activated carbon treated with phosphoric acid may be used for benzene

17. Reference standard traceable zero compressed air purge gas

18. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher

7. Maintenance Activities

The following sections outline the routine checks to be carried out for each analyzer and sensor, followed by maintenance forms (see Section 8) used to indicate when the checks are completed and document any corrective actions taken. These activities are also expected, based upon the project plan, to be logged in a site logbook either in hard or electronic form and can reference this SOP and associated forms.

The following FTIR maintenance activities and performance checks are recommended by the manufacturer:

- Visually inspect the system.

- Confirm the alignment to verify there has been no significant physical movement. Note: this is automatically monitored as well.

- Download data older than 6 months from detector hard drive and if needed delete old files to free space.

- Ensure there are no obstructions between the detector and the retro-reflector.

- Replace air conditioner fans.

- Change out the IR source.

- Realign system after service.

- Check system response (bump test). Take corrective action if % Error exceeds level specified in the QAPP.

- Review and test light and signal levels.

- Verify system settings.

- Perform Cryocooler Check. Replace Cooler or swap detector module assembly if necessary.

7.1 Monthly Visual Inspections

1. Ensure that the instrument is running and the data look reasonable.

2. Clean and correct any obvious problems with the system (cobwebs, rodent nests, broken optics, etc.).

3. Inspect all electrical cables for wear; replace as needed.

4. Indicate these visual checks are complete on the form included at the end of this document.

5. Document any changes to the system in the course of these checks in the site logbook.

7.2 Light Level Check

For good visibility conditions, signal strength is normally >5%. If it is determined that these values are out of range, re-alignment may be needed. Check and record signal strength as reported by the instrument in align mode. If the value is <2%, corrective action should be taken. Common instrumental problems resulting in low signal strength include retroreflector fouling, poor internal alignment, suboptimal software and electronic gain, low source intensity, and failing detector.

Check for Stray Light

Ensure there is sufficient intensity at 966 cm^{-1} compared to the stray light intensity. If there is more than 10 - 20% stray light, advanced optical cleaning, replacement, alignment, or a bulb change may be necessary. To measure stray light, put the instrument in align mode and block the beam from exiting the analyzer with an opaque object (such as a black cloth) and measure the intensity at the wavenumber range of interest (in this case 966 cm^{-1}). Calculate stray light by dividing the intensity of the beam while blocked by the intensity of the unblocked beam and multiplying by 100:

$$\%stray\ light = \frac{Intensity\ of\ blocked\ beam\ (\%)}{Intensity\ of\ unblocked\ beam (\%)} \times 100\%$$

Note: the result of this stray light calculation in the form at the end of this document. 7.3.1 Data Management

7.3 Data Management

7.3.1 Archiving and Deleting Older Data

Note: Data older than twelve months should be deleted from the instrument each month to prevent the instrument from filling its 125 GB internal hard drive.

Raw instrument data are stored on the analyzer computer, the site PC, and the hard drive attached to the site PC. Data consists of (aka "spectral data") spectral data containing two columns: one for wavelength and the other for intensity. There are also two types of "summary" files that contain data resulting from the classical least squares analysis of the spectral data as a function of time. These file formats are described in the CMS Software User Manual.[1] Spectral data and summary files are automatically written to the site PC and moved to the external hard drive after a regular interval. Deliver the external hard drive to Chevron on an annual basis. Data on the instrument must be deleted at monthly intervals. Details on the proper procedure for deleting data files from the instrument are as follows.

1. Confirm that the data files have been successfully written to the external hard drive attached to a separate PC also located in the instrument shelter.

2. Make a note of the amount of available space on the instrument internal drive on the maintenance form.

3. Locate files older than 12 months on the instrument file directory here: C:\Users\CMS-USER\Documents\Cerex\Data\.

   Note: This excludes the Bump Test folder, which should always remain on the instrument computer.

4. Log into the brick PC located in the instrument shelter and locate the data files written from the instrument onto the external hard drive.

5. Confirm all Complete Data Summary files and Simple Data Summary files for the desired month have transferred over completely to the external hard drive attached to the brick PC.

6. Once you have confirmed that those files have been transferred over to the external hard drive, delete those exact Complete Data Summary and Simple Data Summary files from the instrument data folders.

7. For each individual day of single beam folders, ensure that the amount of single beam files are the same on both the external hard drive located on the brick pc and the internal hard of the instrument.

8. If both folder locations match and you have ensured proper file download, you may permanently delete the Single Beam folders from the instrument computer.

9. After all data older than 12 months have been deleted, note how much free space is now available on the instrument's internal drive. If removal of the files does not result in enough free disk space, the disk drive may need to be reindexed (see Section 7.3.2).

7.3.2 Rebuilding the Instruments Indexing Preferences

If deleting data from the instrument does not increase available storage space on the instrument, you may need to reindex files. To rebuild the index preferences, follow these steps.

---

[1] CMS Software User Manual Rev 4. CMS Version 4.0.298.1, CEREX Monitoring Solutions, December 5, 2017.

1. Navigate to the **Control Panel Menu** by using the search function in the lower left-hand corner of the task bar.

2. Once in the control panel menu, click **Indexing Option.**

3. Click on the **Advanced** tab with the shield logo.

4. Click **Rebuild**.

Note: Once rebuild has been selected, a message saying that it might slow user activity will appear. This will not affect the instruments' ability to perform data collection. On the original indexing option screen, the magnifying glass in the upper right-hand corner will move and the number of items indexed will slowly increase. Take note of the available space on the instrument's internal drive once the indexing has been completed.

7.4 Clean Optics on Detector and Retroreflector

Cleaning the retroreflector is an important part of the maintenance plan. Over time the retroreflector will collect debris that can alter the performance of the instrument. Caution should be taken, as there are electrical fan heaters that are used to keep moisture and particulates from collecting on the retroreflectors.

7.4.1 Retroreflector Cleaning

1. Power down any equipment to prevent electrical shock or damage to the system.

2. Use a gentle stream of distilled water, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust build-up on the retroreflector.

3. Use a gentle stream of 80% isopropyl alcohol, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust build-up on the retroreflector.

4. Once the retroreflector has been cleaned and dried, repower the any electrical equipment you have powered down, and clean any spills you have created while cleaning.

7.4.2 Optic Cleaning

If light levels are low or visual inspection reveals soiled optics, cleaning optical surfaces can improve light throughput. This applies to the primary mirror, secondary mirror, and windows. In general, if the optic is not dirty, don't clean it. Excessive cleaning of optics can result in scratches and wear over time. If the optic is obviously soiled and is affecting performance, take the following steps. Mirrors with metallic coatings should be treated with extra care because these surfaces are easily damaged on contact.

1. Wear powder-free gloves to avoid transferring skin oils onto the optics.

2. Use compressed air/canned air to remove particles from the surface of the optic. If the optic is sufficiently clean after this step stop here.

3. Rinse the optic with a gentle stream of solvent. If using acetone, make sure to use acetone-impenetrable gloves.

7.4.3 Replace AC Fans

Two AC fans are necessary to control the temperatures inside the FTIR. The preventative maintenance procedure of replacing the AC fans every 2-3 years is needed to ensure proper operations and prevent critical components from being damaged due to high heat exposure.

1. Turn off MDAs and place unit into Planned Maintenance.

2. Close CMS, Shut down operating system.

3. Unplug power to unit.

4. Open FTIR lid.

    a. Note: (place barrier to prevent screws from falling into the FTIR assembly).

5. Remove shroud fan cover on the underside of the FTIR lid.

6. Make note of fan orientation before removal (i.e. front facing).

    a. Unplug each fan, then remove the four screws holding each fan for removal.

7. Install new fans with screws, then plug fans into power source.

8. Close FTIR lid.

9. Plug in the FTIR power source and begin operations.

10. Start CMS and align FTIR if needed.

7.5 Perform Bump Test and Attach Bump Check Form to This Document

This section addresses the commissioning and performance test procedure for Cerex Monitoring Solutions AirSentry units. The procedure is intended to verify that the equipment is performing to expectations, and that the detection and communication links are functioning correctly.

<div align="center">

***NOTE ***
THIS IS A WORKING DRAFT FOR INITIAL SYSTEM VALIDATION.
IT SHOULD BE REVIEWED FOR COMPLIANCE WITH LOCAL SAFETY AND QUALITY ASSURANCE PRACTICES.
This procedure should only be used by personnel with experience in the safe use of the analyzer and test equipment.

</div>

The purpose of the QA Test procedure is field verification of the factory calibration of the AirSentry. The QA Test process challenges the instrument using known concentrations of Hexane, Ammonia, and/or isobutylene to verify proper detection and quantification under field conditions.

7.5.1 Apparatus Setup

This procedure is to be carried out when using the Internal AirSentry FTIR QA Cell.

Verify system is set up (minus the instrument connections) as depicted in **Figure 4**.
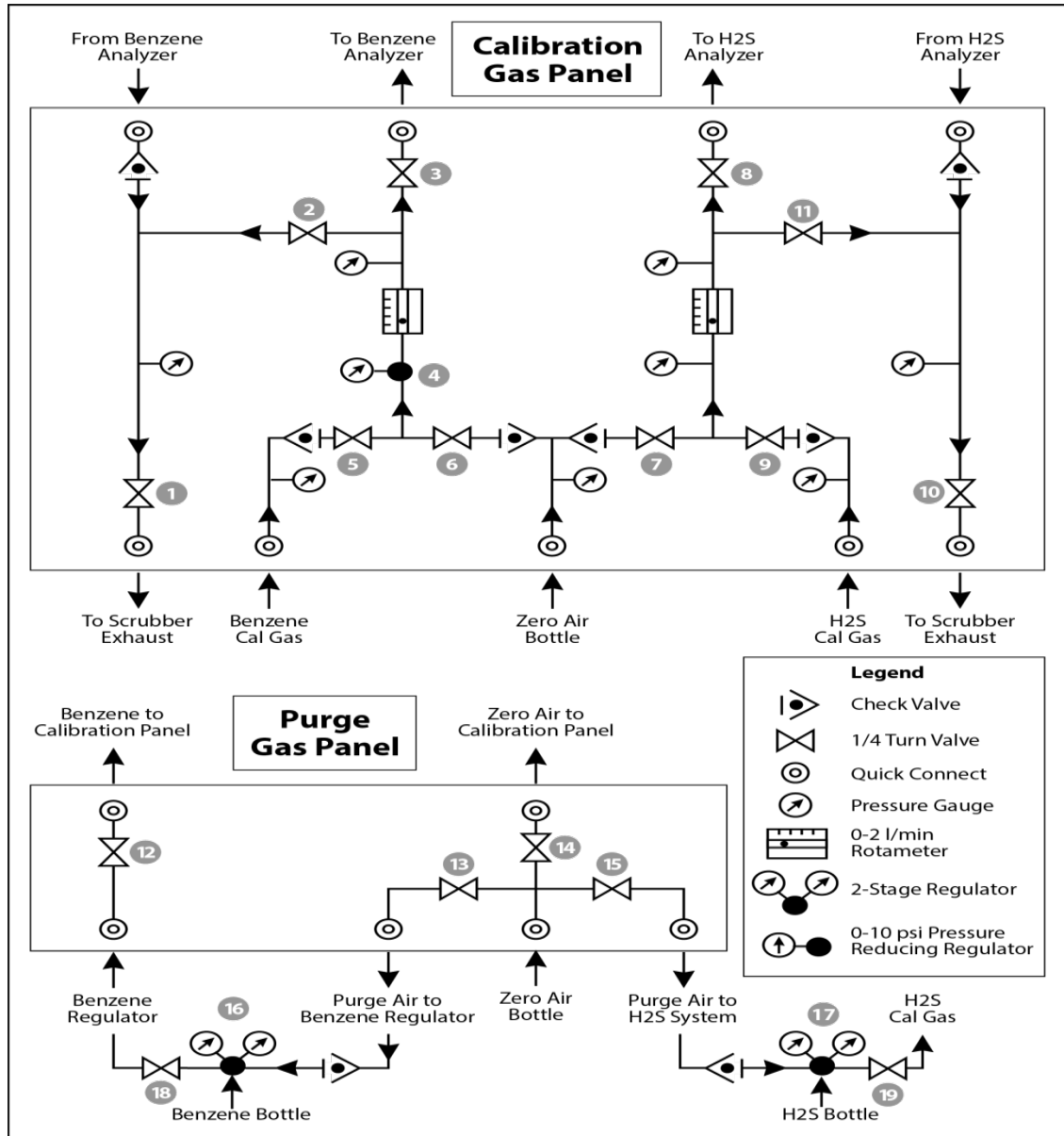

Figure 4. Diagram of the calibration gas panel (top) and purge gas panel (bottom) used for gas delivery. Note that the gas used will change depending on the instrument.

Materials Required

1. Operator-supplied Standard Operating Procedure approved by the End-User and in compliance with End-User's Health and Safety Plan.

2. Cell bump test purge apparatus, including:

    a. Tubing as required: 1/4" PTFE tubing for gas supply from the calibration gas panel to the QA cell.

    b. Tubing as required: 3/8" PTFE tubing for gas supply from the QA cell to the calibration gas panel.

    c. All necessary tubing for supplying calibration and zero reference gas to calibration gas panel.

    d. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less.

3. Purge gas; typically, Zero Air.

4. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher.

5. All relevant PPE, hardware and procedural guidance per SOP, Safety Plan, and Safe Work Permit.

6. Local or remote network link device (as required).

7. External laptop computer with network interface device to the AirSentry FTIR unit (as required).

7.5.2 Configure CMS for Test - (This may be concurrent with Gas Purge System setup)

1. The analyzer should be powered on and running for <u>at least 30 minutes prior to testing</u>.

2. Stop CMS data collection by pressing the **STOP** button.

7.5.3 Gas Test System Setup

1. Connect the ¼" reference cell line coming from the calibration panel to the ¼" reference cell connection on the Cerex MS Air Sentry FTIR.

2. Connect the 3/8" reference cell line coming from the calibration panel to the 3/8" reference cell connection on the Cerex MS Air Sentry FTIR located just below the ¼" refence cell inlet.

3. Ensure all valves on the calibration gas panel are in the closed position.

4. Make all necessary connections from Zero Air and calibration gas standard cylinders to the Gas Calibration Panel.

7.5.4 Verify Proper AirSentry Alignment

1. Open the CMS window.

2. Click on the **FTIR** tab.

3. If **Run** is active, press **STOP**.

4. Click the **ALIGN** button at the bottom left of the plot display.

5. Select 32 cm^{-1} and wait for resolution change.

6. Aim the AirSentry FTIR at the retroreflector and adjust the alignment until the signal intensity is optimized.

    a. **The target intensity should be the highest achievable intensity, which varies based on instrument, but should be above 5% at minimum. Once a stable signal is obtained, select the desired operating resolution (1 cm^{-1} is required unless otherwise directed by Cerex).**

7. **Record** the signal intensity.

    a. **Optional – at this point you may wish to record the current field pathlength and create a backup of the existing configuration file.**

8. Press **OK** and **SAVE** or **ACCEPT** (when prompted) to exit the CMS Alignment window.

7.5.5 Leak Check

1. Ensure that all tubing from the purging panel is connected to the calibration panel in the mobile van. Ensure gas cylinders are connected to the purge panel as depicted in Figure 4. Then attach the calibration panel to the analyzer connection in the analyzer shelter.

2. Connect the PTFE tubing containing the activated carbon scrubber to the analyzer exhaust.

3. Close all valves on the calibration and purging panel.

4. Verify that the regulators on the zero air and benzene cylinders are completely closed (**all the way to the left**!) to prevent any pressure buildup at the regulator.

5. Open high-pressure valves on both the calibration gas and zero air bottles.

6. Open valve (14) and slowly open the regulator on the zero-air cylinder to a pressure of 5-10 psi, observed on the calibration panel zero gas pressure gauge. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

7. Open valve (12) and slowly open the regulator on the calibration gas cylinder to a pressure of 5-10 psi on the pressure gauge on the benzene calibration gas channel of the panel. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

8. Open the bypass valve (2).

9. Open the zero-air valve (6) and slowly open the regulator (4) to a final pressure of about 2 psi (as read on cell and exhaust pressure gauges). **DO NOT pressurize above 3 psi**.

10. Now pressurize the cell. Slowly open the valve going to the cell (valve 3). Close the bypass valve (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve pressure on the cell. Wait until the same pressure is reached on the exhaust-side calibration panel pressure gauge.

11. Close the zero-air valve (6) going to the benzene regulator on the panel so the system is now fully closed off to external pressure.

12. Watch the system for a minimum of five minutes to ensure there is no drop in pressure and the system is leak free.

13. Open the leak check valve (1) to release the pressure from the system, and then close all the valves on both panels.

14. Record leak check.

7.5.6 Configure Test Files

1. Click **Advanced** on the left side of the CMS software window. The password is *advanced*.

2. Under **Advanced** -> **Settings** -> **Runtime -> File**, turn off **Secondary Logging**. Note current file logging paths.

3. Change both of the primary file logging paths to: C:\Users\CMS-USER\Documents\Cerex\Data\bumptest. Then select **File** and **Save**.

7.5.7 Gas System Purge

1. Close the secondary pressure regulator (4) on the panel by turning all the way to the left.

2. Open the leak check (1) and bypass valve (2).

3. Open the zero-air valve (6).

4. Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

5. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve the pressure on the cell. Wait until the desired flow rate has stayed the same and the pressure on the entire system has not increased.

6. Press **RUN** to start background acquisitions.

7. Allow the analyzer to complete **three** or more acquisitions.

   a. If after two acquisitions the absorbance graph shows negative features greater than 3X the peak-to-peak baseline noise level, take another clean air background.

8. Repeat this process until the sequential absorbance acquisition seen in the absorbance graph remains near zero (straight baseline with only normal noise peaks).

9. Once the instrument has performed ten or more acquisitions, close the zero-gas valve (6).

10. Close all valves.

11. Close the secondary pressure regulator (4) on the panel.

7.5.8 Gas Span and QA Test

1. Open the leak check (1) and the bypass valve (2).

2. Open the calibration gas valve (5).

3. Adjust the flow of calibration gas going through the bypass and scrubber until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

4. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve the pressure on the cell. Ensure the desired flow rate has stayed the same and adjust as needed.

5. Wait 10 minutes to fill and condition lines and cell.

6. After 10 minutes of calibration span gas flow, press **Start** in CMS.

7. Collect span gas data.

    a. Observe the concentration reported on the **DATA** tab.

    b. After the concentration becomes stable, allow the analyzer **to run until at least seven stable measurements are made.**

    c. **Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).**

    d. **Verify client system** is receiving and displaying instrument information correctly.

    e. After seven stable measurements are observed, **close the reference gas cylinder valve (6)**. Allow the pressure to fall to zero and the flow to stop.

7.5.9 Completion of Test and Purge of Instrument Calibration Cell

1. Close the calibration gas cylinder. You will see calibration gas pressure increase and/or fluctuate as the pressure on the bottle regulator drops. This is normal - be patient and wait for the benzene pressure to zero out.

2. Close all valves on the calibration and purging panel.

3. Open the zero-air valve (6).

4. Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

5. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve the pressure on the cell. Wait until the desired flow rate has stayed the same and the pressure on the entire system has not increased.

6. **Verify that the target gas(es) concentration has returned to 0 ppm** with non-detect R^2.

NOTE If the concentration has not returned to 0 ppm, this means ambient background target gas concentration has changed during the procedure and testing may need to be repeated to verify results.

7. Once a zero reading is indicated on the FTIR, close all valves.

8. Close the zero-air cylinder and allow all the pressure to be released from the system.

9. Close all valves and ensure there is zero pressure on the system.

10. Disconnect tubing to the analyzer and the activated carbon scrubber.

11. Remove the hoses and cap the connectors.

7.5.10 Restore Normal Operation

1. **Restore** Normal Operation.

   Note: When restoring normal operation, you will change the file storage path in the settings menu back to the normal file path (this is slightly different for each unit, so make a note when first setting up the instrument for the QA test). Once you restart CMS, you will see the file number located on the FTIR main menu of CMS. If the file count starts at file 1, you have the incorrect file writing path because it is starting a new folder for the entire day. If this happens:

   a. **STOP** CMS.

   b. Click **Advanced** on the left side of the CMS software window; password is *advanced*.

   c. Under **Advanced** -> **Settings** -> **Runtime** -> **File**, turn On **Secondary Logging**. Change the primary file logging paths (both of them) to: C:\Users\CMS-USER\Documents\Cerex\Data. Then select **File** and select **Save**.

2. **Check the system alignment** as previously described.

3. Press **RUN** to begin monitoring.

Test Suspension

In the event of a leak or plant alarm requiring suspension of work, the process should be safely suspended. If a plant or site alarm sounds during the validation, stop the test immediately as follows.

1. Close the reference gas bottle valve completely.

2. Allow the system to flow purge gas to the scrubber/vent.

7.5.11 Data Evaluation, Reporting, and Corrective Action

During these tests, a number (N) of replicated measurements (x_i) of a standard reference material of known magnitude (x_{std}) will be measured. Here, an acceptable number of trials will be defined as 7≤N≤15. The average value of these measurements is calculated as:

$$\bar{x} = \frac{\sum_i x_i}{N} \qquad (1)$$

and the sample standard deviation (σ) as:

$$\sigma = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{N-1}}. \qquad (2)$$

From these definitions, % error (accuracy) is defined as:

$$\% \; error = \left| \frac{\bar{x} - x_{std}}{x_{std}} \right| \times 100\% \qquad (3)$$

and precision as the coefficient of variation expressed as a percentage (% CV):

$$Precision \equiv \% \; CV = \frac{\sigma}{\bar{x}} \times 100\% \qquad (4)$$

1. Concentration

   a. Average the concentration of 7 - 15 consecutive stable measurements.

   b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

      Note: To calculate the certified value that will be seen on the Cerex instrument from the actual certified instrument calibration gas concentration, multiply the certified gas concentration by the calibration cell length (0.047 meters), and divide that answer by the path length set in the instrument software. For most Cerex instruments in operation by Sonoma Technology, the path length is set to 2 meters for monostatic instruments and 1 meter for bistatic instruments.

2. Calculate the Limits of Detection and Quantitation

   a. Calculate the mean (average), sample standard deviation, and %error (sometimes also referred to as % difference) of the selected results.

   b. Report the Detection Limit as three times the standard deviation.

   c. Report the Quantitation Limit as five times the standard deviation.

3. Compile all configuration files, spectra files, and log files into a single folder.

   a. The folder should be named "CUS LOC QATest IR# YearMoDy" where CUS is a three-letter designator for the customer, and LOC is a three-letter designator for the facility location.

The QAPP contains the acceptance criteria and warning levels to be used for the test.

Note:

- **If the test produces an error or precision greater than the warning level:** corrective action should be taken so that the precision and error are below the warning levels.

- **If the test produces an error or precision greater than the acceptance criteria:** corrective action should be taken so that the precision and error are below the warning levels. Equipment will not be placed into service until it meets all measurement criteria.

If the measurements do not meet the data quality objectives listed in the QAPP, repeat the procedure without adjustment. If the instrument still fails to meet the QA criteria, retest the following day with no adjustment. If these repeated tests continue to fail, initiate corrective actions, such as:

- Reviewing data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features

- Consulting with the project technical lead to identify abnormal changes to the background

- Check wavelength calibration

- Checking for large changes in stray light since the last test and adjusting calibration factors as necessary

- Reviewing gas testing apparatus for leaks or other similar problems

- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

In the event of a failed test after following all steps outlined above, inform the Sonoma Technology Project Manager and Quality Assurance Manager who will review the instrument performance parameters in the list above.

If all parameters indicate that the instrument was performing properly since the last test, data since the last test will be flagged as suspect. If an issue with the instrument is identified, data since the date and time of the instrument issue will be flagged as invalid. All data flagging will be performed by Data Analysts in consultation with the Quality Assurance Manager.

7.6 Cryocooler Replacement and Calibration

1. Remove Cryocooler
    a. Turn off the power to the instrument. Please follow the proper shutdown procedure.

b. Unplug the power connector (two-pin Molex with gray cable) from the cryocooler engine (**Figure 5**).
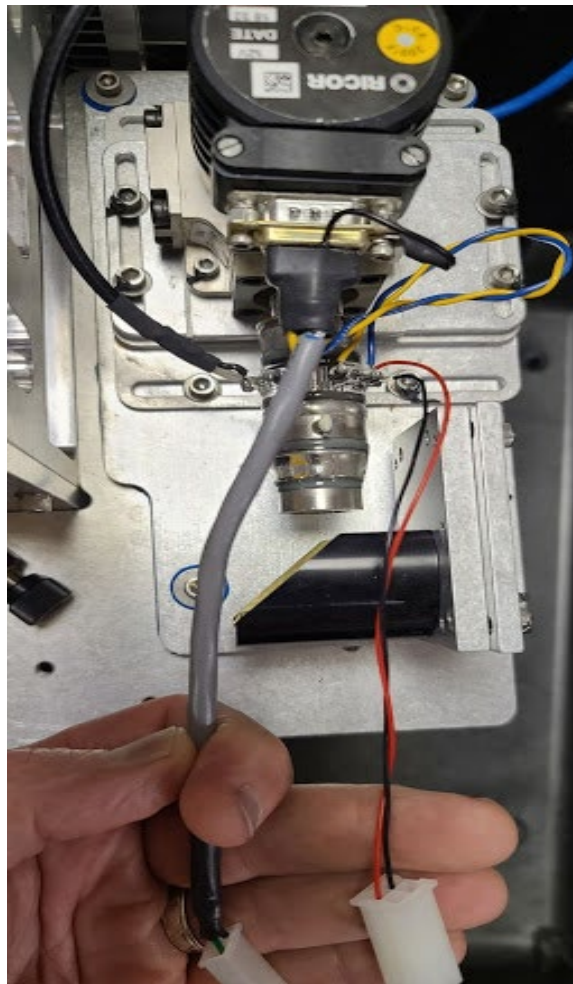

Figure 5. Detector assembly showing RICOR cryocooler, glass detector, DB9 connector, two white Molex connectors, and mirror.

c. Unplug the black and red cable molex connector coming from the glass detector assembly.

d. In some installations there is a ground cable coming from connector and going to the chassis. Remove the ground cable by unscrewing it from the chassis.

e. Take out the 3 #8 screws that hold the detector assembly to the baseplate - these will have blue grommets in the holes (See image below). Only remove 3 screws to release the entire assembly (**Figure 6**).

Figure 6. Image showing baseplate and screws with rubber grommets.

f.   Follow the black coax connector to the small "Preamp" box - silver in color. This is held to the baseplate with 2 screws (**Figure 7**).

Figure 7. Preamp assembly (with orange, black and purple wires) between the heatsink (left) and interferometer (right).

g. Disconnect power to the preamp - this is a 4-pin molex connector that can be pulled apart. The connector has purple, orange, and black wires.

h. Follow the second black coax cable from the preamp over the 4" x 6" heatsink assembly. Remove the BNC connection to this heatsink by hand twisting 1/4 turn counterclockwise and pulling it off.

i. The detector assembly and the preamp will come out together as they are attached to each other by a coax cable.

j. Pack the detector assembly and the preamp in the same box. But wrap both items separately so they can not touch. Immobilize all items in the box. Use protective case to transport entire assembly securely.

2. Re-install cryocooler

    a. The installation process is the opposite of removal.

    b. Make sure all screws and connectors are secured and tightened.

3. Optics Calibration

    a. After replacing or installing a new detector and optics optimization is required using a small test retroreflector array.

        i. Place the test retroreflector array about 2 feet from the front of the FTIR scope. Alternatively, use a small "bike reflector" in the outgoing beam path, just before the light enters the bump test cell.

        ii. With the instrument powered on and using the Align window, set the resolution to 64 ms and align the scope to obtain the maximum signal strength possible.

        iii. Open the instrument and carefully use the beam splitter adjustment screws to maximize signal strength. This means making small adjustments to each screw until you reach the maximum signal strength (Figure 8).
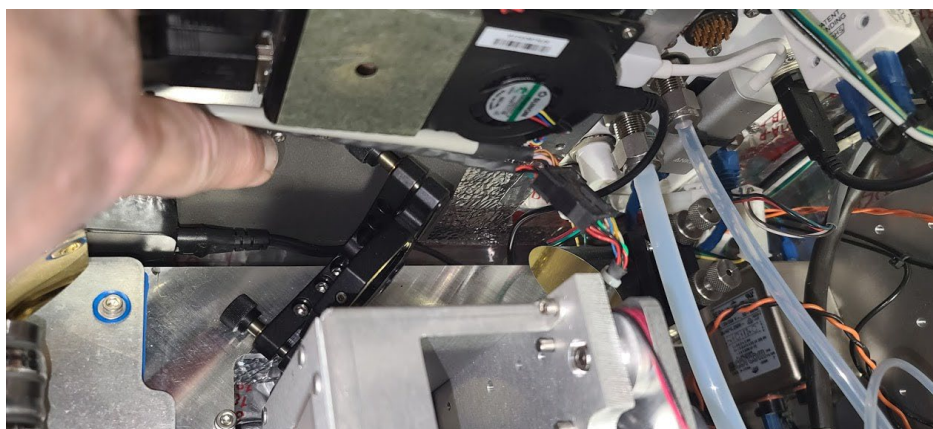

Figure 8. Beamsplitter (black object at 45-degree angle) with adjustment screws.

Repeat the same steps with the beam steering mirror. Keep in mind that the secondary mirror has two lower thumb screw nuts that lock the adjustment in place. You will have to unscrew those nuts before making any adjustments. Tighten the nuts once you have reached the desired adjustment. The beam splitter and the beam steering mirror work in tandem, so you may have to go back and forth between the two to optimize the signal strength (Figure 9).
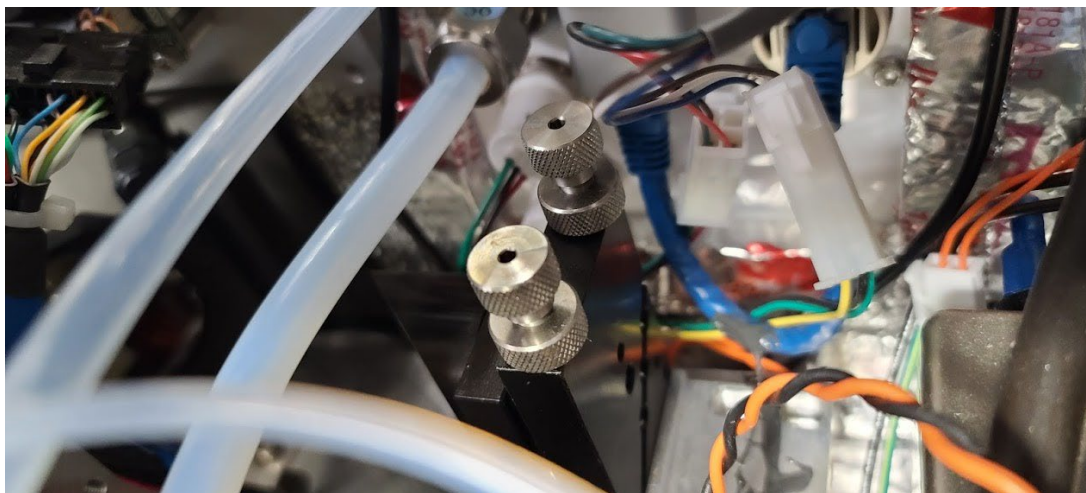
Figure 9. Beam steering mirror with sliver adjustment screws.

8. Monthly Maintenance Forms

Path:_____

Technician:_____

Date:_____

Instructions: complete checks described below, and enter data or initial next to each one once complete. Make note of any corrective action.

Please check off the following steps before conducting maintenance. Doing so reduces the chances of false notifications to the public and clients.

✕ Notify the client and project manager of maintenance tasks.

✕ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.

✕ Confirm that the data is invalidated on the public website before proceeding with maintenance.

✕ When maintenance is complete check the public site <u>for at least 15 min</u> to ensure proper reporting (no missing data, no high values, etc.).

✕ Take out of maintenance mode.

✕ Notify the project manager and client when maintenance is complete.

Upon completion, sign and date:_____

Table 2. Maintenance activities and performance indicator checks for the FTIR.

Activity	Completed (Y/N)
Visually inspect the system (an evolving checklist will be maintained).	
Current source service hours.	
Check light levels	
Confirm the alignment to verify there has not been significant physical movement. This is also automatically monitored.	
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, or vehicles).	
Move data older than 1 week old into an archive folder & note location.	
Ensure data are backed up on external drive. Delete files older than 12 months from the instrument computer.	
Realign instrument.	
Perform bump test. Analyzer should be with 25% of target value.	
Check system performance indicators.	
Inspect and clean optics on detector.	
Verify system settings.	
Inspect air conditioner heat sinks and clean, if necessary.	
Inspect and clean AC system interior heat sink.	
Review and test light and signal levels.	
Check average light intensity to establish baseline for IR Source.	
Change frequency and retro-reflector wear.	
Replace Cryocooler.	
Change out the IR source.	

Corrective Actions for FTIR:

Cerex FTIR Air Sentry Gas Test Summary

DATE: _____   Location: _____

Test Technician 1:_____ 2:_____

Sentry Alignment

Signal Intensity (average)   _____

Signal Intensity at 966 cm^{-1} _____

Blocked Beam Intensity at 966 cm^{-1} _____

% Stray Light   _____

Gas Purge System

Flow purge Start Time _____

Prepare CMS

Path length in the CMS Configuration   _____ m

Configure Test Files

Site File (i.e., QA Audit UV# YearMoDy) _____

Baseline Check   _____ init

Reference Gas

Concentration   _____ ppm

Source   _____

Date   _____

NOTES:

Gas Test Summary – Cerex FTIR - Page 2

Purge Flow Conditions

Start Time   _____

NOTES:

Check Gas Test

Initial Gas Flow   _____ L/min

Start Time   _____

Collect Check Gas Data Start Time   _____

Data Record:

TIME	PPM	R2
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Verify Client   _____ Init

Stop Time   _____ Init

Open the PURGE Gas   Time   _____

Reference Concentration   _____ ppm

Average Concentration   _____ ppm

% error   _____ %

% Spectral Match   _____ %

Standard Deviation   _____ ppm

Estimated MDL (3X Standard Dev)   _____ ppm

Restore Normal Operation

Restore running data file   _____ Init

Press **RUN** to begin monitoring.   _____ Init

Appendix C. Unisearch LasIR Tunable Diode Laser System (TDLAS) Maintenance and Audit Procedure

Appendix C

Unisearch LasIR Tunable Diode Laser System (TDLAS)
Maintenance and Audit Procedure

September 5, 2023   STI-7801
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Contents

1.   Summary

This document addresses the maintenance, commissioning, and performance audit procedure for Unisearch Tunable Diode Laser System (TDLAS) open-path analyzers. The document describes maintenance procedures that enable technicians to verify that equipment is performing to expectations and detection and communication links are functioning correctly.

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***NOTE ***

THIS IS A WORKING DRAFT FOR INITIAL SYSTEM VALIDATION.
IT SHOULD BE REVIEWED FOR COMPLIANCE WITH LOCAL SAFETY AND QUALITY ASSURANCE PRACTICES.

This procedure should only be used by personnel with experience in the safe use of the analyzer and test equipment.

</div>

A number of these maintenance procedures closely follow the manuals provided by Unisearch.[1] Field staff should obtain access to and read these. The Quality Assurance (QA) Audit procedure ensures field verification and calibration of the TDLAS by challenging the instrument with a known concentration of hydrogen sulfide (H_2S) and verifying proper detection and quantification under field conditions.

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[1] Unisearch Associates: A. Preinstallation Manual, B. Installation Manual, C. Networking Manual, D. Remote Sensing Optics Manual, E. Operations Manual, H. Troubleshooting Manual, I. Laser Safety Manual, J. Maintenance Manual, LasIRView 2015 Manual, 2018.

2.   Safe Work and Hazard Identification

The following information should be noted when preparing work plans and permits for safe work practices.

2.1   Laser Safety
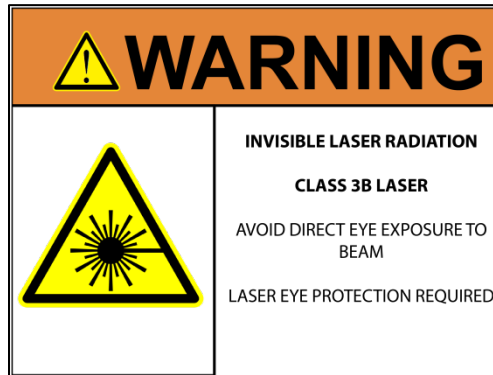
The Unisearch TDLAS produces a class IIIB LASER EMISSION that is INVISIBLE. The laser can cause eye damage if the laser is viewed directly. Unisearch recommends the use of safety procedures consistent with Class II and IIIA lasers. **PROTECTIVE EYEWEAR SHOULD BE WORN WHEN WORKING WITH THE SYSTEM**. Always avoid looking directly into any part of the instrument that can produce laser light, including the transceiver head. Make sure to read the laser safety manual and all other manuals provided with the Unisearch TDLAS instrument.

2.2   Operator Qualifications

Installing, operating, and servicing Unisearch analyzers should only be performed by personnel who are trained in the operation of the system components and are familiar with handling gas delivery and testing equipment. These procedures should not be performed by personnel who do not understand the system, technology, or hazards of the materials involved.

2.3   Safe Work and Hazardous Environment Operation

Work should conform to manufacturer guidance and site health and safety practices.

The Unisearch TDLAS are not rated for safe operation in hazardous or explosive environments. Using the TDLAS in an area that may contain flammable mixtures or highly corrosive vapors requires special preparation to ensure human safety and safe operation of the equipment.

WARNING – Toxic Gas and Eye Hazard. H_2S is a highly toxic gas that can cause death and other adverse health effects at concentrations above 100 ppm. This procedure requires the use of concentrations as high as 750 ppm H_2S for the span check. This procedure must be conducted in a well-ventilated area and requires gas monitors, respirators, and the use of fume scrubbers. Make sure you and others fully understand the safety procedures and gas-handling systems required. Always wear proper eye protection having OD>4 above 900 nm. Improper handling of materials or hardware may result in death, serious injury, destruction of property, or damage to the TDLAS. Only qualified individuals should perform analyzer quality assurance audit activities.

3. Overview and Operating Principle

The Unisearch LasIR open-path H_2S monitoring system (**Figure 1**) is a monostatic open-path remote sensor that uses direct absorption technique. The LasIR sensor consists of an analyzer, transmitter/receiver and retro-reflector array. The tunable infrared (IR) laser for the LasIR system is housed in the analyzer box and scanned over a small range of wavelengths at high frequency. The laser light is guided to the transmitter/receiver telescope via fiber optic cable where it is collimated and sent across the atmospheric path. The retroreflector array at the other end of the path returns the signal to the off-axis parabolic mirror that focuses the light onto a photodiode detector. The electrical signal from the photodiode detector is amplified and returned to the analyzer box where the absorption spectrum is analyzed to produce concentration data.

Classical least squares fitting of the absorption spectrum allows elucidation of low-H_2S concentrations by simultaneously accounting for overlapping water (H_2O) and carbon dioxide (CO_2) absorbance bands. As a result, concentration data for H_2S, H_2O, and CO_2 are provided with correlation coefficients that indicate the "goodness of fit."

The purpose of this procedure is to check the system for expected H_2S response under the installed operating conditions. H_2S standard reference gas is introduced into the optical path by means of a flow-through or sealed cell, meaning the entire sample path is included at the time of testing.
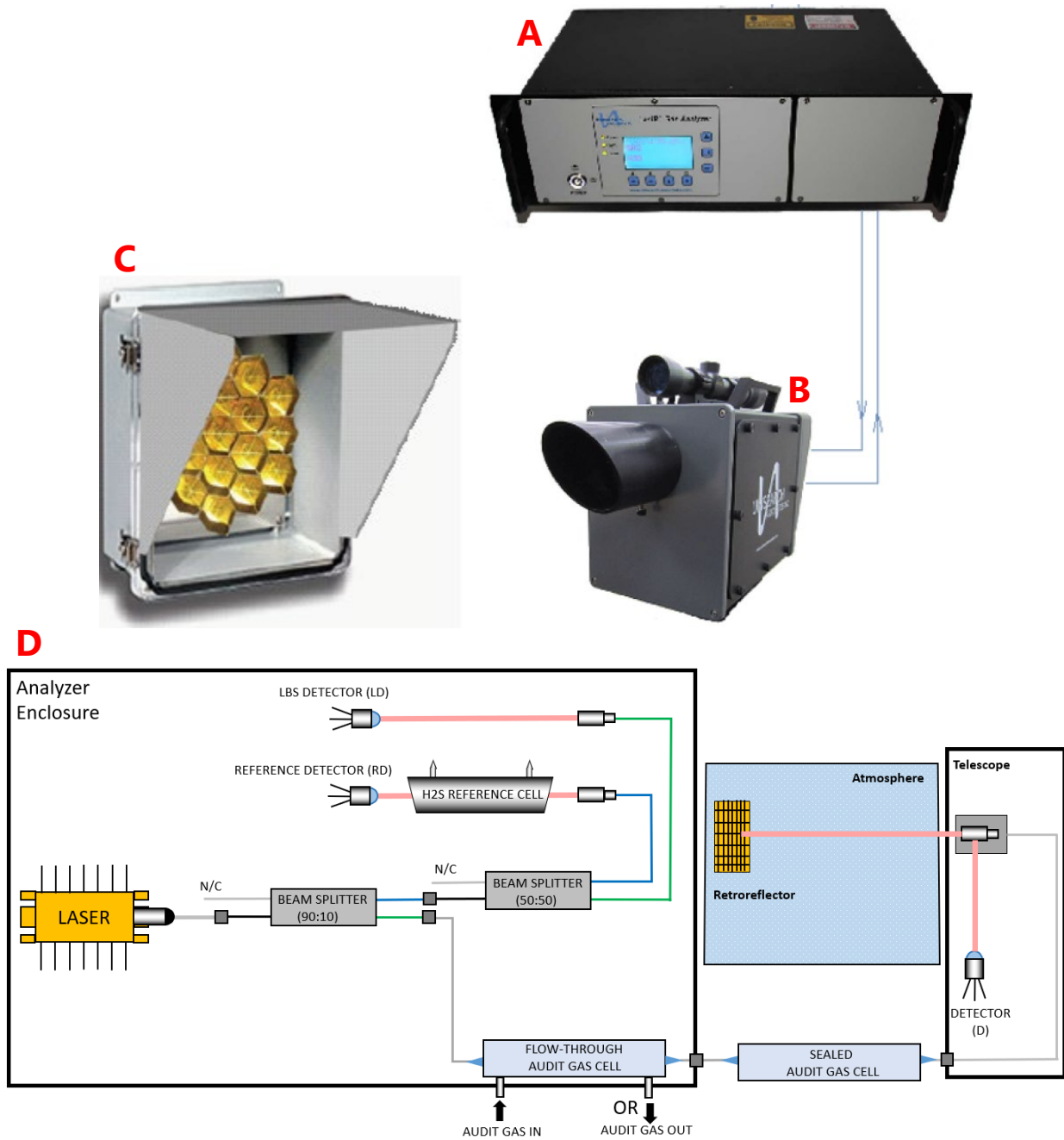
Figure 1. (a) Unisearch TDLAS Analyzer box, (b) telescope, (c) retroreflector, and (d) schematic diagram showing the optical fiber paths and detection points.

3.1　Safety

3.1.1　*Exposure Control*

H_2S is a colorless gas that has an odor of rotten eggs. It is hazardous at low concentrations (Immediately dangerous to life or health [IDLH] is 100 ppm, National Institute for Occupational Safety & Health [NIOSH] 10-min Reference Exposure Level [REL] is 10 ppm, California Office of Environmental Health Hazard Assessment [OEHHA] 1-hr REL is 30 ppb). The odor is not a reliable indicator of the presence of hazardous concentrations of H_2S, because olfactory senses may be deadened by exposure to concentrations below safe exposure levels. A system for scrubbing H_2S gas from a test apparatus vent is used to prevent release and worker exposure.

This procedure has been written to limit exposure potential and mitigate the hazards of accidental release of the reference gas. Only personnel experienced with handling this material who are familiar with the test procedures and apparatus should perform these testing procedures.

3.1.2　*Personal Protection*

Standard refinery personal protective equipment (PPE) should be worn at all times, including laser safety glasses with side shields, a hard hat, goggles, steel-toed boots, hearing protection, fire-retardant clothing (FRC), an H_2S monitor, and appropriate gloves that are adequate for this procedure. For testing with the flow-through cell using H_2S concentrations in excess of 100 ppm, a second person should always be present as a safety monitor. H_2S levels should be monitored inside the enclosure. Two self-contained breathing apparatuses should be on standby.

4.　Routine Maintenance

The TDLAS system is designed to require only modest service and maintenance. Table 1 summarizes TDLAS maintenance activities, as recommended by the manufacturer. The frequency of activities may vary from site to site, so always check the QAPP for facility-specific maintenance schedules and acceptance criteria.

Table 1. List of maintenance activities and performance indicator checks for the TDLAS.

Activity	Section(s)
Visually inspect the system. Inspect electrical and optical cables for wear.	4.1
Inspect optics and clean if necessary	4.2, 4.3
Check the alignment to verify there has not been significant physical movement; note that this is automatically monitored as well	4.4
Download data from detector hard drive and delete old files to free space, if needed	4.5
Ensure there are no obstructions in the beam path	4.6
Review and test light and signal levels	4.6
Verify system settings	4.7
Perform bump test and take corrective action as needed	5.2 (flow-through) 6.1 (sealed cell)
3-point calibration check	6.2

4.1 Visual Inspection

During visual inspection of the analyzer, note and clean any excessive dust buildup on the equipment or analyzers. Eliminate any pests from the sample site, including birds, spiders, rodents, etc. Note the condition of the analyzer cabinet internals. Inspect wiring and note and correct any corrosion or cracking insulation.

In summary, ensure you correct and note the following: HVAC operation, corrosion, condensation, door operation, excessive dust, rodents/pests, and anything that may result in eventual degradation of the LasIR system.

4.2 Cleaning the Transmitter/Receiver Optics

Only the front surface of the window on the telescope assembly may need to be cleaned on a monthly basis. Use a clean cloth to lightly wipe the front surface of the window. Normal lens cleaner solution can be used if necessary, but dust can usually be wiped away with a dry cloth. Be careful not to scratch the window surface by pressing too hard. The shroud protecting the window from the elements may be removed for this purpose. If necessary, loosen the locking screw on the bottom of the shroud and pull the shroud away from the window housing. On telescopes designed for permanent installation, a "purge air" port is provided so that clean, dry air may be flushed over the window to help minimize any dust build-up or condensation.

If the inside of the window gets dirty, it is best to remove the window from the housing and clean it rather than open the telescope side covers, as access from these points is limited. You may either remove the shroud and unscrew the locking ring that holds the window in place or remove the entire front cover by loosening the four screws in the corners. In either case be careful to keep the O-ring seals properly seated. Improper seating may result in leaks if rain falls on the telescope, which could possibly damage sensitive electronic components inside.

4.3   Cleaning Retroreflector Array

Only the front surface of the acrylic protective window for the retro-reflector needs to be cleaned on a monthly basis. Use a clean cloth to lightly wipe the front surface of the window. A lens cleaner solution can be used if necessary, but dust can usually be wiped away with a dry cloth. Be careful not to scratch the window surface by pressing too hard. If, for some reason, the inside of the window gets dirty, this can be cleaned by opening the enclosure front cover. Reflector elements may also be cleaned if necessary, but this should be done with extreme care to prevent damage to their gold-coated surfaces.

4.4   Optical Alignment

Adjust the vertical and horizontal adjustment knobs to maximize the power as reported on the OPM-15 power meter. Lock the adjustment knobs (**Figure 2**) in place. Once aligned, it should be possible to push on the telescope top and side without disturbing the alignment. The spot size at the retro-reflector should be 2-3 times the diameter of the retro-reflector for this to be true. It may be necessary to adjust the collimator to obtain the best beam size and return power. If the beam is smaller than this, variation in the power will be observed, which may affect the alignment over time due to flexing of the mounting structure. When the vertical alignment is correct, tighten the locking thumbscrew. For the horizontal sweep, loosen the 5/8" locking nut located underneath the mount base and use the thumbscrew on the right hand side of the mount base (looking from the back) to adjust the horizontal position. When adjustment is complete, tighten the locking nut. Slight adjustment of the vertical alignment may be required after tightening the horizontal alignment-locking nut as this tightens the rear end of the telescope to the mount, which affects the tilt.
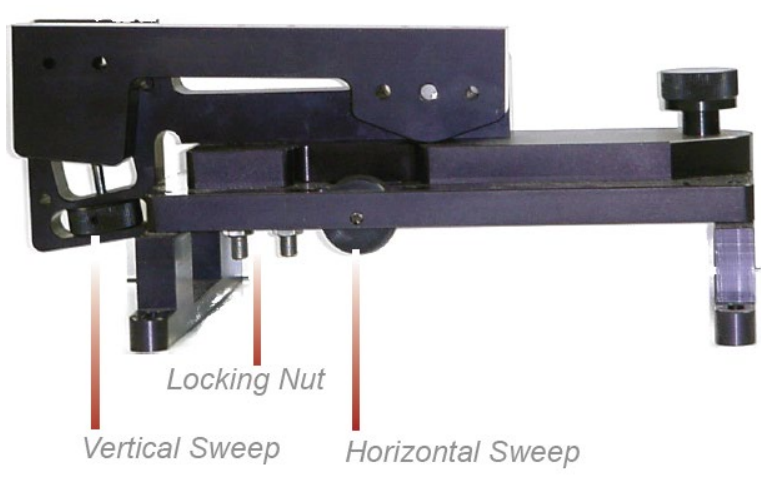
Figure 2. Location of adjustment knobs used for alignment of the Unisearch TDLAS.

4.5 Data Management

Under normal operations, the LasIR system works together with a separate program called the TASDAcc to acquire and process raw TDL data, and reports 5-min data to the Sonoma Technology-operated data system. The TASDAcc software is developed and maintained by Terra Applied Systems (TAS), the integrator of the Unisearch TDL. As depicted in **Figure 3**, the LasIR, TASDAcc, and the cellular modem are all connected through a network switch, which is located in the same cabinet as the Unisearch analyzer box. The TASDAcc software handles three main data types: (1) raw data tables from the LasIR Analyzer, (2) spectral data from the LasIR Analyzer, and (3) 5-min data for ingestion to the Sonoma Technology data system and display on the public-facing website.
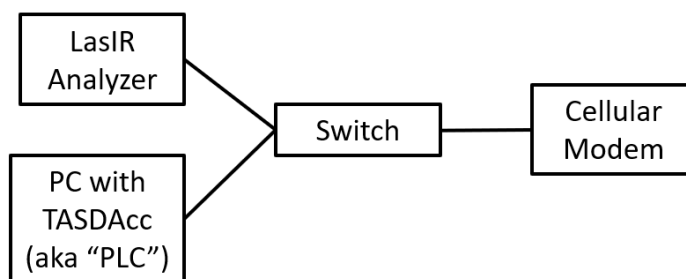

Figure 3. Diagram of local network configuration for the LasIR system.

On a routine basis, data from the PC running the TASDAcc software should be backed up and, eventually, removed from the local hard drive to prevent it from reaching capacity, which would stop proper functioning of the TASDAcc software. In the future, removable hard disk drives together with automated scripts will be used to automate some aspects of this data management and to ensure a redundant copy of data exists for the current year before delivery.

To perform data backup, transfer spectral data and raw data tables provided by the TASDAcc to a removable storage device. This enables the storage of two copies of the data. After data delivery at the beginning of the year, remove the previous year's data from the PC by deleting it.

On a routine basis, according to the maintenance schedule in the QAPP, check the hard drive space to ensure there is enough space for the following measuring period. If enough free space cannot be created on the drive, take corrective action with support from the IT department.

4.6   Test Light Levels

Although the return light level is monitored continuously and reported with the 5-min data, it is important to verify and document observations of light level during routine maintenance. Testing light levels on site allows for the determination of root-cause for problems involving low signal return. The effect of cleaning on light levels should be noted. Testing of light levels at various points in the system can be used to troubleshoot damaged optical components, such as fibers.

To check the light levels, observe the power bar (S) in the scope display or the bar at the bottom of the "Main Running" display (**Figure 4**) on the analyzer. In the host trend display it should be green. If it is yellow it indicates the power is low. If it is purple, the power is very low and the instrument will have stopped recording data. On the analyzer, the bar is normally between 25% and 75%. You may also check the percent (P) values on the analyzer display (**Figure 4**) by cycling to the "Species Information Screen." It should be greater than 5% for proper operation. Low power generally indicates a need for maintenance, such as cleaning the optics, or a problem with the process that is releasing dust into the duct and cutting down the power.
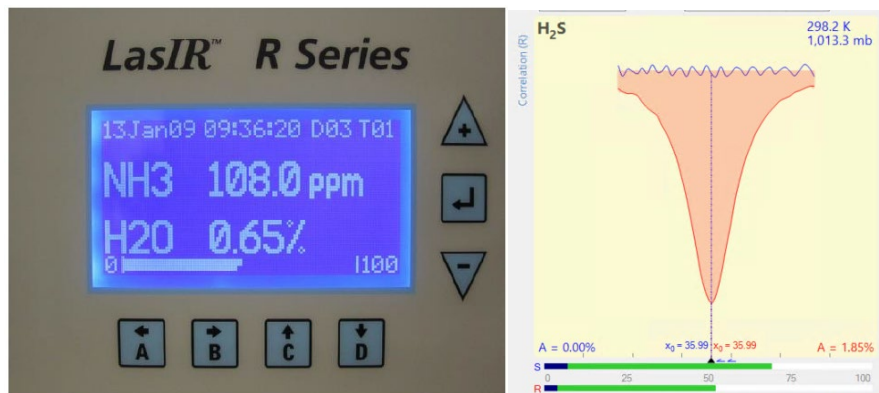

Figure 4. Main running window on instrument front panel (left) and scope display in LasIR View software (right).

4.6.1   Signal Strength Measurements

Measurement of light power at the detector can occur at several points in the system. There are two gains associated with these measurement points, as indicated in **Table 2**. The "signal gain" is the

amplification placed on the signal itself through electronic hardware, and the "IO gain" is a multiplicative modification of the input-output data streams. Using this table together with the method-appropriate use case, the actual light power at the detector can be determined.

For example, if the signal gain is 2 (signal multiplier of 2), the IO gain stage is 3 (multiplier of 5), and the peak power at the detector is 0.12 mW, then the power displayed via RS232 data stream is:

RS232 **SignalPower** = Signal Multiplier x IO Multiplier x Peak Power = (2)(5)(0.12 mW) = 1.2

The ratio of MODBUS to RS232 signal powers is always 2.5, so in this case the **SignalPower** transmitted via MODBUS is: (1.2) (2.5) = 3

Following this example, by ratioing the power at the detector to the power of the laser (say, 18 mW for this example, can be obtained from instrument data sheets), a %transmission may be calculated.

%transmission = (0.12 mW / 18 mW) 100% = 0.67%

However, if the gains are set to "auto," as they are during normal operations, it is impossible to know what gain settings are applied and, therefore, what the actual power at the detector is. Therefore, %transmission can only be assessed during routine maintenance.

Table 2. Multiplicative factors associated with gain stages and how they are translated to the Unisearch data files (SignalPower) and through the MODBUS data connection. Note that the ratio of MODBUS to RS232 is 2.5. The ratio of RMS power to peak power is 0.83.

Signal Gain	Signal Multiplier	IO Gain Stage	IO Multiplier	Power at Detector (mA or mW)	Peak Power at Detector (mA or mW)	MODBUS/ Display Power	RS232/TXT Signal Power
1	1	2	1	1	1.2	3	1.2
2	2	2	1	0.5	0.6	3	1.2
2	2	3	5	0.1	0.12	3	1.2
2	2	4	25	0.02	0.024	3	1.2
1	1	3	5	0.32	0.4	5	2
2	2	3	5	0.2	0.24	6	2.4
3	4	3	5	0.25	0.3	15 (or 1.0 if not in Fast gain with error)	6 (or 2.5 if not in Fast gain with error)
4	8	3	5	0.1	0.12	12 (or 1.0 if not in Fast gain with error)	4.8 (or 2.5 if not in Fast gain with error)
2	2	4	25	0.05	0.06	7.5 (or 1.0 if not in Fast gain with error)	3 (or 2.5 if not in Fast gain with error)
3	4	4	25	0.015	0.018	4.5	1.8

Using the OPM-15 Power Meter: When working with the laser power meter (OPM-15, provided with the analyzer, shown in Figure 5) plugged into the back of the telescope "coax out" port, the units the meter provides are in mA, which has a 1:1 conversion to laser power in mW. If a triangle appears on the screen, units will be in µA or µW. If the IO Gain is configured, the power reading will need to be adjusted by that amount, according to Table 2.

Figure 5. Measuring laser power with the OPM-15 meter provided.

Power reported in Unisearch files: The units for "Signal Power" reported in the raw data files downloaded from the LasIR analyzer are in units of mW. If the signal gain is configured to have a multiplier, the reading will need to be divided with that multiplier (Table 2) in order to get the signal power in mW.

Power reported in TASDAcc files: The power reported in the TASDAcc files are pulled from the MODBUS data stream provided by the instrument. Table 2 shows how this power is related to laser power elsewhere in the system.

4.7   System Settings

In the LasIR instrument software, select File > Configure Analyzer. Select "Expert" on the upper right corner of the Configure Analyzer window. View settings for H_2S, CO_2, and H_2O. Compare these settings with historical settings and provide any explanation for change. For a complete description of the settings and their typical ranges, consult the LasIRView software manual[2]. If you change any settings, document how the settings were changed in the instrument logbook present at the site. Note that all instrument settings are saved on the analyzer on a daily basis.

5.   Flow-Through Response Test

The Unisearch analyzer enclosure comes equipped with a flow-through cell for use in response testing the LasIR units. This setup requires high-concentration compressed gases to be flowed

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[2] Mackay, K., Chanda, A., Mackay, G. Software Manual: LasIRView2015, Application Software for LasIR Analyzers. Rev. 2015-10-01

through in order to affect a response from the analyzer. An alternate way to response-test the analyzers is to use sealed cells; this procedure is described in Section 6.

5.1   Supplies

1. Nitrogen gas

2. H_2S reference gas blend

   - Note that the H_2S reference gas tank and as much of the gas lines as possible should be outside the shelter in the open air; all gas lines should be tested for leaks while filled with nitrogen gas

3. 1/8" PTFE tubing for the reference and purge gas lines into the quality assurance (QA) cell

4. 1/8" PTFE Swagelok tee union to couple the reference and purge gas feed lines into the QA cell

5. 1/4" PTFE tubing for gas flow lines on the outlet of the QA cell

6. Unisearch external 0.167-m flow cell

7. Length of PTFE 1/4" tubing with PTFE Swagelok nuts on both ends

8. Length of PTFE tubing to go from external flow cell to scrubbing system

9. A scrubbing system consisting of ½" ID PTFE tubing, 6" long, filled with GC Sulfursorb Plus activated carbon absorbent, or equivalent; this volume of absorbent has a minimum capacity of 38 grams of H_2S, which is approximately 1,000 times the amount of H_2S existing in 750 ppm H_2S gas flowing at 0.3 l/min for 100 minutes.

10. A max 5 l/min rotameter attached at the exhaust line to view that flow is occurring

5.2   Test Preparation

Depending on the requirements of the QAPP, the path-average concentration will need to be determined using the flow-through cell length, the concentration of standard gas, and the pathlength of the open-path. Note that because this is a monostatic system, the total optical pathlength is twice the distance between the telescope and the retroreflector. For example, a 750-ppm blend of H_2S (in nitrogen or air) delivered to the optical path through the 0.167-m flow-through cell and a total path length of 1000 m provide approximately 125-ppb path average H_2S. An example calculation of this is as follows:

(H_2S concentration in cylinder) (flow cell length) = Path Integrated Concentration ppm-m

(750 ppm) (0.167 m) = 125.25 ppm-m

Path Integrated Concentration divided by the total optical path length = Path Average Concentration (ppm)

$$125.25 \text{ ppm-m} / 1000 \text{ m} = \textbf{0.125 ppm or 125 ppb H}_2\textbf{S}$$

5.3   Gas Testing Procedure

1. Flow nitrogen gas and perform internal zero with nitrogen. Gas delivery should be about 5-10 psi from regulator/cylinder, at a flow rate of 0.25 to 0.5 L/min.
2. Assemble test configuration with the Unisearch short flow-through cell (0.167 m) in the path.
3. Assemble the H_2S gas scrubbing system, with gas flow coming from the external flow cell into the column packed with absorbent.
4. Flow nitrogen to a stable baseline, typically about five volumes of the cell. The flow of nitrogen can be verified by viewing the rotameter at the exhaust.
5. Monitor readings until a stable zero reading is reached. Continue reading 7-15 measurement cycles.
6. Flow the H_2S reference gas. The H_2S should flow at 0.3 L/min.
7. Acquire 7 to 15 measurement cycles, or the number of samples required by the QAPP.
8. Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).
9. Stop the H_2S flow and flow nitrogen to purge the H_2S gas to a stable baseline, typically about five volumes of the cell.
10. Disconnect H_2S and nitrogen gases and remove the external flow cell to return the TDLAS system to open-path monitoring of ambient air.

5.3.1   *Clean-Up*

1. Dispose of the waste PTFE tube filled with GC Sulfursorb Plus appropriately.
2. Download .cfg and .spectrum files and save along with the form at the end of this document.

6.   Sealed-Cell Response Testing

Sealed cells filled with a known concentration of H_2S may be used for response testing the LasIR analyzers. These sealed cells are fiber coupled and may be connected into the light path as indicated in Figure 1.

6.1 Test Preparation

To meet the testing requirements, you must determine path average concentrations using the certified cell concentration and the pathlength. An example calculation of expected path average concentration for a 250 ppm-m sealed cell together with a 500 m one-way path is as follows:

$$Path\ Average\ Concentration = (\frac{250\ ppm - m}{(2 * 500\ m)})(\frac{1000\ ppb}{ppm}) = 250\ ppb$$

Prior to testing, you will need to ensure that the cells you have will satisfy the testing requirements of the QAPP.

6.2 Single-Point Bump Test

1. Disable alerts on Sonoma Technology Field Tech Tool (FTT) and put instrument into planned maintenance mode.

2. Disconnect optical fiber from instrument "Fiber In" port.

3. Connect optical fiber from Step 2 to inlet of sealed cell.

4. Connect optical fiber from outlet of sealed cell to instrument "Fiber In" port.

5. Wait for response to stabilize before collecting data.

6. Collect between 7 and 15 data measurements for averaging, or the number of samples required by the QAPP.

7. Calculate the average, % error, standard deviation, % CV, and average detection r. Record these values in the test form (Section 7).

8. **Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).**

9. Disconnect sealed cell outlet optical fiber from instrument and reconnect optical fiber from Step 2 to instrument "Fiber In" port.

10. Verify baseline of instrument and turn alerts back on in FTT; take out of planned maintenance mode.

11. Download .cfg and .spectrum files and save along with the form at the end of this document.

6.3 Three-Point Calibration

1. For the three-point calibration test, repeat the measurements described in Section 6.1 for the remaining concentrations using additional sealed cells.

2. Plot a curve of measured concentration vs. expected concentration. The record the r^2, slope, and intercept.

3. Download .cfg and .spectrum files and save along with the form at the end of this document.

7. Data Evaluation, Reporting, and Corrective Action

During these tests, a number (N) of replicated measurements (x_i) of a standard reference material of known magnitude (x_{std}) will be measured. Here, an acceptable number of trials will be defined as $7 \leq N \leq 15$. The average value of these measurements is calculated as

$$\bar{x} = \frac{\sum_i x_i}{N} \tag{1}$$

and the sample standard deviation (σ) as:

$$\sigma = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{N-1}}. \tag{2}$$

From these definitions, % error is defined as:

$$\% \, error = \left| \frac{\bar{x} - x_{std}}{x_{std}} \right| \times 100\% \tag{3}$$

and precision as the coefficient of variation expressed as a percentage (% CV):

$$Precision \equiv \% \, CV = \frac{\sigma}{\bar{x}} \times 100\% \tag{4}$$

1. Calculate the Concentration

    a. Average the concentration of "N" stable measurements.

    b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

       Note: To calculate the certified value that will be seen on the TDL from the actual certified instrument calibration gas concentration, you multiply the certified gas concentration by the calibration cell length (0.167 meters) and divide that answer by the path length set in the instrument software. For most TDL instruments in operation by Sonoma Technology, the path length is set to 2 meters for monostatic instruments and 1 meter for bistatic instruments.

2. Calculate the Limits of Detection and Quantitation.

    a. Calculate the mean (average), sample standard deviation, and %error (sometimes also referred to as % difference) of the selected results.

    b. Report the Detection Limit as two times the standard deviation.

    c. Report the Quantitation Limit as equal to the detection limit.[3]

3. Compile all configuration files, spectra files, and log files into a single folder.

    a. The folder should be named "CUS LOC QATest TDL# YearMonDy" where CUS is a 3-letter designator for the customer and LOC is a three-letter designator for the facility location.

The QAPP contains the acceptance criteria and warning levels to be used for the test.

Note:

- **If the test produces an error or precision greater than the warning level**: corrective action should be taken so that the precision and error are below the warning levels.

- **If the test produces an error or precision greater than the acceptance criteria**: corrective action should be taken so that the precision and error are below the warning levels. Equipment will not be placed into service (taken out of "maintenance mode") until it meets all measurement criteria.

If the measurements do not meet the data quality objectives listed in the QAPP, repeat the procedure without adjustment. If the instrument still fails to meet the QA criteria, retest the following day with no adjustment. Confirm that atmospheric conditions were acceptable for bump testing. If these repeated tests continue to fail under acceptable atmospheric conditions, initiate corrective action to include the following:

- Review data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features

- Consult with the project technical lead to identify abnormal changes to the background

- Examine wavelength calibration

- Investigate any large changes in stray light since the last test and adjust calibration factors as necessary

- Review gas testing apparatus for leaks or other similar problems

- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

In the event of a failed test after following all steps outlined above, inform the Sonoma Technology Project Manager and Quality Assurance Manager who will review the instrument performance parameters in the list above.

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[3] In accordance with guidance from BAAQMD in their letters to refineries dated Dec 22, 2022, and subsequent statements that the December 2022 specification (requiring LOQ of 3-25 ppb) was not a significant change from – and was no more stringent than – the October 2021 specification (which required a detection limit of 3-25 ppb)..

If all parameters indicate that the instrument was performing properly since the last test, data since the last test will be flagged as suspect. If an issue with the instrument is identified, data since the date and time of the instrument issue will be flagged as invalid. All data flagging will be performed by Data Analysts in consultation with the Quality Assurance Manager.

8. LasIR Response Test Form

Date: _____ Location: _____

Test Technician 1:_____ 2:_____

Alignment

Signal Intensity as found(MODBUS)_____ (Target: >0.4)

Response Tests

	Trial 1	Trial 2	Trial 3
Reference ID			
Reference Concentration			
Start Time			
Stop Time			
Average			
% error			
Standard Deviation			
% CV			
Average Detection r			

Three-point Calibration Summary

	Value
Slope	
Intercept	
r^2	

Notes: