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

Valero Benicia 12-15
Quality Assurance Project Plan

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1.1 Background

1.1.1 Purpose

The Valero Refining Company (Valero) is conducting air quality monitoring at its refinery in Benicia, California, in response to the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15).[1] The monitoring is following a facility-specific air monitoring plan consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.[2] Rule 12-15 requires routine monitoring near the fencelines of all San Francisco Bay Area refineries for specific air compounds, with data reported to the public.

1.1.2 Rationale

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

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, and quality assurance (QA), field, and website personnel. **Figure 1** shows an organization chart for the project.

[1] Petroleum Refining Emission Tracking (Rule 12-15; approved by the BAAQMD on April 20, 2016).

[2] Bay Area Air Quality Management BAAQMD (2016) Air monitoring guidelines for petroleum refineries. April. Available at baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en.

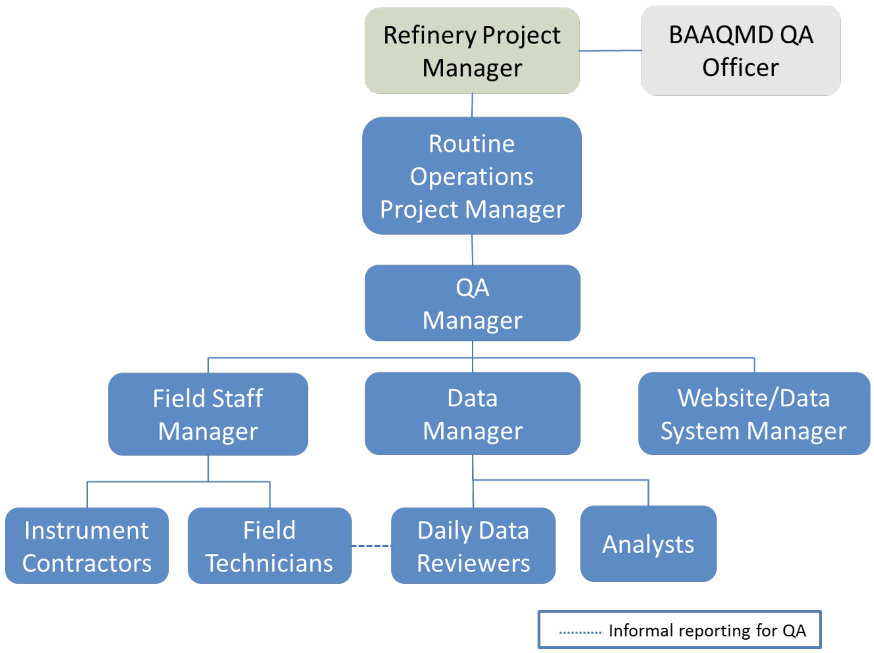

Figure 1. Organizational chart for this project.

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

The Routine Operations Project Manager is responsible for overseeing the day-to-day monitoring operations and reports to the Refinery Project Manager. The **QA Manager** is responsible for ensuring the quality of data collected in this project. The QA Manager oversees data collection and review, provides QA oversight during the study, and oversees and reports on QA activities to the Routine Operations Project Manager. The QA Manager oversees daily data review and data management; works with the Field Staff Manager to ensure any data issues are promptly addressed by the field technicians; and works with the Website/Data System Manager to ensure that data provided to the public are of high quality. The QA manager additionally 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 the necessary instrument maintenance. The technicians ensure that all measurements are collected in accordance with maintenance and audit procedures (see Appendices), standard methods, and regulations, where applicable. Technicians (1) perform the required quality checks on instruments and document all work in site logs; (2) are trained on the operation and maintenance of each instrument; and (3) have the necessary and current training required to be on refinery property.

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

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

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

The **Website/Data System Manager** is responsible for properly displaying data on the website. The website uses automated alerting to notify the Website/Data System Manager when the real-time data are not available. This manager will be responsible for assessing and fixing data communication and other information technology–related issues concerning the website and 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), plus sulfur dioxide (SO_2) and hydrogen sulfide (H_2S). These compounds are measured at a 5-minute resolution. Taking into account the (1) distances that need to be covered by measurements (hundreds of meters), (2) data time-resolution requirements (5 minutes), and (3) current measurement technology, open-path instruments (CEREX UV-DOAS and Unisearch TDLAS) were selected.

Along all measurement paths (see Section 2.2), BTEX and SO_2 are measured by monostatic Ultra Violet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. As currently installed, the xenon light is required to achieve measurements over paths about 300 meters long, and achieve reasonable minimum detection limits (MDL) for BTEX. 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 classical least squares regression analysis. Beer's Law is then used to report gas concentrations. This approach is the same as that specified in the Environmental Protection Agency's TO-16 Methodology,[3] although not written specifically for UV-DOAS. Closeness of fit is indicated by the correlation coefficient (R^2) derived from the fit of the measured spectra to the reference spectra. The R^2 is provided with each concentration so that potential interference can be detected if it is present. Selection of analysis regions that are free of absorbance due to other gases within the sample is the primary means of avoiding cross-interference. Spectral subtraction is used in cases with overlapping absorbance features; the subtraction technique is proprietary to the instrument manufacturer.

Along all measurement paths, H_2S is measured by monostatic Tunable Diode Laser Absorption Spectroscopy (TDLAS) instruments. A tunable diode laser emits light at a very small range of wavelengths, which allows the measurement to avoid potential interferents. The TDLAS technology is not currently ready for production quality systems, especially when the data are to be made publicly available. For H_2S, manufacturers report that the TDLAS has detection limits on the order of 50 ppb over a 500 m path length; however, further instrument adjustments and a passing field accuracy test (FAT) are necessary to confirm the TDLAS minimum detection limit for this system and its actual minimum detection limit will depend on atmospheric conditions. In accordance with the

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

"Air Monitoring Plan –Notification of Extension for H_2S Monitoring Selection Submittal" BAAQMD letter received December 6, 2018, Valero has until December 6, 2020 (or December 6, 2022 with approved extension) to begin operation of open path monitoring for H_2S. Alternatively, if open path monitoring is deemed infeasible, Valero may elect to use fixed measurements for H_2S monitoring and has until December 6, 2019 (or December 6, 2020 with approved extension) to begin operation of fixed measurements for H_2S monitoring.

Heavy fog, heavy rain, or smoke may block the signal from an open-path instrument and prevent data collection; however, even light fog can absorb the signal partially and interfere with measurements. Tule fog forms when there is high relative humidity (typically after rain), light wind, and rapid cooling. Tule fog typically forms in the California Central Valley, and extends into the marshlands along the Sacramento and San Joaquin Rivers and the Carquinez Strait, especially during the rainy season of 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. Using a Belfort Instrument Visibility Sensor Model 6400, visibility measurements are made at two locations—one at a low-elevation monitoring path and one at a higher-elevation monitoring path—and provide evidence when low-visibility conditions cause the open-path instruments to miss measurements.

Table 1 summarizes the estimated MDL and upper detection limit (UDL) for each species by instrument for each measurement path, as provided by instrument manufacturers. The MDL is the lowest concentration that can be measured at the path length, while the UDL is the highest concentration that can be measured. The detection limits are presented as the average species concentration along a path; when a narrow plume covers only a portion of the path, a higher concentration than the MDL is needed for the species to be detected.

Table 1. Open-path instruments and approximate detection limits by pollutant and path. Actual limits will be different and depend on ambient conditions, final path length, and a passing field accuracy test (FAT).

Path		1-1'		1-1"		2-2''		2-2'		3-3'		3-3"	
Distance (meters)		321		523		598		572		574		527	
Technology	Compound	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)
TDLAS	Hydrogen Sulfide	~50*	15,600*	~50*	95,600*	~50*	83,600*	~50*	87,400*	~50*	87,100*	~50*	94,900*
UV-DOAS (Xenon)	Benzene	0.4	23,900	0.3	14,700	0.2	12,800	0.2	13,400	0.2	13,400	0.3	14,600
	Toluene	1.3	13,600	0.8	8,300	0.7	7,300	0.7	7,600	0.7	7,600	0.8	8,300
	Ethylbenzene	0.5	2,900	0.3	1,800	0.3	1,600	0.3	1,600	0.3	1,600	0.3	1,800
	Total Xylene	1.4	7,300	0.9	4,500	0.8	3,900	0.8	4,100	0.8	4,100	0.9	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

* These values indicate a target MDL and UDL only. For H2S, manufacturers report that the TDLAS has detection limits on the order of 50 ppb over a 500 m path length; however, further instrument adjustments and a passing field accuracy test (FAT) are necessary to confirm the TDLAS minimum detection limit for this system and its actual minimum detection limit will depend on atmospheric conditions.

2.2 Monitor Siting Rationale

For the fenceline monitoring program, Valero uses open-path instruments to measure the required compounds—BTEX, SO_2, and H_2S—along three paths. The three measurement paths, composed of two segments each, have been implemented to cover Valero's fencelines in consideration of (1) nearby local receptors (e.g., residences and businesses), (2) dominant winds that blow from west to the east, and (3) infrequent winds that blow from the northeast to the southwest to 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 from the northeast toward the southwest. Over the course of a year, these northeast winds occur less than 7% of the time. Because of terrain effects and the orientation of the Carquinez Strait, the northeasterly wind direction is well-defined and has little directional variability; therefore, the downwind areas that could be affected under these wind conditions are very narrow.
- Path 3 covers the eastern fenceline to assess potential transport toward the business/commercial area east of the refinery. This transport direction is common in the spring, summer, and early fall, when winds often blow from the west toward the east.
- 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 that vehicle traffic will not block the open-path sensor light.
- Open-path analyzers are located at all of the sites. Sites 1 and 2 each have two UV-DOAS and two TDLAS instruments. Each pair of analyzers at each site point roughly 180 degrees 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 sites 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 built into operations and maintenance. For all instruments, scheduled maintenance will occur monthly, quarterly, and/or annually. Emergency maintenance will occur as needed when problems are identified during daily data review and auto-screening of real-time data. All actions performed to the instruments will be recorded and filed in a site log book.

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

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

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving check list will be maintained).	✓		
Inspect optics on detector and retro-reflector; clean if necessary.	✓		
Inspect and clean system filters.	✓		
Confirm the alignment to verify there has not been significant physical movement. This is accomplished by noting the integration time and signal strength – both should be less than 250 ms and greater than 90%, respectively.	✓		
Download data older than 6 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	✓		
Inspect all electrical cables for wear; replace as needed.	✓		
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency. Realign system if integration time exceeds 250 ms or signal intensity is less than 15% at 250 nm under high (>20 mi) visibility conditions.	✓		
Change out the UV source if the intensity has dropped below acceptable range (service hours >2000 hrs or intensity at 250 nm >15% with 40 ms dwell time under high visibility conditions)		✓	
Replace ventilation exit and intake filters.		✓	
Clean and inspect optics on detector and retro-reflector.		✓	
Realign system after service. Ensure integration time is less than 250 ms and intensity is greater than 90% under high visibility conditions.		✓	
Check other system performance indicators, if necessary.		✓	
Perform bump test (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 25% different from expected value (% Accuracy).	✓*		
Verify system settings.			✓

*Bump tests 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 bump test frequency should come as a request to BAAQMD and be agreed to by BAAQMD in cooperation with the Valero, Benicia Refinery.

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. Table 9 further defines operational limits that will be used to trigger corrective actions during separate site visits. Maintenance schedules will be altered as needed.

Table 3. Schedule of maintenance activities for the TDLAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓		
Inspect optics on detector, clean if necessary.	✓		
Check the alignment to verify there has not been significant physical movement and confirm signal levels. Signal power should be greater than 7.5 mW.	✓		
Download data older than 6 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure no obstructions between the detector and the retro-reflector (such as equipment, vegetation, or vehicles).	✓		
Inspect all electrical and optical cables for wear; replace as needed.	✓		
Check system performance indicators (an evolving checklist will be maintained).		✓	
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 7.5 mW.		✓	
Verify system settings.			✓

*Bump tests 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 bump test frequency should come as a request to BAAQMD and be agreed to by BAAQMD in cooperation with the Valero, Benicia Refinery.

2.3.3 Belfort Model 6400 Visibility Sensor

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

Table 4. Schedule of maintenance activities for this visibility sensor.

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

*Calibration checks may be performed less frequently in the future if the measurements prove adequately stable, or additional metadata provides assurance that instruments are working properly. Any reduction in the calibration frequency 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. Because the fenceline monitoring system is composed of two major components—field hardware, and the website software—two separate rotating teams are on-call 24/7 to respond to any issues that can be dealt with remotely. Any field work will occur the next business day. The two teams are (1) the STI on-call field operations team (field ops team, led by the Field Staff Manger and Data Manager, and supported by Terra Applied Systems), and (2) the STI IT operations team (the IT ops team, led by the Website/Data System Manager). The overall STI field ops team consists of one field technician; the IT ops team consists of one IS engineer and one IT specialist. STI manually checks the website twice daily, and automated checks are enabled. If the automated checks identify a problem, the system will immediately send an alert to the field ops team and/or the IT ops team. This approach helps guarantee that problems are identified and addressed in a timely manner. The on-call teams are required to investigate alerts within 30 minutes of their receipt. Refinery personnel will be notified if a solution for issues affecting data availability cannot be resolved within an hour. If the system is offline, a maintenance message will be put on the public website. BAAQMD staff will be notified of monitoring downtime according to BAAQMD Regulation 1-530.[4]

The rotating field ops team will remotely monitor the status of the field sites 7 days a week and use automated checks such as those listed below to determine actions.

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

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

Problems with the analyzers or any associated hardware in the shelters will be addressed on the following business day. As soon as a problem is identified, the STI field ops team will work with the IT ops team to ensure the proper error message for the effected variables is displayed on the website by the following business day.

The IT ops team will remotely monitor that status of the website and associated equipment using automated system checks such as those listed below to determine actions. These checks are detailed in Table 5.

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

Item	Parameter	Monitoring Frequency	Parameter Limit/Threshold for Alert
Website goes down	HTTP test on the: - public website - Administrator website DMS API	Every 300 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 expected to respond within 30 minutes of any system alert and triage the problem as needed. 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 STI. If deemed necessary, STI 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 the following business day, and any issues that occur during weekday nights will be addressed the next 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. The daily data reviewers will review data to identify issues, and 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 issues and fixes are in place, a summary of the problems and solutions will be sent to the program manager via email. In the event that an issue not included in this list is discovered by field or IT personnel, it will be documented, along with the corrective actions taken. The QAPP and relevant SOP will also be updated. Updated QAPPs will be submitted to BAAQMD for approval.

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

Item	Problem	Action	Notification	Person Responsible
Erratic data (e.g., data that is not physically possible)	Possible instrument malfunction	Contact Field Staff Manager and Instrument Contractor	Document in logbook, notify Field Staff Manager	Field Technician
Power	Power interruptions	Check line voltage, reset or restart instruments	Document in logbook, notify Field Staff Manager	Field Technician
Data downloading	Data will not transfer 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
Website	Website is down	Contact Website/Data System Manager	Notify QA Manager	Website/Data System Manager
Server	Not working properly	Contact Website/Data System Manager	Notify QA Manager	Website/Data System Manager
Network	Network is down	Contact Website/Data System Manager	Notify QA Manager	Website/Data System Manager
Data Flow	Data flow interruption	Contact Website/Data System Manager	Notify QA Manager	Website/Data System Manager
Data Flow	Errors in Processing	Contact Website/Data System Manager	Notify QA Manager	Website/Data System Manager

3. Quality Objectives and Criteria

3.1 Data and Measurement Quality Objectives

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

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

For all instrument/parameter combinations, data completeness requirements are provided in Table 7. Percent data recovery (or data capture) for 1-hr data is the percentage of valid 5-minute data values that were collected divided by 12. An hour starts at the top of the hour and must contain 75% complete data for that 60 minute time period. Percent data recovery for a day (starting at 12:00 a.m.) is the number of valid 1-hr values collected divided by 24. Percent data recovery for the calendar quarter is the number of days of valid data collected divided by the total number of days in the date range. For communication purposes, the Percent Data Valid—the percentage of data values that are valid divided by the number of captured data values, corrected for low-visibility conditions—will also be computed. Rule 12-15 allows for the omission of time periods from the completeness calculation when atmospheric conditions prevented measurement, as proven using an independent measure of visibility.

Table 7. Data recovery requirements.

Completeness Requirement	Relevant to	Minimum No. of Values Needed
75% per hour	5-minute average data	9 per hour
75% per day	1-hr average data	18 per day
90% per calendar quarter	Daily data	81 days per 90-day quarter[a]

[a] The exact number of days in the quarter will be used; this example is for illustration only.

Other factors that affect data availability include instrument calibrations or bump tests (approximately every month for a few hours), annual maintenance, and other maintenance.[5] Regular maintenance and careful, responsive operation, will minimize instrument downtime.

3.2 Precision Checks, Bump Test, and Verification

All measurements outlined here are subjected to precision and accuracy tests. During these tests, a number (N) of replicated five-minute 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 N≥15. The average value of these measurements is calculated as

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

and the standard deviation (σ) as:

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

From these definitions, %Accuracy 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 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 will be performed on a monthly basis during the first year and potentially less frequently in the future if the measurements prove adequately stable, or should additional metadata provide assurance that instruments are working properly. If and after the TDLAS technology is determined to provide consistent and reliable data and passes the FAT, a single-species bump test using H_2S will be performed on a monthly basis during the first year and potentially less frequently in the future should the measurements prove adequately stable. The QAPP will be evaluated continuously; if updates are needed, it will be updated and sent to the BAAQMD for approval before implementation.

For the visibility instruments, the sensors are calibrated in the field using a manufacturer-specific calibration kit. A calibration kit consists of (1) a blocking plate or block for checking the sensor zero, and (2) a scatter plate for checking the sensor span. The scatter plate is assigned a factory-traceable extinction coefficient (EXCO) used to calculate the expected values during calibrations. Calibrations will be performed annually.

[5] Bump tests may be performed less frequently in the future if the measurements prove adequately stable, or additional metadata provides assurance that instruments are working properly.

For the open-path systems, precision is 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, five-minute data will be selected during periods of low variability, but when concentrations are well above the MDL. The precision will then be evaluated by calculating the coefficient of variation (CV) during the period of low variability, as shown in the equations on the previous page. If there are no periods of low variability with concentrations above the MDL, bump test data will be used to calculate precision.

3.3 Instrument or Standard Certifications

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

4. Data Management

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

4.1 Data Acquisition and Communications

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 will be transferred from infield instruments through a data acquisition system (DAS) to a DMS using a cell modem. Data are also stored onsite on instrument computers in case of cell modem failure. The DMS uses a Microsoft SQL relational database with stored procedures.

The DMS automatically quality-controls data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities are used for continuous examination of data quality. The DMS feeds auto-screened data to the field operations website and notification system to inform and alert project and facility staff. The operations website shows maps and time series plots of BTEX and SO_2; wind data is also displayed on the maps. The operations website will add open path H_2S to the maps and time series plots after the technology is proven to be consistent and reliable for this application and the TDLAS passes the FAT.

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

4.2 Automated Data Screening

Automated data screening is conducted within the DMS upon data ingest. Automated screening checks of data feeds are used to screen out invalid data for public display, and are helpful to focus the data reviewer's efforts on the data that need the most attention. Initial screening checks, along with actions to be taken, are summarized in **Table 8**. The screening check concentration criteria are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. All screening criteria (flags and rates of change) are preliminary and will be refined during the project based on actual observations and are expected to be finalized after six months of operations. 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 will verify that the instrument is not reporting values outside of reasonable minimum and maximum concentrations.
- **Sticking.** If values are repeated for a number of sampling intervals, data will be reviewed for validity. Typically, four or more intervals of sticking values are a reasonable time span to indicate that investigation is needed. Sticking checks will not be applied to data below the instrument detection limit.
- **Rate of Change.** Values that change rapidly without reasonable cause will be flagged and reviewed.
- **Missing.** If data are missing, data during those time periods will be coded as missing. Missing data may indicate a power issue, an instrumentation problem, or a data communication problem. The time period allowed for missing data may be adjusted as the project proceeds to reduce false or excessive alerting. The alerting will be set for six missing 5-minute values (i.e., 30 minutes).
- **Sensor OP Codes and Alarms.** If the instrument assigns operation (op) codes to data automatically (e.g., for bump tests, internal flow rate checks), the data 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 the twice the path length (two times the path length is used because the open-path sensor light travels to the mirror and back to the analyzer).

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, wavelength versus intensity, and visual review of peaks. There are no previously set data quality objectives for these parameters; we will need to develop objectives for these parameters if we find that they are useful indicators for automated data quality screening or for data validation. The QAPP will be updated as needed to include addition or revision of any data quality indicators that are determined to improve data quality (for example, fewer false positives and false negatives).

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

Table 8. Initial screening checks for 5-minute data. All valid and flagged data values will be displayed to the public in real time. If data are invalid, they will not be included in the public display. All screening values below (flags and rates of change) are preliminary and will be refined during the project. During data validation, flagged data will be further investigated. The screening criteria for H2S has not yet been determined. If and after the Unisearch TDLAS technology is determined to provide consistent and reliable data and passes the FAT, the H2S screening criteria will be added to this table.

Measurement (units)	Approximate MDL for a 598 m Path*	DMS Auto-Screening Checks					
		Range	Sticking	Rate of Change	Missing	Sensor OP Codes and Alarms	Visibility Impairment
Benzene (ppb)	0.2 ppb. If below MDL, flag as below MDL.	If above 24 ppb, flag data as suspect on the website and conduct investigation on validity	If same value observed for four or more intervals, flag data as suspect on the website and conduct investigation on validity	If value changes by more than 12 ppb, flag data as suspect on the website and conduct investigation on validity	If data are missing, code 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 path length, code as invalid on the website due to low visibility
Toluene (ppb)	0.7 ppb. If below MDL, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and conduct investigation on validity		If value changes by more than 50 ppb, flag data as suspect on the website and conduct investigation on validity			
Ethylbenzene (ppb)	0.3 ppb. If below MDL, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and conduct investigation on validity		If value changes by more than 50 ppb, flag data as suspect on the website and conduct investigation on 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)	0.8 ppb. If below MDL, flag as below MDL.	If above 100 ppb, flag data as suspect on the website and conduct investigation on validity	If same value observed for four or more intervals, flag data as suspect on the website and conduct investigation on validity	If value changes by more than 50 ppb, flag data as suspect on the website and conduct investigation on 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 path length, code as invalid on the website due to low visibility
SO_2	0.6 ppb. If below MDL, flag as below MDL.	If above 37.5 ppb, flag data as suspect on the website and conduct investigation on validity		If value changes by more than 19 ppb, flag as suspect on the website and conduct investigation on validity			
Visibility (meters)	If value less than 0, flag data	Not applicable		Not applicable			Not applicable

*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 will be 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 three- to five-day time-series plot of selected parameters for each instrument—allows the analyst to see common problems and verify instruments are operational. If it appears that an instrument is not operating or the data are missing, the field operator will be notified and further investigation and corrective action, if needed, will be taken.

4.3.2 Assess Data Reasonableness

The data reviewer quickly assesses whether the pollutant concentrations are reasonable with respect to the time of day, season, meteorology, and concentrations expected and observed along other paths. For example, data checks for negative values, stuck values, high rate of change, etc., show whether the data are physically reasonable. Other 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, during the process of data validation, it is determined 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 monthly (for first six months) to 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 Quality Control (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-minute 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[6]
- Inspecting several sampling intervals before and after data issues or instrument bump tests or repairs to ensure all affected data have been properly flagged
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on observations by site operator
- 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 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:

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

Additional QC checks for the instruments are summarized in **Table 9**. Data that fail checks are flagged in the DMS and brought to the attention of the reviewer in the graphic summaries. Common reasons for invalidation include instrument malfunction, power failure, and bump-test data that were not identified as such. As the measurements progress, the QA Manager updates and refines the screening checks. Screening checks are typically specific to the site, instrument, time of day, and season, and are adjusted over time as more data are collected. The data checks listed in Table 9 are generally robust, but are actively revised if evidence of ineffectiveness is found during daily and quarterly data validation.

[6] Measurements below the method detection limit will be flagged in the DMS for review by an analyst.

Table 9. Instrument QA/QC checks.[a]

QA/QC Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test (accuracy)	Monthly[b] and after major service	±20%
Baseline stability	Continuous	±5%
Measurement quality – R^2	Continuous	0.8 to 1.0
Integration time	Continuous	80-250 ms *>250 ms integration time results in a warning notification*
Signal intensity	Continuous	>90% *Data may be invalidated only if signal intensity is below 90% and integration time is greater than 250 ms.*
TDLAS		
Bump test	Monthly	±25%
Correlation coefficient (R^2) during bump test	Monthly	0.8 to 1.0
Signal Power	Continuous	7.5 mW
Visibility Sensor		
Accuracy	Annually	±25%

[a] 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 will be flagged as below MDL on the public website and in the database.

[b] Bump tests 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 bump test frequency should come as a request to BAAQMD and be agreed to by BAAQMD in cooperation with the Valero, Benicia Refinery.

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 will be documented in the data file.

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

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

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

- Assigning invalid data a null Code (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 will be documented in the DMS, which retains raw data and traceability of all actions that result in the final data.

On an annual basis, the refinery or its designated 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

The DMS data will be backed up on a daily basis. Backup media are moved weekly to a secure offsite facility. The data will be stored for a period of five years after sampling.

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 upon request; data will be delivered within 30 days of the request. Concentrations of species will be provided in .csv format along with Site Code, Local Standard Time, Measurement Duration, Concentration Value, Concentration Unit, and QC Code. QC Codes are defined as follows:

0 = Valid
5 = Suspect based on instrument operating conditions
7 = Invalid based on additional post-processing checks
9 = Invalid based on poor instrument operating conditions

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 will be removed from the public display. Data issues identified during the automated quality control process will trigger a notification to the Data Manager to conduct further investigation. The Data Manager and team will then decide on the appropriate action to resolve the problem.

Data are screened in real time upon ingest into the DMS, as described in 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 will be presented in a time series of benzene, toluene, ethylbenzene, total xylenes, SO_2, and H_2S. The operations website will add open path H2S to the maps and time series plots after the technology is proven to be consistent and reliable for this application and the TDLAS passes the FAT. Data will be provided as 5-minute averages. Data will be annotated for quality (valid, invalid, flagged, or missing).

4.7.2 Data Backfill Process and Schedule

All data, raw and validated, are retained in the DMS.

Appendix A. CEREX UV-DOAS Audit Procedures

Appendix A

CEREX UV-DOAS Audit Procedures

May 19, 2019 STI-918045-7024-SOP

Contact: Ryan Moffet
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Contents

QA Audit Procedure Summary

This document addresses the commissioning and performance audit procedure for Cerex Monitoring Solutions UV Sentry units. 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 the 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.

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

The purpose of the QA Audit procedure is field verification of the factory calibration of the UV Sentry. The QA Audit 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.

QA audits (bump tests) are to be performed on a quarterly basis.

Safe Work and Hazard Identification

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

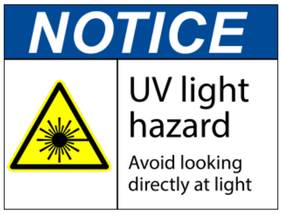
Operator Qualifications

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

Safe Work and Hazardous Environment Operation

Work should conform with 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. 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 UVDOAS 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

This QA Audit procedure requires the handling of toxic 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 quality assurance audit activities. Cerex assumes no liability for the use or misuse of this guidance document, or for operator-performed QA Audits, Calibration or Gas Handling activities. No claims are made by Cerex as to the compliance of this procedure with any regulations or engineering best practices. The operator is solely responsible for safety of personnel and property.

Preliminary Preparation

Safe Operating Precautions

1. Field at least 2 people for the validations.
2. Ensure that a clear escape path is identified.
3. Standard site personal protective equipment (PPE) is appropriate. If gloves are required, nitrile or latex should be used.

Test Apparatus Setup

Materials Required

1. Operator supplied Standard Operating Procedure approved by the End-User and in compliance with End-User's Health and Safety Plan.
2. This procedure is for the Internal UV Sentry QA Cell.
3. Cell bump test purge apparatus including:
   a. Tubing as required: 1/8" PTFE tubing for gas supply from the bottle to the QA cell
   b. Tubing as required: 1/4" PTFE tubing with inline flow indicator from the QA cell to the vent
   c. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less.

4. Purge gas
5. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher.
6. All relevant PPE, hardware and procedural guidance per SOP, Safety Plan, and Safe Work Permit.
7. Local or remote network link device (as required).
8. External laptop computer with network interface device to the Sentry unit (as required).

Verify Proper Sentry Alignment

1. Open the CMS window.
2. Click on the **UV** tab.
3. If Run is active, press **STOP**.
4. Click the **ALIGN** button at the bottom left of the plot display.
5. Adjust the alignment until the signal intensity is optimized.
   a. **Target intensity is 140,000 – 170,000.**
   b. **Target integration time is between 10mS and 55mS.**
6. **Record** the intensity and integration time
7. Press **OK and SAVE** or **ACCEPT** (if prompted) settings to exit the CMS Alignment window.
8. Press **RUN** to resume operation.

Gas Purge System Setup and Purge

1. Connect the reference cell vent line to the reference cell and route it through an appropriate vapor scrubber (as required) and outside the structure.
2. Connect the purge gas cylinder to the internal test cell.
3. Ensure the cell vent is open and unobstructed to atmosphere by monitoring vent flow
4. Flow purge gas at vent flow of 3 L/min for 1 minute to purge the system.
5. Reduce flow to 0.3 L/min

Prepare CMS for Gas Testing

Configure CMS for Audit (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.

Configure Test Files

1. On the CMS **OPERATION** tab enter the site file name, "QA Audit UV# YearMoDy" where # is the UV identification number and YearMnDy indicates the date of the test (i.e., 1969Aug09). Click the **APPLY** button.
2. Click the **RUN** button and allow the analyzer to complete 3 or more acquisitions.
3. Click the **RUN** button and allow the analyzer to complete two sequential acquisitions.
4. Click the **UV** Tab and inspect the absorbance plot for background target gas detection or optical ringing (See page A-9).
5. If no target gas background or optical ringing is observed, proceed to the next step. If optical ringing is observed, delete the QA Audit folder located in D:\Data\, take corrective action, and start over from Step 2 of this section. If target gas or ringing is persistent, make note and continue.
6. Click the **RUN** button and allow the analyzer to continue operation.

Gas Check and QA Audit

Check Gas Test

1. Start Check Gas flow.
    a. Close the purge gas to stop flow.
    b. Allow residual pressure to vent (approximately 10 seconds).
    c. Open the Test gas flow control.
    d. Set vent flow to 3 L/min.
    e. After 1 min, reduce flow to 0.3 L/min.

***NOTE *** Pressurizing the cell to above 3 psig may cause breakage of the optical windows.

2. 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 (±25% of reference standard).** If the measurements do not meet specifications, repeat the procedure. If repeated measurements appear nonconforming, initiate corrective action investigation.
    d. **Verify client system** is receiving and displaying instrument information correctly.
    e. After 15 stable measurements are observed, **close the Reference bottle valve**. Allow the pressure to fall to zero and flow to stop.

3. Purge the Reference gas
    a. **Open the purge gas** valve to flow nitrogen through the system.
    b. **Set the flow** rate to 3 L/min.
    c. **Purge the QA cell** with nitrogen for at least 2 minutes.
    d. **Verify that the target gas(es) concentration has returned to 0 ppm** with non-detect R2.

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

    e. Once the target gas value returns to non-detect, stop flow.
    f. Remove the hoses and cap the connectors.

Restore Normal Operation

1. **Restore** Normal Operation.
2. **STOP** CMS.
3. On the CMS **OPERATION** tab enter the site name "UV# YearMoDy" and click **APPLY.** Click the **RUN** button and allow the analyzer to complete at least one acquisition.
4. Press **STOP.**
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

1. Concentration
    a. Average the concentration of 15 consecutive stable measurements.
    b. Report the percent difference between the average and the certified value.
2. Calculate the Limits of Detection and Quantitation

   a. Calculate the sample standard deviation of the 15 selected results.
   b. Report the Detection Limit as three times the standard deviation.
   c. Report the Quantitation Limit as five times the standard deviation.
3. Compile all configuration files, spectra files, and log files into a single folder.
   a. The folder should be named "CUS LOC QATest UV# YearMonDy" where CUS is a three letter designator for the customer and LOC is a three letter designator for the facility location.

QA Audit Record Template

UV Sentry Fenceline Detection System

DATE: ______________ Location: ___________________________

Test Technician 1 :________________________

Test Technician 2 :________________________

Sentry Alignment

Intensity ______________________ Target 140,000 – 170,000

Integration time ______________________ Target 10mS and 55mS.

Gas Purge System

Flow purge gas Start Time_________________

Stop Time_________________

Prepare CMS

Saved "**Run Configuration**" in _______________________________________

Path length in the CMS Configuration _________________ m

Save "**Audit Configuration**" in the default directory. _________________ init

Configure Test Files

Site File (QA Audit UV# YearMoDy) __________________________________

Optical Ringing Check _________________ init

NOTES:

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

Purge Flow Conditions

Initial Gas flow__________________ L/min
Start Time__________________
End Time__________________
Reduced Gas flow__________________ L/min

Check Gas Test

Initial Gas flow __________________ L/min
Start Time__________________
End Time__________________
Reduced Gas flow time__________________
Start Time__________________
End Time__________________
Collect Check Gas data
Start Time __________________
Concentration__________________ ppm
Verify Client __________________ Init
End Time __________________ Init

Close Reference Gas

Start Time __________________
Open the **PURGE** gas
Time__________________
End Test Gas Concentration ________________ ________ppm_______ R2
________________ ________ppm_______ R2
________________ ________ppm_______ R2
________________ ________ppm_______ R2
________________ ________ppm_______ R2
________________ ________ppm_______ R2
________________ ________ppm_______ R2

Restore Normal Operation

Settings > **Configuration** > **File** > **Load** > **C:\User\Documents\Cerex\CMS** > **'Run Configuration'**
Operation > Benzene UV# > **Apply**.
RUN > complete one acquisition > **STOP**
Verify Benzene Background Benzene ________ppm_______ R2
Press **RUN** to begin monitoring. ____________________ Init

Data Files (CUS LOC QATest UV# YearMonDy) ___________________________________

NOTES:

Results Record

Instrument ID ____________________ Location ____________________

Technician ____________________ Date ____________________

Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
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Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2
Time ____________ ________ppm_______ R2

Reference Concentration ________ ppm
Average Concentration ________ ppm
% difference ________ %
Std Deviation ________ ppm
Estimated MDL (3X Std Dev) ________ ppm

NOTES:

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

Appendix B

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

August 21, 2019 STI-918045-6987-SOP

Contact: Ryan Moffet
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Contents

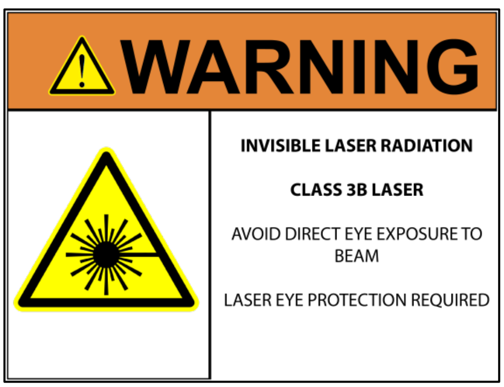
QA Audit Procedure Summary

This document addresses the commissioning and performance audit procedure for Unisearch TDLAS units. The procedure is intended to verify that the equipment is performing to expectations and that the detection and communication links are functioning correctly.

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

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.

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.

Safe Work and Hazard Identification

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

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.

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_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 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.

Overview and Operating Principle

The Unisearch LasIR H_2S monitoring system is a monostatic open-path remote sensor for path integrated monitoring of gases using direct absorption tunable diode laser techniques. Multicomponent analysis using classic least squared fitting provides enhanced detection for low levels of H_2S by adjusting for overlapping water and carbon dioxide absorbance bands. The purpose of this procedure is to check the system for correct H_2S response in the installed operating conditions. H_2S 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.

Safety

Exposure Control

Hydrogen sulfide 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.

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_2S 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_2S reference gas. H_2S levels should be monitored inside the enclosure. Two self-contained breathing apparatuses shall be on standby.

Supplies

Gas Flow

1. Nitrogen gas
2. H_2S reference gas blend (750 ppm is used in this procedure).
3. The H_2S reference gas tank and as much of the gas lines as possible should be outside the shelter in the open air. All gas lines should be tested for leaks while filled with nitrogen gas.
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

Gas Scrubbing System

1. Length of PTFE tubing to go from external flow cell to scrubbing system
2. A scrubbing system consisting of ½″ ID PTFE tubing, 6″ long, filled with GC Sulfursorb Plus activated carbon absorbent, or equivalent. This volume of absorbent has a minimum capacity of 38 grams of H_2S, which is approximately 100 times the amount of H_2S existing in 750 ppm H_2S gas flowing at 0.3 l/min for 100 minutes (one test).
3. A max 5 l/min rotometer attached at the exhaust line to view that flow is occurring.

Detailed Approach

Purge the system with nitrogen to establish a baseline. Then challenge with H_2S 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_2S delivered to the optical path through the 0.167-m flow-through cell and a total path length of 1000 m provide approximately 125 ppb path average H_2S. 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_2S concentration in cylinder * flow cell length = Path Integrated Concentration (ppm-m)

750 ppm * 0.167 m = 125.25 ppm-m

Path Integrated Concentration divided by the total optical path length = Path Average Concentration (ppm)

125.25 ppm-m / 1000 m = **0.125 ppm or 125 ppb H_2S**

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_2S 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_2S flow and flow nitrogen to purge the H_2S 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_2S and nitrogen gases and remove the external flow cell to return the TDLAS system to open-path monitoring of ambient air.

Clean-Up

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

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

February 20, 2019 STI-918045-6991-SOP

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Contents

Summary

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

General Maintenance

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

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.

Visibility Sensor Maintenance Schedule:

Monthly:	Inspect and clean optics
Monthly:	Inspect cables
Annually:	Check calibration

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.

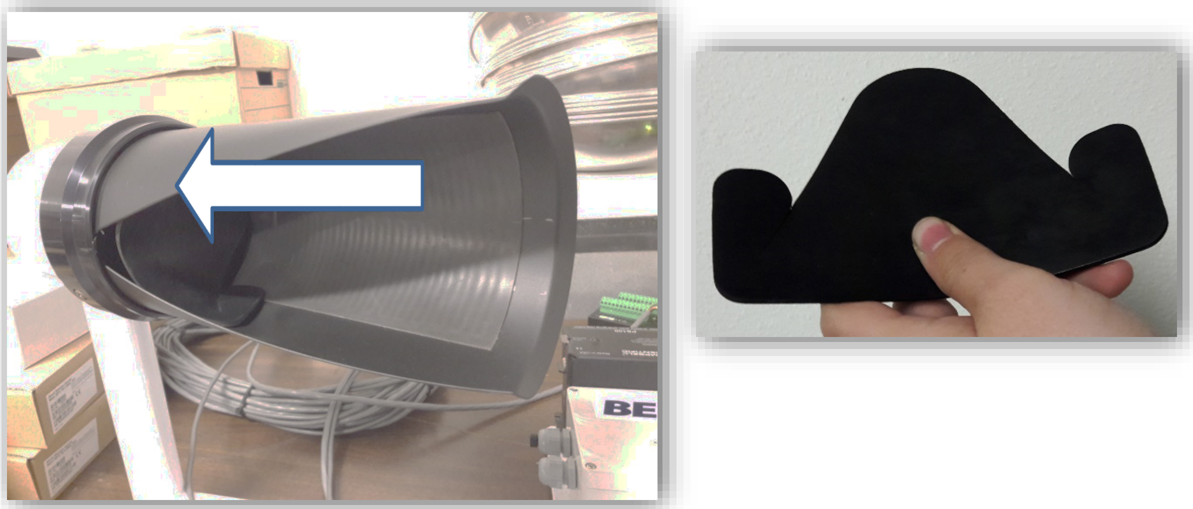

Figure C-1. Inserting the Opaque Filter.

Span Calibration

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

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

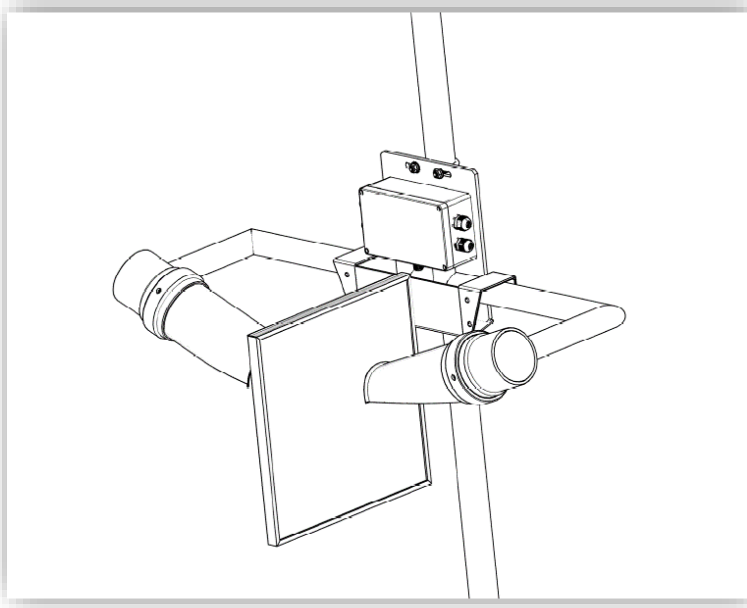

Figure C-2. Scatter Plate Mounting.

Completing the Process

1. Disconnect the serial cable from the laptop, disconnect the Belfort 6400's three serial wires from the cable, and reconnect them to the CR310 data logger. The red wire goes to the C1 terminal, the brown wire goes to the C2 terminal, and the bare wire goes to the G terminal of the CR310.
2. Connect to the CR310 through Loggernet (either via a micro-USB cable to a field laptop or via the DMZ server connection) and check to see if values are coming in and if they make

sense. Note: the values might initially be lower than expected; wait 5 to 10 minutes for the sensor to readjust itself.

QA Audit Record Template

Belfort Model 6400 Visibility Sensor Audit Record

DATE:________________ Location: ______________________________

Test Technician 1 :___________________________
Test Technician 2 :___________________________

Zero State Calibration

Start Time: ____________________________________

Previous Zero Offset: ___________________________

New Zero Offset: ______________________________

Stop Time: _____________________________________

Notes:

Span Calibration

Start Time: _____________________________

Scatter Plate ExCo: _____________________

Span Factor: ___________________________

New Span Factor: ______________________

Stop Time: _____________________________

Notes: