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

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# Valero Benicia 12-15 Quality Assurance Project Plan

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# 1. Project Background and Management

# 1.1 Background

### 1.1.1 Purpose

The Valero Refining Company (Valero) is conducting air quality monitoring at its refinery in Benicia, California, in response to the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15).<sup>1</sup> The monitoring is following a facility-specific air monitoring plan that is consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.<sup>2</sup> Rule 12-15 requires routine monitoring near the fencelines of all San Francisco bay area refineries for specific air compounds, with data reported to the public. On October 6, 2021, the BAAQMD provided updated requirements for refineries to conduct additional H<sub>2</sub>S monitoring along refinery fenceline paths and to implement the enhanced monitoring by January 1, 2023. Valero implemented H<sub>2</sub>S monitoring on December 8, 2022. BAAQMD issued updated specifications on December 22, 2022. Valero's response to the updated specifications is located in Appendix E.

## 1.1.2 Rationale

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

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

# 1.2 Roles and Responsibilities

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

<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. Available at baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en.



Figure 1. Organizational chart for this project.

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

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

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

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

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

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

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

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

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

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

# 2. Measurements

# 2.1 Instrument Selection and Descriptions

The required compounds to be measured are benzene, toluene, ethylbenzene, and xylenes (known together as BTEX), sulfur dioxide (SO<sub>2</sub>), and hydrogen sulfide (H<sub>2</sub>S). These compounds are measured at a 5-min resolution. Open-path instruments (CEREX UV-DOAS and Unisearch TDLAS) were selected after consideration of (1) the distances that need to be covered by measurements (hundreds of meters), (2) data time resolution requirements (5-min), and (3) current measurement technology.

Along all measurement paths (see Section 2.2), BTEX and SO<sub>2</sub> are measured by monostatic Ultraviolet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. As currently installed, the xenon light is required to achieve measurements over paths that are approximately 300 meters long, and achieve reasonable minimum detection limits (MDL) for BTEX and SO<sub>2</sub>. The analyzer records the intensity of light at discrete wavelengths. Any UV-absorbing gas present in the beam absorbs at a specific wavelength of light. Each species of gas has a unique absorbance fingerprint (i.e., peaks in absorbance at different wavelengths are unique to that gas). The analyzer compares regions within the sample absorbance spectra to the same regions within the calibrated reference absorbance spectra using a classic least squares regression analysis. Beer's Law is then used to report gas concentrations. This approach is the same as what was specified in the Environmental Protection Agency's TO-16 Methodology,<sup>3</sup> although this was not written specifically for UV-DOAS. Closeness of fit is indicated by the correlation coefficient (R<sup>2</sup>) derived from the fit of the measured spectra to the reference spectra. The  $R^2$  is provided with each concentration so that potential interference can be detected if present. Selection of analysis regions that are free of absorbance due to other gases within the sample is the primary means of avoiding cross interference. Spectral subtraction is used in cases with overlapping absorbance features; the subtraction technique is proprietary to the instrument manufacturer.

Along all measurement paths, H<sub>2</sub>S is measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instruments. A tunable diode laser emits light at a very small range of wavelengths, which allows spectral measurement of a H<sub>2</sub>S absorption peak. Because the Unisearch TDL operates in a wavelength range that also contains an absorbance feature for water vapor, water vapor correlation can be used as a performance metric. If the water vapor correlation drops below a threshold value, data are flagged as invalid since water vapor is always present in the atmosphere. The signal strength of the light transmitted through the atmosphere is recorded using a photodiode detector and reported in the data file. Together with an independent visibility measurement, the signal strength can be used to evaluate the impact of atmospheric conditions or misalignment on

<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.

data quality. Manufacturers report that the TDLAS has H<sub>2</sub>S detection limits below 25 ppb over a 500 m path length under good atmospheric conditions. The actual MDL depends on atmospheric conditions.

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

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

Table 1. Open-path instruments and approximate detection limits by pollutant and path. Actual detection limits will be different and depend on ambient conditions. H<sub>2</sub>S MDLs will be evaluated in real-time.

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

# 2.2 Monitor Siting Rationale

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

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

- Paths 1 and 2 cover the southwest fenceline to assess potential transport toward the city of Benicia. This transport direction is infrequent and only occurs on an occasional basis in the winter when winds sometimes blow northeast to southwest. Over the course of a year, these northeast winds occur less than 7% of the time. Due to terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability. Therefore, the downwind areas that could be affected under these wind conditions are very narrow.
- Path 3 covers the eastern fenceline to assess potential transport toward the business/commercial area located east of the refinery. This transport direction is common in spring, summer, and early fall, when winds often blow west to east.
- Instruments on Paths 1 and 2 are elevated about 7 feet above ground level (AGL).
   Instruments on Path 3 are elevated about 15 feet AGL so vehicle traffic does not block the open-path sensor light.
- Open-path analyzers are located at all sites. Sites 1 and 2 each have two UV-DOAS and two TDLAS instruments. Each pair of analyzers at each site point roughly 180° from each other. Sites 3' and 3" each have one UV-DOAS and one TDLAS analyzer. The remaining numbered sites (1', 1", 2', 2", and 3) have retroreflectors (i.e., mirrors). This setup provides maximum spatial coverage along the critical paths.



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

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

# 2.3 Instrument Operations and Maintenance

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

### 2.3.1 CEREX UV-DOAS

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

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving check list is maintained).	~		
Inspect optics on detector and retro-reflector; clean if necessary.	√		
Inspect and clean system filters.	$\checkmark$		
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.	V		
Download data older than 6 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	V		
Ensure 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. Realign system if integration time exceeds 250 ms.	V		
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.		✓	
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.		✓	
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. Change calibration factors if the concentration is more than 20% different from expected value (% Accuracy).	¥		
Verify system settings.			$\checkmark$

Table 2. Schedule of maintenance activities 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 3 summarizes TDLAS maintenance activities, as recommended by the manufacturer and required by the BAAQMD. Table 9 further defines operational limits that is used to trigger corrective actions during separate site visits. Maintenance schedules are altered as needed.

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. Signal power should be greater than 0.4.	$\checkmark$		
Download data older than 6 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure 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.	$\checkmark$		
Check system performance indicators (an evolving checklist is maintained).		$\checkmark$	
Perform bump test using sealed cells (simulates system- observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit. Take corrective action if % accuracy is more than 25%.	✓		
Review and test light and signal levels.** Signal power should be greater than 0.4.		✓	
3-point calibration check using sealed cells.		$\checkmark$	
Verify system settings.			$\checkmark$

#### Table 3. Schedule of maintenance activities for the TDLAS.

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

### 2.3.3 Belfort Model 6400 Visibility Sensor

For the visibility instruments, monthly maintenance includes inspecting the sensor for dirt, spider webs, bird nests, or other obstructions (see Table 4). Obstructions are removed and the glass windows are cleaned with glass cleaner if the sensor is dirty. There are no serviceable components in the sensor. Calibration is performed annually per the instruction manual. Table 9 further defines operational limits that are used to trigger corrective actions during separate site visits. Maintenance schedules will be altered as needed.

Table 4. Schedule of maintenance activities for the Belfort Model 6400 Visibility Sensor.

Activity	Monthly	Annually
Visually inspect the system, including all cables.	$\checkmark$	
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 should come as a request to BAAQMD and be agreed to by BAAQMD in cooperation with the Valero, Benicia Refinery.

## 2.4 Emergency Maintenance Procedures

When a major problem is discovered with the fenceline monitoring system, corrective actions and maintenance procedures are required. The fenceline monitoring system is composed of two major components, field hardware and website software. Separate rotating teams are on-call 24/7 to respond to issues that can be dealt with remotely. Any required field work will occur the next business day. The two teams that are on-call are (1) the Sonoma Technology field operations (ops) team and (2) the Sonoma Technology IT ops team. The Sonoma Technology field ops team is led by the Field Staff Manger and Data Manager, supported by Terra Applied Systems (an instrument contractor), and includes field technicians. The IT ops team is led by the Website/Data System Manager and consists of IS engineers and IT specialists. Sonoma Technology manually checks the website twice daily, and automated checks are enabled. If the automated checks identify a problem, the system will immediately send an alert to the field ops team and/or the IT ops team. This approach helps guarantee that problems are identified and addressed in a timely manner. The oncall teams are required to acknowledge alerts within 30 minutes of their receipt. Refinery personnel will be notified if a solution for issues affecting data availability cannot be resolved. If the system is offline, a maintenance message will be put on the public website at the direction from Valero. BAAQMD staff will be notified of monitoring downtime according to BAAQMD Regulation 1-530.4

<sup>&</sup>lt;sup>4</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.

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

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

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

The IT ops team remotely monitors the status of the website and associated equipment using automated system checks, such as those detailed in Table 5, to determine actions.

**Table 5.** Parameters monitored by automated system checks, their monitoring frequency, and threshold for alerting.

ltem	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%
Interruption in data flow	- Time since last datum received	Every 30 min	Most recent measurement is behind collection by more than 30 minutes
Test for errors in data processing pipeline	- Process scheduler	Every 300 seconds	Pass/Fail

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

Corrective action will be taken to ensure that data quality objectives are met. **Table 6** lists the types of issues that require corrective actions. This table is not all-inclusive and additional checks may be added as the project progresses. Issues will be identified daily upon review by Daily Data Reviewers, who will work with the field technicians and instrument contractors to resolve issues that need to be addressed on site. Further details on the manual daily data checks are provided in Section 4.3. After all issues have been addressed, a summary of the problems and solutions will be sent to the project manager via email. In the event that an issue is discovered by field or IT personnel that is not included in this list, the issue and corrective actions taken will be documented and the QAPP and relevant SOP will be updated. Updated QAPPs will be submitted to BAAQMD for approval.

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

Table 6. Potential sampling and data reporting problems and corrective actions.

# 3. Quality Objectives and Criteria

# 3.1 Data and Measurement Quality Objectives

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

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

# 3.2 Data Completeness Objectives

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

- i. Valid Data are within normal operating parameters.
- ii. Invalid Data do not meet the QC criteria.
- iii. Suspect/Questionable Data should be reviewed further.
- iv. Missing Data have not been received by the DMS for more than 10 minutes.

Automated QC processes for open-path data include assessment of visibility conditions in conjunction with instrument parameters, such as signal strength and/or integration time. This allows automatic screening for invalid data due to weather, as well as for suspect/questionable data due to marginal operating conditions. Data below the MDL are flagged accordingly. The automated data QC process flags any data with poor spectral matches to reference libraries, according to the defined acceptance criteria. These criteria are manually reviewed on a regular basis to ensure thresholds are appropriately defined. All data in exceedance of RELs are automatically flagged as

suspect/questionable for additional manual review and verification. The final step of the automated data QC process flags any data with high concentrations (range check), large fluctuations (rate-of-change), or stuck data values (sticking check) as suspect/questionable for additional manual review and verification.

Automated QC processes for point monitors are less complex because their measurement technique is more straightforward. 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 assigned to provide additional diagnostic information. Table 7 presents an overview of relevant QC/OP codes that are used throughout the QC process, including manual QC.

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

Table 7. Overview of data quality control (QC) and operational (OP) codes.

Data completeness is assessed by reviewing the data flags assigned for each 5-min binned average data point. A 1-hr rolling average data point will be considered incomplete if (1) more than 25% of the 5-min binned 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 and 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 rolling average data points.
- **Incomplete**: The number of 1-hr rolling average data points that do not meet completeness criteria.

- % Incomplete: The percentage of Incomplete relative to Possible.
- Complete: The number of 1-hr rolling average data points that do meet completeness criteria.
- % **Complete**: The percentage of Complete relative to Possible.

For all instrument/parameter combinations, data completeness requirements are provided in Table 8.

Table 8. Data recovery requirements.

Completeness Requirement	Relevant to
75% per hour	5-min binned average data
90% per calendar quarter	1-hr rolling average data

Other factors that affect data availability include instrument calibrations or bump tests (a few hours every month), annual maintenance, and other maintenance activities. Regular maintenance and careful, responsive operations will minimize instrument downtime.

# 3.3 Precision Checks, Bump Tests, and Verification

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

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

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

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

From these definitions, %Accuracy is defined as:

$$\%Accuracy = \frac{\bar{x} - x_{std}}{x_{std}} \times 100\%$$

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

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

In the field, a bump test is used to verify that the system can detect at or below the target bump test concentration. To confirm high-quality, reliable performance by the UV-DOAS system, a single-

species bump test using benzene is performed monthly and will potentially be performed less frequently in the future if the measurements prove adequately stable or should additional metadata provide assurance that instruments are working properly. The QAPP will be evaluated continuously and will be updated and sent to the BAAQMD for approval if updates are needed before implementation.

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

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

# 3.4 Instrument or Standard Certifications

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

# 4. Data Management

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

# 4.1 Data Acquisition and Communications

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

The DMS automatically QCs data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities are used for continuous examination of data quality. The DMS provides auto-screened data to the field ops website and notification system to inform and alert project and facility staff. The ops website displays maps and time series plots for BTEX and SO<sub>2</sub>, along with wind data.

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

# 4.2 Automated Data Screening

Automated data screening checks are conducted within the DMS upon data ingest and screen out invalid data for public display. These screening checks help focus the Daily Data Reviewers' efforts on data that need the most attention. Initial screening checks, along with actions to be taken, are summarized in Table 9. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. If, based on a detailed manual review of the data as described in Section 4.3, it is determined that the automated screening criteria are sufficient, they will be left as is. However, if the criteria listed in Table 8 result in erroneous flagging of data, the thresholds will be revised and this QAPP will be updated accordingly. The DMS auto-screening checks include:

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

- Sticking. If values are repeated for a number of sampling intervals, data are reviewed for validity. Typically, four or more intervals of sticking values are a reasonable time span to indicate that investigation is needed. Sticking checks are not applied to data that are below the instrument detection limit.
- Rate of Change. Values that change rapidly without reasonable cause are flagged and reviewed.
- Missing. If data are missing, data during those time periods are coded as missing. Missing data may indicate a power issue, an instrumentation problem, or a data communication problem. The time period allowed for missing data may be adjusted as the project proceeds to reduce false or excessive alerting. The alerting is set for six missing 5-min values (total time span of 30 minutes).
- Sensor OP Codes and Alarms. If the instrument assigns operation (op) codes to data automatically (e.g., for bump tests and internal flow rate checks), the data will be reviewed, codes confirmed, and data flags checked.
- Visibility Impairment. While the exact relationship between visibility and open-path measurements is not established, the expectation is that there would be no measurements when visibility is less than 2.5 miles.

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

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

Table 9. Initial screening checks for 5-min data. All valid and flagged data values are displayed to the public in real time. If data are invalid, they are be included in the public display. During data validation, flagged data will be further investigated.

	Approximate MDL for a 598 m Path*		DMS Auto-Screening Checks						
Measurement (units)		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment		
Benzene (ppb)	0.2 ppb. lf below, flag as below MDL.	If above <u>24 ppb</u> , flag data as suspect on the website and investigate validity.	If the same value is observed for four or more intervals, flag data as suspect on the website and investigate	If value changes by more than 12 ppb, flag data as suspect on the website and investigate validity.		If sensor indicates malfunction or bump test data, code as appropriate and do not display the data.	If visibility is less than 2.5 miles, code as invalid on the website due to low visibility.		
Toluene (ppb)	0.7 ppb. lf below, flag as below MDL.	If above <u>100 ppb</u> , flag data as suspect on the website and investigate validity.		If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.	If data are missing, code as missing on the website and investigate the cause.				
Ethylbenzene (ppb)	0.3 ppb. lf below, flag as below MDL.	If above <u>100 ppb</u> , flag data as suspect on the website and investigate validity.	validity.	If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.					

Measurement (units)	Approximate MDL for a 598 m Path*	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
Total Xylene (ppb)	3.2 ppb. lf below, flag as below MDL.	If above <u>100 ppb</u> , flag data as suspect on the website and investigate validity.	If the same value is observed for four or more intervals, flag data as suspect on the website and investigate validity.	If value changes by more than 50 ppb, flag data as suspect on the website and investigate validity.	If data are missing, flag as missing on the website and investigate cause.	If sensor indicates malfunction or bump test data, code as appropriate and do not display data.	If visibility is less than 2.5 miles, code as invalid on the website due to low visibility.
SO <sub>2</sub> (ppb)	0.6 ppb. lf below, flag as below MDL.	If above <u>37.5 ppb</u> , flag data as suspect on the website and investigate validity.		If value changes by more than 19 ppb, flag as suspect on the website and investigate validity.			
H₂S (ppb)	25 ppb.	If above 30 ppb, flag data as suspect on the website and investigate validity.		If value changes by more than 30 ppb, flag as suspect on the website and investigate validity.			
Visibility (meters)	lf value is less than 0, flag data.	Not applicable		Not applicable			Not applicable

\*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.

# 4.3 Data Verification

### 4.3.1 Confirm Daily Operation

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

## 4.3.2 Assess Data Reasonableness

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

# 4.4 Data Validation Approach

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

Data validation activities include:

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

- Ensuring the data or measurements are realistically achievable and not outside the limits of what can be measured.<sup>6</sup>
- Inspecting several sampling intervals before and after data issues occurred, instrument bump tests were conducted, or repairs were completed to ensure all affected data have been properly flagged.
- Referring to logbooks to see if some values may be unusual or questionable based on observations.
- Assessing instrument metadata (e.g., light intensity, operation codes) to confirm reasonableness.
- Assessing visibility measurements to ensure an adequate signal was obtained to quantify pollutant concentrations.
- Confirming that bump tests or factory calibrations were conducted and results were within specifications.

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

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

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

<sup>&</sup>lt;sup>6</sup> Measurements below the MDL will be flagged in the DMS for review by an analyst.
QA/QC Checks	Frequency	Acceptance Criteria					
UV-DOAS							
Bump test (accuracy)	Monthly and after major service	±20%					
Measurement quality – R <sup>2</sup>	Continuous	0.8 to 1.0					
Integration time	Continuous	≤250 ms					
Signal intensity	Continuous	≥70%					
TDLAS							
Bump test <sup>b</sup> accuracy and repeatability (as $%$ CV) <sup>d</sup> ; H <sub>2</sub> S at a concentration differing from 3-point calibration points.	Monthly	±25%					
3-point calibration accuracy and repeatability (as %CV) <sup>b, d</sup>	Quarterly	$\pm 25\%$ for [H <sub>2</sub> S] < 2000 ppmm $\pm 10\%$ for 2000 $\leq$ [H <sub>2</sub> S] $\leq$ 7000 ppmm $\pm 10\%$ for [H <sub>2</sub> S] > 7000 ppmm					
5-min MDL	Continuous	≤25 ppb					
H <sub>2</sub> S correlation coefficient (r)	Continuous	0.72 to 1.0					
Signal Power <sup>d</sup>	Continuous	≥0.4					
H <sub>2</sub> O correlation coefficient (r)	Continuous	≥0.95					
Visibility Sensor							
Accuracy	Annually	±25%					

#### Table 10. Instrument QA/QC checks.<sup>a</sup>

<sup>a</sup> 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> Sealed cell development is in process to enable bump checks and 3-point calibration checks; the accuracy of tests using this equipment still needs to be determined for the TDLAS.

<sup>c</sup> Data are invalid below this threshold because previous measurements suggest degraded instrument performance below this threshold.

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

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

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

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

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

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

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

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

## 4.5 Data Storage and Processing

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

## 4.6 Data Delivery

Final data sets will be compiled quarterly—60 days after each quarter—and provided to the BAAQMD by the Refinery PM. Outside of the normal quarterly delivery, data will be made available to the BAAQMD within 30 days of a request. Rolling hourly and 5-min concentrations of species will be provided in .csv format along with Site Code, Local Standard Time, Measurement Duration, Concentration Value, Signal Strength, Concentration Unit, and QC and OP codes defined in Table 7. Signal power and real time 5-min MDLs will be provided for the TDL. Raw spectral data files will be saved as single files and made available to the Air District upon request.

In addition to chemical concentration data, meteorological data will be provided as a .csv file that includes Site Code, Local Standard Time, Duration, Wind Speed, Visibility, Wind Speed Unit, Wind Direction, and Wind Direction Unit.

## 4.7 Data Flow to Website

## 4.7.1 Auto-Screening and Alert Review

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

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

The preliminary QA/QC'd concentration data are presented in a time series of benzene, toluene, ethylbenzene, xylenes, SO<sub>2</sub>, and H<sub>2</sub>S. Data are provided as 5-min averages. Data are annotated for quality (valid, invalid, suspect, or missing). Additionally, for the Unisearch TDL, 5-min MDLs will be displayed in real-time.

## 4.7.2 Data Backfill Process and Schedule

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

# Appendix A. CEREX UV-DOAS Audit Procedures

*STi* Sonoma Technology

## Appendix A.

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

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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 A-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. 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 300 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. Hard copies of this procedure and the associated test forms will be kept on site. Upon completion of the test procedure, a copy of the test form showing the results will be sent to the Refinery Project Manager.



Figure A-1. Schematic of the 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. A test where gas of a known concentration is introduced to the analyzer to check for response accuracy.		
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		
QA	Quality Assurance		
UV-DOAS	Ultraviolet Differential Absorption Spectroscopy		

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

## 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 uses in an area that may contain flammable mixtures or highly corrosive vapors require special preparation to address safety and ensure 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 for at least 15 min 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 A-2.



Figure A-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 A-3.



**Figure A-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 A-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 5% 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. 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 =  $\frac{Intensity of blocked beam (\%)}{Intensity of unblocked beam (\%)} \times 100\%$ 



Take corrective action if stray light exceeds 5%.

**Figure A-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, go to **File**, **Save**, and click **Save As Default.** You will be prompted for a password, which is **cerexconfig** 

#### <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
- $\circ$  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
  - o Concentration
    - Zero Readings on Non-Detect: OFF

- Zero Readings on Negative concentrations: OFF
- Display BDL: OFF
- Quick Analysis MDL Wave length Range: 276 -280 (Doesn't Matter the Range)
- 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
      - Integration Time (ms): Always will change if Auto integration is turned on
      - Path Length (m): 2
      - Trigger Mode: Normal
    - Auto Routine
      - Auto Integration: ON
      - Intervals (s): 300
      - Wavenumber Range: 300-310 (This is different on all instruments due to Spectral Background and Intensity Range)
      - Intensity Range 75-85 (This is based on intensity range)
      - Maximum Integration: 300
      - Auto Background: ON
      - Interval (Acquisitions): 5
      - Wavenumber Range: 266-270
    - Verification
      - Verification: OFF (This inactivates all inputs)
- Controller
  - o **General** 
    - Serial Port: n/a
    - Sensor Refresh Interval (s): 15
  - o 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>
  - 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
- 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 checks 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 or electronic form and can reference this SOP and associated forms.

Table A-2 lists the schedule of visual inspections and maintenance procedures that should be performed on the UV-DOAS systems.

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 6 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	$\checkmark$		
Ensure 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. Realign system if integration time exceeds 250 ms or stray light is greater than 5% at 250 nm.	✓		
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 (simulates system-observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit. Change calibration factors if the concentration is more than 20% different from expected value (% Accuracy).	~		
Verify system settings.			$\checkmark$

Table A-2. Schedule of maintenance activities for the UV-DOAS.

#### 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 Monthly 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 by here. Replace if necessary. Ensure fans are running (they should make an audible sound) when 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.

#### **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 A-5).
- 3. Use a 7/64 hex driver to remove the six socket-head cap screws that retain the Filter Access Panel.



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



Figure A-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 Check Signal Strength and Integration Time

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 5%. If the value is less than 5% at 250 nm, the bulb should be changed.

#### 7.4 Data Management

#### 7.4.1 Archiving and Deleting Older Data

**Note:** Data older than six 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 on an annual basis.

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.
- 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.

<sup>&</sup>lt;sup>1</sup> CMS Software User Manual Rev 4. CMS Version 4.0.298.1, CEREX Monitoring Solutions, December 5, 2017.

- 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.

- 10. Under the **Control Panel Menu**, use the search function in the lower left-hand corner of the task bar to search for "Indexing Options".
- 11. Click on the **Advanced** tab with the shield logo.
- 12. Click Rebuild.

**Note**: Once "Rebuild" has been selected, a message staying 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 Monthly: 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.

#### UV Sentry 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.

#### Xenon UV Source Handling

The UV Sentry Xenon Source is shipped from Cerex in a protective plastic enclosure (see Figure A-8). The (+) Anode end of the UV Source is labeled "UP". The UV Source must be installed with the (+) side UP. Always wear clean 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.





#### 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 (Figure A-9).



Figure A-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 (Figure A-10).



Figure A-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.
- Loosen the retaining thumbscrew on the Cathode block at the bottom of the source (Figure A-11).



Figure A-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.

#### UV Sentry Xenon UV Source Installation

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



Figure A-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.

#### 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 preform 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 A-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 A-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 A-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 and Attach Bump Check Form to This Document

#### 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 system is set up (minus the instrument connections) as depicted in Figure A-13.



**Figure A-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 A-8. 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.

#### 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 15 stable measurements are made.**
  - c. Verify that the value is near the expected concentration. If the measurements do not meet the data quality objectives listed in the QAPP, repeat the procedure. If repeated measurements appear nonconforming, initiate corrective action investigation.

#### 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.

#### 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. Once you restart CMS, you will see the file number located on the UV main menu of CMS. If the file count restarts at file 1, it is starting a new folder for the entire day, which means you have the incorrect file writing path. Also, once you restart CMS, take a look at the spectrum graph 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.
- 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.

#### 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.

#### Data Evaluation and Reporting

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 if 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, %Accuracy is defined as:

$$\%Accuracy = \frac{\bar{x} - x_{std}}{x_{std}} \times 100\%$$
(3)

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

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

- 1. Concentration
  - a. Average the concentration of consecutive stable measurements.
  - b. Report the percent accuracy between the average and the certified value. Note the warning and acceptance criteria that is discussed in Table A-2. Take action if the % Accuracy is above the acceptance criteria. 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.
- 2. Calculate the Limits of Detection and Quantitation.
  - a. Calculate the mean (average), sample standard deviation, and %accuracy (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.

Table A-3 shows the type of gas to be used, the warning level, and the acceptance criteria to be used for the bump test.

Sensor	Test	Warning Level for Precision and Accuracy	Acceptance Criteria for Precision and Accuracy
UV-DOAS 5 ppmm benzene (5 ppb path average for 500 m one-way path) bump test		15%	±20%*

 Table A-3.
 Warning and acceptance criteria for the Valero UV-DOAS bump tests.

#### Note:

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

### 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

- 1. Data will be checked daily to ensure instrument performance. Both public website and admin website need to be checked twice daily (for example, before 10 a.m. and 10 p.m.). Ensure that the site is operating properly by pointing your browser to elsegundo1180.com.
- 2. View the data display at https://elsegundo1180.com/data. Take note of any outages by selecting All Compounds from the pollutant dropdown menu.
- View the timeseries graphs for each species by selecting them in the pollutant dropdown menu. Verify that pollutant concentrations are reasonable by using the guidance in Table A-4. Notify the field operations team if anything seems erroneous.
Table A-4. List of parameters measured by the UV-DOAS, with notes on the typical characteristics of the data.

Parameter	Observational Notes
Visibility	~30 miles is the maximum distance measured by the sensor. Values are typically less than 30 miles due to smog and fog reducing visibility.
Integration Time	Should generally be <250 ms. Report values that are stuck at 300 ms to the project manager and fieldopsalerts. Should be anticorrelated with visibility for fog events.
Winds	Typically there is a sea breeze during the day and a land breeze at night.
HCN	Typically below MDL (~1 ppb) – note any high values above REL.
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.
VOCs	Sum of C2 through C5 alkanes. Typically the UV-DOAS will show VOC concentrations at zero, although this is suspect and subject to change.
SO <sub>2</sub>	Concentrations typically can range from 0 to 100 ppb, but are usually measured at zero. Refineries are a local source – note any high values above REL.
NO <sub>2</sub>	Concentrations typically can range from 0 to 200 ppb. Values typically peak at night. Sunlight destroys it, while traffic and combustion produce it. Some instruments may not detect NO <sub>2</sub> if they are saturated.

#### 8.2 Quarterly Validation

Quarterly validation activities involve looking at the data collected from a longer time period (3 months) than the daily checks (typically a few days). The quarterly validation steps are listed below.

- 4. Plot time series and look for statistical anomalies. If problems are found, they may be flagged using the DMS.
- 5. Review any instrument bump test results.
- 6. Verify that daily instrument checks were acceptable.
- 7. Review manual changes to operations/data, and verify that the changes were logged and appropriately flagged; ensure that logged information is complete and understandable.
- 8. Ensure that instrument checks have the appropriate QC codes applied.
- 9. Assign invalid data a Null Code, and provide a reason for data being invalid.
- 10. If a record is not created for a particular site/date/time/parameter combination, create a null record for data completeness.
- 11. Inspect data consistency.
- 12. Review collected data ranges for consistency ranges should remain within the expected values over months of monitoring.
- 13. Check bump test values for completeness; ensure they meet acceptance criteria.
- 14. Review quarterly data completeness.

## 9. 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 below.

- □ 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	Monthly
Visually inspect the system (an evolving checklist will be maintained).	
Clean and inspect optics on detector and retroreflector.	
Current bulb service hours.	
Signal Intensity at 250 nm (% at 40 ms integration time).	
Inspect system filters on optics and retroreflectors (clean or replace if necessary).	
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 retroreflector (such as equipment, vegetation, or vehicles).	
Inspect all electrical cables for wear; replace as needed.	
Remove archive data that is older than 6 months from the instrument computer.	
Realign instrument.	
Perform bump test.	
Activity	Quarterly
Replace UV source. May be changed out less frequently depending on performance. Note recommendations here.	
Inspect and replace system filters.	
Activity	Annually
Verify system settings.	
Deliver past years' data to client.	

Table A-5. Checklist of maintenance activities for the UV-DOAS.

Note any corrective actions for UV-DOAS:

# **UV Sentry Fenceline Detection System**

DATE:	Location:	
Test Technician 1:	2:	
Sentry Alignment		
Integration time	Target 20-24 ms	
300 nm Intensity	Target 80-120%	
254 nm Intensity	Target >5%	
Stray light at 254 nm & 40 ms	Target <5%	
Gas Purge System		
Flow purge gas	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		
Cylinder Pressure		

NOTES:

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

#### **Purge Flow Conditions**

Start tir	me	
Purge g	gas flow	L/min
	NOTE: Should be around 1 LPM	
Check Gas Test	t	
Initial ga	as flow	L/min
	NOTE: should be around 1 LPM	
Start tim	ne	
Reduced	d gas flow	L/min
Start tim	ne	
Collect c	check gas data start time	
Data record		

#### Data record

TIME	PPM	R2	
Verify client			Init
Stop time			Init
Open the PURGE gas		Time	
Reference concentration			ppm
Average concentration			ppm
% Accuracy (+/- 20% Acc	ceptable, take action if g	reater than 15%)	%
Standard deviation	lard doviation)		ppm
Estimated MDL (SX stand	laru ueviation)		ppm
Restore Normal Operation			
Restore running data file			Init
Press <b>RUN</b> to begin moni	toring		Init
5	-		

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



## Appendix B

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

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#### 1. Summary

This document addresses the maintenance, commissioning, and performance audit procedure for Unisearch TDLAS units. The procedure is intended to (1) describe maintenance procedures, (2) verify that the equipment is performing to expectations, and (3) verify 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.

A number of the maintenance procedures closely follow the manuals provided by Unisearch<sup>1</sup>; field staff should obtain access and read electronic copies of these. This QA Audit procedure ensures field verification and calibration of the TDLAS. The QA Audit process challenges the instrument using a known concentration of hydrogen sulfide to verify 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 LASER EMISSION that is INVISIBLE and can damage the eye if the laser is viewed directly. The laser within the instrument is class IIIB. 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 into any part of the instrument that can produce laser light, including the transceiver head. Make sure to read the laser safety manual (as well as 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 trained in the operation of the system components and familiar with handling gas delivery and testing equipment. This procedure should not be performed by someone who does not understand the system, the technology, or the hazards of the materials used.

#### 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. TDLAS use 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.** Hydrogen sulfide (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 750 ppm hydrogen sulfide 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 attempt or perform analyzer quality assurance audit activities.

## 3. Overview and Operating Principle

Along all measurement paths, H<sub>2</sub>S will be measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instruments. The Unisearch LasIR H<sub>2</sub>S monitoring system (Figure B-1) is a monostatic open-path remote sensor for path integrated monitoring of gases using the direct absorption tunable diode laser technique. The LasIR sensor consists of a transmitter/receiver mounted on a tripod and a retro-reflector array. The transmitter/receiver sends a signal across an open path onto a retro-reflector array which returns the signal to the detector. A hybrid lens/mirror system employing an aspheric lens is used to launch the beam to a retro-reflector array. A 25 mm diameter off-axis parabolic mirror is used to collect the returning light and focus it onto the detector. The receiver contains a lens, a detector with preamplifier and driver electronics for the optical return signal. The lens in the receiver focuses the incoming laser light on the detector where it is converted to an electrical signal. This signal is amplified and converted to an optical signal and returned to the central controller.

Multicomponent analysis using classic least squares fitting provides enhanced detection for low levels of H<sub>2</sub>S by adjusting for overlapping water and carbon dioxide absorbance bands. The purpose of this procedure is to check the system for correct H<sub>2</sub>S response in the installed operating conditions. H<sub>2</sub>S standard reference gas is introduced into the optical path by means of a 0.167 meter low volume flow cell that is fiber coupled between the laser source and the path transceiver optics. This enables measurement of the response to the reference gas in the optical conditions of the full path length. Response testing is typically conducted on a quarterly basis.



Figure B-1. Unisearch TDLAS analyzer and retroreflector array.

#### 3.1 Safety

#### 3.1.1 Exposure Control

 $H_2S$  is a colorless gas, with an odor of rotten eggs. It is hazardous at low concentrations. The odor is not a reliable indicator of the presence of hazardous concentrations of  $H_2S$ , because olfactory senses may be deadened by exposure to concentrations below safe exposure levels. A system for scrubbing  $H_2S$  gas from a test apparatus vent is used to prevent release and worker exposure.

This procedure is written to limit exposure potential and mitigate hazards of accidental release of the reference gas. Only personnel experienced with handling this material and familiar with the test procedures and apparatus should perform this testing procedure.

#### 3.1.2 Personal Protection

Standard refinery PPE (personal protective equipment) should be worn at all times, including laser safety glasses with side shields, hard hat, goggles, steel toed boots, hearing protection, FRC (fire-retardant clothing), an H<sub>2</sub>S monitor, and appropriate gloves that are adequate for this procedure. A second person should always be present as a safety monitor when using the H<sub>2</sub>S reference gas. H<sub>2</sub>S levels should be monitored inside the enclosure. Two self-contained breathing apparatuses shall be on standby.

### 4. Routine Maintenance

#### 4.1 Maintenance Schedule

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 B-1 summarizes TDLAS maintenance activities, as recommended by the manufacturer.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓		
Inspect optics on detector, clean if necessary.	$\checkmark$		
Check the alignment to verify there has not been significant physical movement and confirm signal levels. Signal power should be greater than 0.4.	$\checkmark$		
Download data older than 6 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, or vehicles).	✓		
Inspect all electrical and optical cables for wear. Replace as needed.	$\checkmark$		
Check system performance indicators (an evolving checklist is maintained).		$\checkmark$	
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. Take corrective action if % accuracy is more than 25%.	~		
Review and test light and signal levels. Signal power should be greater than 0.4.		√	
3-point calibration check. Take corrective action if % Accuracy is greater than 25%.		$\checkmark$	
Verify system settings.			$\checkmark$

#### Table B-1. Schedule of maintenance activities for the TDLAS.

#### 4.2 Cleaning the Transmittor/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 if necessary for this purpose. 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 on the window.

If, for some reason, the inside of the window gets dirty it is best to remove the window from the housing and clean it rather than opening the telescope side covers, as access from these points is limited. You may either remove the shroud and unscrew the locking ring holding the window in place or remove the entire front cover by removing the 4 screws in the corners. In either case be careful to keep the o-ring seals properly seated. Improper seating may result in leaking if rain is to fall on the telescope, possibly damaging sensitive electronic components inside.

#### 4.3 Cleaning Retroreflector Array

Only the front surface of the acrylic protective window for 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 damaging their gold-coated surfaces.

#### 4.4 Optical Alignment

Adjust the vertical and horizontal adjustment knobs to maximize the power as reported on the OPM-XX power meter. Lock the adjustment knobs (refer to picture below) 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 adjust the horizontal position with the thumbscrew on the right hand side of the mount base (looking from the back). When adjustment is complete tighten the locking nut. Slight adjustment of the vertical alignment may be required after tightening the horizontal alignmentlocking nut as this tightens the rear end of the telescope to the mount affecting the tilt (Figure B-2).



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

#### 5. Flow-Through Response Test

#### 5.1 Supplies

#### 5.1.1 Gas Flow

- 1. Nitrogen gas
- 2. H<sub>2</sub>S reference gas blend (750 ppm is used in this procedure)
- 3. 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
- 4. 1/8" PTFE tubing for the reference and purge gas lines into the quality assurance (QA) cell
- 5. 1/8" PTFE Swagelok tee union to couple the reference and purge gas feed lines into the QA cell
- 6. 1/4" PTFE tubing for gas flow lines on the outlet of the QA cell
- 7. Unisearch external 0.167-m flow cell
- 8. Length of PTFE 1/4" tubing with PTFE Swagelok nuts on both ends

#### 5.1.2 Gas Scrubbing System

- 1. Length of PTFE tubing to go from external flow cell to scrubbing system
- 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 100 times the amount of H<sub>2</sub>S existing in 750 ppm H<sub>2</sub>S gas flowing at 0.3 I/min for 100 minutes (one test)
- 3. A max 5 l/min rotometer attached at the exhaust line to view that flow is occurring

Purge the system with nitrogen to establish a baseline. Then challenge with H<sub>2</sub>S reference gas and collect data for the operating instrument averaging interval (2-5 minutes). The laser spectrometer measures by direct absorbance of the gas according to Beer's Law. A 750-ppm blend of H<sub>2</sub>S 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. A 750 ppm calibration check is what the manufacturer recommends for testing the TDLAS instrument; while the concentration is low enough to be near the detection limit, the concentration is high enough to allow for measurements of sufficient accuracy and precision.

H<sub>2</sub>S concentration in cylinder \* flow cell length = Path Integrated Concentration (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

#### 5.2 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. Perform a bump test by installing the external reference cell fiber optic cables into the Unisearch analyzer. Verify calibration, and remove the cell.
- 3. Assemble test configuration with the Unisearch short flow-through cell (0.167 m) in the path.
- 4. Assemble the H<sub>2</sub>S gas scrubbing system, with gas flow coming from the external flow cell into the column packed with absorbent.
- 5. Flow nitrogen to a stable baseline, typically about 5 volumes of the cell. The flow of nitrogen can be verified by viewing the rotameter at the exhaust.
- 6. Monitor 5-minute averages until a stable zero reading is reached; continue reading 15 measurement cycles.
- 7. Flow the  $H_2S$  reference gas. The 750-ppm cylinder of  $H_2S$  should flow at 0.3 L/min.
- 8. Monitor at least 15 measurement cycles.

- 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 5 volumes of the cell.
- 10. Perform another bump test using the external reference cell.
- 11. 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.

#### 5.2.1 Clean-Up

Dispose of the waste PTE tube filled with GC Sulfursorb Plus in cooperation with Valero.

#### 6. Sealed Cell Response Test

- 1. Disable alerts on FTT and put instrument into planned maintenance.
- 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 15 minutes' worth of data and verify integrity.
- 7. Disconnect sealed cell outlet optical fiber from instrument and reconnect optical fiber from Step 2 to instrument "Fiber In" port.
- 8. Verify baseline of instrument and turn alerts back on in FFT and take out of planned maintenance.

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:

 $Path Average \ Concentration = \frac{250 \ ppm - m}{(2 * 500 \ m)} * \frac{1000 \ ppb}{ppm} = 125 \ ppb$ 

## 7. LasIR Response Test Form

DATE:	Location:	
Test Technician 1 :	2 :	
Alignment		
Signal Intensity		_ Target: >0.4
Gas Purge System		
Flow Purge Gas	Start Time	
	Stop Time	
Calibration Check		
Reference		
Concentration		ppm
Start Time		
Reading		ppm
Stop Time		
Reference Gas		
Concentration		ppm
Source		
Date		

#### NOTES:

## QA Audit Record - LasIR Detection System - Page 2

#### **Purge Flow Conditions**

. 0	Start Time			
	NOTES:			
Chec	k Gas Test			
	Initial Gas flow			L/min
	Start Time			
	Reduced Gas flow			L/min
	Start Time			
	Collect Check Gas Data Start Ti	ime		
	Data Record			
	TIME	РРМ	R2	
		<u> </u>		
	Verify Client			Init
	Stop Time			Init
	Open the PURGE gas		Time	
	Reference Concentration			ppm
	Average Concentration			ppm
	% Difference			%
	Standard Deviation			ppm
	Estimated MDL (3X Standard D	eviation)		ppm
Resto	ore Normal Operation			
	Restore running data file			Init
	Press <b>RUN</b> to begin monitoring	5.		Init

••• Appendix B. Unisearch LasIR TDLAS Maintenance and Audit Procedures

Notes:

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

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

# *STi* Sonoma Technology

## Appendix C

## 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 C-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.

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%.		$\checkmark$

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

\*Calibration checks may be performed less frequently in the future if the measurements prove adequately stable or additional metadata provides assurance that instruments are working properly. Any reduction in the calibration frequency should come as a request to BAAQMD and be agreed to by BAAQMD in cooperation with the Valero, Benicia Refinery.

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 C-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 three minutes allowing the sensor to reach a stable zero state, after which it will run for two 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 three 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.





## 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 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.
- 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 C-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 don't 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 three minutes, allowing the sensor to reach a stable Span state, after which it will run for two 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 three 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 C-2. Scatter Plate Mounting.

#### **Completing the Process**

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

## QA Audit Record Template

# Belfort Model 6400 Visibility Sensor Audit Record

DATE:	Location:
Test Technician 1 : Test Technician 2 :	
Zero State Calibration	
Start Time:	
Previous Zero Offset:	
New Zero Offset:	
Stop Time:	

Notes:

#### Span Calibration

Start Time:	

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

Span Facto	r:
------------	----

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

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

Notes:

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

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

# Appendix D

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

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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 procedure is intended to describe maintenance procedures and 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.  $H_2S$  is a highly toxic gas that can cause death and other adverse health effects at concentrations above 100 ppm. This procedure requires the use of 750 ppm  $H_2S$  for the span check. This procedure must be conducted in a well-ventilated area and requires gas monitors, respirators, and the use of fume scrubbers. Make sure you and others fully understand the safety procedures

and gas-handling systems required. Always wear proper eye protection having OD>4 above 900 nm. Improper handling of materials or hardware may result in death, serious injury, destruction of property, or damage to the TDLAS. Only qualified individuals should perform analyzer quality assurance audit activities.

# 3. Overview and Operating Principle

The Unisearch LasIR open-path H<sub>2</sub>S monitoring system (Figure D-1) is a monostatic open-path remote sensor that uses direct absorption technique. The LasIR sensor consists of an analyzer, transmitter/receiver and retro-reflector array. The tunable infrared (IR) laser for the LasIR system is housed in the analyzer box and scanned over a small range of wavelengths at high frequency. The laser light is guided to the transmitter/receiver telescope via fiber optic cable where it is collimated and sent across the atmospheric path. The retroreflector array at the other end of the path returns the signal to the off-axis parabolic mirror that focuses the light onto a photodiode detector. The electrical signal from the photodiode detector is amplified and returned to the analyzer box where the absorption spectrum is analyzed to produce concentration data.

Classical least squares fitting of the absorption spectrum allows elucidation of low- $H_2S$  concentrations by simultaneously accounting for overlapping water ( $H_2O$ ) and carbon dioxide ( $CO_2$ ) absorbance bands. As a result, concentration data for  $H_2S$ ,  $H_2O$ , and  $CO_2$  are provided with correlation coefficients that indicate the "goodness of fit."

The purpose of this procedure is to check the system for expected H<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 D-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 (IDLH is 100 ppm, NIOSH 10-min REL is 10 ppm, California 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 D-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	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
Inspect electrical and optical cables for wear	4.1
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 if % accuracy exceeds the limits listed in the QAPP	5.2 (flow-through) 6.1 (sealed cell)
3-point calibration check	6.2

Table D-1. List of maintenance activities 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 is to fall 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 damaging 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 D-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 alignmentlocking nut as this tightens the rear end of the telescope to the mount, whichaffects the tilt.



Figure D-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 perform acquisition and processing of the raw TDL data for reporting 5-min data to the Sonoma Technology-operated data system. The TASDAcc software is developed and maintained by Terra Applied Systems (TAS), the integrator of the Unisearch TDL. As depicted in Figure D-3, the LasIR, TASDAcc, and the cellular modem are all connected through a switch, which is located in the same cabinet as the Unisearch analyzer box. The TASDAcc software collects 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 used to display the data on the public-facing website.



Figure D-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 it is delivered to the client.

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 to the client 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 D-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 D-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 D-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 D-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," it is impossible to know what gain settings are applied and, therefore, what the actual power at the detector is.

**Table D-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 D5) 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 D-2.



Figure D5. 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 D-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 D-2 shows how this power is related to laser power elsewhere in the system.

# 4.7 Verify System Settings

In the LasIR instrument software, select File > Configure Analyzer. Select "Expert" on the upper right corner of the Configure Analyzer window. View settings for  $H_2S$ ,  $CO_2$ , and  $H_2O$ . Compare these settings with historical settings and provide any explanation for change.

# 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 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.

Supplies:

- 1. Nitrogen gas
- 2. H<sub>2</sub>S reference gas blend (750 ppm is used in this procedure)
- 3. 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
- 4. 1/8" PTFE tubing for the reference and purge gas lines into the quality assurance (QA) cell
- 5. 1/8" PTFE Swagelok tee union to couple the reference and purge gas feed lines into the QA cell
- 6. 1/4" PTFE tubing for gas flow lines on the outlet of the QA cell
- 7. Unisearch external 0.167-m flow cell
- 8. Length of PTFE 1/4" tubing with PTFE Swagelok nuts on both ends
- 9. Length of PTFE tubing to go from external flow cell to scrubbing system
- 10. A scrubbing system consisting of <sup>1</sup>/<sub>2</sub>" 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 100 times the amount of H<sub>2</sub>S existing in 750 ppm H<sub>2</sub>S gas flowing at 0.3 I/min for 100 minutes (one test)
- 11. A max 5 l/min rotameter attached at the exhaust line to view that flow is occurring

## 5.1 Test Preparation

Purge the system with nitrogen to establish a baseline. Then challenge the system with H<sub>2</sub>S reference gas and collect data for the operating instrument averaging interval (2 to 5 minutes). The laser spectrometer measures by direct absorbance of the gas according to Beer's Law. 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. A 750-ppm calibration check is what the manufacturer recommends for testing the TDLAS instrument. While the concentration is low enough to be near the detection limit, the concentration is high enough to allow for measurements of sufficient accuracy and precision.

(H<sub>2</sub>S concentration in cylinder) (flow cell length) = Path Integrated Concentration 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

#### 5.2 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. Perform a bump test by installing the external reference cell fiber optic cables into the Unisearch analyzer. Verify calibration, and remove the cell.
- 3. Assemble test configuration with the Unisearch short flow-through cell (0.167 m) in the path.
- 4. Assemble the H<sub>2</sub>S gas scrubbing system, with gas flow coming from the external flow cell into the column packed with absorbent.
- 5. 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.
- 6. Monitor 5-min averages until a stable zero reading is reached. Continue reading 15 measurement cycles.
- 7. Flow the H<sub>2</sub>S reference gas. The 750-ppm cylinder of H<sub>2</sub>S should flow at 0.3 L/min.
- 8. Acquire 7 to 15 measurement cycles.
- 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. Perform another bump test using the external reference cell.
- 11. 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.

#### 5.2.1 Clean-Up

Dispose of the waste PFTE tube filled with GC Sulfursorb Plus appropriately.

# 6. Sealed-Cell Response Testing

Sealed cells filled with a known concentration of  $H_2S$  may be used for response testing the LasIR analyzers. These sealed cells are fiber coupled and may be connected into the light path as indicated in Figure D-1.

#### 6.1 Single-Point Bump Test

- 1. Disable alerts on 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.
- Calculate the average, %difference, standard deviation, %CV, and average detection r<sup>2</sup>. Record these values in the test form (Section 7)
- 8. Disconnect sealed cell outlet optical fiber from instrument and reconnect optical fiber from Step 2 to instrument "Fiber In" port.
- 9. Verify baseline of instrument and turn alerts back on in FFT and take out of planned maintenance mode.

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:

 $Path Average \ Concentration = (\frac{250 \ ppm - m}{(2 * 500 \ m)})(\frac{1000 \ ppb}{ppm}) = 250 \ ppb$ 

#### 6.2 Three-Point Calibration

- 1. For the three-point calibration test, repeat the measurements described in Section 6.1 for the remaining concentrations.
- 2. Plot a curve of measured concentration vs. expected concentration. The record the r<sup>2</sup>, slope, and intercept.

# 7. 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			
% Difference			
Standard Deviation			
% CV			
Average Detection r			

# Three-point Calibration Summary

	Value
Slope	
Intercept	
r <sup>2</sup>	

# Notes:

Appendix E. Valero's Response to BAAQMD's "RE: Refinery Fenceline H<sub>2</sub>S TDL Monitoring System Specification" Letter • • Appendix E. Valero's Response to BAAQMD's "RE: Refinery Fenceline H2S TDL Monitoring System Specification" Letter

# Appendix E.

# Valero's Response to BAAQMD's "RE: Refinery Fenceline H2S TDL Monitoring System Specification" Letter

	Specification from BAAQMD	Response
1	A Limit of Quantitation (LOQ), <sup>1</sup> which ranges from 3 to 25 ppb H2S, depending on environmental and operational conditions, with an average integrated path LOQ of 15 ppb H2S. The stated LOQ limits can	These are substantially different requirements compared to the October 6, 2021 letter issued by the BAAQMD. Most notably, by the requirements above, the BAAQMD requires the measurement to meet precision and accuracy requirements at 3 to 25 ppb path- average concentrations. These specifications have not yet been proven for the Unisearch system under routine operations given how we define LOQ and MDL.
	be converted to a path length equivalent (i.e., ppb-m) value, based on the actual installation path length, for convenience if	Our MDL is defined as 3s with s being the standard deviation of a 5-min average blank sample. With this definition in place, there is only a 1% probability that a reading above the MDL is a false positive.
	<b>Necessary.</b> <sup>1</sup> For reference, the minimum detection limit (MDL) of a measurement process is defined as the lowest concentration of the analyte that can be reliably detected (i.e., distinguished from zero), and the LOQ is the lowest concentration at which the analyte can not only be reliably detected but at which predefined goals for accuracy and precision are met. The LOQ may be equivalent to the MDL, or it could be at a higher concentration. All LOQ specifications provided here are established with respect to the accuracy and precision requirements stated in this attachment.	In a similar fashion, the LOQ is set to 10s. This standard methodology helps to ensure that data above LOQ can be accurately quantified and reported to the public. See references below for the origins of our definitions for MDL and LOQ. Currie, L.A., Horwitz, W., "IUPAC Recommendations for Defining and Measuring Detection and Quantification Limits", Analysis 22 (1994) 24 Danzer, K. and Currie, L.A., "Guidelines for Calibration in Analytical Chemistry", Pure Appl. Chem. 1998, 70, 993 Harris, D.C. (2007) Quantitative Chemical Analysis ISBN-13: 978-0- 7167-7041-1
2	An LOQ of 25 ppb at a light transmission less than or equal to 1%, or at a signal power equivalent to 1% light transmission, provided the equivalency is demonstrated and documented in the quality assurance project plan (QAPP).	The manufacturer recommendation for acceptable signal strength at the detector is greater 0.4 mW which corresponds to greater than 3 to 5% transmission, depending on the initial laser power. We currently invalidate data with a signal power less than 0.4 mW if there is no fog present according to a collocated visibility sensor. With this automated quality control in place, we can commit to 90% data completeness.

3	A path integrated measurement range of 3 to 5,000 ppb H2S with a measurement accuracy within 15% of the reference standard and a coefficient of variation not greater than 15% using a concentration of 40 to 60 ppb H2S equivalent integrated path average.	Measurements become less accurate as the concentration approaches the MDL (Albert and Horowitz, 1997). It is therefore critical to consider the concentration and averaging time of any bump test or calibration. BAAQMD has specified 15% precision and accuracy at concentration equivalents as low as 40 ppb, but an averaging time has not been prescribed. For example, a bump test could be assessed against (1) raw 8-sec acquisitions of a 50- ppb sealed cell averaged to 5 min, or (2) data with a 5-min average consisting of a single 2,000-ppb acquisition averaged with the remainder of instrument blanks. Both techniques would effectively challenge the instrument with comparable average concentrations, but instrument performance in either case would differ significantly. It is unclear what methodology the BAAOMD has in mind or whether
		their requirements are appropriately specified. Based on recent testing, the Unisearch TDL system is capable of a concentration-dependent accuracy, using raw 8-sec data as follows:
		Determination of the lower limit at which calibration and bump testing can be routinely performed, and performance criteria reliably achieved, is ongoing. Note that ppmm is equivalent to ppb for a one-way path length of 500 m.
		<ul> <li>±25% for [H2S] &lt; 2,000 ppmm</li> <li>±10% for 2,000 ≥ [H2S] ppmm</li> </ul>
		Similar to current requirements for other open-path systems, accuracy and precision should be specified at 25% until it is clear that commercially available TDL systems can achieve better performance on a routine basis for a given averaging time and test method.
		With the existing installations, we ask the BAAQMD to allow sufficient time (at least one year) to develop and test these procedures under a variety of conditions.

4	Equipment calibration performed at	Flow through-gas cells can be used with NIST
	least on a quarterly basis to validate	traceable gases. Methodology needs to be
	monitor performance under real-	developed at the concentrations required in this
	world operating conditions and	most recent BAAOMD letter to show that feasibility
	potential ambient concentrations	of flow-through cells
	- Calibration checks must be	
	performed at a minimum of three	If using sealed cells, NIST traceable sealed cells will
	concentration points (low mid	need to be procured and we are not currently aware
	concentration points (low, mid,	of a supplier offering such sealed cells
	high), using sealed or flow-	
	through cells and NIST traceable	See comment #3 for issues surrounding the lower
	standards.	concentration tests.
	<ul> <li>The low calibration point must be</li> </ul>	
	in the range of 40 to 60 ppb H2S	
	equivalent integrated path	
	average. Two reasonable upscale	
	(mid, high) calibration	
	concentrations should be chosen	
	to confirm the accuracy and	
	precision of the system over the	
	measurement range, without	
	adjustment after each calibration	
	noint measurement: these	
	calibration concentrations should	
	be commensurate with ambient	
	concentrations that may result	
	from process upgets looks or	
	itom process upsets, leaks, or	
	- The accuracy and precision	
	specifications of 15% must be met	
	at each calibration point. Failure to	
	meet these specifications must	
	trigger repair, maintenance, and	
	root cause analysis, followed by	
	repeat calibration checks until a	
	passing calibration check is	
	completed. All steps in this	
	process, including results of each	
	passing and failed calibration	
	check, and monitor response or	
	calibration adjustments must be	
	fully documented in the quarterly	
	report submitted to the Air District	

• • • Appendix E. Valero's Response to BAAQMD's "RE: Refinery Fenceline H2S TDL Monitoring System Specification" Letter

as described in the requirements below and subsequent attachments. Standard operating procedures, which describe the calibration checks and corrective actions, must also be attached to the QAPP.

- Cells must be placed in the light path, however correction for the effects of the equipment on the light transmission may be proposed and implemented upon approval. Correction procedures must be fully documented in the QAPP, and any correction of actual data must be explained in the associated quarterly reports when the data are submitted to the Air District.

5	Bump tests performed at least monthly	The QAPP and SOPs can be revised to cover
	at a unique concentration that differs	corrective actions in the case of a failed test.
	from the calibration checks. The bump	
	check concentration should be 50 to	See summary of issues under point #3 for low
	100 ppb to confirm accuracy and	concentration tests. These would be an issue for the
	precision are maintained near the low	50 to 100 ppb bump test requested here.
	calibration point during routine	
	operation. The accuracy and precision	
	specifications of 15% must be met for	
	the bump test. Failure to meet the	
	monthly bump test accuracy and	
	precision specifications must trigger	
	repair, maintenance, and root cause	
	analysis, followed by repeat bump	
	testing until a passing bump test is	
	completed. All steps in this process,	
	including results of each failed bump	
	test, must be fully documented in the	
	quarterly report submitted to the Air	
	District as described in the	
	requirements below and subsequent	
	attachments. These specifications, and	
	any associated procedures, must be	
	clearly documented in the QAPP.	

6	Failure to meet the monthly accuracy or precision requirements during two or more bump tests in any quarter, or four bump tests in any 12-month period, will result in a violation of the accuracy and/or precision specifications and QAPP requirements. Such occurrences will invalidate all data prior to the failed bump test going back to the last bump test passed. Invalidated data will be counted against data completeness requirements.	We ask for the BAAQMD to allow for sufficient time to develop and test these procedures under a variety of conditions; we propose at least one or two years.
7	Real time validation of TDL data must be performed using measurement of another common ambient air component, such as methane, water, or carbon monoxide if present in the spectra.	The details of using water vapor for data validation can be described in the QAPP.
8	LOQ quantification and verification must be performed continuously in near real time, reported in near real time on the refinery fenceline monitoring website, and included in the quarterly reports along with the measurement data as specified in the requirements below and subsequent attachments.	See comments under point #1 regarding appropriate definitions of MDL and LOQ. We propose to continue quantifying MDL in real time.
9	Percent light transmission received at the detector, including the signal or power strength, must be measured in real time, and provided in the quarterly reports as specified in the requirements below and subsequent attachments. All data, metrics, and procedures used to exclude data due to environmental conditions must be fully documented in the QAPP and explained/supported in the quarterly reports as specified in the requirements below and subsequent attachments.	The current Unisearch implementation can report signal power. The instrument does not currently report % transmission in real time.

10	Raw spectral data files must be saved as single files and made available to the Air District upon request. File formats must be specified in the QAPP.	Spectral data for the Unisearch instrument is saved as a single file for each day. Together with the configuration file for the instrument, this data is readable with the LasIR software.
11	All quality assurance and quality control metrics and procedures must be clearly and completely documented in the AMP and QAPP.	We strive to accomplish this with every AMP and QAPP submission.
12	Standard operating procedures (SOPs) for all quality assurance, quality control, and maintenance activities must be attached to the AMP and QAPP. For any SOP that contains confidential information, two copies must be submitted – one that has the confidential information redacted and that can be made available to the public, and another unredacted copy for internal Air District reference.	We will include SOPs with the AMP and QAPP submission.
13	Quarterly reports must be submitted to the Air District consistent with the specifications outlined in attachments 2 and 3 to this letter.	See our comments on attachments 2 and 3.
14	Optional - The Air District recommends that system operation and performance is based on a standardized method, such as EPA Method TO-16, or a method developed by a credible standardization body, such as ASTM International or the International Organization for Standardization (ISO).	We recommend inclusion of IUPAC to this list of credible organizations.