Air Monitoring Plan for the Tesoro Refining & Marketing Company, LLC Martinez Renewable Fuels Facility in Martinez, California

Submitted by Martinez Renewable Fuels Facility Martinez, California

September 5, 2023

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Air Monitoring Plan

September 5, 2023

Prepared in consultation with Sonoma Technology

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# Version History

Version Number	Date	Description of Change
1	September 7, 2017	Initial AMP submittal to BAAQMD.
2	June 1, 2022	Updated QAPP submittal to BAAQMD – includes addition of open-path H <sub>2</sub> S measurement technology and data quality objectives.
3 (rescinded)	December 1, 2022	Updated AMP and QAPP submittal to BAAQMD – includes revisions pursuant to AQMD review and comments.
4	February 17, 2023	Resubmittal of December version – includes updates and revisions following revised TDLAS specifications issued by BAAQMD in December 2022.
5	September 5, 2023	Revised in response to July 19, 2023, feedback from BAAQMD

## 1. Introduction

Tesoro Refining & Marketing Company, a subsidiary of Marathon Petroleum Corporation, monitors fenceline concentrations of certain compounds at the Martinez Renewable Fuels Facility in Martinez, California, in compliance with the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15). The monitoring program follows a facility-specific air monitoring plan consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.<sup>1,2</sup> Rule 12-15 requires refineries to monitor multiple species in a manner that achieves a minimum detection limit (MDL) in the parts-per-billion (ppb) concentration range, using measurement technology such as "open-path" or an equivalently sufficient method, with all data reported to the public.<sup>1</sup> Rule 12-15 requires monitoring for concentrations of benzene, toluene, ethylbenzene, xylenes (BTEX), and hydrogen sulfide (H<sub>2</sub>S). In addition, sulfur dioxide (SO<sub>2</sub>), alkanes, 1,3-butadiene, other organics, and ammonia (NH<sub>3</sub>) were considered for measurement. This Monitoring Plan was approved in June 2018, with conditions to: (1) update the Quality Assurance Project Plan (QAPP, located in Appendix A) and (2) select H<sub>2</sub>S monitoring technology. On October 6, 2021, BAAQMD provided updated requirements for refineries to conduct additional H<sub>2</sub>S monitoring along refinery fenceline paths and implement this enhanced monitoring by January 1, 2023. These requirements were met and the Martinez Facility notified the BAAQMD within seven days of the H<sub>2</sub>S systems becoming fully operational. BAAQMD issued updated specifications on December 22, 2022. The Martinez Facility's response to the updated specifications was submitted on February 23, 2022. This version of the monitoring plan addresses feedback from BAAQMD received July 19, 2023.

### 1.1 Plan Summary

### 1.1.1 General Principles of Proposed Measurement Techniques

The Martinez Facility monitors concentrations of the aforementioned compounds using open-path instruments placed at or near the refinery's property fencelines. Open-path instruments operate based on the following principles of physics:

- Each gas species absorbs light energy at characteristic wavelengths; thus, a target gaseous species can be specifically identified by monitoring for light absorption at a specific wavelength.
- The extent of light absorption is proportional to the path-average concentration of the target gaseous species. The greater the absorption, the higher the concentration.

<sup>&</sup>lt;sup>1</sup> Petroleum Refining Emission Tracking (Rule 12-15; approved by the BAAQMD on April 20, 2016).

<sup>&</sup>lt;sup>2</sup> Bay Area Air Quality Management BAAQMD (2016) Air Monitoring Guidelines for Petroleum Refineries. April 2016. Available at baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016hearing/1215-amg-041416-pdf.pdf?la=en.

Open-path instruments transmit light or infrared energy across a long open path. Energy absorption relates to the average concentration of gases of interest along the path, according to the Beer-Lambert absorption law. Individual gases absorb most effectively at characteristic wavelengths; therefore, measurements of energy absorption at specific wavelengths can be used to infer path-average concentrations for species of interest. The transmitted energy signal is typically either detected remotely by a targeted detector or reflected for detection elsewhere. Often a combined transmitter-detector unit is positioned at one end of a path, and a retroreflector—a type of mirror with a geometric shape that gathers and re-focuses the transmitted energy—is positioned at the other end of the path. The retroreflector returns the transmitted energy to the transmitter-detector unit for detection. Figure 1 illustrates the basic concepts of open-path measurements.

Note that open-path instruments are not able to distinguish between a widely dispersed, lowconcentration plume and a narrow, high-concentration plume. Rather, the instruments detect average concentrations across the entire distance from the transmitter to the detector (or the distance from the transmitter-detector to a retroreflector, and back again). Periods of poor visibility due to weather-related conditions (e.g., fog) are known to interfere with open-path measurements. Rule 12-15 anticipates some data loss due to poor visibility and allows for such data loss if supported by visibility measurements. The Refinery will monitor visibility using a standard light-scattering device to identify periods of poor visibility that may cause data loss.



Figure 1. Schematic illustrating the basic premise for open-path instrument operation.

### 1.1.2 Measurement Sites

The Martinez Facility monitors concentrations across four open paths (shown in Figure 2). The Facility selected these locations after consideration of dominant wind patterns, sources of potential air emissions on the refinery property, nearby local receptors, and logistical feasibility (Section 2). Transmitter-detectors are located at sites 1S-A, 2E-A, 3N-A, and 4N-A (identified in Figure 2), and

retroreflectors are placed at sites at 1N-R, 2W-R, 3S-R, and 4S-R. A summary of the exact shelter coordinates, elevation (analyzer and retroreflector), and optical path lengths is provided in Table 1.



**Figure 2.** Open-path monitoring sites for the Martinez Facility. The four paths are labeled 1N-1S, 2E-2W, 3N-3S, and 4N-4S, with 'A' and 'R' denoting whether the site is the location of an analyzer or reflector, respectively.

Table 1. Summary of each open-path system (analyzer and retroreflector) at the Martinez
Facility, including geographic coordinates, path length, and shelter elevation.

Path No.	Path Length	Equipment	Coordinates	Elevation
1	654	UV-DOAS, FTIR, TDLAS Analyzers	38.0226437, - 122.0432505	1.5 m
(East)	654 m	Reflector	38.0286053, - 122.0414416	4.5 m
2	40.4	UV-DOAS, TDLAS Analyzers	38.0105084, - 122.048323	1.5 m
(Southeast)	) 484 m	Reflector	38.0101376, - 122.0540906	4.5 m
3 (Southwest)		UV-DOAS, TDLAS Analyzers	38.0120123, -122.06357	1.5 m
	598 m	Reflector	38.007080, -122.060473	4.5 m
4	574	UV-DOAS, FTIR, TDLAS Analyzers	38.0208706, - 122.0690485	1.5 m
(West)	571 m	Reflector	38.0161463, - 122.0671891	4.5 m

The following provides an explanation of the rationale that the Martinez Facility used in selecting the open-path monitoring locations identified in Figure 2. Additional information is provided in Section 2.2.

- Path 1 is positioned between the Facility's main processing block and the community of Clyde. Clyde is further than 1 mile from the eastern fenceline and even further from any emission sources, and therefore, Rule 12-15 requirements do not apply. However, the Martinez Facility considers that the community is directly east and downwind from the Facility's main processing block during wind conditions that are predominate in the region (i.e., winds blowing from the west to the east). Thus, the Martinez Facility included monitoring on Path 1.
- Path 2 is positioned between the Facility's main processing block, storage tanks, and the occupied areas of Concord towards the southeast: the Concord-Northwood residential community, the Sun Terrace neighborhood, and a zone of light industry and office parks that borders the south and eastern sides of the Mallard Reservoir. While wind blowing from the refinery in this direction is not frequent, the Martinez Facility recognized that these receptor areas are close to the Facility and established monitoring on Path 2.

- Paths 3 and 4 provide coverage when winds blow from the northeast to southwest. Northeasterly winds are infrequent; however, they occasionally occur during the winter.
  - Path 3 lies between a battery of crude oil storage tanks and residential neighborhoods of Martinez, off north Blum Road.
  - Path 4 lies between the refinery's main center of processing operations and the Vine Hill neighborhood of Martinez.

A visibility monitor is located on the Path 2 instrument shelter.

#### 1.1.3 Parameters and/or Species Measured

Species that are measured include BTEX, 1,3-butadiene, hexane, SO<sub>2</sub>, and NH<sub>3</sub>. H<sub>2</sub>S measurements were added along the fenceline paths starting January 1, 2023. Other species were ruled out based on an understanding of the operations and materials existing at the Martinez Facility. H<sub>2</sub>S and BTEX emissions are distributed across the refinery property and concentrations of BTEX and H<sub>2</sub>S are currently measured along all four of the refinery fenceline paths. Sources of NH<sub>3</sub> and 1,3-butadiene are present only near the refinery's main processing block; therefore, given the annual and seasonal wind patterns, these species are measured only along Path 1 and Path 4. Hexane, which serves as a surrogate for alkane emissions, is also measured along Path 1 and Path 4 because hexane measurements will be available from the same instruments used to measure NH<sub>3</sub> and 1,3-butadiene.

#### 1.1.4 Instrument Selection and Configuration

BTEX and SO<sub>2</sub> are measured by Ultraviolet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. NH<sub>3</sub> and 1,3-butadiene are measured with a Fourier Transform Infrared spectroscopy (FTIR) instrument. H<sub>2</sub>S is measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instruments. To the extent practicable, instruments have been installed and are operated as follows:

- Instruments are mounted in a monostatic configuration, which means the light source and analyzer detector point at a retroreflector array that is approximately 300-700 meters away. The light is reflected off of the array and back to the detector for analysis.
- Instruments generally are elevated about 5 ft above ground level (AGL).
- Instruments are configured and operated following manufacturers specifications, including necessary bump tests. A bump test challenges an instrument using known gas concentrations to confirm accurate instrument response.
- Instruments are operated with the goal of achieving 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 less than 5 minutes and averaged to 5-min and 1-hr values for reporting (based on clock hours). Rolling hourly averages are used for data display to the public website and comparison to health thresholds.

#### 1.1.5 Data Management and Reporting

Data collected by the fenceline monitors is transmitted to a website where the near-real-time results can be viewed by the public. Prior to display on this website, data generated by the fenceline monitors undergo a review throughout the measurement and reporting process. Included in this process are automated QA/QC checks, as well as more detailed reviews conducted by trained data analysts (more details on data review processes are provided in the QAPP). Under normal circumstances, a 5-min average measurement will appear on the website within 10 minutes of the end of the measurement period. However, the data upload may be impacted by internet traffic. A rolling 1-hr average of the 5-min data for each gas is also reported on the website to allow for comparisons to health thresholds. The website also contains a mechanism for collecting public feedback.

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 open-path UV-DOAS, FTIR, and H<sub>2</sub>S raw spectral data will be saved as single files and made available to BAAQMD upon request. BAAQMD may make publicly available any of the data routinely submitted in a quarterly report.

All data collected as part of the fenceline monitoring system is retained for a period of five years, consistent with Rule 12-15-502.

# 2. Monitoring Plan Design Considerations

The Martinez Facility's Monitoring Plan was developed in consideration of the following elements.

- Rule 12-15 and related BAAQMD guidance documents.
- Monitoring objectives, which were established in consideration of Rule 12-15 and related guidance.
- The findings of a preliminary scoping study, which involved assessments of the geographic setting around the Martinez Facility and meteorological conditions that impact the area. The preliminary scoping study is discussed in Section 2.2.
- Technical and engineering feasibility related to available monitoring technologies and instrument siting.
- Data management and quality assurance/quality control (QA/QC) requirements.

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

### 2.1 Key Elements of Rule 12-15 and Guidance

According to the Guidance Document,<sup>3</sup> 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 will lower emissions."

Key guidance for designing a monitoring plan to meet these goals is summarized below. The Martinez Facility monitoring program achieves the goals listed above and meets the following provisions:

<sup>&</sup>lt;sup>3</sup> Bay Area Air Quality Management BAAQMD (2016) Air Monitoring Guidelines for Petroleum Refineries. April 2016. Available at <u>baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en</u>.

- Conduct "fenceline" measurements of BTEX and H<sub>2</sub>S and consider measuring other compounds, including SO<sub>2</sub>, alkanes, 1,3-butadiene, other organics, and NH<sub>3</sub>. 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 impact populated areas on a frequent basis. Specifically,
  - "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 percent 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 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 species at the ppb level or as technology allows.
- Conduct measurements using open-path instruments or an appropriate alternative.
- Provide rationale for the species 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 Preliminary Scoping Study

### 2.2.1 Geographic Study Setting

The Martinez Facility is located east of the City of Martinez and north of the City of Concord in Contra Costa County, California (see Figure 3). Refinery operations occupy approximately 2,200 acres, including a 50-acre main block of processing operations, with the center of the facility located approximately at 38.025° latitude, -122.063° longitude (see Figure 4). The area surrounding the refinery includes:

- North Wetlands, the Point Edith Wildlife Area, and Suisun Bay sit to the north of the refinery. There are no receptors within one mile of the Facility in this direction. The Valero Refinery is about three miles north of the Marathon facility, across the Suisun Bay.
- West The Shell Martinez Refinery is about two miles west of the Facility. The Vine Hill and Blum Road neighborhoods of Martinez are the nearest residential areas to the west and portions of these areas are within 1 mile of the refinery. Low coastal hills rise to elevations of 400 to 600 feet within 5 miles west of the refinery.
- South Highway 4 passes by directly south of the Facility. Toward the southeast, the Concord-Northwood residential community and the Sun Terrace neighborhood are the nearest residential areas, and a zone of light industry and office parks sits just south of the Mallard Reservoir.
- East Low coastal hills rise to elevations of 400 to 600 feet within 2.5 miles east of the Facility. Areas east of the refinery include former and current military lands, but aside from the community of Clyde (slightly beyond 1 mile east of the refinery), the lands within 5 miles to the east are only lightly populated.

The nearby populated public areas represent air quality "receptors" that may at times sit downwind from the Facility. The positions of these receptors received careful consideration during the design of the Monitoring Plan.

The Martinez Facility also maintains an auxiliary tank battery and a marine unloading terminal just west of the south end of the Benicia-Martinez Bridge across the Carquinez Strait, about 2.8 miles west of the refinery. Potential receptors near this facility were also considered for the Monitoring Plan.



Figure 3. Geographic setting of the Martinez Facility.



Figure 4. Layout of the Martinez Facility.

### 2.2.2 Local Meteorology

Contracted meteorologist reviewed the refinery's routinely collected surface wind measurements in the context of expert knowledge about the Bay Area regional wind patterns. The Martinez Facility 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. Figure 5 illustrates the predominant wind flow patterns: (1) winds occasionally blowing from the south (most often occurring during winter storms); (2) winds blowing from northeast to southwest (regional offshore flow, most often occurring in winter); (3) winds blowing from the northwest and west to southeast (onshore flow, most often occurring in spring, summer, and early fall).<sup>4</sup>

<sup>&</sup>lt;sup>4</sup> 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. Typical wind flows influencing the Martinez Facility.

Radial histograms (wind roses) were prepared to determine the frequencies of wind speeds and directions as directed by Rule 12-15 Guidance (i.e., annual mean wind direction distributed by 22.5-degree arcs) and for other relevant data groupings (e.g., seasonal, monthly, and/or narrower arcs). Using data from 2011 through 2016, Figure 6 provides the annual wind roses recorded from the refinery's meteorological station, while Figure 7 provides seasonal wind roses. Key findings are summarized as follows:

- Onshore winds westerly winds (from west to east) occur with frequencies greater than 10% on an annual basis. Winds from these directions are most common in spring, summer, and early fall. The town of Clyde is located more than one mile downwind of the facility's process operations during westerly wind flow.
- Southerly winds winds blowing from south to north occur about 10% of the time on an annual basis. However, there are no receptors downwind during southerly wind flow.
- Offshore winds northeasterly winds do not occur with a frequency greater than 10% on an annual basis, but do occur with a frequency greater than 10% during the winter season. The Vine Hill and north Blum Road neighborhoods of Martinez are the nearest residential areas to the west and are within one mile of the fenceline.

- Southeasterly winds southeasterly winds (winds blowing from southeast to the northwest) do not occur with a frequency greater than 10% on an annual basis, but do occur more than 10% of the time during the winter; however, there are no receptors within one mile downwind of the refinery during southeasterly flows.
- Other winds winds from other directions occur with lesser frequencies, whether data are grouped annually, monthly, or seasonally. While winds blowing from approximately northwest to southeast are very infrequent, the Concord-Northwood residential community, the Sun Terrace neighborhood, and a zone of light industry and office parks next to the Mallard Reservoir are downwind and within one mile of the fenceline under these conditions.

#### ••• 2. Monitoring Plan Design Considerations



Figure 6. Annual wind roses plotted from the Martinez Facility's surface meteorological station, from 2011-2016 (top left to bottom right).



**Figure 7.** Seasonal wind roses plotted from the Martinez Facility's surface meteorological station from spring, summer, fall, and winter of 2011 through 2016.

To better identify and illustrate the areas located downwind from the refinery during onshore and offshore winds, maps highlighting these areas were created (Figures 8 and 9). The edges of the refinery boundaries were coupled with leeward projections of onshore and offshore winds to highlight any areas sitting downwind from the Martinez Facility during the wind conditions of interest. In addition, the outline of the refinery boundary was projected outwards to a distance of one mile. The illustrations confirm the above findings and show that:

- During infrequent offshore winds, portions of Martinez are downwind, but only a few Martinez neighborhoods are within one mile.
- During infrequent northwesterly winds, a few neighborhoods of Concord sit within one mile downwind of the refinery.
- During dominant westerly winds, the community of Clyde is downwind, but more than one mile downwind of refinery process areas.

In consideration of the above, general paths for monitoring were considered and are shown in Figures 8 and 9 as black bold lines. These general paths were then refined based on detailed wind data, population areas, and emission locations to develop the final monitoring paths shown in Figure 2.



**Figure 8.** Areas downwind of the Martinez Facility property boundaries during infrequent offshore and southerly winds. Black lines are the initial monitoring paths that were considered.



**Figure 9.** Areas downwind of the Martinez Facility property boundaries during onshore winds. Black lines are the initial monitoring paths that were considered.

As shown in Figure 2, monitoring Path 1 upwind of Clyde addresses the scenarios of onshore winds. Monitoring Path 2 addresses the few neighborhoods of Concord that are located to the south within one mile downwind of the Facility.

Optimally, the refinery had hoped that Path 2 would cover the very southern end of the facility; however, the location was not logistically feasible for a number of reasons, including the presence of large trees and several public baseball fields. Although Path 2 is north of a few storage tanks, these tanks contain diesel, which is a finished product that is inherently low in emissions: it has very low vapor pressure and only trace amounts of BTEX, H<sub>2</sub>S, and other compounds of relevance to this rule. The gap in monitoring between Path 1 and 2 exists because there are no nearby populated areas downwind of the refinery in this direction; thus, measurements are not needed.

To further refine the paths west of the refinery, one-mile pie segments that encompass the northeasterly wind segments were created and overlaid at various points on the western refinery boundary – these pie segments are shown in Figure 10. Based on this analysis, monitoring Paths 3 and 4 capture the needed monitoring paths for the areas to the west of the refinery.

A small gap necessarily exists between Paths 3 and 4 because of steep terrain to the west, making it logistically infeasible to monitor between these two paths.

While not required by Rule 12-15 because there is no population downwind within a mile of the refinery, consideration was given to extending Path 4 north by a few hundred yards. However, due to terrain, infrastructure, and trees, it is not feasible to extend the monitoring north. Importantly, any emissions leaving the refinery from this area are very unlikely to impact populated areas because winds from the northeast to the southwest are infrequent. Furthermore, given the terrain and distances from the refinery to populated areas, any emissions that moved toward the southwest would be well-diluted.

Similar illustrations were prepared for the Martinez Facility's auxiliary tank battery near the Martinez-Benicia Bridge (Figure 11). Figure 11 shows one-mile pie segments that encompass the northeasterly wind segments. The transparent pie segment uses the wind data from the meteorological station located in the main refinery area. The green pie segments illustrate the probable wind pattern in this area as the winds follow the terrain through Carquinez Strait. As observed in Figure 11, there are no downwind areas of concern near the Martinez Facility's auxiliary tank battery; thus, there is no openpath monitoring in this area.



**Figure 10.** Open-path monitoring sites for the Martinez Facility. Four paths are labeled 1n-1s, 2e-2w, 3n-3s, and 4n-4s. Analyzers are located at sites 1s, 2e, 3n, and 4n, while reflectors are located at sites 1n, 2w, 3s, and 4s. The annual wind rose is shown in the top left.



Figure 11. Areas downwind of the Martinez Facility's auxiliary tank battery during offshore flow.

### 2.3 Instrument Selection

The Martinez Facility served as a petroleum refinery producing fuel products—primarily gasoline, diesel, liquefied petroleum gas (LPG), residual fuel oils, and petroleum coke—through distillation of crude oil, including cracking, alkylation, and reforming processes. The facility also has a chemical plant, where salable sulfuric acids, molten sulfur, and liquid ammonia are produced. In consideration of the refinery's products, processes, and potential emissions sources, the rationales summarized in Table 2 were applied to determine which species would be proposed for inclusion in the Monitoring Plan. 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 minutes), and current measurement technology, various open-path instruments were selected to best measure the target species.

Pollutant	Required by the BAAQMD	To Be Measured (paths)	Instrument(s)	Rationale for Inclusion or Exclusion if Not Required
Benzene	Yes	Yes (1,2,3,4)	UV-DOAS with Xenon	Required
Toluene	Yes	Yes (1,2,3,4)	UV-DOAS with Xenon	Required
Ethylbenzene	Yes	Yes (1,2,3,4)	UV-DOAS with Xenon	Required
Xylenes	Yes	Yes (1,2,3,4)	UV-DOAS with Xenon	Required
$H_2S$	Yes	Yes (1,2,3,4)	TDLAS	Required
SO <sub>2</sub>	No, if justified	Yes (1,2,3,4)	UV-DOAS with Xenon	Included
$\mathrm{NH}_3$	No, if justified	Yes (1,4)	FTIR	Impact unlikely other than on Paths 1 and 4 because NH <sub>3</sub> is only located in the main processing area.
1,3-butadiene	No, if justified	Yes (1,4)	FTIR	Although not needed due to coincident with benzene and low concentrations, will report 1,3- butadiene, since FTIRs will be implemented for NH <sub>3</sub> .
Alkanes	No, if justified	Yes (1,4)	FTIR	Will report hexane since FTIRs will be implemented for NH <sub>3</sub> and hexane is a reasonable surrogate for alkanes. On paths without FTIR, benzene will be measured and is a good surrogate for hexane except for diesel tanks. For diesel tanks, any emissions would be negligible due to low vapor pressure.
Other organics	No, if justified	No	N/A	Benzene measurement is reasonable surrogate.

Table 2. Summary of rationale supporting selection of species for inclusion in the Monitoring Plan.

Along all paths, BTEX and SO<sub>2</sub> are measured using a monostatic UV-DOAS with a xenon light source. The xenon light is used to achieve the desired MDLs for BTEX compounds and collect measurements over paths that are about 300 to 700 meters long. H<sub>2</sub>S is measured using monostatic TDLAS instruments as of January 1, 2023. The basic principle of TDLAS is to measure the absorption of a single absorption line for the target species. A tunable diode laser can emit light over a small range of very specific wavelengths, which allows spectral measurement over a narrow range to minimize interference. Based on field measurements collected at a refinery location, it has been determined that MDLs or level of quantitation (LOQ) lower than 25 ppb can be achieved on a routine basis. Per the December 22, 2022, letter from BAAQMD,<sup>5</sup> the LOQ is taken to be equivalent to the MDL, and is

<sup>&</sup>lt;sup>5</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

calculated as twice the standard deviation of a blank sample. The resulting MDL is reported alongside every 5-min average concentration value. In theory, one can monitor H<sub>2</sub>S using UV-DOAS, but its absorption spectra overlaps with BTEX and can generate false positives. While FTIR technology was considered for measurements of BTEX and H<sub>2</sub>S, instrument manufacturers informed Tesoro that FTIR is not suitable for these species because of poor detection limits and overlap in absorption with other species (such as carbon dioxide with benzene). NH<sub>3</sub>, 1,3 butadiene, and alkanes are measured using FTIRs.

Table 3 summarizes the MDLs and upper detection limits (UDLs) by instrument expected for Tesoro's monitoring program. 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.

The detection limits in Table 3 are approximate and are based on the theoretical capabilities of the instruments. Actual MDLs can change depending on atmospheric or operational conditions. For instance, under acceptable operating conditions, the MDL/LOQ of the Unisearch TDLAS is expected to be between 3 to 25 ppb below 1% transmission. The MDL may be higher than 25 ppb if there is poor atmospheric visibility, the instrument is misaligned, there are hardware problems, or an interferant is present. For the Unisearch TDLAS, a real-time MDL is calculated continuously in real time using the standard deviation of the last seven 5-min average concentration values containing no measurable analyte (as determined by the correlation coefficient). The MDL is defined at three times this standard deviation; it is determined by the analyzer software and reported alongside every 5-min average concentration value data. Real-time MDL values greater than 25 ppb will be flagged for additional review and, in the absence of marginal operating conditions or an instrument malfunction, will be considered to not meet the performance criteria. Real-time MDLs for the TDLAS will be displayed on the public-facing website.

Monostatic (as opposed to bistatic) instruments have been selected to reduce the need for substantial power at the mirror sites and improve minimum detection limits by increasing effective path lengths. Thus, substantial power, communications, and shelter are required at the light-source/ detector end of the monitoring path only. Limited power is needed at the retroreflectors. The retroreflector needs to be aligned at the other end of the path for maximum performance and should be cleaned regularly. An example of a UV-DOAS analyzer and receiver in a shelter is shown in Figure 12, and a retroreflector is shown in Figure 13.

Path		Pat	th 1	Pat	th 2	Pat	h 3	Pat	:h 4
Distance (m)	Compound	654 meters		484 meters		598 meters		571 meters	
Technology	Compound	MDL (PPB)	UDL (PPB)	MDL (PPB)	UDL (PPB)	MDL (PPB)	UDL (PPB)	MDL (PPB)	UDL (PPB)
	1,3-Butadiene	1.4	873	1.9	940	1.5	980	1.6	857
FTIR	Ammonia	0.3	707	0.4	761	0.4	794	0.4	694
	Hexane	0.7	693	0.9	712	0.8	662	0.8	834
TDLAS	Hydrogen Sulfide	3-25	5,700	3-25	7,700	3-25	6,200	3-25	6,500
	Benzene	0.4	10,867	0.6	11,694	0.5	12,195	0.5	10,671
	Toluene	1.2	6,169	1.7	6,638	1.4	6,922	1.5	6,057
UV-DOAS	Ethylbenzene	0.5	1,312	0.6	1,411	0.5	1,472	0.5	1,288
	Total Xylenes	2.2	4,998	3.0	5,378	2.4	5,609	2.5	4,907
	Sulfur Dioxide	1.0	3079	1.4	3,159	1.1	2,938	1.2	3,702

Table 3. Open-path instrument detection limits by technology, species, and path length. TDLAS MDLs for H<sub>2</sub>S will be evaluated in real time<sup>a</sup>.

<sup>a</sup> Per the December 22, 2022, letter from BAAQMD,<sup>6</sup> 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.

<sup>&</sup>lt;sup>6</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022



Figure 12. A UV-DOAS analyzer.



Figure 13. A UV-DOAS retroreflector.

### 2.4 Data Management Requirements

#### 2.4.1 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 that create low-visibility (such as dense fog), invalid data during low-visibility conditions do not count against completeness requirements. Visibility measurements are made at one location to document the time periods of poor visibility. The threshold for impairment of the open-path measurements is approximately 2.5 miles. This is based on path length, manufacturer specifications, and review of the observed instrument performance metrics such as signal strength (e.g., signal to noise ratio), since the equipment has been operating. Visibility measurements are made at least every 5 minutes to coincide with the open-path measurements.

Data completeness is assessed by reviewing the data flags assigned for each 5-min average data point. A 1-hr average data point (based on clock hours) will be considered incomplete if (1) more than 25% of the 5-min average data points within the averaging window are missing or do not meet acceptance criteria, and (2) exclusionary conditions do not exist. Exclusionary conditions include low-visibility atmospheric conditions beyond the control of the refinery, as well as planned maintenance activities, which are not counted against the refinery for data completeness calculations. Completeness is calculated as follows:

- Possible: The theoretical maximum number of 1-hr average data points in a clock hour.
- Incomplete: The number of 1-hr average data points that do not meet the completeness criteria.
- % Incomplete: The percentage of Incomplete data points relative to Possible data points.
- Complete: The number of 1-hr average data points that do meet the completeness criteria.
- % Complete: The percentage of Complete data points relative to Possible data points.

Other factors that affect data availability include instrument bump tests (approximately every month for a few hours), routine maintenance (e.g., replacement of analyzer consumables or annual checks), and emergency or unplanned maintenance. In the event that an analyzer is offline for an extended period of time, repairs are made as quickly as possible. A spare analyzer, if available, may be installed while repairs occur. Regular maintenance and careful, responsive operation will minimize instrument downtime.

### 2.4.2 Data Quality Assurance/Quality Control

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, suspect, or invalid. Data review consists of the following types of actions.

A data manager reviews the 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 are verified. Throughout operations, the project QA/Data Manager ensures that (1) Standard Operating Procedures (SOPs) are being followed, (2) operators are documenting field operations in field data sheets and logbooks, (3) instrument performance checks are being conducted, and (4) 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. A data analyst 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 is achieved.

Details regarding the QA/QC process can be found in Sections 3 and 4 in the QAPP, located in Appendix A.

# 3. Routine Operations

For this monitoring program, four UV-DOAS analyzers, two FTIR analyzers, and one visibility sensor were originally installed, and four TDLAS analyzers were added as of January 1, 2023. Instrument operations, routine maintenance and bump tests (monthly, quarterly, or annual), and daily checks work to ensure that data are flowing consistently. Further details are provided in the following sections, which describe routine instrument and data management operations. Additional details and documentation, including standard operating procedures (SOPs), for example, are included in the QAPP.

### 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 the typical UV-DOAS maintenance activities as recommended by a manufacturer. Preventive maintenance frequency depends on the operating environment and may need to be adjusted beyond manufacturers' recommendations depending on field conditions. On an as-needed basis, system status alarms will alert operators to specific issues needing to be addressed.

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

Table 4. Schedule of maintenance activities and performance indicator checks for the UV-DOAS.

#### 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 a typical manufacturer and required by the BAAQMD. 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 immediately addressed. Calibration is typically done at the factory. Field calibration will be performed on a quarterly basis in addition to monthly bump tests. Where commercially available, NIST-certified sealed cells will be used for bump tests and calibrations.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	$\checkmark$		
Inspect optics on detector. Clean if necessary.	$\checkmark$		
Check the alignment to verify there has not been significant physical movement and confirm signal levels.	$\checkmark$		
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.	$\checkmark$		
Perform bump test	~		
Review and test light and signal levels. <sup>a</sup>		$\checkmark$	
3-point calibration check		$\checkmark$	
Verify system settings.			$\checkmark$

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

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

#### 3.1.3 FTIR

The FTIR has similar maintenance activities to the UV-DOAS. The FTIR system is also designed to require only modest service and maintenance. Table 6 summarizes FTIR maintenance activities, as recommended by a typical manufacturer. Preventative maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed. Bump tests are performed on site.

Table 6. Schedule of maintenance activities and performance indicator checks for the FTIR.

Activity	Monthly	Quarterly	Annually	18-24 months	Five Years
Visually inspect the system.	$\checkmark$				
Inspect optics on detector and retro-reflector; clean if necessary.	~				
Confirm the alignment to maximize signal intensity.	~				

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

### 3.1.4 Visibility Sensor

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 semi-annually. Maintenance schedules for the visibility sensor are listed in Table 7.
Activity	Monthly	Quarterly	Semi- Annually
Inspect optics on detector, clean if necessary.	$\checkmark$		
Visually inspect the system including all cables.		$\checkmark$	
Check calibration. An acceptable $\%$ error is less than $\pm 25\%$ .			✓

Table 7. Schedule of maintenance activities for the visibility sensor.

# 3.2 Data Management Operations

Data management occurs on a daily, monthly, quarterly, and annual basis. In near-real time, data are transferred from infield instruments through a data acquisition system (DAS) to the Data Management System (DMS) using a cellular modem. Data are also stored onsite on instrument computers in case of cell modem failure.

The DAS performs data averaging to 5-min values, requiring that raw data completeness meets prescribed thresholds for each analyzer to calculate an average. These thresholds differ by each analyzer according to the time resolution of the raw data. Values that meet these completeness criteria are transferred to the DMS. The DAS also assigns initial data flags to each data value, based on operating characteristics information collected from the analyzers, as well as the data values. All data are stored in the DMS, which uses a Microsoft SQL relational database with stored procedures for data processing.

The DMS automatically quality-controls data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities will be used for continuous examination of data quality. The DMS feeds auto-screened data to an internal field operations website and notification system to inform and alert project and facility staff if there is a data issue. The non-public operations website shows time series plots of BTEX, SO<sub>2</sub>, H<sub>2</sub>S, 1,3-butadiene, hexane, and NH<sub>3</sub> concentrations, as well as wind speed, wind direction, visibility, and other analyzer metadata.

### 3.2.1 Quality Assurance and Quality Control (QA/QC)

All data values that are not associated with bump tests or other instrument maintenance are displayed to the public in near-real time (i.e., about 10 minutes or less). If data are subsequently proven to be invalid, they are removed from the public display, and the rationale for data removal is recorded.

The DAS and DMS that process data automatically apply flags assessing data quality to all collected data points. 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 quality control criteria.
- iii. Suspect/Questionable. Data should be reviewed further.
- iv. Missing. Data have not been received by the DMS for more than 10 minutes.

In addition to the QC flags described above, operational codes (OP) are also assigned to provide additional diagnostic information. Table 8 presents an overview of relevant QC/OP codes, which are used throughout the QC process, including manual QC efforts (described in Section 4 of the (QAPP).

#### Table 8. Overview of data quality control (QC) and operational (OP) codes.

	Data QC/OP Codes						
	Quality Control (QC) Codes						
0	Valid						
5	Suspect/Questionable						
7	Insufficient valid/suspect data to calculate an hourly average						
8	Missing						
9	Invalid						
	Operational (OP) Codes						
0	Valid						
5	Hourly data is suspect (general classification); due to range, rate of change, or sticking						
7	Insufficient valid/suspect data to calculate an hourly average						
9	No valid/suspect data to calculate an hourly average; due to invalid 5-min data						
17	Below MDL						
28	Planned Instrument Maintenance						
29	Unplanned Instrument Maintenance						
70	Instrument Malfunction						
72	Marginal Operating Conditions-Elevated Integration Time indicating low signal return						
73	Poor Visibility (Weather)						
74	Goodness of fit (R <sup>2</sup> ) is below threshold, this occurs when compound is below detectable levels						
76	Marginal Operating Conditions–R <sup>2</sup> below threshold; signal return is marginal and compound concentration below detectable levels						
100	Flagged by Manual Review						
101	Flagged by Range Check						
102	Flagged by Rate of Change Check						
103	Flagged by Sticking Check						

A non-public field operations website will be used for daily graphical review of the data (an example is provided in Figure 14). Common data problems include flat signal/constant values, no signal/missing data, extremely noisy signal, rapid changes (spikes or dips), and negative concentrations (see annotated Figure 15 for some examples). An initial review, typically of a one-to three-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 routine operations manager and field technicians are notified and further investigation and corrective action, if needed, is taken.



Figure 14. Example of a non-public field operations website used for daily review of instrument operations.



Figure 15. Example of species concentration time series showing stuck values, wild swings, large negative values, and a data gap. Such features in the data indicate instrument issues.

Automated data screening is conducted within the DMS upon data ingest. Automated screening checks of data feeds are used to screen out invalid data for public display and are helpful to focus the Data Reviewer's efforts on the data that need the most attention. 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. 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 below the instrument detection limit.
- Rate of Change Values that change rapidly without reasonable cause are flagged as suspect and reviewed.
- Missing If data are missing, data during those time periods are marked as missing.
- 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, OP codes confirmed, and data flags checked.
- Visibility impairment The expectation is that measurements are severely impacted when visibility is less than 2.5 miles, as this results in marginal operating conditions for the analyzer (e.g., decreased signal strength or increased integration time). If open-path data are missing or invalid due to low light, and visibility is low, data are flagged as invalid due to low visibility.

Additional QC checks for the instruments are summarized in Table 9. Data that fail checks will be flagged in the DMS and brought to the attention of the reviewer. 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 or invalid. Common reasons for invalidation include instrument malfunction, power failure, and bump test data that were not identified as such. A summary of issues leading to invalidated data will be documented in the data file. Screening checks are typically specific to the site, instrument, time of day, and season, and may be adjusted over time as more data are collected.

**Table 9.** Initial screening checks for 5-min data. Valid and suspect data values will be displayed to the public in real-time. If they are subsequently proven invalid, they will be removed from the public display. Screening values (flags and rates of change) presented herein should be considered as preliminary and may be refined either during the project.

	Checks							
Measurement (units)	Minimum Detection Limit (MDL <sup>a</sup> ): If concentration is below MDL, flag as below MDL	Range: If concentration is above value listed, flag as suspect, conduct investigation	Sticking: If same value observed for 4 or more intervals, flag as suspect, conduct investigation	Rate of Change Between Intervals: If concentration changes by more than value listed, flag as suspect and conduct investigation	Missing: If data are missing, flag as missing and investigate cause	Sensor OP Code/Alarm: If sensor indicates malfunction or bump test data, flag as appropriate	Visibility: If visibility is <2.5 miles and data are invalid, flag as appropriate	
Benzene (ppb)	0.5 ppb	>24 ppb		±12 ppb		Same for all pollutants	Same for all pollutants	
Toluene (ppb)	1.4 ppb	>1,000 ppb		±500 ppb	Same for all pollutants			
Ethylbenzene (ppb)	0.5 ppb	>1,000 ppb		±500 ppb				
Xylenes (ppb)	2.4 ppb	>1,000 ppb		±500 ppb				
SO <sub>2</sub> (ppb)	1.1 ppb	>75 ppb	Same for all	±150 ppb				
Ammonia (ppb)	0.4 ppb	>500 ppb	pollutants	±250 ppb				
1,3 –Butadiene (ppb)	1.5 ppb	>900 ppb		±300 ppb				
Hexane (ppb)	0.8 ppb	>200 ppb		±100 ppb				
H <sub>2</sub> S (ppb)	3-25 ppb <sup>b</sup>	>50 ppb		±30 ppb				
Visibility (miles)	If value is <0, flag as suspect	>50		Not applicable				

<sup>a</sup> 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. <sup>b</sup> Per the December 22, 2022 letter from BAAQMD,<sup>7</sup> 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.

<sup>&</sup>lt;sup>7</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

Additional parameters that are monitored as indicators of data quality include signal strength, correlation between measured and reference spectra, wavelength versus intensity, and visual review of peaks. The QA/QC checked used are listed in Table 10.

Instrument Checks	Frequency	Acceptance Criteria
	-DOAS	
Bump test with benzene (accuracy and precision)	Monthly and after major service	±20%ª
Measurement quality (R <sup>2</sup> )	Continuous	0.8 to 1.0
Integration time	Continuous	≤250 ms
Signal intensity	Continuous	≥80% <sup>b</sup>
Т	DLAS	
Bump test <sup>a</sup> (accuracy and precision) H <sub>2</sub> S at a concentration between 50 and 100 ppb which differs from 3-point calibration points.	Monthly	±15%
3-point calibration <sup>a, b, c</sup> (accuracy and precision) The lowest calibration concentration must be in the range of 40 to 60 ppb.	Quarterly	±15% for each calibration point
5-min LOQ <sup>d</sup>	Continuous	3-25 ppb
H <sub>2</sub> S correlation coefficient (r)	Continuous	0.72 to 1.0
Power	Continuous	0.1 mW (corresponds to <1% transmission)
H <sub>2</sub> O correlation coefficient (r)	Continuous	≥0.95
	FTIR	
Bump test with ammonia (accuracy and precision)	Monthly	±20%ª
Signal intensity	Continuous	≥2% <sup>b</sup>
Measurement quality (R <sup>2</sup> )	Continuous	0.7 to 1.0
Visibil	lity Sensor	
Accuracy	Annually	±25%

#### Table 10. Instrument QA/QC checks.

<sup>a</sup> 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.

<sup>b</sup> NIST TN 1297: Appendix D1. Terminology.

<sup>c</sup> For test concentrations requiring greater than 750 ppm H<sub>2</sub>S, safety considerations necessitate certified sealed cells be used. For test concentrations requiring lower than 750 ppm, certified flow-through cells may be used.

<sup>d</sup> Per the December 22, 2022 letter from BAAQMD,<sup>8</sup> 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.

<sup>&</sup>lt;sup>8</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

For those data points that are collected with a signal strength percentage outside of an acceptable range, will be flagged as either invalid or undergo additional screening. For UV-DOAS analyzers, signal strength is assessed with the integration time (which increases as signal intensity decreases). The correlation between measured spectra and reference spectra is also used to filter data. Measurements with less than 80% (UV-DOAS) or 70% (FTIR) spectral match are flagged as poor spectral match (ambient interference and spectral noise are believed to impact measurements). TDLAS signal power can be measured with a photodiode detector and used to evaluate the impact of atmospheric conditions or misalignment on data quality. During normal operations, the photodiode detector has an auto-gain feature that resets when the signal power is at 20% on the low end and 80% on the high end. Because the Unisearch TDLAS operates in a wavelength range that also contains an absorbance feature for water vapor and carbon dioxide, the 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.

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.

Any corrections or updates will be copied to the website. Validation checks will include:

- Looking for and investigating 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 data reasonableness by comparing data to other sources of data.
- Ensuring the data or measurements are realistically achievable and not outside the limits of what can be measured.
- Inspecting several sampling intervals before and after data issues, instrument bump tests, or repairs to ensure all affected data have been properly flagged.
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on manual changes to operations/data, and verify that the changes were logged and appropriately flagged.
- Assessing instrument meta-data to confirm reasonableness.
- Assessing visibility measurements to ensure adequate signal was obtained to quantify pollutant concentrations.
- Confirming that bump tests were conducted and were within specifications.

On a quarterly basis, to ensure 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 bump tests or instrument checks have the appropriate data flags are applied.

On a quarterly basis, analysts subject the data to final QC. In this review, analysts:

- Create a null record for data completeness purposes if a record is not created for a particular site/date/time/parameter combination.
- Assign a Null Code to Invalid data (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 data completeness.

Actions will be documented to retain the raw data and support traceability of actions taken to produce the data on the website. Additional details on the final QC process are provided in the QAPP (Appendix A).

On an annual basis, the Facility Program Manager and the QA Manager will review the performance of the network by (1) reviewing the data completeness by monitoring path, instrument, and species; (2) reviewing results of bump tests; (3) analyzing the reported values in context of refinery operations; and (4) analyzing the data in context of the meteorology.

### 3.2.2 Public Data Availability and Display

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

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

The preliminary quality-controlled data are presented as time series of species concentrations, visibility, and wind speed and direction. Data are provided on the website as 5-min averages and rolling 1-hr averages. Data are annotated for quality (valid, invalid, suspect, missing). In the event that high concentration levels occur, Tesoro will follow its existing procedures to determine whether any additional information needs to be provided to the public.

An image of the Tesoro (Marathon) Martinez Refinery's public-facing website is shown in Figure 16. Information is written at a public-friendly level with links to additional resources for members of the public who want to delve deeper into the science.



Figure 16. Screenshot of the Martinez fenceline monitoring public-facing web page.

The data collected 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.
- Discussion of levels of concern, with links to third-party sources such as the Office of Environmental Health Hazard Assessment website on the health effects of each species.
- Discussion of non-refinery sources that could affect the measured concentrations.
- Definitions of abbreviations.
- Discussion of data below MDL.
- Definition of data QC flags and their meaning.
- Frequently asked questions (FAQs; to be updated over time).

To facilitate public feedback, a feedback mechanism is provided on the web page. This allows users to submit questions or comments about the website. An email is delivered to a Martinez Facility contact and the website host, who are 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, they can be made available to BAAQMD upon request. Some of the comments can aid in the creation of FAQs.

# Appendix A: Quality Assurance Project Plan

Quality Assurance Project Plan for the Tesoro Refining & Marketing Co., LLC, Martinez Renewable Fuels Facility in Martinez, CA.

# Appendix A. Quality Assurance Project Plan

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# **Version History**

Version Number	Date	Description of Change
1	December 7, 2019	Initial QAPP submittal to BAAQMD.
2	August 24, 2019	Updated QAPP submittal to BAAQMD – includes updates and revisions pursuant to AQMD review and comments (received in 07/19).
3	January 8, 2020	Updated QAPP submittal to BAAQMD – includes updates and revisions pursuant to AQMD review and comments. Updated analyzer SOPs.
4	June 1, 2022	Updated QAPP submittal to BAAQMD – includes addition of open-path H <sub>2</sub> S measurement technology and data quality objectives. Updated analyzer SOPs.
5 (rescinded)	December 1, 2022	Updated QAPP submittal to BAAQMD — includes updates and revisions pursuant to AQMD review and comments (received in 07/22) and the addition of an SOP for the H <sub>2</sub> S open path analyzer.
6	February 17, 2023	Resubmittal of December revision – includes updates and revisions following revised TDL specifications issued by BAAQMD in December 2022.
7	September 5, 2023	Revised in response to July 19, 2023, comments from the BAAQMD

# 1. Project Background and Management

# 1.1 Background

### 1.1.1 Purpose

Tesoro Refining & Marketing Company, a subsidiary of Marathon Petroleum Corporation, monitors fenceline concentrations of certain compounds at the Martinez Renewable Fuels Facility located in Martinez, California ("Martinez Facility" or "Facility"), in compliance with the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15) and consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.<sup>1,2</sup> Rule 12-15 requires monitoring for specific air compounds, with data reported to the public. On October 6, 2021, the BAAQMD provided updated requirements for refineries to conduct additional hydrogen sulfide (H<sub>2</sub>S) monitoring along Facility fenceline paths and to implement the enhanced monitoring by January 1, 2023. The Martinez Facility met this requirement within the timeframe specified. BAAQMD issued updated specifications on December 22, 2022. The Martinez Facility'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 using "open-path technology capable of measuring in the parts-per-billion range regardless of path length" or an alternative measurement technology.<sup>2</sup> The Martinez Facility is conducting open-path pollutant monitoring with visibility and meteorological measurements to meet the regulations.

This document is a quality assurance project plan (QAPP), which documents the actions that the Martinez Facility fenceline monitoring project team will take to ensure that the data collected are credible and meet the requirements of Rule 12-15.

<sup>&</sup>lt;sup>1</sup> Petroleum Refining Emission Tracking (Rule 12-15; approved by the BAAQMD on April 20, 2016).

<sup>&</sup>lt;sup>2</sup> Bay Area Air Quality Management BAAQMD (2016) Air Monitoring Guidelines for Petroleum Refineries. April 2016. 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.

# 1.2 Roles and Responsibilities

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



Figure 1. Organizational chart for this project.

The overall program will be run by a **Program Manager** (PM) appointed by the Facility. This PM acts as the central point of contact for the BAAQMD and the Project Manager. The PM is responsible for overseeing the program and reporting directly to the BAAQMD.

The Project Manager serves as the primary technical advisor for the program and measurements. They work with the Routine Operations Manager to ensure that program requirements are being met and the Data/QA Manager to ensure data quality is being maintained. The project manager also works with the Website Manager to ensure that data are being reported to the public in real time and are of high quality. The Project Manager ensures that quarterly reporting is completed and delivered to the Facility PM.

The Routine Operations Manager is responsible for overseeing the day-to-day monitoring operations and reports to the Project Manager. They coordinate directly with Field Technicians to ensure the fenceline network is being maintained according to schedule and as described in SOPs. They also work with the Data/QA Manager to ensure that issues impacting data delivery or data quality are addressed.

The Data/QA Manager is responsible for ensuring the quality of data collected in this program. The Data/QA Manager oversees data collection and review, provides QA oversight, and oversees and reports on QA activities to the Project Manager. The QA Manager oversees daily data review and data management, works with the Routine Operations Manager to ensure that any data issues are addressed by the field technicians.

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

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

The Daily Data Reviewers assess data every day and conduct data validation. They communicate with the QA/Data Manager when issues arise and may also interact with Field Technicians when they notice an issue that needs to be addressed. They are the primary data analysts who conduct quarterly review and validation of the data.

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 will be responsible for assessing and fixing data communication issues and other information technology–related problems concerning the website and data system.

# 2. Measurements

## 2.1 Instrument Selection and Descriptions

The compounds measured are benzene, toluene, ethylbenzene, and xylenes (referred to collectively as BTEX), sulfur dioxide (SO<sub>2</sub>), hydrogen sulfide (H<sub>2</sub>S), 1,3-butadiene, hexane, and ammonia (NH<sub>3</sub>). These compounds are measured at a 5-min resolution. Because of the distances that need to be covered by measurements (hundreds of meters), data time-resolution requirements (5 minutes), and current measurement technology, open-path instruments (CEREX UV-DOAS, Unisearch TDLAS, and CEREX FTIR) were selected.

### 2.1.1 UV-DOAS

Along all measurement paths (see Section 2.2), BTEX and SO<sub>2</sub> are measured by monostatic Ultraviolet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. The light source and detector on one end of the open-path point at a retroreflector some 300 to 700 meters away (monostatic configuration). The xenon light is required to achieve measurements over these path lengths at the minimum detection limits (MDL) required. The analyzer detector records the intensity of light at discrete wavelengths. Any UV-absorbing gas that is present in the beam path absorbs at a specific wavelength of light. Each species of gas has a unique absorbance fingerprint (i.e., the ratios between the absorbance at several different wavelengths are unique to that gas). The analyzer compares regions within the sample absorbance spectra to the same regions within the reference absorbance spectra. The analyzer uses a classical least squares regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files. Beer's Law is used to report gas concentrations. Though not written specifically for UV-DOAS, this approach is the same as that specified in the Environmental Protection Agency's (EPA) TO-16 Methodology.<sup>3</sup> Closeness of fit is indicated by the coefficient of determination ( $R^2$ ) describing agreement between the measured spectra and the reference spectra. A related term, spectral match, is defined as R<sup>2</sup> multiplied by 100 and is used here to validate data. The spectral match is provided continuously with each concentration value so that interference can be detected if it is present. Selection of regions of analysis 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.

<sup>&</sup>lt;sup>3</sup> 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.

#### 2.1.2 TDLAS

Along all measurement paths, H<sub>2</sub>S is measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) open-path instruments. A tunable diode laser emits light at a very small range of wavelengths, which allows spectral measurement of an H<sub>2</sub>S absorption peak. The system measures (1) sample path absorbance in a region where  $H_2S$  absorbs infrared (IR) light, and (2) through an internal reference cell that contains a known concentration of H<sub>2</sub>S. The two resultant spectra are compared to each other using analytic software that determines the concentration of H<sub>2</sub>S in the sample path. The software also reports a correlation coefficient (r), with larger values reflecting higher confidence in the analyte detection. TDLAS signal power can be measured with a photodiode detector and used to evaluate the impact of atmospheric conditions or misalignment on data quality. During normal operations, the photodiode detector has an auto-gain feature that resets when signal power is at 20% on the low end and 80% on the high end. 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.

#### 2.1.3 FTIR

Hexane, NH<sub>3</sub>, and 1,3-butadiene are measured with a Fourier Transform Infrared (FTIR) Spectroscopy instrument. The FTIR operates similarly to the UV-DOAS analyzer and sends an infrared light beam through the open air. It is then reflected back to the analyzer detector (monostatic configuration), where the absorption due to target gases is measured and recorded. The analyzer uses a classical least squares regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files according to the EPA's TO-16 Methodology. Beer's Law is used to report accurate gas concentrations. A combination of industry standard methods and proprietary methods are used to mitigate interference from both water vapor and interference gases, including spectral subtraction, path length adjustments, selecting isolated absorbance peaks for the gases of interest, and multi-peak analytics.

### 2.1.4 Instrument Performance Considerations

Heavy fog, rain or smoke may block the signal from an open-path instrument and prevent data collection; however, even light fog or smoke 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, typically in the California Central Valley. It extends into the marshlands along the Sacramento River, San Joaquin River, and Carquinez Strait, especially during the rainy season from late fall to early spring. Visibility measurements are made at one representative location and provide evidence when low-visibility conditions cause the open-path instruments to miss measurements.

Table 1 summarizes the MDL, which is the lowest concentration that can be measured, and upper detection limits (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 for the average species concentration along a path. Per the December 22, 2022, letter from BAAQMD,<sup>4</sup> 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. The MDL is defined at two times this standard deviation and is reported alongside every 5-min average concentration value.

The detection limits provided in Table 1 represent expected values, as actual MDLs/LOQs are not fixed and can change depending on atmospheric or operational conditions. For instance, under acceptable operating conditions, the MDL/LOQ of the Unisearch TDLAS is expected to be between 3 to 25 ppb, below 1% transmission. The MDL/LOQ may be higher than 25 ppb if there is poor atmospheric visibility, if the instrument is misaligned, if there are hardware problems, or if an interferant is present. For the Unisearch TDLAS, a real-time MDL/LOQ is calculated continuously in real time using the standard deviation of the last seven 5-min average concentration values containing no measurable analyte (as determined by the correlation coefficient). The MDL/LOQ is defined at two times this standard deviation; it is determined by the analyzer software and reported alongside every 5-min average concentration value data. Real-time MDL/LOQ values greater than 25 ppb are flagged for additional review and, in the absence of marginal operating conditions or an instrument malfunction, are considered to not meet the performance criteria. Real-time MDLs/LOQs for the TDLAS are displayed on the public-facing website.

<sup>&</sup>lt;sup>4</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

Path		Pat	:h 1	Pat	:h 2	Patl	h 3	Pat	h 4
Distance (m)	Compound	654 n	neters	484 n	neters	598 m	eters	571 m	neters
Technology		MDL (PPB)	UDL (PPB)	MDL (PPB)	UDL (PPB)	MDL (PPB)	UDL (PPB)	MDL (PPB)	UDL (PPB)
	1,3-Butadiene	1.4	873	1.9	940	1.5	980	1.6	857
FTIR	Ammonia	0.3	707	0.4	761	0.4	794	0.4	694
	Hexane	0.7	693	0.9	712	0.8	662	0.8	834
TDLAS	Hydrogen Sulfide	3-25	5,700	3-25	7,700	3-25	6,200	3-25	6,500
	Benzene	0.4	10,867	0.6	11,694	0.5	12,195	0.5	10,671
	Toluene	1.2	6,169	1.7	6,638	1.4	6,922	1.5	6,057
UV-DOAS	Ethylbenzene	0.5	1,312	0.6	1,411	0.5	1,472	0.5	1,288
	Total Xylenes	2.2	4,998	3.0	5,378	2.4	5,609	2.5	4,907
	Sulfur Dioxide	1.0	3,079	1.4	3,159	1.1	2,938	1.2	3,702

Table 1. Instruments and approximate detection limits by species, and path length. Actual detection limits will depend on ambient conditions, visibility, and instrument performance.  $H_2S$  MDLs/LOQs will be evaluated in real-time.<sup>a</sup>

<sup>a</sup> Per the December 22, 2022, letter from BAAQMD,<sup>5</sup> 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.

<sup>&</sup>lt;sup>5</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

# 2.2 Monitor Siting Overview and Rationale

The Martinez Facility monitors concentrations across four open paths, shown in Figure 2. The Facility selected these locations after consideration of dominant wind patterns, sources of potential air emissions on the property, nearby local receptors, and logistical feasibility. Detectors/analyzers are located at monitoring sites 1S, 2E, 3N, and 4N, and retro-reflectors are placed at the remaining identified sites at 1N, 2W, 3S, and 4S. On public facing website, the sites are also labeled as East (Path 1), Southeast (Path 2), Southwest (Path 3), and West (Path 4). The BAAQMD previously approved the locations of the four open paths.



**Figure 2.** Open-path monitoring sites for the Martinez Facility. Four paths are identified, labeled 1n-1s (yellow), 2e-2w (blue), 3n-3s (blue), and 4n-4s (yellow). Analyzers are located at sites 1s, 2e, 3n, and 4n, while reflectors are located at sites 1n, 2w, 3s, and 4s.

A description of the exact shelter coordinates, elevation (analyzer and retroreflector), and optical path lengths is provided in Table 2.

Path No.	Path Length	Equipment	Coordinates	Elevation
1 (East)	654 m	UV-DOAS, FTIR, TDLAS Analyzers	38.0226437, -122.0432505	1.5 m
		Reflector	38.0286053, -122.0414416	4.5 m
2 (Southeast)	484 m	UV-DOAS, TDLAS Analyzers	38.0105084, -122.048323	1.5 m
· · ·		Reflector	38.0101376, -122.0540906	4.5 m
3 (Southwest)	598 m	UV-DOAS, TDLAS Analyzers	38.0120123, -122.06357	1.5 m
(00000000)		Reflector	38.007080, -122.060473	4.5 m
4 (West)	571 m	UV-DOAS, FTIR, TDLAS Analyzers	38.0208706, -122.0690485	1.5 m
(,		Reflector	38.0161463, -122.0671891	4.5 m

 Table 2. Summary of each open-path system (analyzer and retroreflector) including

 geographic coordinates, path length, and shelter elevation at the Martinez Facility.

The Martinez Facility used the following rationale in selecting the open-path monitoring locations identified in Figure 2:

- Path 1 is positioned between the Facility's main processing block and the community of Clyde. Clyde is further than 1 mile from the eastern fenceline and even further from any emission sources, and Rule 12-15 requirements therefore do not apply. However, the Facility considers that the community is directly east and downwind from the Facility's main processing block during wind conditions that predominate in the region (i.e., winds blowing from the west to the east).
- Path 2 is positioned between the Facility's main processing block, storage tanks, and the occupied areas of Concord toward the southeast: the Concord-Northwood residential community, the Sun Terrace neighborhood, and a zone of light industry and office parks that borders the southern and eastern sides of the Mallard Reservoir. While wind blows from the Facility in this direction infrequently, the Facility recognizes that these receptor areas are close to the Facility and plans to establish monitoring on Path 2.
- Paths 3 and 4 provide coverage when winds blow from the northeast to southwest. Northeasterly winds are infrequent; however, they occasionally occur during the winter.

- Path 3 lies between a battery of crude oil storage tanks and residential neighborhoods of Martinez off Blum Road.
- Path 4 lies between the Facility's main center of processing operations and the Vine Hill neighborhood of Martinez.

H<sub>2</sub>S and BTEX emissions are distributed across the Facility property, and are measured along all four of the open pathways. Sources of NH<sub>3</sub> and 1,3-butadiene are present only near the Facility's main processing block; therefore, given the annual and seasonal wind patterns, measurements of these species are made only along Paths 1 and 4. Hexane, which serves as a surrogate for alkane emissions, is also reported along Paths 1 and 4.

A visibility monitor is located on the Path 2 instrument shelter.

## 2.3 Instrument Operations and Maintenance

Four types of instrument systems are included in this monitoring system: UV-DOAS, TDLAS (effective January 2023), FTIR, and a visibility sensor. Other meteorological data are obtained from existing measurement systems at the Facility. Quality Assurance (QA) is a primary consideration for all operations and maintenance procedures. For all instruments, scheduled maintenance will occur monthly, quarterly, and/or annually. Emergency maintenance will occur as needed when problems are identified during daily data review and auto-screening of real-time data. All actions performed to the instruments are recorded and filed in a site logbook.

### 2.3.1 CEREX UV-DOAS

The UV-DOAS system is designed to require only modest service and maintenance. Table 3 summarizes typical UV-DOAS maintenance activities as recommended by the manufacturer. These actions help ensure data integrity and maximize up-time. Table 11 (see Section 4.4) further defines operational limits that will be used to trigger corrective actions during separate site visits. Maintenance schedules will be adjusted as needed.

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving check list is maintained).	$\checkmark$		
Inspect optics on detector and retro-reflector. Clean if necessary.	$\checkmark$		
Inspect and clean system filters.	$\checkmark$		
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.	$\checkmark$		
Ensure there are no obstructions between the detector and the retro- reflector (such as equipment, vegetation, vehicles).	$\checkmark$		
Inspect all electrical cables for wear. Replace as needed.	$\checkmark$		
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.		$\checkmark$	
Clean and inspect optics on detector and retro-reflector.		$\checkmark$	
Realign system after service. Ensure integration time is less than 250 ms and intensity is greater than 90% under high visibility conditions.		$\checkmark$	
Check other system performance indicators, if necessary.		$\checkmark$	
Perform bump test.	$\checkmark$		
Verify system settings.			$\checkmark$

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

### 2.3.2 UniSearch LasIR TDLAS

Maintenance activities for the TDLAS and the UV-DOAS are similar. The TDLAS system is also designed to require only modest service and maintenance. Table 4 summarizes TDLAS maintenance activities, as recommended by the manufacturer and required by the BAAQMD. Table 11 (see Section 4.4) further defines operational limits that will be used to trigger corrective actions during separate site visits. Maintenance schedules will be altered as needed.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	$\checkmark$		
Inspect optics on detector. Clean if necessary.	$\checkmark$		
Check the alignment to verify there has not been significant physical movement and confirm signal levels.	$\checkmark$		
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.	$\checkmark$		
Perform bump test	~		
Review and test light and signal levels. <sup>a</sup>		$\checkmark$	
3-point calibration check		$\checkmark$	
Verify system settings.			✓

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

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

### 2.3.3 CEREX FTIR

Maintenance activities for the FTIR and the UV-DOAS are similar. The FTIR system is also designed to require only modest service and maintenance. Table 5 summarizes FTIR 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. Audits will be performed on site.

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

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

### 2.3.4 Belfort Model 6400 Visibility Sensor

For the visibility sensor, monthly maintenance includes inspecting the sensor for dirt, spider webs, birds' nests, or other obstructions (see Table 6). If the sensor is dirty, the glass windows are cleaned with glass cleaner. There are no serviceable components in the sensor. Calibration will be performed semi-annually. Table 11 (see Section 4.4) further defines operational limits that will be used to trigger corrective actions during separate site visits. Maintenance schedules will be adjusted as needed.

Activity	Monthly	Quarterly	Semi- Annually
Inspect optics on detector, clean if necessary.	$\checkmark$		
Visually inspect the system including all cables.		$\checkmark$	
Check calibration. An acceptable $\%$ accuracy is less than $\pm 25\%$ .			✓

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

# 2.4 Emergency Maintenance Procedures

When a major problem is discovered with the fenceline monitoring system, corrective actions and maintenance procedures are required. Because the fenceline monitoring system is composed of two major components—field hardware and website software—two separate rotating teams are on call 24/7 to respond to any issues that can be dealt with remotely. Any necessary field work will occur the next business day. The two teams are (1) the Sonoma Technology field operations team (field ops team), and (2) the Sonoma Technology IT operations team (the IT ops team). The overall field ops team will consist of field technicians, and the IT ops team will consist of IS (information systems) engineers and IT specialists. Sonoma Technology staff manually checks the website daily, and automated checks are enabled. If the automated checks identify a problem, the automated system will immediately send an alert to the field ops team and/or the IT ops team. This approach will help to 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 and begin investigation within 75 minutes thereafter. Facility personnel will be notified if a solution for issues affecting data availability cannot be resolved within an hour of investigation. BAAQMD staff will be notified of monitoring downtime according to BAAQMD Regulation 1-530.<sup>6</sup>

The rotating field ops team will remotely monitor the status of the field sites 7 days per week and use automated checks such as the following to determine actions:

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

Problems with the analyzers or any associated hardware in the shelters will be addressed on the following business day. The IT ops team will remotely monitor the status of the website and associated equipment using automated system checks such as those listed in Table 7 to determine actions. Automated alerts are triggered when any of the parameters surpasses their limit or threshold.

<sup>&</sup>lt;sup>6</sup> 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.

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

Item	Parameter	Monitoring Frequency	Parameter Limit/Threshold for Alert
Website goes down	HTTP test on the: - public website - Administrator website DMS API	Every 300 seconds	Websites not reachable
DMS systems	- CPU utilization - Memory use - Disk space used	Every 300 seconds	- CPU utilization >60% - Memory used >75% - Disk used >75%
Other network- related issues	<ul> <li>Database replication</li> <li>API load balancer</li> <li>System services</li> <li>Network connections</li> </ul>	Every 300 seconds	Status either - OK - Insufficient - Unhealthy
Test for errors in data processing pipeline	- Process scheduler	Every 300 seconds	Status either - OK - Insufficient - Unhealthy

The IT ops team is expected 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 the Facility of any issues affecting data availability on the public website. Any instrument-level outages that occur during the weekday nights or weekends will be dealt with the next business day. In the case of any long-term outage or scheduled maintenance at a specific site, a temporary message may be displayed on the public-facing website to alert the public. If there is an outage lasting more than 24 hours, BAAQMD will be notified on the next business day. A spare analyzer may be installed if there is a long-term problem with a piece of operating equipment.

Corrective action will be taken to ensure that data quality objectives are met. Table 8 lists the types of issues that require corrective actions. This table is not all-inclusive, and additional checks may be added as the project progresses. The Daily Data Reviewers will review data daily to identify issues and will work with the field technicians and instrument contractors to resolve issues that need to be addressed on site. Analysts will examine both public facing and internal websites to assess data quality and availability. If issues are noted, the Analyst will further investigate and work with the QA Manager, Project Manager, and Field Technicians to resolve the problem. Furthermore, 24/7 on call field operations will be notified of any data availability issues. If necessary, maintenance tables will be modified and updated in the QAPP and submitted to BAAQMD for approval.

ltem	Problem	Action	Notification	Person Responsible
Erratic data (highly variable or not physically possible)	Possible instrument malfunction	Contact Field Manager and Instrument Contractor	Document in logbook, notify Routine Operations Manager	Field Technician
Power	Power interruptions	Check line voltage, reset or restart instruments	Document in logbook, notify Routine Operations Manager	Field Technician
Data downloading	Data will not transfer to the DMS	Contact Field Manager and Instrument Contractor	Document in logbook, notify Field Manager and Website/Data System Manager	Field Technician
Supplies and consumables	Essential supplies run out	Contact Field Manager	Document in logbook, notify Routine Operations Manager	Field Technician
Access to sites	Technician cannot access the sites	Contact Project Manager	Document in logbook, notify Program Manager	Field Technician
Instrument light level	A low light level alert is observed	Contact Instrument Manufacturer; replace bulb	Document in logbook, notify Routine Operations Manager	Field Technician/Daily Data Reviewer
Website	Website is down	Contact Website/Data System Manager	Notify Program 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

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

# 3. Quality Objectives and Criteria

### 3.1 Data and Measurement Quality Objectives

To ensure 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 measures.

To ensure appropriate spatial coverage of measurements, a thorough meteorological analysis was performed, as documented in the monitoring plan. Comparability among measurements is addressed by using one manufacturer for each system (UV-DOAS, TDLAS, FTIR, visibility) so that hardware and software are consistent among sites.

# 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 cloudbased DMS. The DMS automatically QCs data, detects outliers and problems, and creates alerts, while also tracking 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 integration time (only UV-DOAS reports integration time). This allows automatic screening for invalid data due to weather, as well as for suspect/questionable data due to marginal operating conditions. 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. Data below the MDL are flagged accordingly. 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, as their measurement technique is more straightforward. As with the open-path analyzers, all data in exceedance of RELs are automatically flagged as suspect/questionable for additional manual review and verification. 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 also assigned to provide additional diagnostic information. Table 9 presents an overview of relevant QC/OP codes that are used throughout the QC process including manual QC efforts (described in Section 4 of this document).

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

	Data QC/OP Codes				
Quality Control (QC) Codes					
0	Valid				
5	Suspect/Questionable				
7	Insufficient valid/suspect data to calculate an hourly average				
8	Missing				
9	Invalid				
	Operational (OP) Codes				
0	Valid				
5	Hourly data is suspect (general classification); due to range, rate of change, or sticking				
7	Insufficient valid/suspect data to calculate an hourly average				
9	No valid/suspect data to calculate an hourly average; due to invalid 5-min data				
17	Below MDL				
28	Planned Instrument Maintenance				
29	Unplanned Instrument Maintenance				
70	Instrument Malfunction				
72	Marginal Operating Conditions-Elevated Integration Time indicating low signal return				
73	Poor Visibility (Weather)				
74	Goodness of fit $(R^2)$ is below threshold, this occurs when compound is below detectable levels				
76	Marginal Operating Conditions–R <sup>2</sup> below threshold. Signal return is marginal and compound concentration below detectable levels.				
100	Flagged by Manual Review				
101	Flagged by Range Check				
102	Flagged by Rate of Change Check				
103	Flagged by 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 will be subjected to precision and accuracy tests. 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  $7 \le N \le 15$ . The average value of these measurements is calculated as:

and the standard deviation ( $\sigma$ ) as:

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

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

From these definitions

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 the system can detect at or below the target bump test concentration. To confirm reliable, high-quality performance by the UV-DOAS analyzer, single-species bump tests using benzene will be performed. For the FTIR analyzer, ammonia will be used as the test species. For both systems, bump tests will be performed on a monthly basis and potentially 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; if updates are needed, it will be updated and sent to the BAAQMD for approval before implementation. For the TDLAS analyzer, bump tests will also be performed monthly, using sealed cells containing H<sub>2</sub>S. Where commercially available, NIST-certified cells will be used.

For the visibility instruments, the sensors are calibrated in the field using a manufacturer-specific calibration kit. A calibration kit consists of (1) a blocking plate or block for checking the sensor zero and (2) a scatter plate for checking the sensor span. The scatter plate is assigned a factory-traceable

extinction coefficient used to calculate the expected values during calibrations. Calibrations will be performed on a semi-annual basis.

For the open-path systems, precision will be measured with bump test data by evaluating the coefficient of variation 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). If monthly bump test accuracy and precision specifications are not met, then repair, maintenance, and a root-cause analysis will be triggered, with repeat bump tests performed until a passing test is completed. All steps in this process will be recorded.

## 3.4 Instrument or Standards Certifications

For factory calibrations, a certification of the standard gases used will be requested from the manufacturer. Standards shall not be used past their expiration date. Certificates on reference standards used for bump tests in the field will be closely monitored. File version numbers of the spectral libraries used for signal processing will also be documented and archived.

## 4. Data Management

Data quality criteria are evaluated through (1) automatic data checks conducted through 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

Data management occurs on a real-time, daily, monthly, quarterly, and annual basis. In near-real time, data are transferred from infield instruments through a data acquisition system (DAS) to the DMS using cell modem. Data are also stored onsite on instrument computers in case of cell modem failure. The DAS performs data averaging to 5-min values, requiring that raw data completeness meets prescribed thresholds for each analyzer to calculate an average. These thresholds differ by each analyzer according to the time resolution of the raw data. Values that meet these completeness criteria are transferred to the DMS. The DAS also assigns initial QC codes and OP codes to each data value (Table 9 in Section 3.2), based on operating characteristics information collected from the analyzers as well as the data values. All data are stored in the DMS, which uses a Microsoft SQL relational database with stored procedures for data processing.

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 feed auto-screened data to an internal field operations website and notification system to inform and alert project and Facility staff if there is a data issue. The non-public operations website shows time series plots of BTEX, SO<sub>2</sub>, H<sub>2</sub>S, 1,3-butadiene, hexane, NH<sub>3</sub>, wind speed, wind direction, visibility, and other analyzer metadata.

The data is displayed on the website within 10 minutes of data collection only after it undergoes automated QC (described in Section 4.2) and aggregation to 5-min and running 1-hr values. One-hr average values that do not meet 75% completion criteria are considered invalid, due to insufficient data being collected.

## 4.2 Automated Data Quality Control

Automated data screening is conducted within the DMS upon data ingest. Automated screening checks of data feeds are used to screen out invalid data for public display and are helpful to focus the data reviewer's efforts on the data that need the most attention. Initial screening checks, along with actions to be taken, are summarized in Table 10. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by

compound, and typical ambient concentrations by compound. If, based on a detailed manual review of the data as described in Section 4.3, it is determined that the automated screening criteria are sufficient, they will be left as is. However, if the criteria listed in Table 10 result in erroneous flagging of data, the thresholds will be revised and this QAPP will be updated accordingly. The DMS auto-screening checks include:

- Range. These checks will 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 will be reviewed for validity. Typically, four or more intervals of sticking values are a reasonable time span to indicate that investigation is needed. Sticking checks will not be applied to data below the instrument detection limit.
- Rate of Change. Values that change rapidly without reasonable cause will be flagged and reviewed.
- Missing. If data are missing, data during those time periods will be coded as missing. Missing data may indicate a power issue, an instrumentation problem, or a data communication problem. Alerts are sent to the internal project team when no new data have been ingested over a 30-min period.
- Sensor OP codes and alarms. If the instrument assigns operation (OP) codes to data automatically (e.g., for bump tests or internal flow rate checks), the data will be reviewed, codes confirmed, and data flags checked.
- Visibility impairment. If open-path data are missing or invalid due to low light, and visibility is low, data will be flagged as invalid due to low visibility.

Additional parameters that may be monitored as indicators of data quality include signal strength, correlation between measured and reference spectra, wavelength versus intensity, and visual review of peaks. Signal strength will be used as a data filter. For those data points that are collected with a signal strength percentage outside of an acceptable range, based on will be flagged as either invalid or undergo additional screening. For UV-DOAS, this can also be paired with the integration time (which increases as signal intensity decreases). The correlation between measured spectra and reference spectra also used to filter data. Measurements with less than 80% (UV-DOAS) or 70% (FTIR) spectral match are flagged as below the detection limit of the analyzer (ambient interference and spectral noise are believed to impact measurements). A visual review of peaks can be conducted using manufacturer-supplied data processing software. This visual inspection will be used to determine the validity if peaks with high concentrations. Data quality objectives for these parameters may continue to evolve as the project is in operation; the QAPP will be updated as needed to include addition or revision of any data quality indicators that are determined to improve data quality.

QC flags identified through auto-screening will be 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—i.e., raw data and all changes are preserved. The website "Resources" page provides an explanation of every data flag used on the public website.

**Table 10.** Initial screening checks for 5-min data. All valid and suspect data values will be displayed to the public in real-time. If data are invalid, they will not be included in the public display. All screening values below (flags and rates of change) are preliminary and will be refined during the project. During data validation, flagged data will be further investigated.

	Checks						
Measurement (units)	Minimum Detection Limit (MDL): If concentration is below MDL, flag as below MDL	Range: If concentration is above value listed, flag as suspect and investigate	Sticking: If same value observed for four or more intervals, flag as suspect and investigate	Rate of Change Between Intervals: If concentration changes by more than value listed, flag as suspect and investigate	Missing: If data are missing, flag as missing and investigate cause	Sensor OP Code/Alarm: If sensor indicates malfunction or bump test data, flag as appropriate	Visibility: If visibility is less than 2.5 miles and data are invalid, flag as appropriate
Benzene (ppb)	0.5 ppb	>24 ppb	Same for all pollutants	±12 ppb			
Toluene (ppb)	1.4 ppb	>1000 ppb		±500 ppb			
Ethylbenzene (ppb)	0.5 ppb	>1000 ppb		±500 ppb			
Xylenes (ppb)	2.4 ppb	>1000 ppb		±500 ppb			
SO <sub>2</sub> (ppb)	1.1 ppb	>75 ppb		±150 ppb			
Ammonia (ppb)	0.4 ppb	>500 ppb		±250 ppb	Same for all	Same for all	Same for all
1,3 –Butadiene (ppb)	1.5 ppb	>900 ppb		±300 ppb	pollutants	pollutants	pollutants
Hexane (ppb)	0.8 ppb	>200 ppb		±100 ppb			
H <sub>2</sub> S (ppb)	3-25 ppb	>50 ppb		±30 ppb			
Visibility (miles)	If value is <0, flag as suspect	>50		Not applicable			

\*Valid data below MDL will be 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, the data will be flagged as below MDL on the public website and in the database. Per the December 22, 2022 letter from BAAQMD,<sup>7</sup> 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.

<sup>&</sup>lt;sup>7</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

## 4.3 Routine Data Verification

## 4.3.1 Confirm Daily Operation

Data are reviewed 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 instruments are operational. If it appears that an instrument is not operating, or the data are missing, the field operator will be notified and further investigation and corrective action, if needed, will be taken.

## 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, etc., show whether the data are physically reasonable. Other instrument parameters and correlation among measurements, can also be used to judge the validity of the data. 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 during the data validation process. If, after review, there are no justifiable reasons for invalidating the data, questionable data will be considered valid. All data will be preserved during data reviews and only data flags will be changed, if applicable. Chain-of-custody logs will show all changes to data flags.

## 4.4 Data QA Procedures and Validation

At least quarterly, a Data Reviewer/Analyst will validate data by building on the automated screening results. More frequent review and validation of concentration data may occur as determined by the Facility Program Manager and/or the QA Manager. This process starts with an in-depth review of the data, which includes statistical tests to ensure the data are valid for the intended end use. The QA Manager will evaluate QA/QC procedures and ensure adherence to the methods for meeting data quality objectives. Data validation activities will be reviewed and approved by the QA Manager.

Data validation activities include:

- Looking for and investigating 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 data reasonableness by comparing data to other sources of data
- Ensuring the data or measurements are realistically achievable and not outside the limits of what can be measured

- Inspecting several sampling intervals before and after data issues or instrument bump tests or repairs to ensure all affected data have been properly flagged
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on manual changes to operations/data, and verify that the changes were logged and appropriately flagged
- Assessing instrument meta-data to confirm reasonableness
- Assessing visibility measurements to ensure adequate signal was obtained to quantify pollutant concentrations
- Confirming that bump tests were conducted and were within specifications

Additional QC checks for the instruments are summarized in Table 11. The data checks listed in Table 10 are generally robust but may be actively revised if evidence of ineffectiveness is found during daily and quarterly data validation.

Data are only invalidated if a known 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 as suspect. Additional analysis may be needed to deem data valid or invalid. Voided data will be flagged as invalid in the database. A summary of issues leading to invalidated data will be documented in the data file.

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

#### Table 11. Instrument QA/QC checks.

<sup>a</sup> 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.

<sup>b</sup> NIST TN 1297: Appendix D1. Terminology.

<sup>c</sup> For test concentrations requiring greater than 750 ppm H<sub>2</sub>S, safety considerations necessitate certified sealed cells be used. For test concentrations requiring lower than 750 ppm, certified flow-through cells may be used.

<sup>d</sup> Per the December 22, 2022 letter from BAAQMD<sup>8</sup>, 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.

<sup>&</sup>lt;sup>8</sup> Bovee, J. "Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specifications", Communication to Tesoro, December 22, 2022.

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 instrument checks have the appropriate QC codes applied.

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

- Assigning invalid data a null code (a reason for being invalid).
- Creating a null record if a record is not created for a particular site/date/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 will be documented in the DMS, which retains raw data and traceability of all actions that result in the final data.

On an annual basis, the Facility Program Manager and the QA Manager will review the performance of the network by (1) reviewing the data completeness by monitoring path, instrument, and species; (2) reviewing results of bump tests; (3) analyzing the reported values in context of Facility operations; and (4) analyzing the data in context of the meteorology.

## 4.5 Data Storage and Backup

On-site, raw analyzer backup files are copied to offsite storage on a semi-annual basis. The DMS data is backed up on a daily basis. Stored and retained information includes (1) raw and validated data; (2) QC codes, operational (OP) codes, and metadata associated with each data value; (3) metadata associated with each analyzer; and (4) change-of-custody logs. A complete data repository is kept by Sonoma Technology in the cloud, and the Martinez Facility Environmental Group and the BAAQMD will retain quarterly datasets. The data is stored for a period of five years, consistent with Rule 12-15 requirements.

Access to the DMS data is controlled by username and password (with strong encryption) and is restricted to those designated to perform data validation and analysis. As protection against incorrect modification or deletion, a chain-of-custody record is kept of all changes to the database, and backups are completed frequently.

## 4.6 Data Delivery and Reporting

Final data sets and a quarterly report are compiled quarterly and will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter. Consistent with BAAQMD guidance, quarterly data deliveries will include the following.

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

- A record for each 5-min period of the quarter for all instrument and parameter combinations; records corresponding to missing data will include the facility name, instrument ID, instrument descriptor, parameter, date, time, and error codes with their respective values, and remaining fields will be populated with a value of "NA"
- An assessment of data completeness, as described in Section 3.2
- A summary of bump tests and calibration checks performed according to the QAPP including the instrument or system, the type of test or check, the start and end date and time of the test or check, and the date and time that the instrument or system resumed normal operations; potential failed bump tests or calibration checks will be included
- The results of bump tests and calibration checks performed according to the QAPP including accuracy and precision; root cause analysis and a narrative description of maintenance or repairs performed to return the system to proper operations will be included for potential bump tests or calibration checks with accuracy and precision results that are not within the acceptance criteria
- Data corrections accounting for the effects of gas cells or other equipment on instrument signal
- Meteorological data and a narrative explanation sufficient to justify where data has been excluded due to adverse atmospheric or environmental conditions

The quarterly reports provide a summary of measured data, threshold exceedances, quarterly and monthly statistics, accuracy and precision of instruments, outliers, anomalies, and data QC. The quarterly reports are written at a public-friendly level but still reflect a high level of data validation and QC. Each report is reviewed for accuracy by (1) the Project Manager and another Senior Manager at Sonoma Technology, and (2) the Martinez Facility Environmental staff.

Outside of the normal quarterly delivery, data will be made available to the BAAQMD upon request and will be delivered within 30 days of the request.

## 4.7 Data Flow to Website

All data values that are not associated with bump tests, other instrument maintenance, or instrument problems, will be displayed to the public in near-real time. If data are subsequently proven to be invalid, they will be removed from the public display with the reason for removal flagged on the public display. The website "Resources" page provides an explanation of every data flag used on the public website. Data issues identified during the automated QC process will trigger a notification to the Data Manager to conduct further investigation. The Data Manager and team will then decide on the appropriate action to resolve the problem.

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 the data are collected.

The preliminary QA/QC'd concentration data are presented in a time series of benzene, toluene, ethylbenzene, total xylenes, 1,3-butadiene, hexane, NH<sub>3</sub>, and H<sub>2</sub>S. Data are provided as 5-min averages. Data are annotated for quality (valid, invalid, suspect, or missing).

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

## Appendix A

# Standard Operating Procedures for the CEREX UV Sentry UV-DOAS

STI-7024

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## 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<sub>2</sub>, NO<sub>2</sub>, 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

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

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

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.

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.



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</u> <u>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.

- <u>RunTime</u>
  - o 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
  - o File

- File Type: .CSV
- Primary Data Logging File: ON
  - C:\Users\CMS-USER\Documents\Cerex\Data
- Secondary Data File Logging: ON
  - \\OPT1-PC1\VLOData\OPT1\_Path1\UVSentry\_POC1
    - Note this path will change based on the different computer and path you are working on. This is just a basic file writing path to show you what it should look like.
- Single Data Folder: OFF
- Primary Summary File Logging: ON
  - C:\Users\CMS-USER\Documents\Cerex\Data
- Secondary Summary File Logging: ON
  - \\OPT1-PC1\VLOData\OPT1\_Path1\UVSentry\_POC1
    - Note this path will change based on the different computer and path you are working on. This is just a basic file writing path to show you what it should look like
- Single Summary File: OFF
- o Library
  - Library File: C:\Users\CMS-USER\Documents\Cerex\Library\
- o 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>
  - o 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
  - o Filters
    - Absorbance Savitzhy-Golay: ON
    - Baseline Correction Savitzky-Golay: OFF

- Instruments
  - o 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: Normal
    - 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)
- <u>Controller</u>
  - General
    - Serial Port: n/a
    - Sensor Refresh Interval (s): **15**
  - $\circ \quad \text{Sensors}$ 
    - Don't Touch Anything
  - o Alarms
    - Don't Touch Anything
- <u>Email</u>
  - o 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
  - o SMTP

- Server: **smtp.gmail.com**
- Port: 587
- Username: Blank
- Password: Blank
- Timeout (s): 100
- SSL Authentication: **ON**
- <u>Auxiliary Coms</u>
  - $\circ$  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.



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  $8'' \times 8'' \times 1''$  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.<sup>1</sup> 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.

<sup>&</sup>lt;sup>1</sup> 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



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

- 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.
- 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.
- 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)
- 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).
- 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  $7 \le N \le 15$ . The average value of these measurements is calculated as

$$\bar{x} = \frac{\sum_{i} x_{i}}{N} \tag{1}$$

and the sample standard deviation ( $\sigma$ ) as:

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

From these definitions, % error is defined as:

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

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

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

- 1. Concentration
  - a. Average the concentration of 15 consecutive stable measurements.
  - b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

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

- 2. Calculate the Limits of Detection and Quantitation.
  - a. Calculate the mean (average), sample standard deviation, and % error (sometimes also referred to as % difference) of the selected results.
  - b. Report the Detection Limit as three times the standard deviation.
  - c. Report the Quantitation Limit as five times the standard deviation.
- 3. Compile all configuration files, spectra files, and log files into a single folder.
  - a. The folder should be named "CUS LOC QATest UV# YearMonDy" where CUS is a threeletter 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.

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 <sub>2</sub>	0 to 100 ppb, usually zero. Refineries are a local source – note any high values above REL.
NO <sub>2</sub>	Typically 0 to 200 ppb. Values typically peak at night; sunlight destroys it, traffic and combustion produce it. Some instruments may not detect NO <sub>2</sub> if they are saturated.

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

# 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</u> <u>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.

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. <sup>a</sup>	
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	

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

<sup>a</sup> 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	on (typically 1 m for monostatic and 2 m for
bistatic) r	
Configure Test Files	
Site File (i.e., QA Audit UV# YearMo	DDy)
Baseline Check	init
Reference Gas	
Concentration	ppm
Source	
Date	
Cylinder Pressure	
NOTES:	

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 Tir	ne	-	
Data Record:			
TIME	РРМ	R2	
Verify Client		-	Init
Stop Time		-	Init
Open the PURGE gas		Time	
Reference Concentration			ppm
Average Concentration % error			ppm %
Std Deviation			ppm
% CV			ppm
<b>Restore Normal Operation</b>			
Restore running data file		-	Init
Press <b>RUN</b> to begin monitoring.		-	Init

# QA Audit Record - UV Sentry Detection System - Page 2

# Appendix B. Standard Operating Procedures for the CEREX AirSentry FTIR

# Appendix B

# Standard Operating Procedures for the CEREX AirSentry FTIR

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# 1. Scope and Application

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

# 2. Introduction and Overview

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



Figure 1. Schematic of the instrument.

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

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

# 3. Definitions

 Table 1. List of definitions.

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

# 4. Safe Work and Hazard Identification

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

### Safe Operating Precautions

- 1. Ensure that a clear escape path is identified.
- 2. Standard site PPE is appropriate. If gloves are required, nitrile or latex should be used.

### **Operator Qualifications**

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

# Safe Work and Hazardous Environment Operation

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



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

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

# **Procedure Warnings**

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



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

- □ Notify the client and project manager of maintenance tasks.
- □ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.
- Confirm that the data is invalidated on the public website before proceeding with maintenance.
- When maintenance is complete check the public site <u>for at least 15</u> <u>min</u> to ensure proper reporting (no missing data, no high values, etc.).
- □ Take out of maintenance mode.
- □ Notify the project manager and client when maintenance is complete.

# 5. Routine Operations

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

1. Start the CMS software (if not already initiated). You should see a window similar to the one shown in Figure 2.



**Figure 2.** Screenshot showing the FTIR tab of the CMS software. Note that the Align and Run buttons are grayed out because the instrument is in run mode.

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



ОК

Cancel

Status: Collecting spectrum.



Maximum Intensity: 11.57%

**Figure 3.** Screenshots of Align mode. The spectral resolution can be selected from the dropdown menu. In these particular screenshots, resolutions of 1 cm<sup>-1</sup> (top) and 64 cm<sup>-1</sup> (bottom) are selected.

- 3. Select a spectral resolution of 64 cm<sup>-1</sup> and optimize the signal intensity by adjusting the pan-tilt head of the FTIR unit to adjust the position of the IR beam on the retroreflector.
- 4. Once sufficient alignment is obtained, exit the align mode by pressing Cancel.

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

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

- <u>RunTime</u>
  - o General
    - Operator Name: **Default** (these will change based on the path and site you are working on)
    - Sitename: Cerex (these will change based on the path and site you are working on)
    - Auto Run: ON (ON means the instrument will turn on automatically if the computer is running)
    - Auto Run Delay (s): **15** (time delay for CMS autostart)
  - o File
    - File Type: .CSV
    - Primary Data Logging File: ON
      - C:\Users\CMS-USER\Documents\Cerex\Data (file path will vary by facility)
    - Secondary Data File Logging: ON
      - \\XXX\XXX\... (file path will vary by facility)
        - Note this path will change based on the computer and path you are working on. This is just a basic file writing path to show you what it should look like.
    - Single Data Folder: OFF
    - Primary Summary File Logging: ON
      - C:\Users\CMS-USER\Documents\Cerex\Data
    - Secondary Summary File Logging: ON
      - \\OPT1-PC1\VLOData\OPT1\_Path1\UVSentry\_POC1
        - Note this path will change based on the computer and path you are working on. This is just a basic file writing path to show you what it should look like.
    - Single Summary File: OFF
  - o Library
    - Library File: C:\Users\CMS-USER\Documents\Cerex\Library\
  - o 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>
  - o General
    - Moving Average Interval: 12
    - Display Units: **PPM**
  - Concentration
    - Zero Readings on Non-Detect: **OFF** (zeros reading below threshold % match
    - Zero Readings on Negative concentrations: OFF (zeros reading less than zero)
    - Display BDL: OFF
    - Quick Analysis MDL Wave length Range: 276 -280 (not typically used)
    - Temperature/ Pressure Concentration: OFF
  - o Filters
    - Absorbance Savitzky-Golay: OFF
    - Baseline Correction Savitzky-Golay: OFF
  - Background
    - Auto Background: **ON** (typically ON for fenceline monitoring projects reporting concentration above background)
    - Interval (Acquisitions): **5** (How far back the routine will search for a background)
    - Depth: 4
- Instruments
  - o FTIR
    - Operational;
      - FTIR: **ON** (sets instrument type)
      - Averages/Co-adds: 28 (how many spectra will be averaged together)
      - Path Length (m): 2 (2 for monostatic units)
      - Resolution: 1 cm-1 (spectral resolution)
    - Verification
      - Verification: OFF (This inactivates all inputs)
- <u>Controller</u>
  - o **General** 
    - Serial Port: n/a
    - Sensor Refresh Interval (s): 10
  - o Sensors
    - Don't Touch Anything
  - o Alarms
    - Don't Touch Anything

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

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

# 6. Equipment and Supplies

- 1. Field notebook
- 2. Tool kit, especially including: 7/64 hex driver, complete set of combination wrenches, adjustable wrenches, screwdrivers, etc.
- 3. Cleaning supplies designated to be safe for use on a Cerex FTIR
- 4. All relevant PPE, hardware, and procedural guidance per SOP, Safety Plan, and Safe Work Permit
- 5. Local or remote network link device (as required)
- 6. External laptop computer with network interface device to the Sentry unit (as required)
- 7. Cerex FTIR Sentry Unit equipped with CMS software
- 8. Isopropyl Alcohol (≥80%)
- 9. Distilled water
- 10. Pressurized sprayers
- 11. Powder-free nitrile gloves

- 12. Cell bump test apparatus (including panels, regulators, valves, meters, etc.)
- 13. Tubing as required: 1/4" metal jacketed PTFE tubing for gas supply from the bottle to the QA cell
- 14. Tubing as required: 3/8" metal jacketed PTFE tubing with inline flow indicator from the QA cell to the scrubber
- 15. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less
- 16. Gas scrubber appropriate for gas used. Activated carbon treated with phosphoric acid may be used for benzene
- 17. Reference standard traceable zero compressed air purge gas
- 18. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher

# 7. Maintenance Activities

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

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

- Visually inspect the system.
- Confirm the alignment to verify there has been no significant physical movement. Note: this is automatically monitored as well.
- Download data older than 6 months from detector hard drive and if needed delete old files to free space.
- Ensure there are no obstructions between the detector and the retro-reflector.
- Replace air conditioner fans.
- Change out the IR source.
- Realign system after service.
- Check system response (bump test). Take corrective action if % Error exceeds level specified in the QAPP.
- Review and test light and signal levels.

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

# 7.1 Monthly Visual Inspections

- 1. Ensure that the instrument is running and the data look reasonable.
- 2. Clean and correct any obvious problems with the system (cobwebs, rodent nests, broken optics, etc.).
- 3. Inspect all electrical cables for wear; replace as needed.
- 4. Indicate these visual checks are complete on the form included at the end of this document.
- 5. Document any changes to the system in the course of these checks in the site logbook.

# 7.2 Light Level Check

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

# **Check for Stray Light**

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

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

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

# 7.3 Data Management

# 7.3.1 Archiving and Deleting Older Data

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

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

- 1. Confirm that the data files have been successfully written to the external hard drive attached to a separate PC also located in the instrument shelter.
- 2. Make a note of the amount of available space on the instrument internal drive on the maintenance form.
- 3. Locate files older than 12 months on the instrument file directory here: C:\Users\CMS-USER\Documents\Cerex\Data\.

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

- 4. Log into the brick PC located in the instrument shelter and locate the data files written from the instrument onto the external hard drive.
- 5. Confirm all Complete Data Summary files and Simple Data Summary files for the desired month have transferred over completely to the external hard drive attached to the brick PC.
- 6. Once you have confirmed that those files have been transferred over to the external hard drive, delete those exact Complete Data Summary and Simple Data Summary files from the instrument data folders.
- 7. For each individual day of single beam folders, ensure that the amount of single beam files are the same on both the external hard drive located on the brick pc and the internal hard of the instrument.
- 8. If both folder locations match and you have ensured proper file download, you may permanently delete the Single Beam folders from the instrument computer.
- 9. After all data older than 12 months have been deleted, note how much free space is now available on the instrument's internal drive. If removal of the files does not result in enough free disk space, the disk drive may need to be reindexed (see Section 7.3.2).

# 7.3.2 Rebuilding the Instruments Indexing Preferences

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

<sup>&</sup>lt;sup>1</sup> CMS Software User Manual Rev 4. CMS Version 4.0.298.1, CEREX Monitoring Solutions, December 5, 2017.
- 1. Navigate to the **Control Panel Menu** by using the search function in the lower left-hand corner of the task bar.
- 2. Once in the control panel menu, click **Indexing Option**.
- 3. Click on the **Advanced** tab with the shield logo.
- 4. Click **Rebuild**.

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

# 7.4 Clean Optics on Detector and Retroreflector

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

## 7.4.1 Retroreflector Cleaning

- 1. Power down any equipment to prevent electrical shock or damage to the system.
- 2. Use a gentle stream of distilled water, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust build-up on the retroreflector.
- 3. Use a gentle stream of 80% isopropyl alcohol, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust build-up on the retroreflector.
- 4. Once the retroreflector has been cleaned and dried, repower the any electrical equipment you have powered down, and clean any spills you have created while cleaning.

## 7.4.2 Optic Cleaning

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

- 1. Wear powder-free gloves to avoid transferring skin oils onto the optics.
- 2. Use compressed air/canned air to remove particles from the surface of the optic. If the optic is sufficiently clean after this step stop here.

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

## 7.4.3 Replace AC Fans

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

- 1. Turn off MDAs and place unit into Planned Maintenance.
- 2. Close CMS, Shut down operating system.
- 3. Unplug power to unit.
- 4. Open FTIR lid.
  - a. Note: (place barrier to prevent screws from falling into the FTIR assembly).
- 5. Remove shroud fan cover on the underside of the FTIR lid.
- 6. Make note of fan orientation before removal (i.e. front facing).
  - a. Unplug each fan, then remove the four screws holding each fan for removal.
- 7. Install new fans with screws, then plug fans into power source.
- 8. Close FTIR lid.
- 9. Plug in the FTIR power source and begin operations.
- 10. Start CMS and align FTIR if needed.

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

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

## \*\*\*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.

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

## 7.5.1 Apparatus Setup

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

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



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

# Materials Required

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

- 2. Cell bump test purge apparatus, including:
  - a. Tubing as required: 1/4" PTFE tubing for gas supply from the calibration gas panel to the QA cell.
  - b. Tubing as required: 3/8" PTFE tubing for gas supply from the QA cell to the calibration gas panel.
  - c. All necessary tubing for supplying calibration and zero reference gas to calibration gas panel.
  - d. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less.
- 3. Purge gas; typically, Zero Air.
- 4. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher.
- 5. All relevant PPE, hardware and procedural guidance per SOP, Safety Plan, and Safe Work Permit.
- 6. Local or remote network link device (as required).
- 7. External laptop computer with network interface device to the AirSentry FTIR unit (as required).

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

- 1. The analyzer should be powered on and running for <u>at least 30 minutes prior to testing</u>.
- 2. Stop CMS data collection by pressing the STOP button.

## 7.5.3 Gas Test System Setup

- 1. Connect the <sup>1</sup>/<sub>4</sub>" reference cell line coming from the calibration panel to the <sup>1</sup>/<sub>4</sub>" reference cell connection on the Cerex MS Air Sentry FTIR.
- 2. Connect the 3/8" reference cell line coming from the calibration panel to the 3/8" reference cell connection on the Cerex MS Air Sentry FTIR located just below the 1/4" reference cell inlet.
- 3. Ensure all valves on the calibration gas panel are in the closed position.
- 4. Make all necessary connections from Zero Air and calibration gas standard cylinders to the Gas Calibration Panel.

## 7.5.4 Verify Proper AirSentry Alignment

- 1. Open the CMS window.
- 2. Click on the **FTIR** tab.
- 3. If **Run** is active, press **STOP**.

- 4. Click the **ALIGN** button at the bottom left of the plot display.
- 5. Select 32 cm<sup>-1</sup> and wait for resolution change.
- 6. Aim the AirSentry FTIR at the retroreflector and adjust the alignment until the signal intensity is optimized.
  - a. The target intensity should be the highest achievable intensity, which varies based on instrument, but should be above 5% at minimum. Once a stable signal is obtained, select the desired operating resolution (1 cm<sup>-1</sup> is required unless otherwise directed by Cerex).
- 7. **Record** the signal intensity.
  - a. Optional at this point you may wish to record the current field pathlength and create a backup of the existing configuration file.
- 8. Press OK and SAVE or ACCEPT (when prompted) to exit the CMS Alignment window.

## 7.5.5 Leak Check

- Ensure that all tubing from the purging panel is connected to the calibration panel in the mobile van. Ensure gas cylinders are connected to the purge panel as depicted in Figure 4. Then attach the calibration panel to the analyzer connection in the analyzer shelter.
- 2. Connect the PTFE tubing containing the activated carbon scrubber to the analyzer exhaust.
- 3. Close all valves on the calibration and purging panel.
- 4. Verify that the regulators on the zero air and benzene cylinders are completely closed (**all the way to the** <u>left</u>!) to prevent any pressure buildup at the regulator.
- 5. Open high-pressure valves on both the calibration gas and zero air bottles.
- 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.
- Open valve (12) and slowly open the regulator on the calibration gas cylinder to a pressure of 5-10 psi on the pressure gauge on the benzene calibration gas channel of the panel. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.
- 8. Open the bypass valve (2).
- 9. Open the zero-air valve (6) and slowly open the regulator (4) to a final pressure of about 2 psi (as read on cell and exhaust pressure gauges). **DO NOT pressurize above 3 psi**.
- 10. Now pressurize the cell. Slowly open the valve going to the cell (valve 3). Close the bypass valve (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve pressure on the cell. Wait until the same pressure is reached on the exhaust-side calibration panel pressure gauge.

- 11. Close the zero-air valve (6) going to the benzene regulator on the panel so the system is now fully closed off to external pressure.
- 12. Watch the system for a minimum of five minutes to ensure there is no drop in pressure and the system is leak free.
- 13. Open the leak check valve (1) to release the pressure from the system, and then close all the valves on both panels.
- 14. Record leak check.

### 7.5.6 Configure Test Files

- 1. Click **Advanced** on the left side of the CMS software window. The password is *advanced*.
- 2. Under Advanced -> Settings -> Runtime -> File, turn off Secondary Logging. Note current file logging paths.
- 3. Change both of the primary file logging paths to: C:\Users\CMS-USER\Documents\Cerex\Data\bumptest. Then select **File** and **Save**.

## 7.5.7 Gas System Purge

- 1. Close the secondary pressure regulator (4) on the panel by turning all the way to the left.
- 2. Open the leak check (1) and bypass valve (2).
- 3. Open the zero-air valve (6).
- Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.
- 5. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve the pressure on the cell. Wait until the desired flow rate has stayed the same and the pressure on the entire system has not increased.
- 6. Press **RUN** to start background acquisitions.
- 7. Allow the analyzer to complete three or more acquisitions.
  - a. If after two acquisitions the absorbance graph shows negative features greater than 3X the peak-to-peak baseline noise level, take another clean air background.
- 8. Repeat this process until the sequential absorbance acquisition seen in the absorbance graph remains near zero (straight baseline with only normal noise peaks).
- 9. Once the instrument has performed ten or more acquisitions, close the zero-gas valve (6).
- 10. Close all valves.

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

## 7.5.8 Gas Span and QA Test

- 1. Open the leak check (1) and the bypass valve (2).
- 2. Open the calibration gas valve (5).
- 3. Adjust the flow of calibration gas going through the bypass and scrubber until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.
- 4. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve the pressure on the cell. Ensure the desired flow rate has stayed the same and adjust as needed.
- 5. Wait 10 minutes to fill and condition lines and cell.
- 6. After 10 minutes of calibration span gas flow, press **Start** in CMS.
- 7. Collect span gas data.
  - a. Observe the concentration reported on the DATA tab.
  - b. After the concentration becomes stable, allow the analyzer **to run until at least seven stable measurements are made.**
  - c. Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).
  - d. Verify client system is receiving and displaying instrument information correctly.
  - e. After seven stable measurements are observed, close the reference gas cylinder valve (6). Allow the pressure to fall to zero and the flow to stop.

## 7.5.9 Completion of Test and Purge of Instrument Calibration Cell

- 1. Close the calibration gas cylinder. You will see calibration gas pressure increase and/or fluctuate as the pressure on the bottle regulator drops. This is normal be patient and wait for the benzene pressure to zero out.
- 2. Close all valves on the calibration and purging panel.
- 3. Open the zero-air valve (6).
- Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

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

### 6. Verify that the target gas(es) concentration has returned to 0 ppm with non-detect R<sup>2</sup>.

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

- 7. Once a zero reading is indicated on the FTIR, close all valves.
- 8. Close the zero-air cylinder and allow all the pressure to be released from the system.
- 9. Close all valves and ensure there is zero pressure on the system.
- 10. Disconnect tubing to the analyzer and the activated carbon scrubber.
- 11. Remove the hoses and cap the connectors.

### 7.5.10 Restore Normal Operation

1. Restore Normal Operation.

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

- a. **STOP** CMS.
- b. Click **Advanced** on the left side of the CMS software window; password is *advanced*.
- c. Under Advanced -> Settings -> Runtime -> File, turn On Secondary
   Logging. Change the primary file logging paths (both of them) to:
   C:\Users\CMS-USER\Documents\Cerex\Data. Then select File and select
   Save.
- 2. Check the system alignment as previously described.
- 3. Press **RUN** to begin monitoring.

#### Test Suspension

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

1. Close the reference gas bottle valve completely.

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

#### 7.5.11 Data Evaluation, Reporting, and Corrective Action

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

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

and the sample standard deviation ( $\sigma$ ) as:

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

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

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

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

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

- 1. Concentration
  - a. Average the concentration of 7 15 consecutive stable measurements.
  - b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

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

- 2. Calculate the Limits of Detection and Quantitation
  - a. Calculate the mean (average), sample standard deviation, and %error (sometimes also referred to as % difference) of the selected results.
  - b. Report the Detection Limit as three times the standard deviation.
  - c. Report the Quantitation Limit as five times the standard deviation.
- 3. Compile all configuration files, spectra files, and log files into a single folder.
  - a. The folder should be named "CUS LOC QATest IR# YearMoDy" where CUS is a three-letter designator for the customer, and LOC is a three-letter designator for the facility location.

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

Note:

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

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

- Reviewing data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features
- Consulting with the project technical lead to identify abnormal changes to the background
- Check wavelength calibration
- Checking for large changes in stray light since the last test and adjusting calibration factors as necessary
- Reviewing gas testing apparatus for leaks or other similar problems
- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

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

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

# 7.6 Cryocooler Replacement and Calibration

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

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



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

- c. Unplug the black and red cable molex connector coming from the glass detector assembly.
- d. In some installations there is a ground cable coming from connector and going to the chassis. Remove the ground cable by unscrewing it from the chassis.
- e. Take out the 3 #8 screws that hold the detector assembly to the baseplate these will have blue grommets in the holes (See image below). Only remove 3 screws to release the entire assembly (Figure 6).



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

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



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

- g. Disconnect power to the preamp this is a 4-pin molex connector that can be pulled apart. The connector has purple, orange, and black wires.
- h. Follow the second black coax cable from the preamp over the 4" x 6" heatsink assembly. Remove the BNC connection to this heatsink by hand twisting 1/4 turn counterclockwise and pulling it off.
- i. The detector assembly and the preamp will come out together as they are attached to each other by a coax cable.
- j. Pack the detector assembly and the preamp in the same box. But wrap both items separately so they can not touch. Immobilize all items in the box. Use protective case to transport entire assembly securely.

- 2. Re-install cryocooler
  - a. The installation process is the opposite of removal.
  - b. Make sure all screws and connectors are secured and tightened.
- 3. Optics Calibration
  - a. After replacing or installing a new detector and optics optimization is required using a small test retroreflector array.
    - i. Place the test retroreflector array about 2 feet from the front of the FTIR scope. Alternatively, use a small "bike reflector" in the outgoing beam path, just before the light enters the bump test cell.
    - ii. With the instrument powered on and using the Align window, set the resolution to 64 ms and align the scope to obtain the maximum signal strength possible.
    - iii. Open the instrument and carefully use the beam splitter adjustment screws to maximize signal strength. This means making small adjustments to each screw until you reach the maximum signal strength (Figure 8).



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

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



Figure 9. Beam steering mirror with sliver adjustment screws.

# 8. Monthly Maintenance Forms

Path:\_\_\_\_\_

Technician:\_\_\_\_\_

Date:\_\_\_\_\_

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

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

- □ Notify the client and project manager of maintenance tasks.
- Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.
- Confirm that the data is invalidated on the public website before proceeding with maintenance.
- When maintenance is complete check the public site <u>for at least 15</u> <u>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:\_\_\_\_\_

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

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

# **Corrective Actions for FTIR**:

# Cerex FTIR Air Sentry Gas Test Summary

DATE:	Location:
Test Technician 1:	_ 2:
Sentry Alignment	
Signal Intensity (average)	
Signal Intensity at 966 cm <sup>-1</sup>	
Blocked Beam Intensity at 966 cm <sup>-1</sup>	
% Stray Light	
Gas Purge System	
Flow purge Start Time	
Prepare CMS	
Path length in the CMS Configuration	m
Configure Test Files	
Site File (i.e., QA Audit UV# YearMoDy)	
Baseline Check	init
Reference Gas	
Concentration	ppm
Source	
Date	

NOTES:

# Gas Test Summary – Cerex FTIR - Page 2

<b>Purge Flow Conditions</b> Start Time NOTES:	
Check Gas Test Initial Gas Flow Start Time Collect Check Gas Data Start Time Data Record:	L/min 
TIME       PPM	R2
Verify Client Stop Time Open the PURGE Gas Reference Concentration Average Concentration % error % Spectral Match Standard Deviation Estimated MDL (3X Standard Dev) Restore Normal Operation Restore running data file Press RUN to begin monitoring.	Init Time Init Time ppm ppm % % % ppm ppm ppm Init Init

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

# Appendix C

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

STI-7801

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# 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.<sup>1</sup> 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<sub>2</sub>S) and verifying proper detection and quantification under field conditions.

<sup>&</sup>lt;sup>1</sup> 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<sub>2</sub>S 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<sub>2</sub>S 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<sub>2</sub>S 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<sub>2</sub>S concentrations by simultaneously accounting for overlapping water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) absorbance bands. As a result, concentration data for H<sub>2</sub>S, H<sub>2</sub>O, and CO<sub>2</sub> are provided with correlation coefficients that indicate the "goodness of fit."

The purpose of this procedure is to check the system for expected H<sub>2</sub>S response under the installed operating conditions. H<sub>2</sub>S 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<sub>2</sub>S 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<sub>2</sub>S, because olfactory senses may be deadened by exposure to concentrations below safe exposure levels. A system for scrubbing H<sub>2</sub>S 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<sub>2</sub>S monitor, and appropriate gloves that are adequate for this procedure. For testing with the flow-through cell using H<sub>2</sub>S concentrations in excess of 100 ppm, a second person should always be present as a safety monitor. H<sub>2</sub>S 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.

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		

Table 1. List of maintenance activities and performance indicator checks for the TDLAS.

## 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 Technologyoperated 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  $\mu$ A or  $\mu$ W. 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<sub>2</sub>S, CO<sub>2</sub>, and H<sub>2</sub>O. 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<sup>2</sup>. 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

<sup>&</sup>lt;sup>2</sup> 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<sub>2</sub>S reference gas blend
  - Note that the H<sub>2</sub>S 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 1/2" 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<sub>2</sub>S, which is approximately 1,000 times the amount of H<sub>2</sub>S existing in 750 ppm H<sub>2</sub>S 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<sub>2</sub>S (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<sub>2</sub>S. An example calculation of this is as follows:

(H<sub>2</sub>S 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 ppm-m / 1000 m = **0.125 ppm or 125 ppb H**<sub>2</sub>**S**

### 5.3 Gas Testing Procedure

- 1. Flow nitrogen gas and perform internal zero with nitrogen. Gas delivery should be about 5-10 psi from regulator/cylinder, at a flow rate of 0.25 to 0.5 L/min.
- 2. Assemble test configuration with the Unisearch short flow-through cell (0.167 m) in the path.
- 3. Assemble the  $H_2S$  gas scrubbing system, with gas flow coming from the external flow cell into the column packed with absorbent.
- 4. Flow nitrogen to a stable baseline, typically about five volumes of the cell. The flow of nitrogen can be verified by viewing the rotameter at the exhaust.
- 5. Monitor readings until a stable zero reading is reached. Continue reading 7-15 measurement cycles.
- 6. Flow the  $H_2S$  reference gas. The  $H_2S$  should flow at 0.3 L/min.
- 7. Acquire 7 to 15 measurement cycles, or the number of samples required by the QAPP.
- 8. Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).
- 9. Stop the H<sub>2</sub>S flow and flow nitrogen to purge the H<sub>2</sub>S gas to a stable baseline, typically about five volumes of the cell.
- 10. Disconnect H<sub>2</sub>S 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<sub>2</sub>S 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<sup>2</sup>, 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  $7 \le N \le 15$ . The average value of these measurements is calculated as

$$\bar{x} = \frac{\sum_{i} x_{i}}{N} \tag{1}$$

and the sample standard deviation ( $\sigma$ ) as:

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

$$Precision \equiv \% CV = \frac{\sigma}{\bar{x}} \times 100\%$$
(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.<sup>3</sup>
- 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.

<sup>&</sup>lt;sup>3</sup> 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 <sup>2</sup>	

### Notes:

# Appendix D. Belfort Model 6400 Visibility Sensor Maintenance and Audit Procedures

# *STi* Sonoma Technology

# Appendix D

# Belfort Model 6400 Visibility Sensor Maintenance and Audit Procedures

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# 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 act	ivities for the Belfort Model 6400 '	Visibility Sensor
		• 1510 million 501.

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

\* 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:		
Juit mille.		

Scatter Plate ExCo:	
---------------------	--

Span Factor: \_\_\_\_\_

New Span Factor: \_\_\_\_\_

Stop Time: \_\_\_\_\_

Notes: