Air Monitoring Plan for the Valero Refinery in Benicia, California

Prepared for
Valero Refining Company - CA
Benicia Refinery
Benicia, CA

Updated: September 5, 2023
Original: September 7, 2017

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Air Monitoring Plan
for the Valero Refinery in
Benicia, California

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Air Monitoring Plan, Rev 6
STI-1922002-6601

Updated: September 5, 2023
Original: September 7, 2017

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1.   Introduction

1.1   Background

The Valero Refining Company (Valero) conducts air quality monitoring at its Benicia, California, refinery in response to the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15).[1] The monitoring follows a facility-specific air monitoring plan 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. The rule also requires that refineries submit air monitoring plans to the BAAQMD for approval. This Monitoring Plan was approved on June 8, 2018, with conditions to: (1) update the Quality Assurance Project Plan (QAPP, located in Appendix A) and (2) select hydrogen sulfide (H_2S) monitoring technology. 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 December 8, 2022, Valero implemented H_2S monitoring. BAAQMD issued updated specifications on December 22, 2022, and Valero's response to the updated specifications was submitted on February 23, 2022. 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_2S. In addition, sulfur dioxide (SO_2), alkanes, 1,3-butadiene, other organics, and ammonia should be considered for measurements.

For the Valero fenceline monitoring program, Valero uses open-path instruments to measure the required compounds (BTEX and H_2S) along three paths. The three measurement paths, composed of

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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.

two segments each, are implemented to cover Valero's fencelines in consideration of nearby local receptors (e.g., residences and businesses), dominant winds that blow from west to the east, and infrequent winds that blow from the northeast to the southwest to portions of populated areas in Benicia. As shown in **Figure 1**, the business park east of Valero is the only populated area influenced by the dominant winds; winds blow from other directions less than 10% of the time for 22.5-degree wind direction segments.
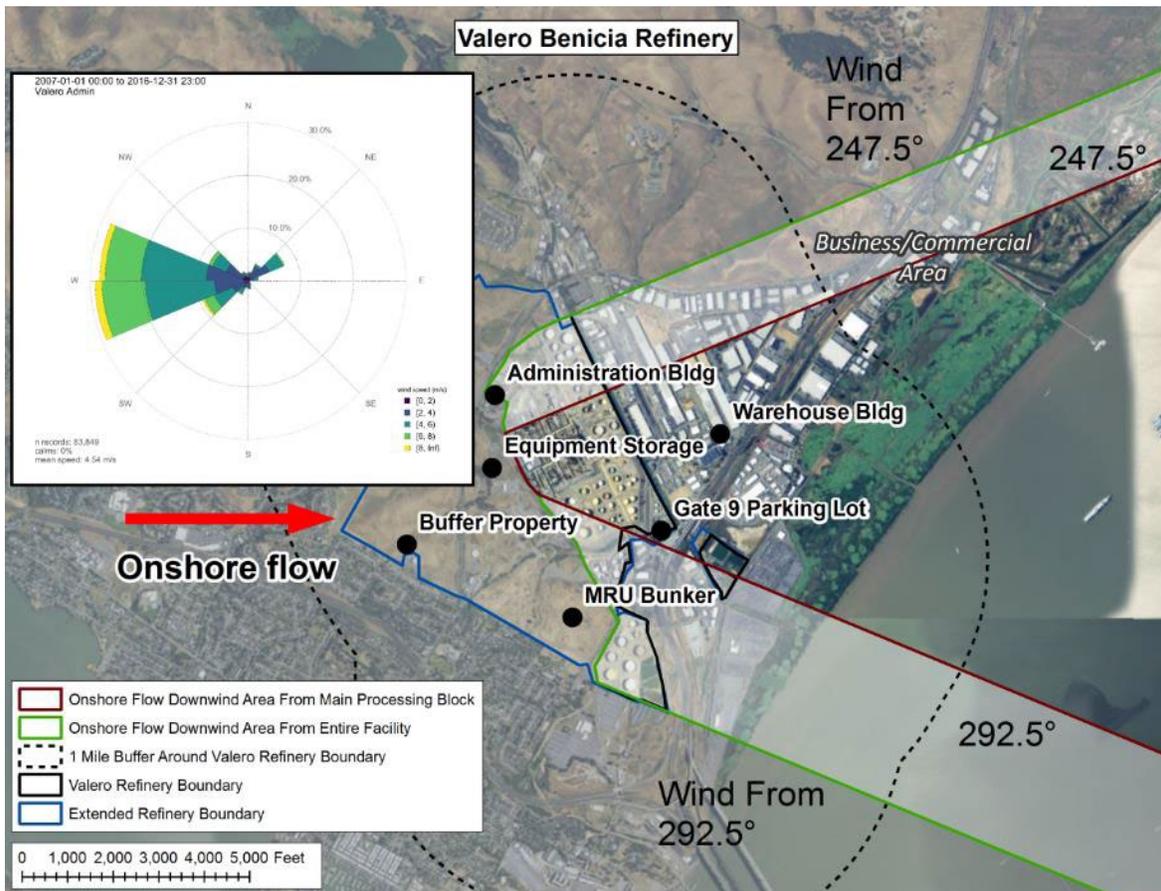
Figure 1. Areas downwind of the Valero Benicia Refinery property boundaries for wind directions that occur more than 10% of the time on an annual basis. The only populated area impacted by the dominant wind direction is the business park to the east of the Valero refinery.

Along all paths, BTEX and SO_2 are measured by monostatic Ultraviolet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. For open-path measurements, "monostatic" refers to the configuration where the light source and detector are at the same location, and the light from the source is reflected straight back at the detector using a special mirror called a retroreflector. H_2S is measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instrument. These open-path instruments transmit light across a given path and detect the amount of energy absorption at a particular wavelength of light to determine the average concentration of a particular pollutant along the path. The three primary monitoring paths, composed of six total segments, are

shown in **Figure 2**. GPS coordinates, elevations, and instrument inventory at each open-path sampling site are shown in **Table 1**.

In addition, as requested by the BAAQMD, monitoring between Paths 2 and 3 occurs at sample locations 10, 11, and 12 (see Figure 2). The sorbent tubes at these point locations will be replaced and analyzed for benzene, toluene, ethylbenzene, and total xylenes approximately every 14 days in accordance with the 40 CFR Subpart CC Fenceline Monitoring program. Please note, all additional discussions in this document, unless otherwise noted, refer to the open-path monitoring and not the monitoring with sorbent tubes.

Figure 2. Open-path monitoring network for Valero's Benicia Refinery. Each primary path is numbered and contains segments that are labeled with the path number and a prime (') or double prime ('') symbol. Yellow "+" symbols indicate the location of point monitoring by sorbent tubes. Main wind flow directions are also shown.

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

Site	Coordinates	Elevation (ft)	Equipment
1″	38.069404, -122.153003	402	1 UV-DOAS 1 TDL Retroreflector
1	38.065527, -122.150574	344	2 UV-DOAS Analyzers 2 TDL Analyzers
1′	38.063530, -122.147851	253	1 UV-DOAS 1 TDL Retroreflector
2″	38.061956, -122.144872	215	1 UV-DOAS 1 TDL Retroreflector
2	38.059251, -122.138816	193	2 UV-DOAS Analyzers 2 TDL Analyzers
2′	38.056332, -122.133499	172	1 UV-DOAS 1 TDL Retroreflector
3″	38.069889, -122.132245	12	1 UV-DOAS Analyzer 1 TDL Analyzer
3	38.074329, -122.134956	28	2 UV-DOAS Retroreflectors 2 TDL Retroreflectors
3′	38.079025, -122.137809	28	1 UV-DOAS Analyzer 1 TDL Analyzer

Paths 1 and 2 cover the southwest fenceline to assess potential transport toward the city of Benicia. This transport direction is infrequent and only occurs on an occasional basis in the winter, when winds sometimes blow from the northeast toward the southwest. Over the course of a year, these northeast winds occur less than about 7% of the time. Because of terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability; therefore, the downwind areas that could be affected under these wind conditions are very narrow.

Path 3 covers the eastern fenceline to assess potential transport toward the business/commercial area east of the refinery. This transport direction is common in the spring, summer, and early fall, when winds often blow from the west toward the east. Monitoring between Path 2 and 3 is not needed, as there are no significantly populated areas downwind of this space between the monitors. In addition, a release that might travel between Path 2 and 3 would likely be seen on Path 2 or 3 monitors because of dispersion. Also, it is not feasible to add monitors between Paths 2 and 3 because of road, rail track, and terrain issues.

Instruments on Paths 1 and 2 are elevated about 5 ft above ground level (agl). Instruments on Path 3 may be elevated to about 15 to 20 feet agl so that vehicle traffic will not block the open-path sensor

light. While instruments are located at the above elevations, the distance between the ground and the light beam along the path vary according to the terrain.

Open-path analyzers are located at sites 1, 2, 3′, and 3″. Sites 1 and 2 each have two UV-DOAS and two TDLAS analyzers. Each pair of analyzers at each site points roughly 180 degrees from each other. The remaining numbered sites (1′, 1″, 2′, 2″, and 3) have retro reflectors (i.e., mirrors). This setup provides maximum spatial coverage along the critical paths.

Visibility instruments are placed at sites 1 and 3′ to measure visibility conditions at different locations and elevations. The visibility measurements are used as evidence of low visibility conditions that cause missing measurements from the open-path instruments. Two sites have been selected because visibility can vary spatially across the refinery. In addition, these locations were selected for ease of access.

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 an internet 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 undergoes 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-minute 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 gas reported. 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 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.

- The findings of a scoping study, which involved assessments of (1) the geographic setting around Valero's Benicia Refinery, (2) the relevant meteorological conditions, and (3) air quality monitoring and dispersion modeling results.

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

- Data management and 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 is 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   Scoping Study

2.2.1   Assessment of the Geographic Study Setting

Valero's Benicia Refinery is located at 3400 East 2nd Street in the eastern part of the City of Benicia, Solano County, California (see Figure 3). The refinery is bounded by Suisun Bay and by the Carquinez Strait on the east and south sides of the property. Low coastal hills rise to elevations of 400 to 1,000 feet on the west and north sides of the refinery. Valero's 800-acre property is largely undeveloped and provides a useful area for air monitoring. Valero's Refinery operations occupy approximately 330 acres, including a 46-acre process block that lies between East 2nd Street and Park Road and a 50-acre crude oil tank farm that lies between Park Road and Interstate 680 (see Figure 4). The PBF Energy Martinez and Tesoro Golden Eagle refineries are located to the south and southeast across the Carquinez Strait.

Figure 3. Geographic setting of the Valero Benicia Refinery.

Figure 4. Layout of the Valero Benicia Refinery (Source of information: Valero Improvement Project Environmental Impact Report, June 2008).

Residential areas are located to the southwest, west, and northwest of the facility and most are at least 1,500 feet from the refinery plant and storage tanks. Businesses are located east and northeast of the refinery, and the business/commercial area begins a short distance from the refinery property. Interstate 680 is adjacent to the eastern side of the refinery and Interstate 780 is located to the south; there are residences between Interstate 780 and the refinery. The nearby public-access areas—e.g., residences, businesses, and public roadways—represent air quality "receptors" that are nearest and at times downwind from Valero's Benicia Refinery. The positions of these receptors received careful consideration during the design of this air quality monitoring plan.

2.2.2 Assessment of Valero Processes

Valero's Benicia Refinery is a petroleum refinery producing fuel products, such as liquefied petroleum gas (LPG), gasoline, jet fuels, diesel fuels, and residual fuel oils through distillation of crude oil, including cracking, alkylation, and reforming. In light of Valero's products, processes, and associated potential emissions, the following rationales in Table 2 were used to determine which compounds need to be measured or not measured:

1. Benzene measurements are a good qualitative indicator for other Hazardous Air Pollutant (HAP) emissions[3]

2. The compound is not a HAP (this is not the sole reason for exclusion, but is provided for completeness)

3. Emissions are low compared to background concentrations

4. Already measured by existing ground level monitors (GLM)

5. Alerting systems already in place at the refinery

6. Not manufactured as a product of the refinery and not used in routine processing.

Table 2. Compounds and the rationale for their exclusion from the fenceline monitoring program.

Compound	Required by the BAAQMD	To Be Measured	Rationale for Exclusion
Benzene	Yes	Yes	N/A
Toluene	Yes	Yes	N/A
Ethylbenzene	Yes	Yes	N/A
Xylenes	Yes	Yes	N/A
Hydrogen sulfide	Yes	Yes	N/A
SO$_2$	No, if justified	Yes	N/A
Alkanes	No, if justified	No	1 (for hexane) 2 (except for hexane) 5
1,3-Butadiene	No, if justified	No	6
Other organics	No, if justified	No	1
Ammonia	No, if justified	No	5, 6

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[3] Background section of Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards.

Exclusion of alkanes. Valero does not include alkanes in its fenceline monitoring program. During normal operations, there is no potential for alkanes to be released at the fenceline without a corresponding benzene release, and as noted in Table 2 above, benzene is included in the fenceline monitoring program. Alkanes are used within the refinery process units; however, the Benicia refinery is unique in its design of integrated process units. This design, intended to maximize energy efficiency and minimize the storage of intermediate products, essentially causes the entire refinery to function as one integrated unit. This means that a release of alkanes from a process unit that *does not* emit BTEX compounds would coincide with a release from a process unit that *does* emit BTEX compounds. Therefore, the proposed fenceline BTEX monitoring would serve as the alert in the event of a release of alkanes used in the process units.

The only location where alkanes could potentially be released without a corresponding benzene release is at tank storage (liquefied petroleum gas [LPG] spheres, one pressurized tank, and two LPG loading racks). However, fenceline monitoring of these alkanes would not serve as a first alert of an alkane leak: any release from one of these sources would be a significant event with refinery alarms that would activate refinery emergency response procedures and evacuation of people downwind. The LPG storage area, including the loading racks, has open-path total hydrocarbon detectors that alarm in the Control House in the event of a release. The pressurized tank is equipped with pressure relief valves (PRVs). These existing open-path analyzers and PRVs serve as the first alert for an alkane release that would activate emergency response procedures; a fenceline monitor would not be used as a first alert of a release in this situation.

Exclusion of 1,3-butadiene. Valero does not include measurements of 1,3-butadiene in its fenceline monitoring program. This is because 1,3-butadiene is not manufactured as an intermediate product or end product of the refinery and is only present in trace quantities.

Exclusion of other organics. Valero does not include measurements of other organics in its fenceline monitoring program. Other organics, with the exception of alkanes, are coincident with BTEX; therefore, the BTEX measurements serve as an excellent surrogate for other organics. The exclusion of alkanes is discussed above.

Exclusion of anhydrous ammonia. Valero does not include measurements of anhydrous ammonia in its fenceline monitoring program because anhydrous ammonia is used in air pollution control devices and is not used in routine processing at the refinery. Anhydrous ammonia is present in only one location, in two 3.5' x 14' drums that have high temp/pressure/level alarms for detection of release at the source. There are also excess flow shutoff valves on the drum, fixed fire monitors around the perimeter, and bollards and elevated foundations to protect the drums.

2.2.3 Assessment of Local Meteorology

Valero's Benicia Refinery is positioned in a wind flow corridor between the San Francisco Bay and the Sacramento Valley. Wind flow through the corridor is driven by seasonally variable regional temperature gradients and large-scale meteorological systems.

To characterize meteorological processes, measurements of wind, mixing height, and visibility were collected and assessed at several sites (see **Figure 5**). Items investigated included the monthly, annual, seasonal, and spatial patterns of winds; the low-level vertical structure of winds and how that structure might impact the transport of elevated sources versus surface sources; and the presence of fog and low clouds (as related to the ability of open-path sensors to obtain measurements). The primary data used in this analysis included:

- **Routine surface winds** – collected at the Valero's Administration building and an offsite warehouse in 2007–2016.

- **Special-study surface winds** – collected at MRU Bunker in 2015.

- **Special-study 1-minute visibility measurements** – collected using a Belfort visibility instrument at the facility's Equipment Storage site (ES) location from January 14 through July 9, 2015.

Surface wind data collected at the special-study Buffer Property site (BP) in winter 2015 were compared to data from the Administration site. It was determined that the wind data collected at BP were very similar to the data collected at the Administration site; thus, the BP data were not included in the detailed analysis summarized in this report. Also, the Administration meteorological site is appropriate for understanding movement of air from the refinery to Benicia because (1) it is located between the refinery and the community to the west and thus better represents transport directions to the community; (2) it is at an elevation that is more representative of winds that blow into the community; and (3) it is not influenced by nearby buildings.

General meteorological patterns were also discussed with experts in meteorological processes in the North Bay Area.

For this analysis, seasons were defined as follows: winter is December, January, February; spring is March, April, May; summer is June, July, August; and fall is September, October, November.
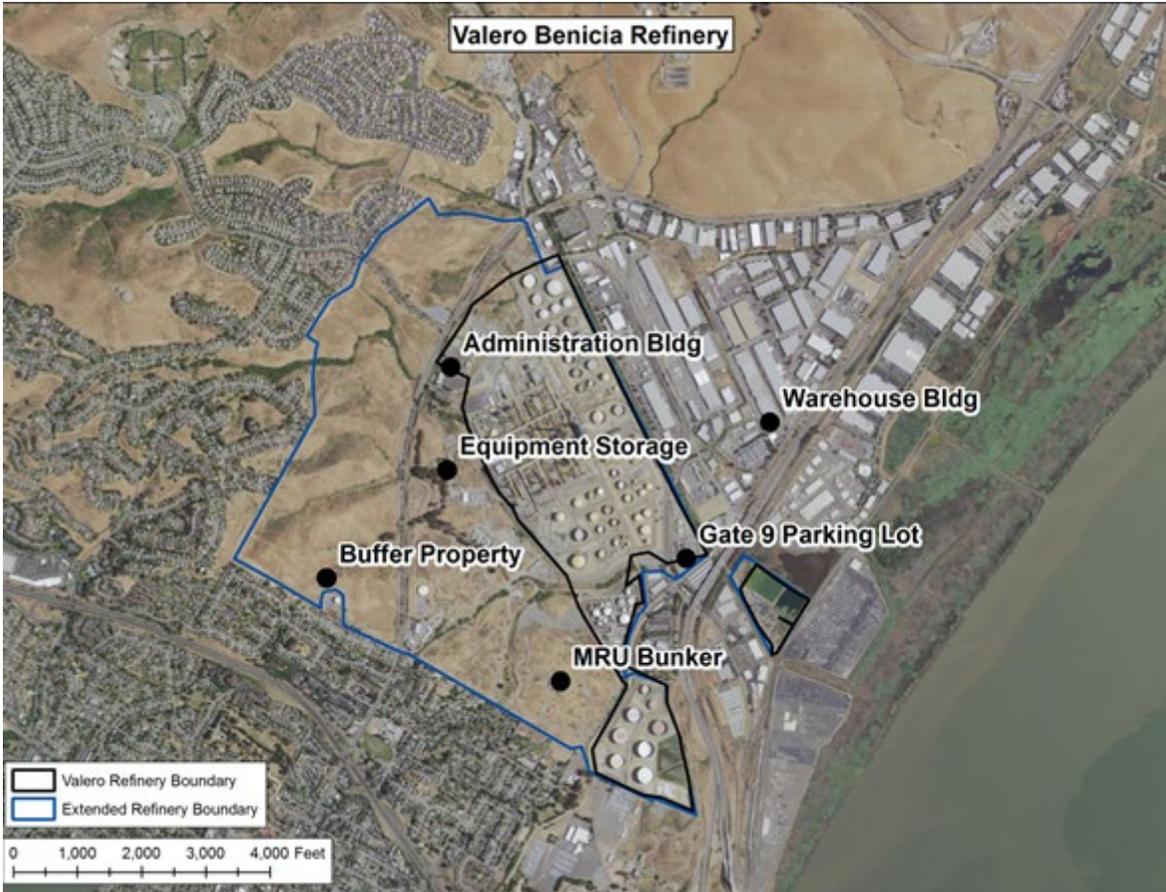
Figure 5. Meteorological monitoring locations.

General Flow Patterns

Figure 6 illustrates the predominant wind flow patterns (1) winds blowing from the northwest and west to the east and southeast (onshore flow, most often occurring in spring, summer, and early fall); and (2) winds blowing from northeast to southwest (regional offshore flow, most often occurring in winter).

Figure 6. Typical wind flows around Valero's Benicia Refinery.

Wind Roses

Wind roses were created to determine the frequency of wind speed and direction for various time periods. To evaluate the actual winds against the wind direction requirement stated in the BAAQMD Guidance document, wind roses showing annual mean wind direction in 22.5-degree segments were created and reviewed. To evaluate seasonal and recurring short-term meteorological events, seasonal and monthly wind roses were created.

The petals of a wind rose show the direction from which the wind is blowing. The wind roses show that:

- **Onshore winds** – Winds blowing from northwest to southeast, west to east, and southwest to northeast are in excess of 10% per year (see **Figure 7**). Winds from these directions are most common in spring, summer, and early fall.

- **Offshore winds** – Winds blowing from the refinery toward the city of Benicia (i.e., winds blowing from northeast to southwest) are infrequent and occur on an occasional basis less than 7% of the time throughout the year (**Figures 8 and 9**). Although the northeasterly winds occur less than 10% of the time annually, they are included for consideration in this Monitoring Plan because portions of the city of Benicia are downwind of the refinery under these conditions and the winds may occur more than 10% of the time *during the winter season only*. Winds from other directions occur a negligible amount of the time.

To better illustrate the downwind areas impacted by the onshore and offshore winds, maps that highlight the areas downwind of the Valero Benicia Refinery property were created. For offshore

winds, more precise modeling was performed because this wind direction is from the refinery toward the residences of Benicia. Details on the modeling are discussed in Section 2.2.4. The downwind areas of influence for onshore flow and offshore flow are shown in Figure 1 and **Figure 10,** respectively. These analyses show that:

- During **dominant** onshore (southwest through northwest) winds, the main area downwind of the refinery is the business/commercial area just to the east.

- During **infrequent** offshore (northeasterly) winds, the main area downwind of the refinery is the city of Benicia, excluding west and northwest Benicia. The offshore wind direction is well defined and has little directional variability (because of terrain effects and the orientation of the Carquinez Strait). Therefore, the downwind areas that could be affected under these conditions are very narrow.

The results of the wind and modeling analyses indicate that air quality measurements are needed along the southwest fenceline (Paths 1 and 2) and eastern fenceline (Path 3) of the Valero Benicia Refinery (see Figure 2). Monitoring between Paths 2 and 3 is not feasible because of road, rail track, and terrain issues. However, monitoring between Paths 2 and 3 is not needed, as there are no significantly populated areas downwind of this space between the monitors. Monitoring north of Path 1 is not needed because it is outside of the area of influence.
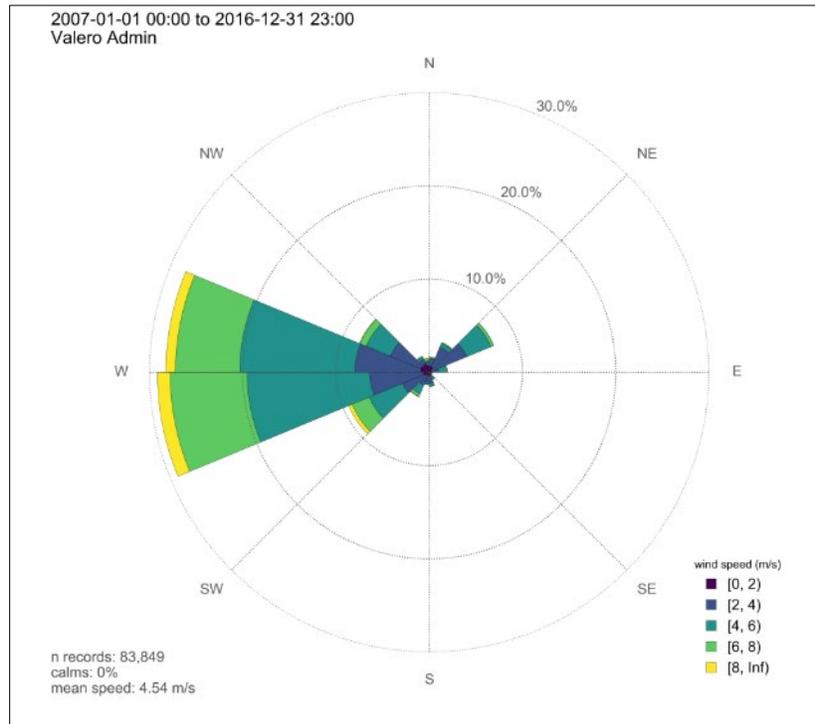
Figure 7. Wind rose for Administration site showing near-surface wind directions for data collected from 2007 through 2016.
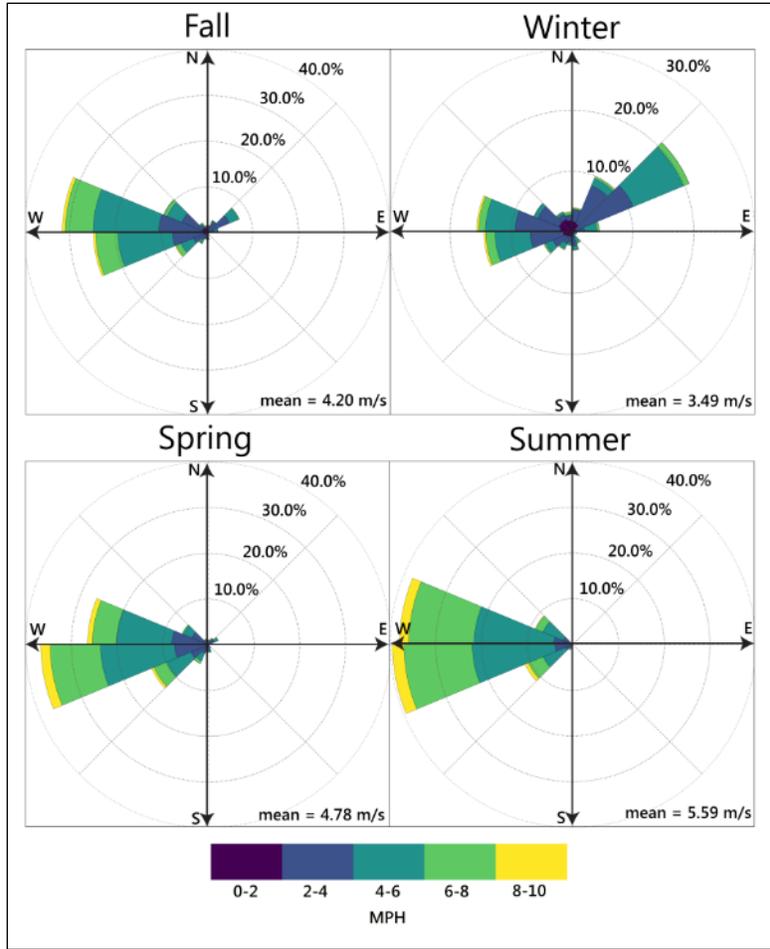
Figure 8. Wind roses at the Administration building (surface winds) by season for data collected from 2007 through 2016.
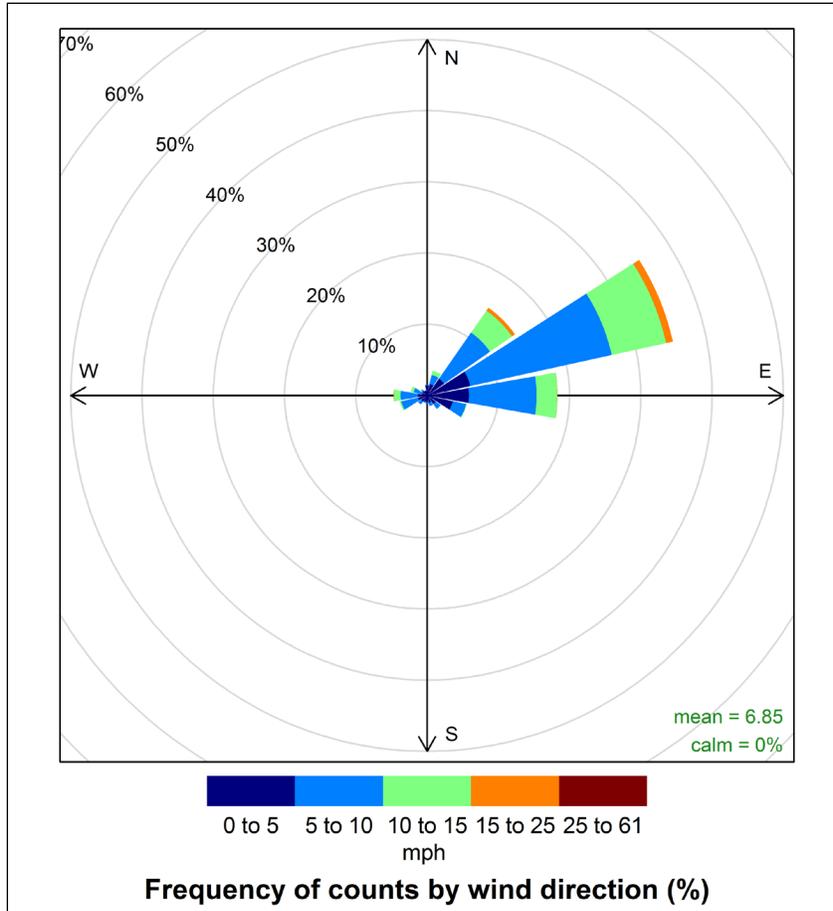
Figure 9. Wind roses at MRU Bunker for January 2015.
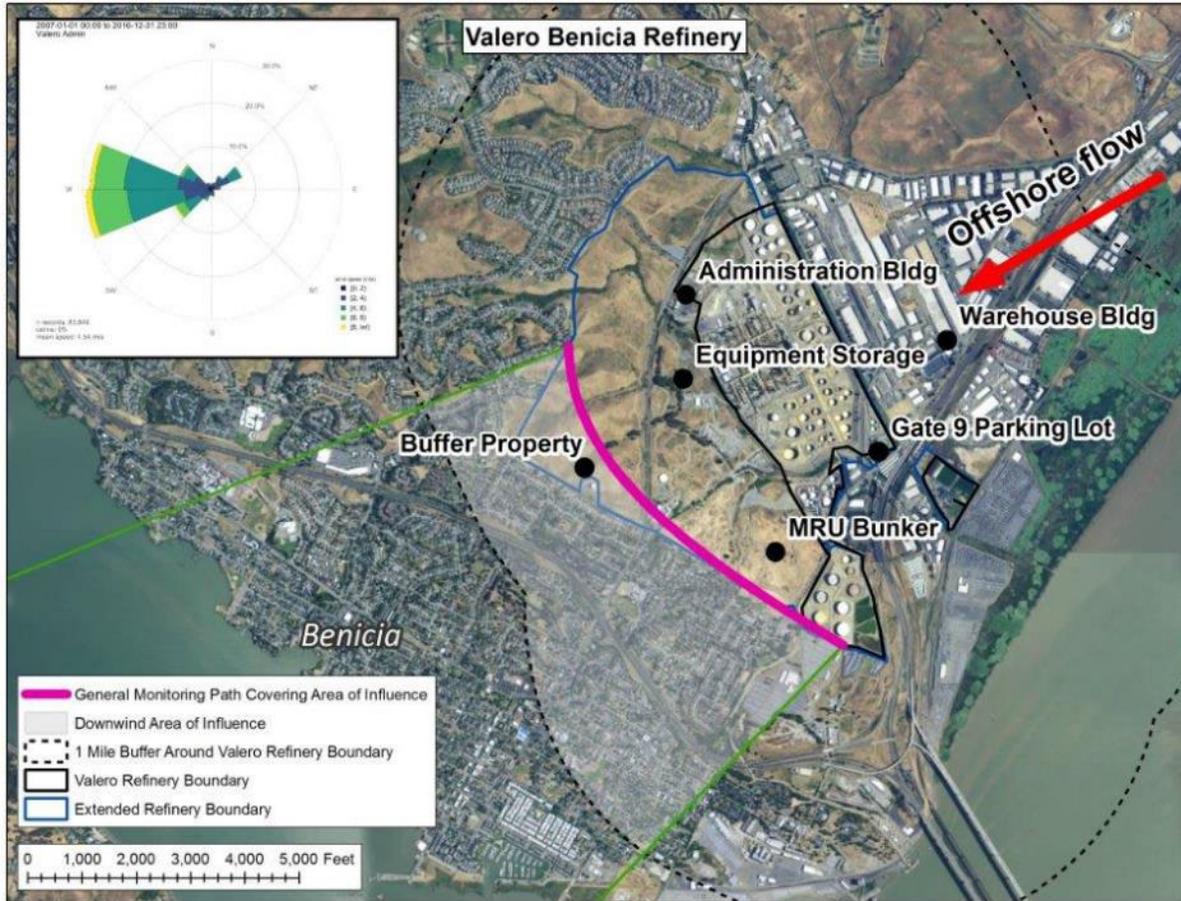
Figure 10. Areas downwind of the Valero Benicia Refinery property boundaries during offshore (northeast to southwest) winds.

2.2.4   Winter Offshore-Flow Dispersion Modeling

Because of terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability; therefore, the downwind areas that could be affected under these wind conditions are very narrow. To provide further evidence that monitoring Paths 1 and 2 upwind of Benicia during winter months are in the correct locations to capture the narrow area of the offshore flow, air pollutant dispersion modeling was performed using the American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD, Version 15181).[4] AERMOD is a steady-state Gaussian plume dispersion model. The advantage of dispersion modeling over wind rose analysis is that it combines winds, topography, atmospheric stability, emissions, and dispersion processes to estimate areas of peak concentrations across the entire downwind area. Importantly, dispersion modeling accounts for the time variability in meteorology to create a more accurate assessment of the locations where fenceline monitoring is needed.

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[4] https://www3.epa.gov/scram001/dispersion_prefrec.htm

AERMOD uses hourly meteorological data to assess the dispersion of emission plumes from several point, area, or volume sources in flat and complex terrain.

Special meteorological measurements were conducted from January 15, 2015, through late spring of 2015, to support the development of this monitoring plan. The data collected during this study were used to support the air pollutant dispersion modeling. Due to the infrequent nature of northeasterly wind events (the meteorological conditions of importance for transport to Benicia and the focus of the modeling), there were only a few days to model; these days included January 24, 2015, January 25, 2015, and January 26, 2015. Meteorological data collected on these days used in the model included sodar winds (continuous winds from about 20 m to 600 m above ground level), ceilometer mixing heights (roughly the height to which any emissions will mix), and surface winds.

Sources of benzene emissions at Valero's Benicia Refinery[5] were identified, and dispersion was modeled for three representative case-study days. Benzene measurement is a reasonable surrogate for other HAP emissions.[6] Maps of the 24-hr accumulative concentrations of benzene were produced for each of the days.

Figures 11 through 13 provide the model results for these case study days. The results predict very low benzene levels downwind of the refinery. The concentrations fields provide further evidence that the monitoring paths (Paths 1 and 2) upwind of the city of Benicia are in the correct location and that monitoring along the western/northwestern fenceline is not required. Any emission that would pass just north of Path 1 would also be captured by Path 1 monitors, because of pollutant dispersion.

Because the east boundary that is upwind of the business/commercial area is covered by Monitoring Path 3, we did not perform modeling for the onshore, westerly wind events.

As noted in Figure 2, there is a small gap in coverage between monitoring Paths 1 and 2 over 2nd Street because it was not logistically feasible to measure in this area. However, the horizontal dispersion of any material released from the refinery would create a wide enough plume by the time the plume reached this gap, such that monitoring along both Paths 1 and 2 would measure any material.

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[5] Based on 2010 EPA ICR data adjusted for the flue gas scrubber.
[6] Background section of Petroleum Refinery Sector Risk and Technology Review and New Source Performance Standards.
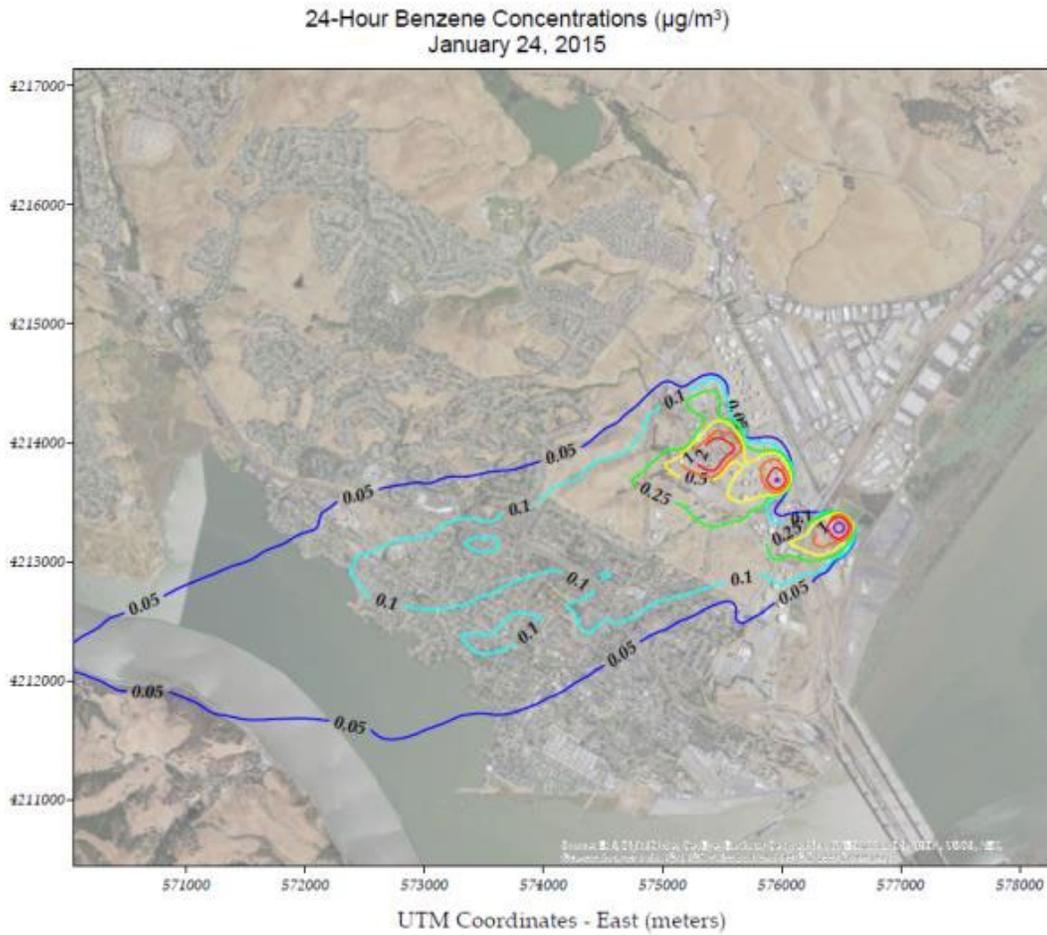
Figure 11. Dispersion modeling results using meteorological data from January 24, 2015, showing predicted 24-hr average benzene concentrations (μg/m³). Note: 1 ppb = 3.2 μg/m³ for benzene at 20°C and 1013 mb.
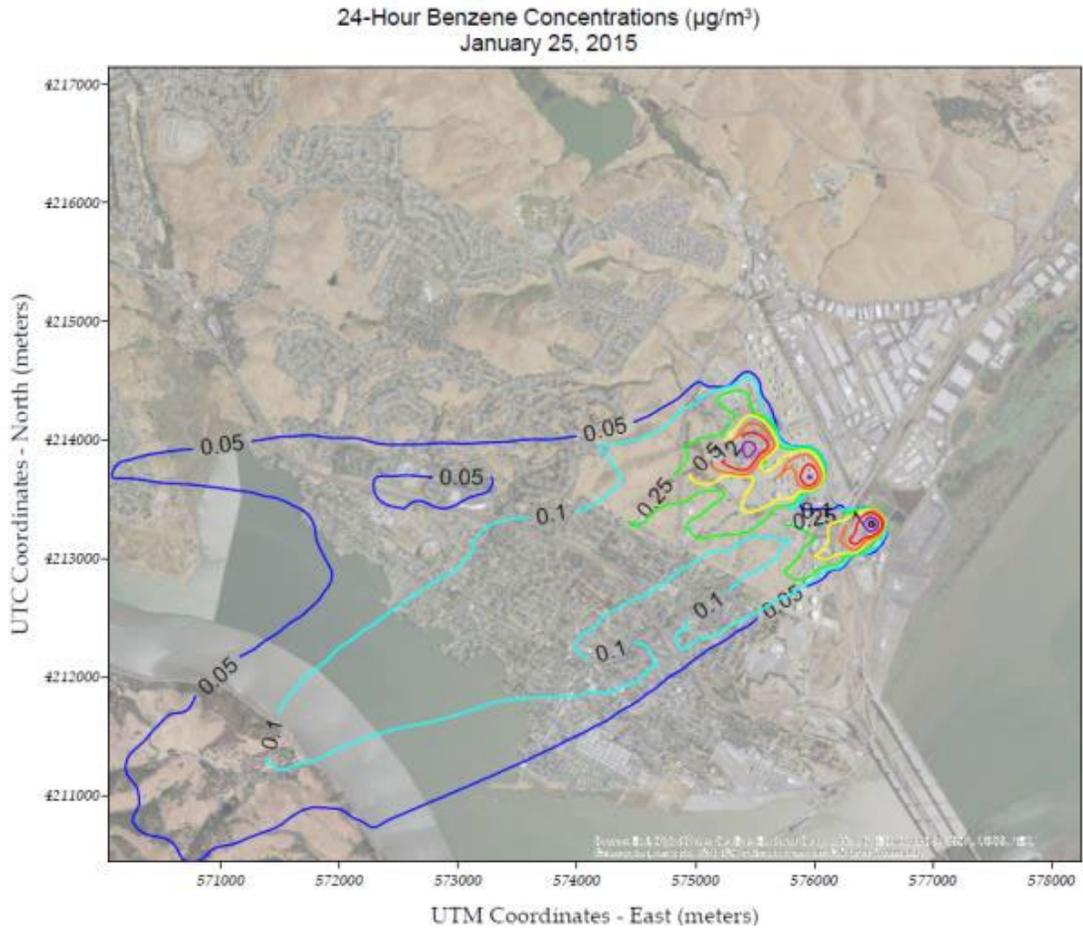
Figure 12. Dispersion modeling results using meteorological data from January 25, 2015, showing predicted 24-hr average benzene concentrations (µg/m³). Note: 1 ppb = 3.2 µg/m³ for benzene at 20°C and 1013 mb.
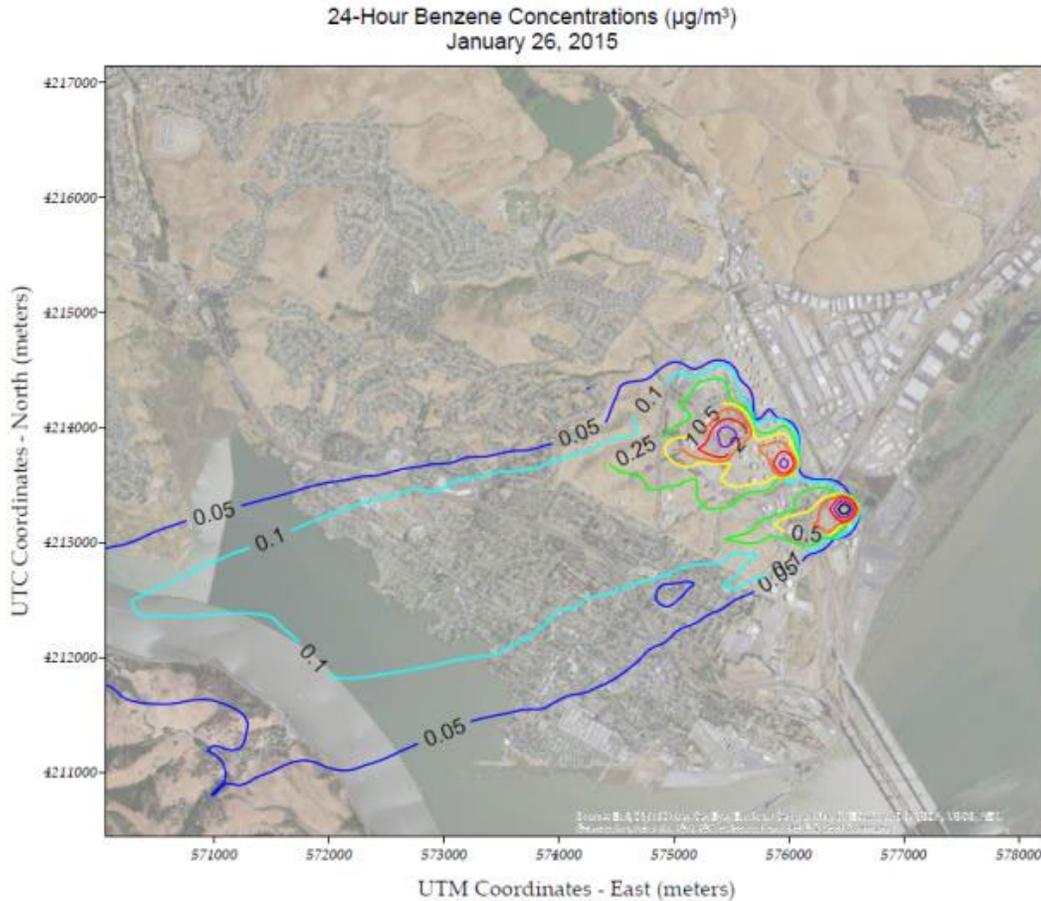
Figure 13. Dispersion modeling results using meteorological data from January 26, 2015, showing predicted 24-hr average benzene concentrations (μg/m³). Note: 1 ppb = 3.2 μg/m³ for benzene at 20°C and 1013 mb.

2.2.5 Visibility Conditions

Tule fog forms when there is high relative humidity (typically after rain), light wind, and rapid cooling. Tule fogs typically form in the California Central Valley, extending into the marshlands along the Sacramento and San Joaquin Rivers and into the Carquinez Straits, especially during the rainy season of late fall through early spring. 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. Tule fogs may occur during periods when pollutant measurements are most critical because (1) the stable atmospheric conditions associated with Tule fogs are unfavorable for pollutant dispersal, and (2) they are most likely to occur during northeasterly wind events when residential receptors in Benicia are downwind from the refinery. **Figure 14** shows an example of the Tule fog at the refinery. To investigate visibility, a visibility monitor was operated at the refinery from January 14 through July 9, 2015.

Figure 14. Example of tule fog at the Valero Benicia refinery.

Figure 15 shows that 617 5-min periods were recorded with visibility below 500 meters, and 839 periods were recorded with visibility below 1,000 meters. Based on these observations, 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. Assuming that the frequency of low visibility observed during mid-January to mid-July is representative of visibility from mid-July through mid-January, and that 2015 is representative of other years, we expect fog to impact open-path measurements about 5% of the time over the course of a year. Rule 12-15 allows for missing or invalid data due to adverse environmental conditions where supported by meteorological measurements and a narrative description. For this reason, visibility measurements are taken as part of the measurement program.

01/14/2015 - 07/09/2015
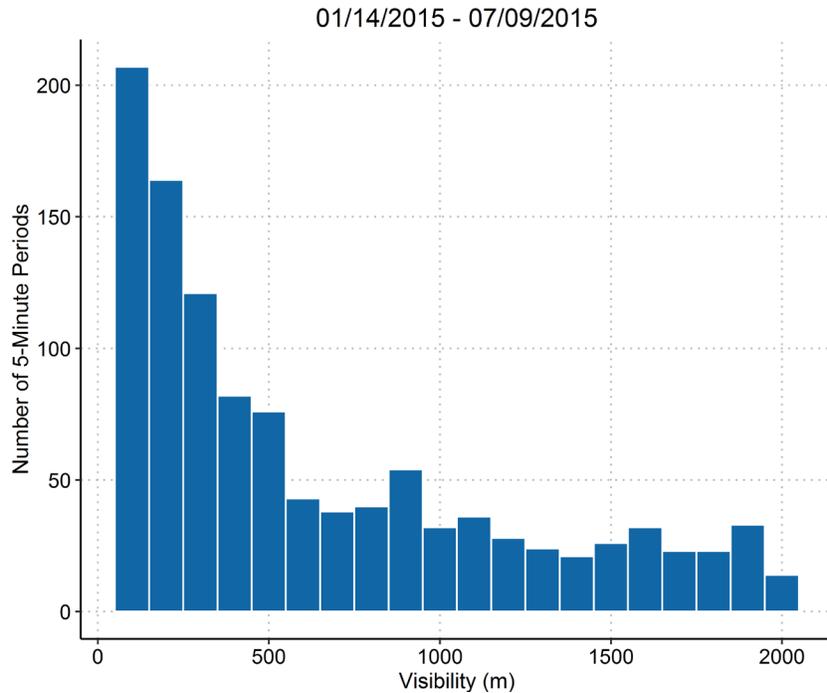
Figure 15. Histogram of 5-min visibility values of less than 2,000 meters during January 14 through July 9, 2015.

2.2.6 Instrument Selection

Literature reviews, site surveys, and interviews with instrument manufacturers were performed to determine the instruments needed to meet Rule 12-15 requirements. Both fixed-site and open-path instruments were investigated. Based on the distances that need to be covered by measurements (hundreds of meters), data time-resolution requirements (5-min), and current measurement technology, open-path instruments were selected.

Monostatic open-path instruments transmit light across a long path, which is reflected straight back by a targeted mirror ("retroreflector") for detection by a sensor located within the same housing as the light source. Energy absorption at different wavelengths is measured and recorded by the detector. Energy absorption relates to the average concentrations of gases of interest along the light path, according to Beer-Lambert's absorption law, with individual gases having characteristic wavelengths at which they absorb most effectively. Therefore, measurements of absorption between the transmitter and detector can be used to infer average concentrations across the length of the path for species of interest. **Figure 16** illustrates the basic concepts of open-path measurements. Note that open-path measurements 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.
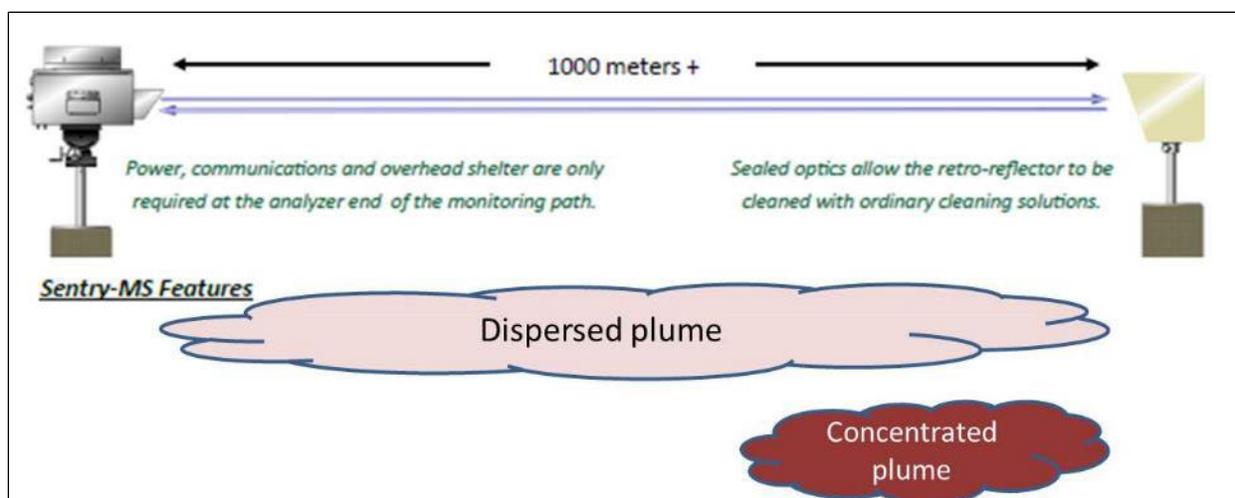
Figure 16. Basic premise for open-path instrument operation. Image from Cerex Sentry-MS monitoring brochure, used with permission from Cerex Monitoring Solutions, LLC.

Along all paths, BTEX and SO_2 is measured using a monostatic UV-DOAS with a xenon light source. The xenon light is required to achieve (1) measurements over paths that are about 300 to 600 meters long, and (2) the minimum detection limits (MDL) for BTEX. H_2S is measured using monostatic TDLAS instruments. The basic principle of TDLAS is to measure the absorption of 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. In theory, one can monitor H_2S using UV-DOAS, but its absorption spectra overlaps with BTEX and generates false positives. While Fourier Transform Infrared Technology spectroscopy (FTIR) technology was considered for measurements of BTEX and H_2S, instrument manufacturers informed Valero that FTIR is not suitable for these compounds because of poor detection limits and overlap in absorption with other compounds (such as carbon dioxide with benzene).

Table 3 summarizes the MDL and upper detection limit (UDL) for each species by instrument for each measurement path, 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.

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[7], 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 will be flagged for additional review and in the absence of marginal operating conditions considered to not meet the

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[7] Bovee, J. "Refinery Fenceline H_2S TDL Monitoring System Specifications", Communication to Valero, December 22, 2022.

performance criteria. 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 3 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 3. Open-path instruments and approximate detection limits by pollutant and path. Actual limits are different and depend on ambient conditions.

Path		1-1'		1-1"		2-2''		2-2'		3-3'		3-3"	
Distance (meters)		326		481		609		567		578		549	
Technology	Compound	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)
TDLAS[a]	Hydrogen Sulfide	3-25	12,000[a]	3-25	7,200	3-25	6,300	3-25	6,500	3-25	6,500	3-25	7,100
UV-DOAS (Xenon)	Benzene	0.4	23,900	0.3	14,700	0.2	12,800	0.2	13,400	0.2	13,400	0.3	14,600
	Toluene	1.3	13,600	0.8	8,300	0.7	7,300	0.7	7,600	0.7	7,600	0.8	8,300
	Ethylbenzene	0.5	2,900	0.3	1,800	0.3	1,600	0.3	1,600	0.3	1,600	0.3	1,800
	Xylenes	5.9	7,300	3.6	4,500	3.2	3,900	3.3	4,100	3.3	4,100	3.6	4,400
	Sulfur Dioxide	1.1	6,800	0.7	4,200	0.6	3,600	0.6	3,800	0.6	3,800	0.9	4,100

[a] Per the December 22, 2022, letter from BAAQMD[8], the level of quantitation (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. This LOQ will be achieved at less than 1% transmission.

[8] Bovee, J. "Refinery Fenceline H_2S TDL Monitoring System Specifications", Communication to Valero, December 22, 2022.

Monostatic (as opposed to bistatic) instruments use mirrors to reflect sensor light; monostatic instruments have been selected to reduce the need for substantial power at the mirror sites and to improve MDL by increasing effective path lengths. Power, communications, and shelter are required at the light-source/detector end of the monitoring path only. The retro-reflector needs only to be aligned for maximum performance at the other end of the path and to be cleaned regularly. An example of a UV-DOAS analyzer and receiver in a shelter is shown in **Figure 17**. The retro-reflector is shown in **Figure 18**. For Path 3, the instruments and retroreflectors are placed on an elevated platform to avoid interference with passing vehicles (see the example in **Figure 19**).

Figure 17. Example of a UV-DOAS analyzer installation.

Figure 18. Example of a UV-DOAS retroreflector installation.
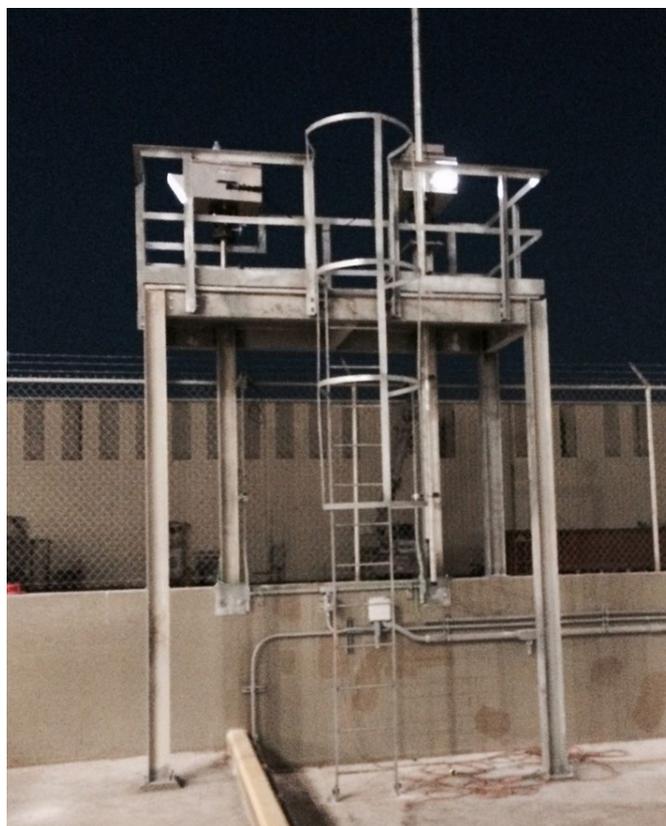
Figure 19. Example of a UV-DOAS analyzer installation on an elevated platform.

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 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. For both UV-DOAS and TDLAS instruments, a backup system will be used when each of the primary instruments are returned to the manufacturer for extended 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 regarding the QA/QC process can be found in Section 3.2.1 and in the QAPP (Appendix A).

3.   Routine Operations

For this monitoring program, 6 UV-DOAS, 6 TDLAS, and 2 visibility instruments have been installed and are currently collecting measurements. 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.

In addition, as requested by BAAQMD, sorbent tubes are used at three locations (labeled 10, 11, and 12 in Figure 2). The sorbent tubes at these locations are replaced and analyzed for benzene, toluene, ethylbenzene, and total xylenes approximately every 14 days in accordance with the 40 CFR Subpart CC Fenceline Monitoring program. Valero reviews the BTEX results and submit them to the District in a District-approved formatted spreadsheet within 30 days after receiving the results. Because the two-week monitoring period results in 26 samples per calendar year, the availability of laboratory results is not expected to align with calendar months. Therefore, Valero submits the results within 30 days of receipt and verification.

Valero follows the 40 CFR 63.658(e)(3) burden reduction schedule for sampling. If an individual monitor consistently achieves benzene results at or below 0.9 µg/m^3, the sampling frequency is reduced. For the purposes of the Rule 12-15 compliance program, the monitoring at locations 10, 11, and 12 will also be reduced.

Should three or more sampling events in one year exceed 9.0 µg/m^3 of benzene at an individual monitor between paths 2 and 3, Valero will increase the submittal frequency to the District to within two weeks after receiving the results from the laboratory. Once there is a 12-month period with no benzene results greater than 9.0 µg/m^3, the results will resume being submitted to the District within one month after receiving the results.

In the event the annual rolling average benzene concentration (deltaC) at sample locations 10, 11, or 12 exceeds the 9.0 µg/m^3 action level (as defined in 40 CFR 63.658), Valero will work with the District to consider installation of a UV-DOAS open-path monitor at this monitoring point location.

3.1   Instrument Operations

3.1.1 UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. Table 4 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 4. 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 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 >2000 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 5 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 5. 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 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 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 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, and SO_2 concentrations, and wind data are also displayed on the maps.

3.2.1   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 20). 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 21 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 20. Example of non-public field operations website used for daily review of instrument operations.
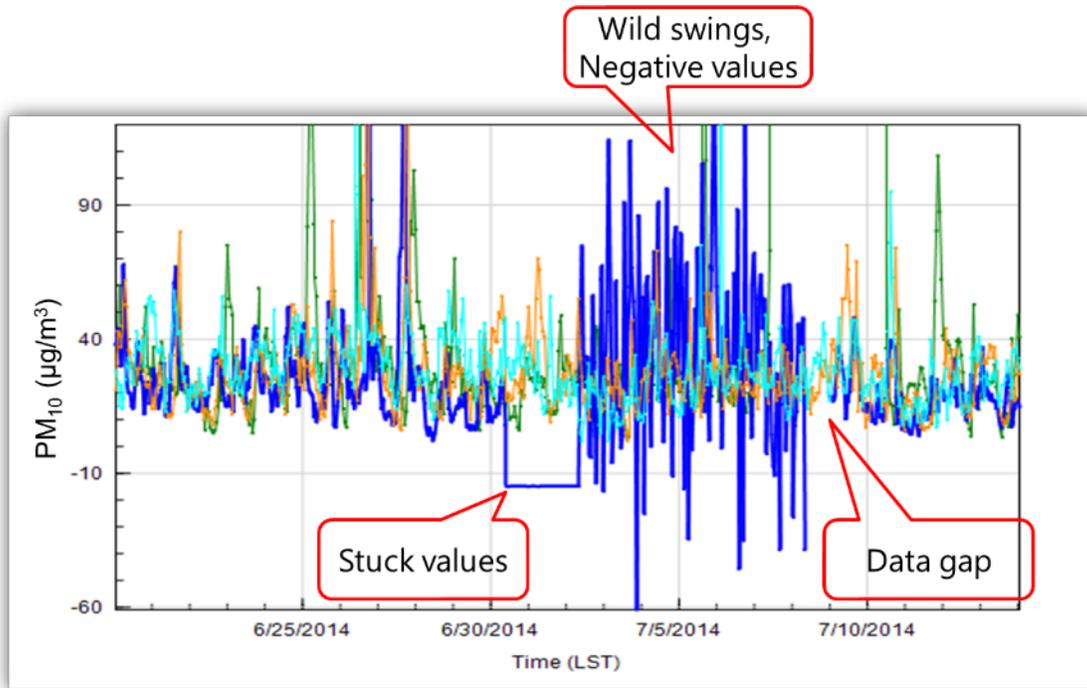
Figure 21. Example of pollutant concentration time series showing stuck values, wild swings, large negative values, and a data gap. All of these are indicators of instrument issues.

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) is 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.

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

On a quarterly basis, analysts subject the data to final QC by:

- Filling in missing records with null values, and add 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, Valero or its designated contractor reviews the performance of the network by reviewing the data completeness by monitoring path, instrument, and species; by reviewing results of bump tests; by analyzing the reported values in the context of refinery operations; and by analyzing the data in the context of the meteorology. The results are summarized in an internal technical memorandum and provided to the BAAQMD upon request.

Table 6. Initial screening checks for 5-min data. All valid and flagged data values are displayed to the public in real time. If data are invalid, they are included in the public display. During data validation, flagged data will be further investigated.

Measurement (units)	Approximate MDL for a 598-m Path[a]	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
Benzene (ppb)	0.2 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 sensor indicates malfunction or bump test data, code as appropriate and do not display the data.	If visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
Toluene (ppb)	0.7 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)	0.3 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.			
Total Xylene (ppb)	3.2 ppb. If below, flag as below MDL.	If above 100 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 50 ppb, flag data as suspect on the website and investigate validity.	If data are missing, flag as missing on the website and investigate cause.	If 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.
SO$_2$ (ppb)	0.6 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 for a 598-m Path[a]	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
H_2S (ppb)	3-25 ppb.[b]	If above 25 ppb, 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.			
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, 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.[9]

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[9] Bovee, J. "Refinery Fenceline H_2S TDL Monitoring System Specifications", Communication to Valero, December 22, 2022.

Table 7. Instrument QA/QC checks.[a]

QA/QC Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test (accuracy)	Monthly and after major service	±20%
Measurement quality – R^2	Continuous	0.8 to 1.0
Integration time	Continuous	≤250 ms
Signal intensity	Continuous	≥70%
TDLAS		
Bump test[a] accuracy (as % Error) 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 is between approx. 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
Visibility Sensor		
Accuracy	Annually	±25%

[a] For the TDLAS, accuracy and repeatability specifications will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions. Valero can currently commit to repeatedly achieving ±25% accuracy and precision using gas concentrations in the upper end of the BAAQMD's required range for bump tests and quarterly calibrations.

[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,[10] 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.

Auto-screening checks were 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 22**). DMS

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[10] Bovee, J. "Refinery Fenceline H_2S TDL Monitoring System Specifications", Communication to Valero, December 22, 2022.

keeps track of data changes in its chain of custody feature—i.e., raw data are preserved as well as all changes.
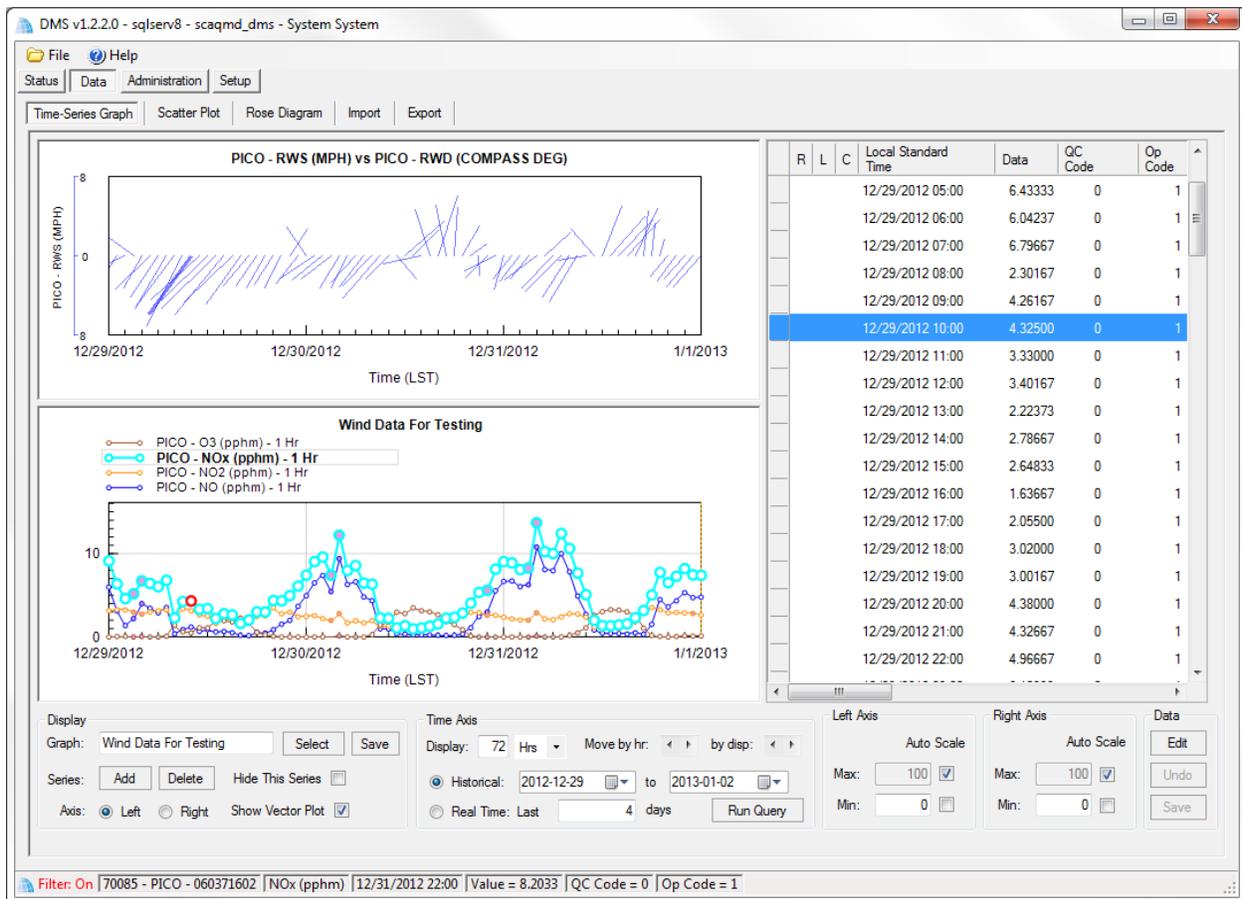
Figure 22. Screenshot of DMS showing winds and pollutant concentrations.

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 and H_2S concentrations, and visibility, wind speed, and wind direction. Data are provided as 5-min binned averages. Additionally, for the Unisearch TDL, 5-min

MDLs will be 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 23**.

In the event that high concentration levels occur, Valero will follow its existing event protocol and the City of Benicia will decide when it is appropriate to activate its emergency alert program. Episodic data will be provided to the BAAQMD upon request, consistent with other regulatory measurements.

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 Air District upon request. BAAQMD may make publicly available any of the data routinely submitted in a quarterly report.

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

Figure 23. Example of a public-facing web page.

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 as compared to other regional air quality measurements and as outlined by BAAQMD.
- Health data provided on the webpage 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 delivered to a Valero contact and a designated consultant responsible for deciding how to respond to the public comments. The emails received through the website are archived. Although not all comments have 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

Document No.	Rev No.	Rev Date	Effective Date	Distribution	Description
AMP	1	4/14/2017		BAAQMD, Refinery Project Manager, QA Manager	Initial Submission
AMP	2	7/24/2017		BAAQMD, Refinery Project Manager, QA Manager	Revised in response to BAAQMD comments
AMP	3	9/7/2017		BAAQMD, Refinery Project Manager, QA Manager	Revised in response to BAAQMD comments
AMP	4	7/23/2018		BAAQMD, Refinery Project Manager, QA Manager	Updated per District requests to (1) include chemical species data collected by sorbent tubes on the southeast corner of the refinery and (2) to reflect that hydrogen sulfide (H_2S) monitoring will be implemented on a different schedule due to unproven H_2S open-path measurement technology at this time
AMP	5	6/1/2022		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Instrument Contractors, Data Manager, Website/Data System Manager, BAAQMD	Revised in response to BAAQMD comments; revised TDL measurement
AMP	6	2/3/2023		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Instrument Contractors, Data Manager, Website/Data System Manager, BAAQMD	Revised in response to BAAQMD comments; revised TDL measurement
AMP	7	9/5/2023		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Instrument Contractors, Data Manager, Website/Data System Manager, BAAQMD	Revised in response to BAAQMD comments

Appendix A to the Air Monitoring Plan for the Valero Refinery in Benicia, California

Prepared for
Valero Refining Company - CA
Benicia Refinery
Benicia, CA

Updated: September 5, 2023
Original: September 7, 2017

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

STi | Sonoma Technology

Valero Benicia 12-15
Quality Assurance Project Plan

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STI-1922002-6990

September 5, 2023

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1.   Project Background and Management

1.1   Background

1.1.1   Purpose

The Valero Refining Company (Valero) is conducting air quality monitoring at its refinery in Benicia, California, in response to 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. Valero implemented H_2S monitoring on December 8, 2022. BAAQMD issued updated specifications on December 22, 2022, and Valero's response to the updated specifications was submitted on February 23, 2022. This revision addresses feedback from BAAQMD received 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] Valero is conducting open-path pollutant monitoring and collecting visibility and meteorological 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**.
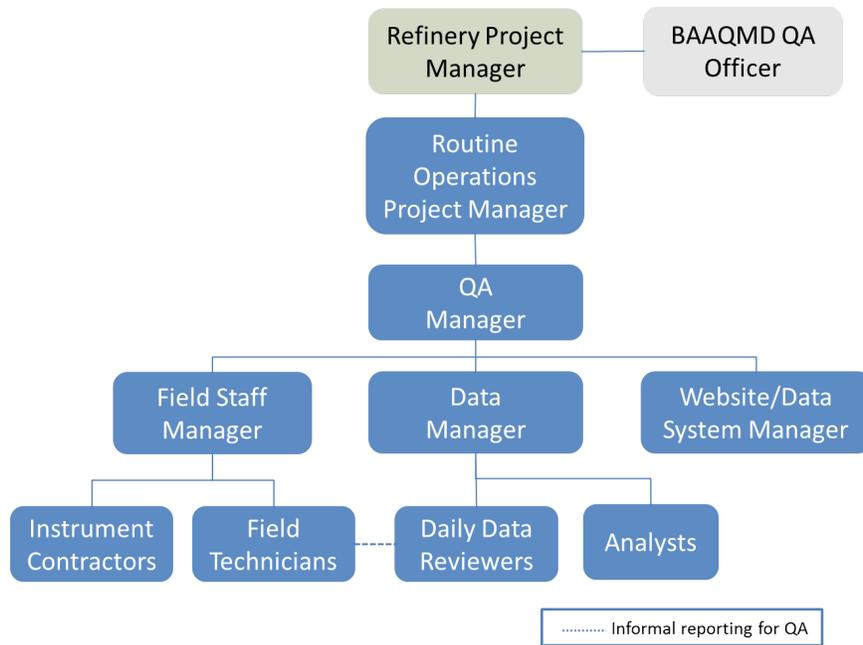
Figure 1. Organizational chart for this project.

The overall project is run by a **Refinery Project Manager** (PM) appointed by Valero. 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), and hydrogen sulfide (H_2S). These compounds are measured at a 5-min resolution. Open-path instruments (CEREX UV-DOAS and Unisearch TDLAS) were selected after consideration of (1) the distances that need to be covered by measurements (hundreds of meters), (2) data time resolution requirements (5-min), and (3) current measurement technology.

Along all measurement paths (see Section 2.2), BTEX and SO_2 are measured by monostatic Ultraviolet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. As currently installed, the xenon light is required to achieve measurements over paths that are approximately 300 meters long, and achieve reasonable minimum detection limits (MDL) for BTEX and SO_2. The analyzer records the intensity of light at discrete wavelengths. Any UV-absorbing gas present in the beam absorbs at a specific wavelength of light. 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. Beer's Law is then used to report gas concentrations. This approach is the same as what was specified in the Environmental Protection Agency's 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.

Along all measurement paths, H_2S is measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instruments. 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 TDL operates in a wavelength range that also contains an absorbance feature for water vapor and carbon dioxide, the correlation coefficient of these gases can be used as a performance metric. If the water vapor correlation drops below a threshold value, carbon dioxide correlation is examined. If that also drops below a threshold value, data are flagged as invalid. This logic reflects that water vapor and carbon dioxide 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

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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.

data file. Together with an independent visibility measurement, the signal strength can be used to evaluate the impact of atmospheric conditions or misalignment on data quality. Manufacturers report that the TDLAS has H_2S detection limits below 25 ppb over a 500 m path length under good atmospheric conditions. The actual MDL depends on atmospheric conditions.

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. Tule fog forms when there is high relative humidity (typically after rain), light wind, and rapid cooling, and is characteristic of the California Central Valley. It extends into the marshlands along the Sacramento River, the San Joaquin River, and the Carquinez Strait, especially during the rainy season from late fall through early spring. Tule fog may occur during periods when pollutant measurements are most critical because (1) the stable atmospheric conditions associated with Tule fog are unfavorable for pollutant dispersal, and (2) Tule fog is most likely to occur during northeasterly wind events when residential receptors in Benicia are downwind from the refinery. A Belfort Instrument Visibility Sensor Model 6400 is used to make visibility measurements at two locations—one at a low-elevation monitoring path and one at a higher-elevation monitoring path. These measurements provide evidence when low-visibility conditions impact invalid or missing data from the open-path instruments.

Table 1 summarizes the estimated MDL, which is the lowest concentration that can be measured, and upper detection limit (UDL), which is the highest concentration that can be measured, for each species by instrument for each measurement path, as provided by instrument manufacturers. The detection limits are presented as the average species 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 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 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 TDL, 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. Open-path instruments and approximate detection limits by pollutant and path. Actual detection limits will be different and depend on ambient conditions. H$_2$S MDLs will be evaluated in real-time.

Path		1-1'		1-1"		2-2''		2-2'		3-3'		3-3"	
Distance (meters)		326		481		609		567		578		549	
Technology	Compound	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)
TDLAS[a]	Hydrogen Sulfide	3-25	12,000	3-25	7,200	3-25	6,300	3-25	6,500	3-25	6,500	3-25	7,100
UV-DOAS (Xenon)	Benzene	0.4	23,900	0.3	14,700	0.2	12,800	0.2	13,400	0.2	13,400	0.3	14,600
	Toluene	1.3	13,600	0.8	8,300	0.7	7,300	0.7	7,600	0.7	7,600	0.8	8,300
	Ethylbenzene	0.5	2,900	0.3	1,800	0.3	1,600	0.3	1,600	0.3	1,600	0.3	1,800
	Xylenes	5.9	7,300	3.6	4,500	3.2	3,900	3.3	4,100	3.3	4,100	3.6	4,400
	Sulfur Dioxide	1.1	6,800	0.7	4,200	0.6	3,600	0.6	3,800	0.6	3,800	0.9	4,100

[a] Per the December 22, 2022, letter from BAAQMD,[4] 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.

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

2.2   Monitor Siting Rationale

For the fenceline monitoring program, Valero uses open-path instruments to measure the required compounds—BTEX, SO_2, and H_2S—along three paths. The three measurement paths, composed of two segments each, have been implemented to cover Valero's fencelines in consideration of (1) nearby local receptors (e.g., residences and businesses), (2) dominant winds that blow from west to the east, and (3) infrequent winds that blow northeast to southwest and affect portions of populated areas in Benicia.

The three monitoring paths, composed of six total segments, are shown in Figure 2.

- Paths 1 and 2 cover the southwest fenceline to assess potential transport toward the city of Benicia. This transport direction is infrequent and only occurs on an occasional basis in the winter when winds sometimes blow northeast to southwest. Over the course of a year, these northeast winds occur less than 7% of the time. Due to terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability. Therefore, the downwind areas that could be affected under these wind conditions are very narrow.

- Path 3 covers the eastern fenceline to assess potential transport toward the business/commercial area located east of the refinery. This transport direction is common in spring, summer, and early fall, when winds often blow west to east.

- Instruments on Paths 1 and 2 are elevated about 7 feet above ground level (AGL). Instruments on Path 3 are elevated about 15 feet AGL so vehicle traffic does not block the open-path sensor light.

- Open-path analyzers are located at all sites. Sites 1 and 2 each have two UV-DOAS and two TDLAS instruments. Each pair of analyzers at each site point roughly 180° from each other. Sites 3' and 3" each have one UV-DOAS and one TDLAS analyzer. The remaining numbered sites (1', 1", 2', 2", and 3) have retroreflectors (i.e., mirrors). This setup provides maximum spatial coverage along the critical paths.

Figure 2. Open-path monitoring network for Valero's Benicia Refinery. Each primary path is numbered, and the endpoints are numbered and labeled with a prime (') or double prime ('') symbol. Main wind flow directions are shown.

Visibility instruments are placed at Sites 1 and 3' to collect measurements at different locations and elevations. These two sites have been selected because visibility can vary spatially across the refinery.

2.3 Instrument Operations and Maintenance

Three types of instrument systems are included in this project: UV-DOAS, TDLAS, and visibility measurements. Other meteorological data are obtained from an existing meteorological station at the refinery. 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 the instruments are recorded in a site-specific logbook.

2.3.1 CEREX UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. **Table 2** summarizes typical UV-DOAS maintenance activities as recommended by the manufacturer. These actions help ensure data integrity and maximize up-time. Table 9 further defines operational limits that are used to trigger corrective actions during separate site visits. Maintenance schedules will be altered as needed.

Table 2. 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 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 6 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure 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 >2000 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.			✓

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 3 summarizes TDLAS maintenance activities, as recommended by the manufacturer and required by the BAAQMD. Table 9 further defines operational limits that is used to trigger corrective actions during separate site visits. Maintenance schedules are altered as needed.

Table 3. 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.* Signal power should be greater than 0.1 mW.		✓	
Perform 3-point calibration check.		✓	
Verify system settings.			✓

  * 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   Belfort Model 6400 Visibility Sensor

For the visibility instruments, monthly maintenance includes inspecting the sensor for dirt, spider webs, bird nests, or other obstructions (see Table 4). 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. Table 9 further defines

operational limits that are used to trigger corrective actions during separate site visits. Maintenance schedules will be altered as needed.

Table 4. Schedule of maintenance activities for the Belfort Model 6400 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 come as a request to BAAQMD and be agreed to by BAAQMD in cooperation with the Valero, Benicia Refinery.

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, supported by Terra Applied Systems (an instrument contractor), 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 from Valero. BAAQMD staff will be notified of monitoring downtime according to BAAQMD Regulation 1-530.[5]

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

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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.

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, such as those detailed in Table 5, to determine actions.

Table 5. 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 Valero 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 6 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 6. 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
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 thorough meteorological analysis was performed and documented in the monitoring plan. Comparability among measurements is ensured by using one manufacturer for each system across every site (UV-DOAS, TDLAS, visibility) so that hardware and software are consistent.

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. All data in exceedance of reference exposure levels (RELs) are automatically

flagged as suspect/questionable for additional manual review and verification. 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 7 presents an overview of relevant QC/OP codes that are used throughout the QC process, including manual QC.

Table 7. 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, a single-species bump test using benzene is performed monthly and will potentially be performed less frequently in the future if the measurements prove adequately stable or should additional metadata provide assurance that instruments are working properly. 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 instruments, 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 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 ten 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 8. 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 8 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 data from open-path analyzers 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 8. Initial screening checks for 5-min data. All valid and flagged data values are displayed to the public in real time. If data are invalid, they are not to be included in the public display. During data validation, flagged data will be further investigated.

Measurement (units)	Approximate MDL for a 598 m Path*	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
Benzene (ppb)	0.2 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 sensor indicates malfunction or bump test data, code as appropriate and do not display the data.	If signal strength is below the threshold value and visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
Toluene (ppb)	0.7 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)	0.3 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.			
Total Xylene (ppb)	3.2 ppb. If below, flag as below MDL.	If above 100 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	If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.	If data are missing, flag as missing on the	If sensor indicates malfunction or bump test data,	If signal strength is below the threshold value and visibility is

Measurement (units)	Approximate MDL for a 598 m Path*	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
SO$_2$ (ppb)	0.6 ppb. If below, flag as below MDL.	If above 37.5 ppb, flag data as suspect on the website and investigate validity.	website and investigate validity.	If value changes by more than 19 ppb, flag as suspect on the website and investigate validity.	website and investigate cause.	code as appropriate and do not display data.	less than 2.5 miles, code as invalid on the website due to low visibility.
H$_2$S (ppb)	3-25 ppb.	If above 30 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 30 ppb, flag as suspect on the website and investigate validity.			
Visibility (meters)	If value is less than 0, flag data.	Not applicable		Not applicable			Not applicable

* MDL is dependent on atmospheric conditions. Data is evaluated on the basis of correlation coefficient and other operational parameters such as signal strength. If data 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 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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[6] Bovee, J. "Refinery Fenceline H$_2$S TDL Monitoring System Specifications", Communication to Valero, 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 9. 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 9 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 9. Instrument QA/QC checks.[a]

QA/QC Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test (accuracy, as % error)	Monthly and after major service	±20%
Measurement quality – R^2	Continuous	0.8 to 1.0
Integration time	Continuous	≤250 ms
Signal intensity	Continuous	≥70%
TDLAS		
Bump test[a] accuracy (as %Error) 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 will be in the range of about 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
Visibility Sensor		
Accuracy (as %Error)	Annually	±25%

[a] For the TDLAS, accuracy and repeatability specifications will be treated as objectives to become requirements once it is proven they can be reliably met under all seasons and atmospheric conditions. Valero can currently commit to repeatedly achieving ± 25% accuracy and precision using gas concentrations in the upper end of the BAAQMD's required test range for bump tests and quarterly calibrations.

[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,[8] the LOQ is taken to be equivalent to the MDL and is calculated as twice the standard deviation of a blank sample for the TDL.

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[8] Bovee, J. "Refinery Fenceline H_2S TDL Monitoring System Specifications", Communication to Valero, December 22, 2022.

4. Data Management

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:

- Data for all instrument and parameter combinations in the comma separated value (.csv) data file template provided by BAAQMD. Data will contain:

    o The name of the facility where the equipment is located

    o A unique identification number assigned to each instrument or system

    o A short descriptive name for the instrument associated with the reported unique ID (e.g. TDL, UV-DOAS)

    o The name of the compound being measured

    o The date of measurement, formatted as "yyyy-mm-dd"

    o 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

    o The mean 5-min concentration, reported as numeric values for detection events above and below the LOQ

    o The unit of measure corresponding to the reported mean concentration

    o The averaging period duration (in minutes) for the reported mean concentration

    o The number of values that comprise the reported mean concentration

    o 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.

    o 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

    o The maximum concentration measured during the averaging period, reported in the same units of measure as the mean concentration

    o The required LOQ for the corresponding instrument, reported in the same units of measure as the mean concentration

    o The real-time LOQ for the averaging period, reported in the same units of measure as the mean concentration

    o The average measured light signal for the corresponding averaging period

    o 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

Document No.	Rev No.	Rev Date	Effective Date	Distribution	Description
QAPP	1	12/7/2018		Refinery Project Manager, QA Manager, Field Staff Manager, Field Technicians, BAAQMD	Initial submission
QAPP	2	3/4/2019		Refinery Project Manager, QA Manager, Field Staff Manager, Field Technicians, Data Manager, Daily Data Reviewers, BAAQMD	Addressed comments from BAAQMD Addition of TDL measurement for H_2S
QAPP	3	8/23/2019		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Field Technicians, Data Manager, Daily Data Reviewers, BAAQMD	Addressed comments from BAAQMD
QAPP	4	1/8/2020		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Field Technicians, Data Manager, Daily Data Reviewers, BAAQMD	Addressed comments from BAAQMD
QAPP	5	6/1/2022		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Field Technicians, Data Manager, Daily Data Reviewers, BAAQMD	Revision of TDL measurement information
QAPP	6	2/3/2023		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Instrument Contractors, Data Manager, Website/Data System Manager, BAAQMD	Revised in response to BAAQMD comments. Adding TDL measurement.
QAPP	7	9/5/2023		Refinery Project Manager, Routine Operations Project Manager, QA Manager, Field Staff Manager, Instrument Contractors, Data Manager, Website/Data System Manager, BAAQMD	Revised in response to BAAQMD feedback

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

Appendix A.

Standard Operating Procedures for the CEREX UV Sentry UV-DOAS

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.
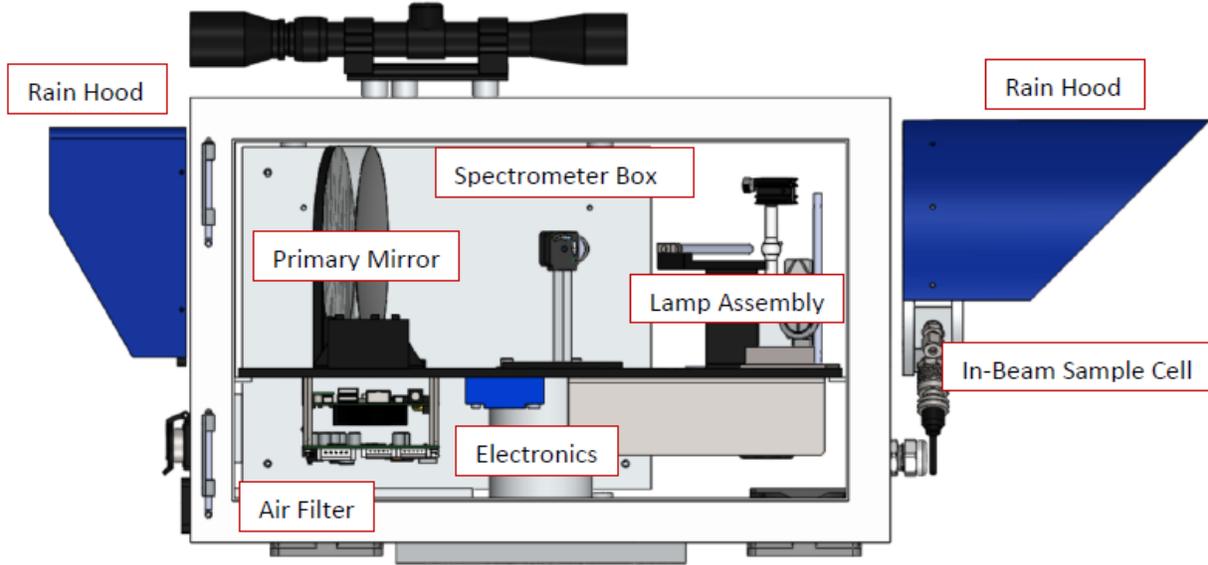
Figure 1. Schematic of the monostatic UV Sentry UV-DOAS analyzer.

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**.
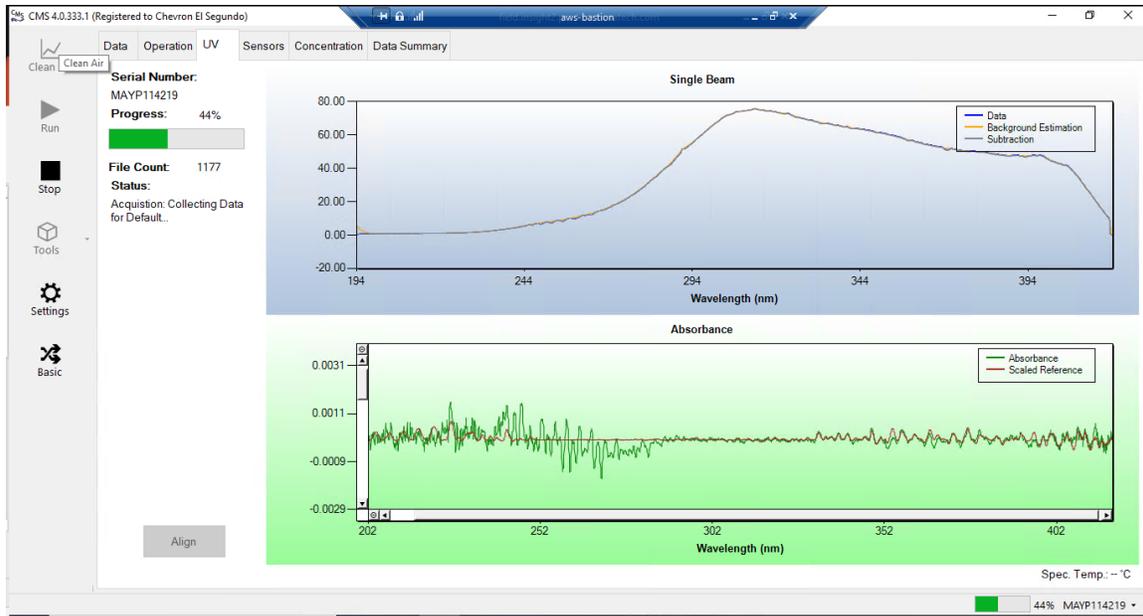
Figure 2. Screenshot showing the **UV** tab of the CMS software. Note that the **Align** button is grayed out because the instrument is in run mode (the **Run** button is also grayed out because the instrument is in run mode).

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.
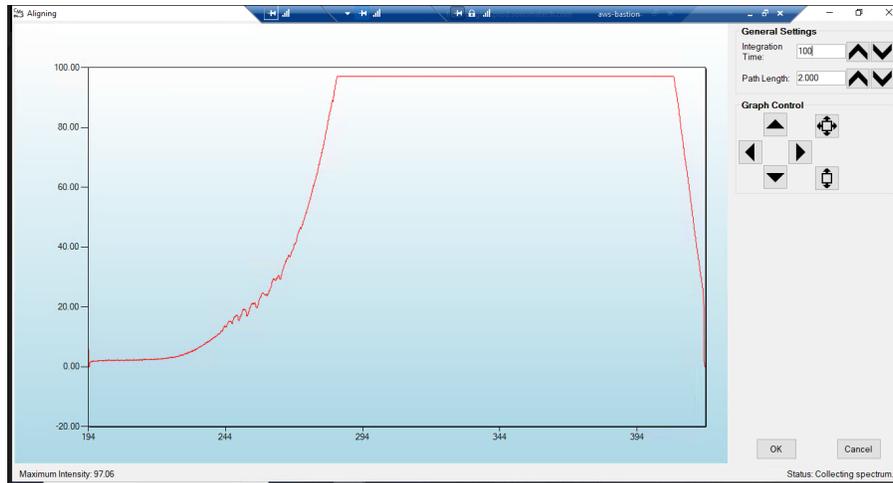
Figure 4. An example of a saturated spectrum when in **Align** mode. Note the "flat top" profile of the spectrum. The spectrum flattens out because the detector has saturated at those wavelengths and cannot quantitatively measure additional light.

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

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- 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**
- <u>Analysis</u>
  - 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
  - o 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.
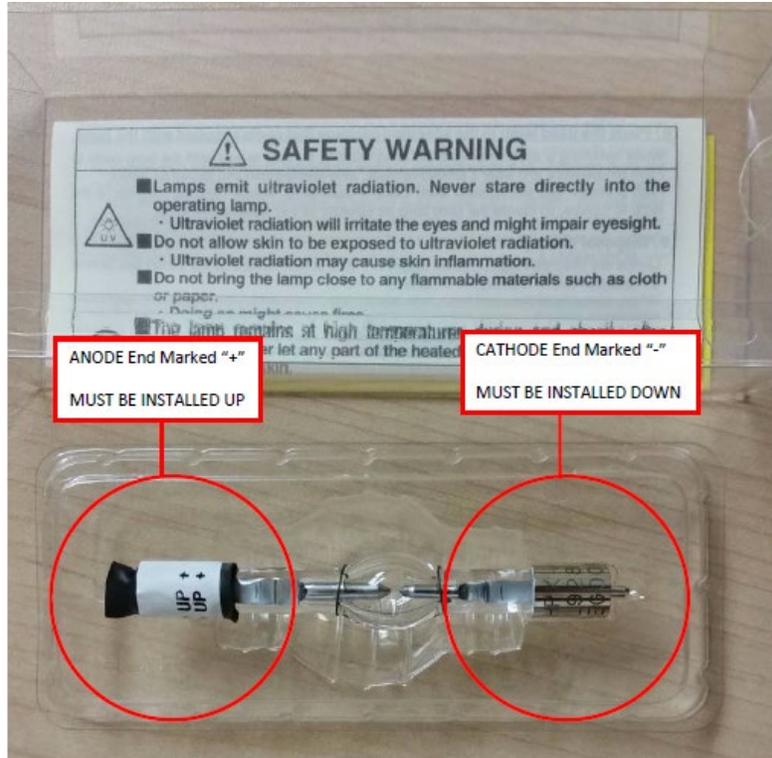
Figure 8. The ANODE end of the UV Source is marked (+). The CATHODE end of the UV Source is marked (-).

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).
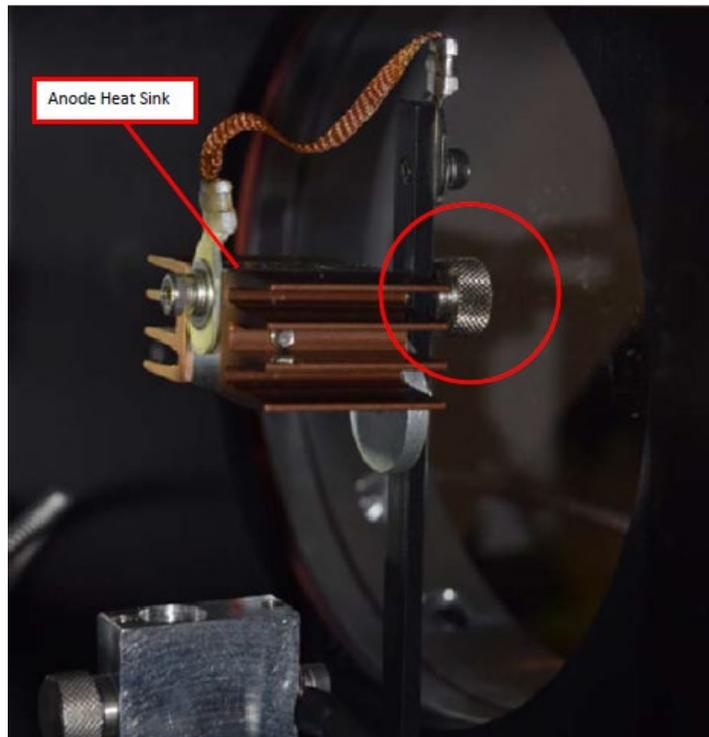
Figure 10. Anode heatsink at the top of the UV source.

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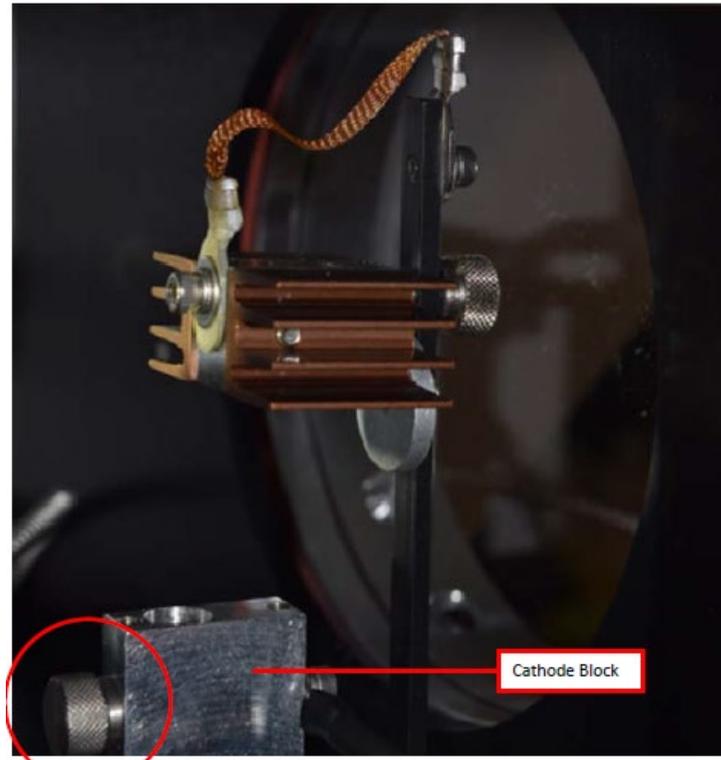
Figure 11. Loosen the thumbscrew on the Cathode block at the bottom of the UV source.

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 (-).
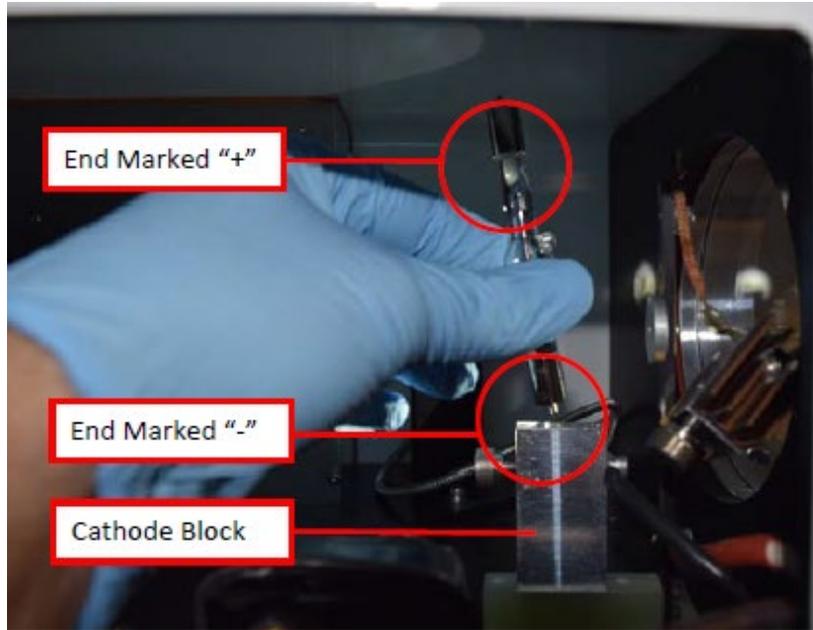
Figure 12. Inserting the Xenon UV Source into the Cathode block.

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**.
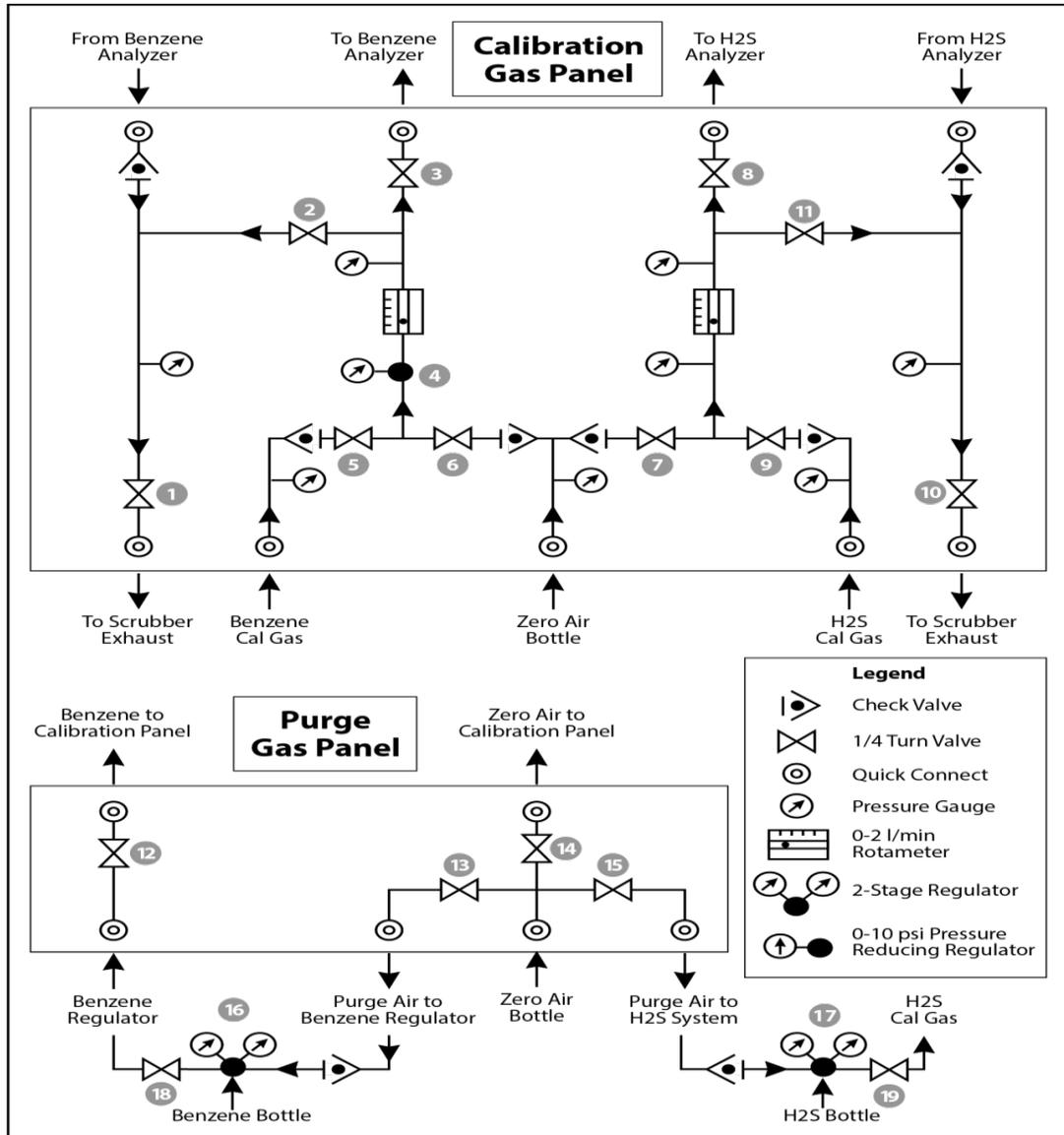

Figure 13. Diagram of the calibration gas panel (top) and purge gas panel (bottom) used for gas delivery.

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 $7 \leq N \leq 15$. 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:

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

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

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.

***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.

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.
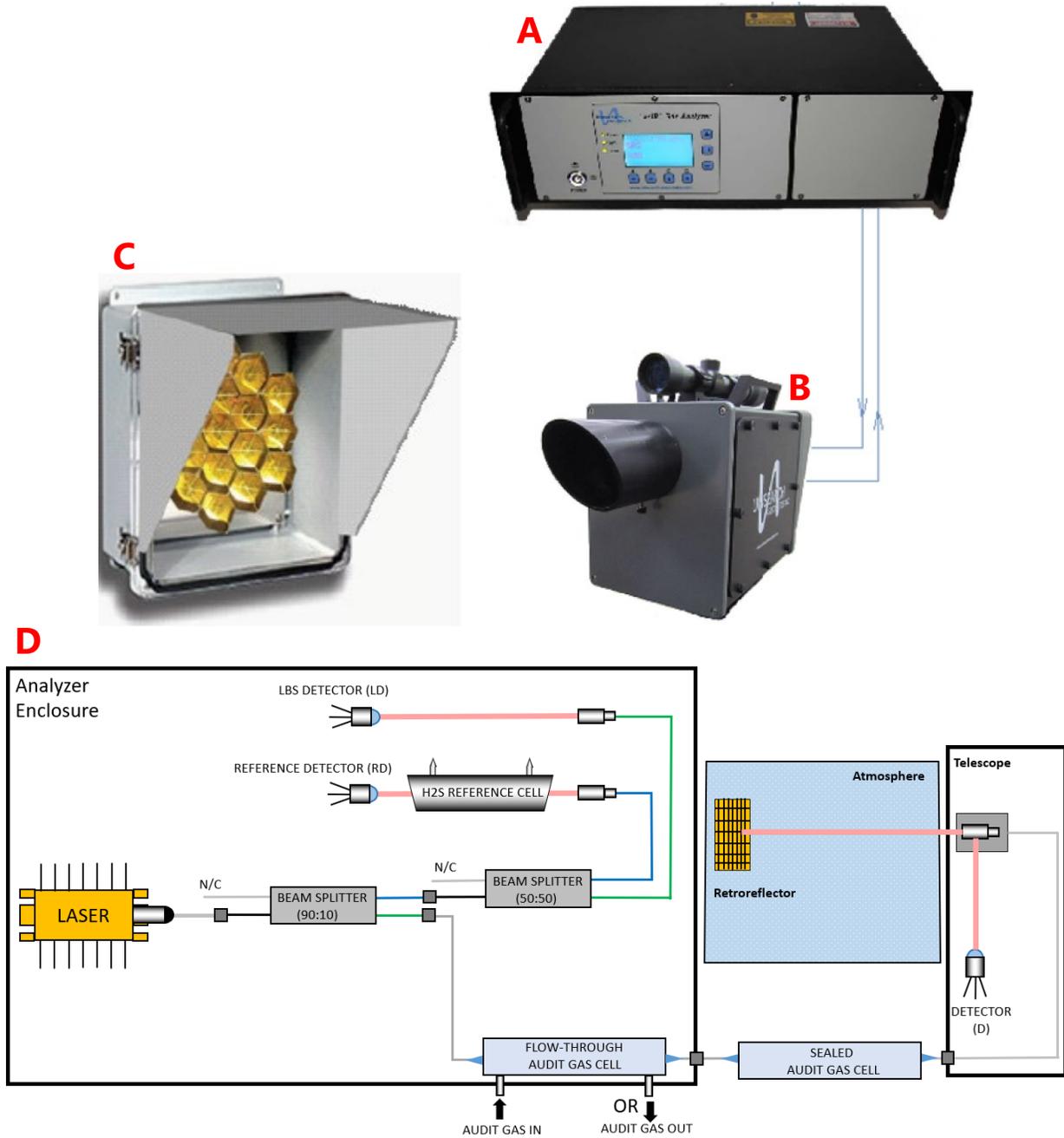
Figure 1. (a) Unisearch TDLAS Analyzer box, (b) telescope, (c) retroreflector, and (d) schematic diagram showing the optical fiber paths and detection points.

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.
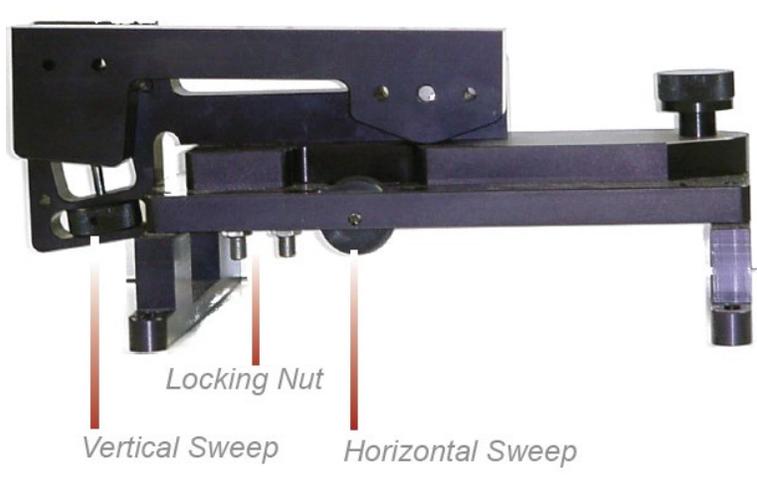
Figure 2. Location of adjustment knobs used for alignment of the Unisearch TDLAS.

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.
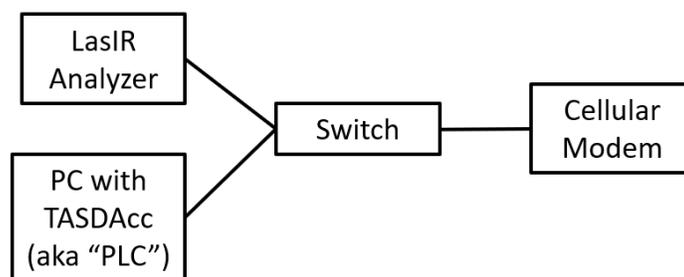

Figure 3. Diagram of local network configuration for the LasIR system.

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.
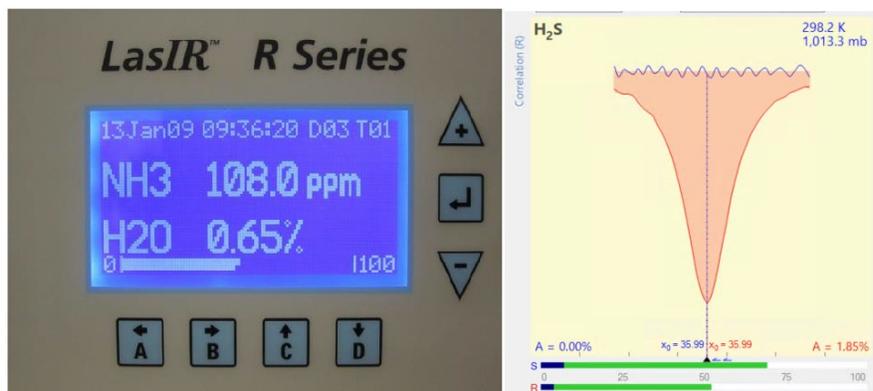

Figure 4. Main running window on instrument front panel (left) and scope display in LasIR View software (right).

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)

$$125.25 \text{ ppm-m} / 1000 \text{ m} = \textbf{0.125 ppm or 125 ppb } \mathbf{H_2S}$$

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 ≤ 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. 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:

Appendix C. Belfort Model 6400 Visibility Sensor Maintenance and Audit Procedures

Appendix C

Belfort Model 6400 Visibility Sensor Maintenance and Audit Procedures

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Contents

Summary

This document describes the steps necessary to calibrate and maintain the Belfort Instrument Visibility Sensor Model 6400. The procedure is intended to verify that the equipment is performing to expectations and that the detection and communication links are functioning correctly. Hardcopies of this procedure and associated audit forms will be kept on site. Upon completion of the audit procedure, a copy of the audit form showing the results will be sent to the Refinery Project Manager.

General Maintenance

Belfort Instrument suggests that the initial maintenance of the Visibility Sensor be conducted three months after installation. The technician will need to adjust this time frame based on the individual site environment in which the instrument is installed. Factors may include, but are not limited to, insects at the site, weather conditions, dust, blowing debris, and deposits from water spray. Table 1 provides a schedule of maintenance activities for the sensor.

The technician should periodically inspect the sensor for dirt, spider webs, bird nests, and other obstructions. When necessary, carefully clean the protective glass windows in the Receiver and Transmitter with a commercially available glass cleaner.

There are no user serviceable components in the sensor. Should a failure occur, return the sensor to Belfort Instrument for repair.

Table 1. Schedule of maintenance activities for the Belfort Model 6400 Visibility Sensor.

Activity	Monthly	Annually
Visually inspect the system, including all cables.	✓	
Inspect optics on detector and clean if necessary.	✓	
Check calibration. An acceptable % accuracy 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 shall be approved by BAAQMD.

Contact Belfort Instruments or Sonoma Technology to receive a digital copy of the manual.

Preparing for Calibration

Before beginning the calibration, make sure to have all of these materials:

- Serial cable with hook or alligator clips

- Opaque filter
- Scatter plate
- Laptop with terminal emulator

If the calibration is being performed in the field, select a clear day with low wind speeds. Fog will affect calibration results; wind speed should be less than 10 knots. For the calibration to be valid, visibility must be at least 1 mile. The sensor needs to have been powered on for at least 45 minutes before beginning calibration. Check that the sensor windows are clean and clear of any noticeable dirt, spider webs, or other obstructions.

The technician will need to set up a serial connection with the sensor, then perform a zero calibration and a span calibration (in that order).

Setting Up the Serial Connection

1. Disconnect the three serial wires connected to the CR310 data logger's terminals and reconnect them to the serial cable with hooks (or alligator clips). Note: the red wire is RX, the brown wire is TX, and the bare wire is the ground. Then connect the serial cable to a laptop.

2. Use **Device Manager** to check the com port you are connected to under the **Ports** section.

3. Open a terminal emulator, such as **Tera Term**, and set it to that com port. Make sure the serial settings match that of the Belfort 6400 (baud rate 9600, 8 bit, no parity, 1 stop bit, no flow control).

4. Test the connection by typing the **FL** command into the terminal without pressing Enter. Immediately, a list of values should be returned similar to this:

   P,00223, 1, 0.19333965, 40.33408642, 1.45484,Mi, 1.281314 0000

   If nothing is returned, try swapping the red and brown wires. If it still doesn't work, check the serial settings to make sure they are correct.

5. Before the calibration commands can be entered, the terminal must be given super user privilege. Hold down the **Ctrl** key and press the **V** key. Then type in the password **foggy** and press **Enter**. You should see the message, "Password accepted, Operator is now Super User." To stop being a super user at any time, press **Ctrl-V** and **Enter** again without entering the password. Turning the sensor off and on will also end super user status. DO NOT USE ANY COMMANDS NOT STATED IN THIS SOP WHILE IN SUPER USER MODE. Doing so could compromise the sensor's functionality.

Zero Calibration

1. Push the black foam opaque filter into the receiver hood on the sensor (see **Figure 1**). This is the hood on the left when facing the front of the sensor. You are facing the front when you can see the "Belfort" logo on the device. Make sure the filter is completely blocking the receiver window. *Warning:* the hood might be hot to the touch if the heaters are on.

2. In the terminal emulator, enter the command **FZ**. The sensor will ask for verification before starting the calibration routine; type the letter **Y** to accept (or **Esc** to abort).

3. The zero calibration routine will run for 3 minutes allowing the sensor to reach a stable zero state, after which it will run for 2 more minutes taking an average of the zero offset.

4. At the end of the zero calibration routine, the operator will be prompted to accept the new zero offset value. If the operator does not respond within 3 minutes, the sensor aborts the calibration (discarding the value generated). After accepting the new value, record it along with the previous value in eSIMS or a laboratory/field notebook.

5. Do not forget to remove the opaque filter after doing the zero calibration; failure to do so will result in constant high visibility readings regardless of actual conditions.
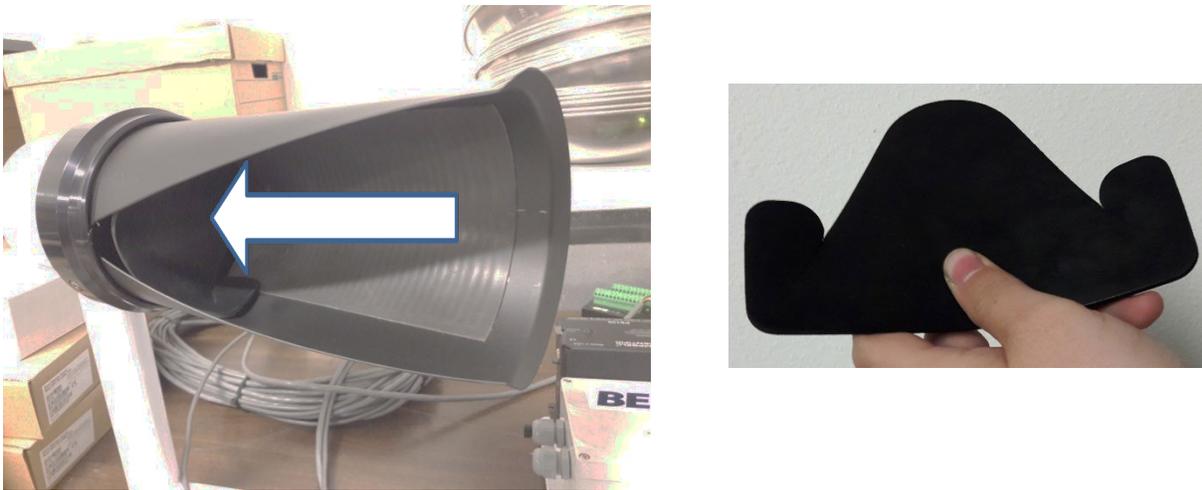

Figure 1. Inserting the opaque filter.

Span Calibration

1. Make sure the opaque filter has been removed from the receiver hood. Check the scatter plate for smudges and scratches. Clean off any smudges with a commercial glass cleaner (do not use harsh solvents as they will melt the plastic on the scatter plate). If the scatter plate is badly scratched, contact the manufacturer before use.

2. Carefully hang the scatter plate on the sensor by hooking the top bracket over the top of the sensor's cross arm. Center the scatter plate on the cross arm an equal distance from the edge of each hood to the plate. Make sure the plate is secure and not swinging or rotating on the sensor's cross arm (see **Figure 2**).

3. In the terminal emulator, enter the command **FN**. A list of configuration parameters will be returned. Verify that the value of **Cal_ExtCo** (Calibration Extinction Coefficient) is equal to the value marked on the scatter plate's label. If they do not match, enter the command **FC**. A similar list of parameters will appear, followed by a prompt to change them. The prompt will

go through each parameter one by one. Press **Enter** to go to the next parameter until you reach the **Cal_ExtCo** parameter. Enter the value found on the scatter plate's label and press **Enter**. Then press **Esc**. **DO NOT CHANGE ANY OTHER PARAMETERS**. Doing so could compromise the sensor's functionality.

4. Enter the **FS** command. When the sensor asks for verification before starting the calibration routine, type the letter **Y** to accept (or **Esc** to abort).

5. The span calibration routine will run for 3 minutes, allowing the sensor to reach a stable span state, after which it will run for 2 more minutes making periodic adjustments to the slope as it attempts to minimize the error.

6. At the end of the span calibration routine, the operator will be prompted to accept the new span factor value. If the operator does not respond within 3 minutes, the sensor aborts the calibration (discarding the value generated). After accepting the new value, record it along with the previous value in eSIMS or a laboratory/field notebook.

7. Do not forget to remove the scatter plate from the sensor and carefully put it away in a safe place.

8. Record procedure details and results, plus date and operator name, etc., in eSIMS or a laboratory notebook.
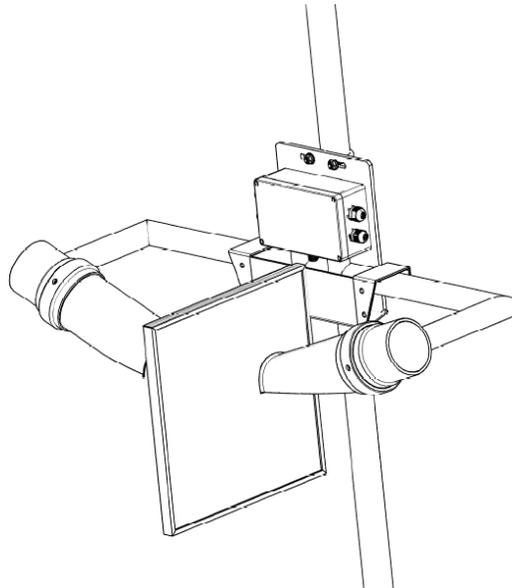

Figure 2. Scatter plate mounting.

Completing the Process

1. Disconnect the serial cable from the laptop, disconnect the Belfort 6400's three serial wires from the cable, and reconnect them to the CR310 data logger. The red wire goes to the **C1**

terminal, the brown wire goes to the **C2** terminal, and the bare wire goes to the **G** terminal of the CR310.

2. Connect to the CR310 through Loggernet (either via a micro-USB cable to a field laptop or via the DMZ server connection) and check to see if values are coming in and if they make sense. Note: the values might initially be lower than expected; wait 5-to-10 minutes for the sensor to readjust itself.

QA Audit Record Template

Belfort Model 6400 Visibility Sensor Audit Record

DATE:_____   Location: _____

Test Technician 1 :_____
Test Technician 2 :_____

Zero State Calibration

Start Time: _____

Previous Zero Offset: _____

New Zero Offset: _____

Stop Time: _____

Notes:

Span Calibration

Start Time: _____

Scatter Plate ExCo: _____

Span Factor: _____

New Span Factor: _____

Stop Time: _____

Notes: