Tesoro Refining & Marketing Co., LLC*

*A subsidiary of Marathon Petroleum Corporation

Martinez Refinery Quality Assurance Project Plan

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1. Project Background and Management

1.1 Background

1.1.1 Purpose

Tesoro Refining & Marketing Co., LLC (Tesoro), a subsidiary of Marathon Petroleum Corporation, plans to monitor fenceline concentrations of certain compounds at their refinery located in Martinez, California ("Martinez Refinery" or "Refinery"), in compliance with the Bay Area Air Quality Management District's (BAAQMD) Regulation 12, Rule 15 (Rule 12-15) and consistent with the BAAQMD's Air Monitoring Guidelines for Petroleum Refineries.^{1,2} Rule 12-15 requires monitoring 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 The Martinez Refinery will conduct open-path pollutant monitoring, and collect visibility and meteorological measurements, to meet the regulations.

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

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



Figure 1. Organizational chart for this project.

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

The QA Manager is responsible for ensuring the quality of data collected in this program. The QA Manager oversees data collection and review, provides QA oversight, and oversees and reports on QA activities to the Refinery PM. The QA Manager oversees daily data review and data management, works with the Field Staff Manager to ensure that any data issues are addressed by the field technicians promptly, and works with the Website Manager to ensure that data provided to the public are credible and meet the requirements of Rule 12-15.

The Field Staff Manager ensures that field technicians (site operators) are meeting the requirements of the program. The Field Staff Manager coordinates staff coverage and serves as a technical resource for site measurements.

Field Technicians perform necessary instrument maintenance. The technicians will be trained on the operation and maintenance of each instrument to ensure that all measurements are collected in accordance with standard operating procedures (SOPs), standard methods, and regulations, where applicable. Technicians perform the required quality checks on instruments and document all work in

site logs. Technicians will also have the necessary and current training required to safely work 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, that data that fail auto-screening are inspected, and that data validation follows the proper schedule and procedures. The Data Manager is also responsible for delivering the validated data to the PM.

Daily data review and data validation are conducted by experienced air quality analysts. The Data Reviewers communicate with the Data Manager when there are issues 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 and ensuring that validated data are prepared for reporting to the BAAQMD on a quarterly basis. Automated alerting will notify the Website/Data System Manager when the real-time data are not available on the website. 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 compounds to be measured are benzene, toluene, ethylbenzene, and xylenes (referred to collectively as BTEX), sulfur dioxide (SO₂), hydrogen sulfide (H₂S), as well as 1,3-butadiene, hexane, and ammonia (NH₃). These compounds will be measured at a 5-minute resolution. Because of the distances that need to be covered by measurements (hundreds of meters), data time-resolution requirements (5 minutes), and current measurement technology, open-path instruments (CEREX UV-DOAS, and CEREX FTIR) were selected.

Along all measurement paths (see Section 2.2), BTEX and SO₂ will be measured by monostatic Ultra Violet-Differential Optical Absorption Spectroscopy (UV-DOAS) with a xenon light source. The xenon light is required to achieve measurements over paths of about 300 to 600 meters long and to achieve the minimum detection limits (MDL) for BTEX. The analyzer records the intensity of light at discrete wavelengths. Any UV-absorbing gas that is present in the beam absorbs at a specific wavelength of light. Each species of gas has a unique absorbance fingerprint (i.e., the ratios between the absorbance at several different wavelengths are unique to that gas). The analyzer compares regions within the sample absorbance spectra to the same regions within the reference absorbance spectra. The analyzer uses a classical least squares regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files. Beer's Law is used to report gas concentrations. Though not written specifically for UV-DOAS, this approach is the same as that specified in the Environmental Protection Agency's (EPA) TO-16 Methodology.³ Closeness of fit is indicated by the correlation coefficient (R^2) of agreement between the measured spectra and the reference spectra. The R² is provided with each concentration so that interference can be detected if it is present. Selection of regions of analysis that are free of absorbance due to other gases within the sample is the primary means of avoiding cross-interference. Spectral subtraction is used in cases with overlapping absorbance features; the subtraction technique is proprietary to the instrument manufacturer.

The measurement technique for hydrogen sulfide has yet to be established. Once an instrument has been selected, this QAPP and associated SOPs will be updated.

Hexane, NH₃, and 1,3-butadiene will be measured with a *Fourier Transform Infrared (FTIR) Spectroscopy* instrument. The FTIR operates by sending a beam of infrared light through the open air. The IR beam is reflected back to the analyzer by a retro-reflector array (monostatic), where 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/ttnamtil/files/ambient/airtox/tocomp99.pdf.

absorption due to target gases is measured and recorded. The analyzer uses a classical least squares regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files according to the EPA's TO-16 Methodology. Beer's Law is used to report accurate gas concentrations. The FTIR operates on a similar premise as the UV-DOAS by using reference spectra. There are a variety of industry standard methods to mitigate interference from both water vapor and interference gases, including spectral subtraction, path length adjustments, and selecting isolated absorbance peaks for the gases of interest. Proprietary methods include multi-peak analytics.

Heavy fog or smoke (from wildfires) may entirely block the signal from an open-path instrument and prevent data collection; however, even light fog or smoke can extinguish the light and degrade the 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. Visibility measurements will be made at one representative location and will provide evidence when low-visibility conditions cause the open-path instruments to miss measurements.

Table 1 summarizes the MDL and upper detection limits (UDL) for each species by instrument foreach measurement path, as provided by instrument manufacturers. The MDL is the lowestconcentration that can be measured at the path length, and the UDL is the highest concentrationthat can be measured. The detection limits are for the average species concentration along a path;narrow plumes that only cover a portion of the path would need to have a higher concentration thanthe MDL to be detected.

Table 1. Instruments and approximate detection limits by species, and path length. Actual detection limits will depend on ambient conditions, visibility, final path lengths, and instrument performance.

Path		Path 1		Path 2		Path 3		Path 4	
Approximate Distance		654 meters		484 meters		598 meters		571 meters	
			UDL	MDL	UDL			MDL	UDL
Technology	Compound	MDL (PPB)	(PPB)	(PPB)	(PPB)	MDL (PPB)	UDL (PPB)	(PPB)	(PPB)
	1,3-Butadiene	1.4	873.1	1.9	939.5	1.5	979.8	1.6	857.3
FTIR	Ammonia	0.3	707.2	0.4	761.0	0.4	793.7	0.4	694.4
	Hexane	0.7	693.3	0.9	711.5	0.8	661.5	0.8	833.7
То Ве	Hydrogen								
Determined	Sulfide	TBD	TBD	TBD	TBD	TBD	TBD	TBD	TBD
	Benzene	0.4	10866.8	0.6	11693.8	0.5	12194.9	0.5	10670.6
	Toluene	1.2	6168.5	1.7	6637.9	1.4	6922.4	1.5	6057.1
UV-DOAS	Ethylbenzene	0.5	1311.6	0.6	1411.4	0.5	1471.9	0.5	1287.9
	Total Xylenes	2.2	4997.6	3.0	5378.0	2.4	5608.5	2.5	4907.4
	Sulfur Dioxide	1.0	3079	1.4	3159	1.1	2937.5	1.2	3701.8

2.2 Monitor Siting Overview and Rationale

The Martinez Refinery will monitor concentrations across four open paths, shown in Figure 2. The Refinery selected these locations after consideration of dominant wind patterns, sources of potential air emissions on the property, nearby local receptors, and logistical feasibility. Detectors/Analyzers will be located at monitoring sites 1A, 2E, 3N, and 4N, and retro-reflectors will be placed at the remaining identified sites at 1N, 2W, 3S, and 4S. The BAAQMD previously approved the locations of the four open paths.



Figure 2. Selected open-path monitoring sites for the Martinez Refinery. Four paths are identified, labeled 1N-R-1S-A (yellow), 2E-A-2W-R (blue), 3N-A-3S-R (blue), and 4N-A-4S-R (yellow), where "A" and "R" denote locations of analyzers and reflectors, respectively.

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

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

H₂S and BTEX emissions are distributed across the refinery property, and these species will be measured along all four of the open pathways. Sources of NH₃ and 1,3-butadiene are present only near the refinery's main processing block; therefore, given the annual and seasonal wind patterns, measurements of these species will be made only along Path 1 and Path 4. Hexane, which serves as a surrogate for alkane emissions, will also be reported along Path 1 and Path 4.

A visibility monitor will be located on the Path 2 instrument shelter.

2.3 Instrument Operations and Maintenance

Four instrument systems will be included in this monitoring system: UV-DOAS, FTIR, a visibility sensor, and a hydrogen sulfide analyzer. Other meteorological data will be obtained from existing measurement systems at the refinery. Quality assurance is built into operations and maintenance. For all instruments, scheduled maintenance will occur monthly, quarterly, and/or annually. Maintenance schedules may be altered as needed. Emergency maintenance will occur as needed when problems are identified during daily data review and auto-screening of real-time data.

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.

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving checklist will be maintained).	✓		
Inspect optics on detector and retro-reflector; clean if necessary.	\checkmark		
Inspect system filters.	\checkmark		
Confirm the alignment to verify there has not been significant physical movement. This is automatically monitored as well.	✓		
Download data older than 6 months from the hard drive, move to a permanent archive, and delete old files from the analyzer.	✓		
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, vehicles).	✓		
Inspect all electrical cables for wear; replace as needed.	\checkmark		
Change out the UV source.		\checkmark	
Replace ventilation exit and intake filters.		\checkmark	
Clean optics on detector and retro-reflector.		\checkmark	
Realign system after service. Ensure integration time is less than 250 ms and intensity is greater than 90% under high visibility conditions.		~	
Check system performance indicators.		\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).*	~		

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

Activity	Monthly	Quarterly	Annually
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 visibility conditions.	¥		
Verify system settings.			\checkmark

*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. Frequency will be reduced only if agreed to by BAAQMD in cooperation with refinery personnel.

2.3.2 CEREX FTIR

Maintenance activities for the FTIR and the UV-DOAS are similar. The FTIR system is also designed to require only modest service and maintenance. Table 3 summarizes FTIR maintenance activities, as recommended by the manufacturer. Preventative maintenance frequency depends on the operating environment and may need to be adjusted. On an as-needed basis, system status alarms may alert operators to specific issues that need to be addressed. Audits will be performed on site.

Activity	Monthly	Quarterly	Semi- Annually	Annually	~18 months	Five Years
Visually inspect the system.	\checkmark					
Inspect optics on detector and retro- reflector; clean if necessary.	\checkmark					
Confirm the alignment to maximize signal intensity. Signal should be greater than 5%	V					
Download data older than 6 months from the hard drive, move to a permanent archive, and delete old files from the analyzer.	~					
Ensure there are no obstructions between the detector and the retro- reflector (such as equipment, vegetation, vehicles).	~					

Table 3. Schedule of maintenance activities for the FTIR.

Activity	Monthly	Quarterly	Semi- Annually	Annually	~18 months	Five Years
Perform bump test* 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).	✓					
Check system performance indicators (an evolving checklist will be maintained).		\checkmark				
Inspect and clean AC system exterior heat sink.			\checkmark			
Review and test light and signal levels. Check average light intensity to establish baseline for IR Source change frequency and retro-reflector wear.				~		
Replace cryocooler or swap detector module assembly.					\checkmark	
Change out the IR source.						\checkmark

*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. Frequency will be reduced only if agreed to by BAAQMD in cooperation with refinery personnel.

2.3.3 Belfort Model 6400 Visibility Sensor

For the visibility sensor, monthly maintenance includes inspecting the sensor for dirt, spider webs, birds' nests, or other obstructions. 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 (see Table 4).

Activity	Monthly	Quarterly	Annually
Visually inspect the system including all cables.		\checkmark	
Inspect optics on detector, clean if necessary.	\checkmark		
Check calibration. An acceptable % Accuracy is less than 10%.			\checkmark

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

2.4 Emergency Maintenance Procedures

When a major problem is discovered with the fenceline monitoring system, corrective actions and maintenance procedures are required. Because the fenceline monitoring system is composed of two major components—field hardware and the website software—two separate rotating teams will be 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, supported by Terra Applied Systems), and (2) the STI IT operations team (the IT ops team). The overall field ops team will consist of one field technician; the IT ops team will consist of one IS engineer and one IT specialist. STI will manually check the website daily, and automated checks will be enabled. If the automated checks identify a problem, the automated system will immediately send an alert to the field ops team and/or the IT ops team. This approach will help to guarantee that problems are identified and addressed in a timely manner. The on-call teams are required to 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 fenceline monitors are offline, a maintenance message will be put on the public website.

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

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

Problems with the analyzers or any associated hardware in the shelters will be addressed on the following business day. As soon as a problem is identified, the team will work with the IT ops team to ensure that the proper error message for the affected 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 in Table 5 to determine actions. Automated alerts are triggered when any of the parameters surpasses their limit or threshold.

Item	Parameter	Monitoring Frequency	Parameter Limit/Threshold for Alert
Website goes down	HTTP test on the: - public website - Administrator website DMS API	Every 300 seconds	Websites not reachable
DMS systems	- CPU utilization- Memory use- Disk space used	Every 300 seconds	- CPU utilization >60% - Memory used >75% - Disk used >75%
Other network- related issues	 Database replication API load balancer System services Network connections 	Every 300 seconds	Status either - OK - Insufficient - Unhealthy
Interruption in data flow	- Time since last data point received	Every 30 minutes	Most recent measurement is behind collection by more than 30 minutes
Errors in data processing pipeline	- Process scheduler	Every 300 seconds	Status either - OK - Insufficient - Unhealthy

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

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 the Refinery 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. If there is an outage lasting more than 24 hours, BAAQMD will be notified on the next business day (short-term outages less than 24 hours will be identified in the quarterly report). A spare analyzer may be installed if there is a long-term problem with a piece of operating equipment.

Corrective action will be taken to ensure that data quality objectives are met. Table 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. Data Reviewers will review data daily to identify issues, and will work with the field technicians and instrument contractors to resolve issues that need to be addressed on site. Twice daily, Analysts will examine both public facing and internal websites to assess data quality and availability. If issues are noted, the Analyst will further investigate and work with the QA Manager, Project Manager, and Field Technicians to resolve the problem. Furthermore, 24/7 on call field operations will be notified of any data availability issues. If necessary, maintenance tables will be modified and updated in the QAPP and submitted to BAAQMD for approval.

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

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

To ensure appropriate spatial coverage of measurements, a thorough meteorological analysis was performed, as documented in the monitoring plan. Comparability among measurements is addressed by using one manufacturer for each system (UV-DOAS, FTIR, 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 AM) is the number of valid 1-hr values collected divided by 24. Percent data recovery for the calendar year (starting January 1) is the number of days of valid data collected divided by the total number of days in that year. 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.

Completeness Requirement	Minimum No. of Values Needed
75% valid data per hour	9 valid 5-minute averages per clock hour. 3 valid 5-minute averages per clock hour during hours in which instrument maintenance or validation is being performed.
75% valid data per day	18 valid clock hours per calendar day
90% valid data per calendar year	328 days per year

Table 7. Data recovery requirements.

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

3.2 Precision Checks, Bump Tests, and Verification

All measurements outlined here will be subjected to precision and accuracy tests. During these tests, a number (N) of replicated measurements (x_i) of a standard reference material of known magnitude (x_{std}) will be measured. 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 reliable, high-quality performance by the UV-DOAS analyzer, single-species bump tests using benzene will be performed. For the FTIR analyzer, ammonia will be used as the test species. For both systems, bump tests will be performed on a monthly basis and potentially less frequently in the future if the measurements prove adequately stable, or should additional metadata provide assurance that instruments are working properly. The QAPP will be evaluated continuously; if updates are needed, it will be updated and sent to the BAAQMD for approval before implementation. For the 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 calibration fixture is assigned a factory-traceable extinction coefficient (EXCO) used to calculate the expected values during calibrations. Calibrations will be performed as specified by a manufacturer.

For the open-path systems, precision will 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. More specifically, five-minute data will be selected during periods of low variability, when concentrations are above the MDL and are stable, exhibit minimal fluctuations in value, do not contain values not physically reasonable, and were collected without the presence of rain or fog. The precision can then be evaluated by calculating the coefficient of variation (CV) during

this period of low variability, as shown in the above equations. If there are no periods of low variability and concentrations above the MDL, bump test data will be used to calculate precision, as measured concentrations are steady and consistently above MDL during a bump test.

3.3 Instrument or Standards Certifications

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

4. Data Management

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

4.1 Data Acquisition and Communications

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

The DMS automatically quality-controls data, detects outliers and problems, generates reports, and creates alerts. The auto-screening and graphical capabilities will be used for continuous examination of data quality. The DMS will feed auto-screened data to the field operations website and notification system to inform and alert project and facility staff if there is a data issue. The operations website will show maps and time series plots of BTEX, SO₂, H₂S, 1,3-butadiene, hexane, NH₃, wind speed, and wind direction.

The automatically QC'd air quality data will be fed to the public website 10 minutes after 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. The DMS auto-screening checks that will be used include:

- Range. These checks will verify that the instrument is not reporting values outside of reasonable minimum and maximum concentrations. Table 8 summarizes the ranges for each compound.
- 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. These data will be flagged as suspect and reviewed by data quality reviewers on a daily to weekly basis. 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.
- Sensor OP codes and alarms. If the instrument assigns operation (OP) codes to data automatically (e.g., for bump tests or internal flow rate checks), the data will be reviewed, codes confirmed, and data flags checked.
- Visibility impairment. 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, as this results in marginal operating conditions for the analyzer (e.g., decreased signal strength or increased integration time). If open-path data are missing or invalid due to low light, and visibility is low, data will be flagged as invalid due to low visibility.

Additional parameters that may be monitored as indicators of data quality include signal strength, correlation between measured and reference spectra, wavelength versus intensity, and visual review of peaks. Signal strength will be used as a data filter. For those data points that are collected with a signal strength percentage outside of an acceptable range, based on will be flagged as either invalid or undergo additional screening. For UVDOAS, this can also be paired with the integration time (for example: data below 90% signal intensity and an integration time above 250 nm are flagged as invalid). The correlation between measured spectra and reference spectra also used to filter data. Measurements with less than 70% spectral match are flagged as below the detection limit of the analyzer (ambient interference and spectral noise are believed to impact measurements). A visual review of peaks can be conducted using manufacturer-supplied data processing software. This visual inspection will be used to determine the validity if peaks with high concentrations. Data quality objectives for these parameters may continue to evolve as the project is in operation; the QAPP will be updated as needed to include addition or revision of any data quality indicators that are determined to improve data quality.

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. The website "Resources" page provides an explanation of every data flag used on the public website.

Table 8. Initial screening checks for 5-minute data. All valid and suspect data values will be displayed to the public in real-time. If data are invalid, they will not be included in the public display. All screening values below (flags and rates of change) are preliminary and will be refined during the project. During data validation, flagged data will be further investigated.

Measurement (units)	Approvimato			Checks			
	MDL for a 598 m path*	Range	Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility
Benzene (ppb)	0.5 ppb. If below MDL, flag as BD	If above <u>24</u> <u>ppb</u> , flag as suspect and investigate validity	If same value observed for four or more intervals, flag as suspect (Same for all pollutants)	If sameIf value changesIf data areIf svalueby more than 12missing, flagindobservedppb, flag asas missingmafor four orsuspect and(Same for allbutmoreinvestigatepollutants)dataintervals,Value changes(Same for allbutflag asIf value changes(Same for allbutsuspectby more than 50(Same forpol(Same forppb, flag asasflag asallsuspect andinvestigateinvestigatepollutants)investigatevalidity	If sensor indicates malfunction or bump test data, flag as appropriate	If visibility is less than 1,000 m and data are missing, flag as	
Toluene (ppb)	1.4 ppb. If below MDL, flag as BD	If above <u>100</u> <u>ppb</u> , flag as suspect and investigate validity				(Same for all approp pollutants) (Same f pollutan	appropriate (Same for all pollutants)
Ethylbenzene (ppb)	0.5 ppb. If below MDL, flag as BD	If above <u>100</u> <u>ppb</u> , flag as suspect and investigate validity		If value changes by more than 50 ppb, flag as suspect and investigate validity			

Measurement (units)	Approvimate			Checks			
	MDL for a 598 m path*	Range	Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility
Total Xylenes (ppb)	2.4 ppb. If below MDL, flag as BD	If above <u>100</u> <u>ppb</u> , flag as suspect and investigate validity	If same value observed for four or more intervals, flag as suspect (Same for all pollutants)	If sameIf value changesIf data arevalueby more than 50missing, flaobservedppb, flag asas missingfor four orsuspect and(Same for amoreinvestigatepollutants)intervals,validity	If data are missing, flag as missing (Same for all pollutants)	If sensorIf visibilityindicatesless thanmalfunction or1,000 mbump testdata aredata, flag asmissing,appropriateas(Same for allappropriatepollutants)(Same for pollutants)	If visibility is less than 1,000 m and data are missing, flag as
SO ₂ (ppb)	1.1 ppb. If below MDL, flag as BD	If value above <u>37.5 ppb</u> , flag as suspect and investigate validity		If value changes by more than 19 ppb, flag as suspect and investigate validity			appropriate (Same for all pollutants)
NH₃ (ppb)	0.4 ppb. If below MDL, flag as BD	If value above 50 ppb, flag as suspect and investigate validity			If value changes by more than 25 ppb, flag as suspect and investigate validity		
1,3 – Butadiene (ppb)	1.5 ppb. If below MDL, flag as BD	If value above <u>9 ppb</u> , flag as suspect and investigate validity		If value changes by more than 4.5 ppb, flag as suspect and investigate validity			

Measurement (units)	American			Checks				
	MDL for a 598 m path*	Range	Sticking	Rate of Change Between Intervals	Missing	Sensor OP Code or Alarm	Visibility	
Hexane (ppb)	0.8 ppb. If below MDL, flag as BD	If value is above <u>200</u> <u>ppb</u> , flag as suspect and investigate validity	If same value observed for four or more intervals, flag as suspect (Same for all pollutants)	If value changes by more than 100 ppb, flag as suspect and investigate validity	If data are missing, flag as missing (Same for all pollutants)	If sensor indicates malfunction or bump test data, flag as appropriate (Same for all pollutants)	If visibility is less than 1,000 m and data are missing, flag as appropriate (Same for all pollutants)	
Visibility (meters)		Not applicable	Not applicable	Not applicable			Not applicable	

*Valid data below MDL will be evaluated on the basis of correlation coefficient and other operational parameters such as signal strength. If data below the MDL are determined to be valid, but the concentration is below the MDL, the data will be flagged as below MDL on the public website and in the database.

4.3 Data Verification

4.3.1 Confirm Daily Operation

Data are reviewed daily by a data reviewer to assess instrument operation. This initial review, typically of a 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. For an outage lasting more than 24 hours, BAAQMD will be notified on the next business day (short-term outages less than 24 hours will be identified in the quarterly report.

In addition to daily checks of the field website, an automated alerting system will let technicians and managers know when data have been missing for a specified period of time. Missing data may indicate a power issue, an instrument 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 initially for six missing 5-minute values (i.e., 30 minutes).

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 instrument parameters and correlation among measurements, can also be used to judge the validity of the data. If anomalies are observed, additional analysis will be conducted to determine whether there is an instrument malfunction, or if the data are truly anomalous but valid. Data reasonableness is also assessed more thoroughly during the data validation process. If, after review, there are no justifiable reasons for invalidating the data, questionable data will be considered valid. All data will be preserved during data reviews and only data flags will be changed, if applicable. Chain-of-custody logs will show all changes to data flags.

4.4 Data Validation

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

Data validation activities include:

- Looking for and investigating statistical anomalies and outliers in the data
- Ensuring there are not several continuous 5-minute averages of the same number (flatlining)
- Evaluating monthly summaries of the minimum, maximum, and average values
- Ensuring data reasonableness by comparing data to other sources of data
- Ensuring the data or measurements are realistically achievable and not outside the limits of what can be measured⁴
- Inspecting several sampling intervals before and after data issues or instrument bump tests or repairs to ensure all affected data have been properly flagged
- Referring to site and operator logbooks to see if some values may be unusual or questionable based on manual changes to operations/data, and verify that the changes were logged and appropriately flagged
- Assessing instrument meta-data to confirm reasonableness
- Confirming that bump tests were conducted and were within specifications

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.

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

⁴ Measurements below the method detection limit will be flagged in the DMS for review by an analyst.

Instrument Checks	Frequency	Acceptance Criteria			
UV-DOAS					
Bump test (accuracy)	Monthly 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% Signal intensity below 90% with an integration time >250 ms results in a warning notification			
	FTIR				
Bump test	Monthly	±20%			
Baseline stability	Continuous	±5%			
Signal intensity	Continuous	>5% Signal intensity below 5% results in a warning notification			
Measurement quality (R ²)	Continuous	0.7 to 1.0 [^]			
Vis	Visibility Sensor				
Accuracy	Annually	±10%			

Table 9. Instrument parameters and QA/QC checks.

*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. All MDLs are displayed on the public website. ^Correlation coefficient based on recommendation from analyzer manufacturer. On a quarterly basis, to ensure all the daily QC tasks are complete, analysts:

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

Analysts will subject the data to final QC by filling in missing records with null values, and add Null Codes:

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

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

On an annual basis, the Refinery Program Manager and the QA Manager will review the performance of the network by (1) reviewing the data completeness by monitoring path, instrument, and species; (2) reviewing results of bump tests; (3) analyzing the reported values in context of refinery operations; and (4) analyzing the data in context of the meteorology. The QA Manager will also evaluate overall network performance to ensure it is meeting overall objectives, using analyses similar to those used to support the network design. The results will be summarized in a technical memorandum and will be provided to the BAAQMD.

4.5 Data Storage and Processing

The DMS data will be backed up on a daily basis. Backup media will be 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. Hourly 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. Supporting documentation, such as SOPs and raw/spectral data will be made available to BAAQMD upon request.

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, will be displayed to the public in near-real time. If data are subsequently proven to be invalid, they will be removed from the public display with the reason for removal flagged on the public display. The website "Resources" page provides an explanation of every data flag used on the public website. Data issues identified during the automated 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 previous sections. Automated procedures will be 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 QC'd data will be presented in a time series of benzene, toluene, ethylbenzene, total xylenes, 1,3-butadiene, hexane, NH₃, and H₂S concentrations; and visibility, wind speed, and wind direction. 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

Prescreened, raw data will be augmented with validated data files within 60 days after the calendar quarter. All data, raw and validated, will be retained in the DMS.

5. Standard Operating Procedures

Standard Operating Procedures for maintenance and audits of the CEREX UV-DOAS instrument, the CEREX FTIR instrument, and the Belfort Model 6400 visibility sensor are provided in Appendices A through C of this QAPP.

Appendix A

CEREX UV-DOAS Audit Procedures

STI-918045-7024-SOP

January 2, 2020 Contact: Ryan Moffet Sonoma Technology, Inc. rmoffet@sonomatech.com 707-665-9900

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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.



Procedure Warnings

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.

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 (±20% 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.

Checking for Optical Ringing

Optical ringing may appear in the absorbance plot of the UV Tab. Ringing is the result of the angle of the cell optics with respect to the incoming light beam and appears as a sine wave or multiple sine waves of variable amplitude in the absorbance spectrum as displayed in the absorbance plot on the UV tab while the analyzer is in operation. Ringing is capable of causing patterns of detection and non-detection, as well as significant periodic false inflation of gas concentration reported as well as non-detection. The QA audit procedure should not be performed if optical ringing is present in the absorbance spectra.

QA Audit Record Template

DATE: Loc	cation:
Tost Toshnisian 1 :	
Test Technician 2 :	
Sentry Alignment	
Intensity	_ Target 80-90%
Integration time	_ Target 20 – 40 mS
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 di	rectory init
Configure Test Files	
Site File (QA Audit UV# YearMoDy)	
Optical Ringing Check ir	nit

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/mir	n		
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				
End Test Gas Concentration			nnm	P2
			ppm ppm	R2
			ppm	R2
Destans Normal Onemation				
Settings > Configuration > F	ile > Load > C	:\User\Document	s\Cerex\CMS\	, > 'Run
Configuration'				
Operation > Acrolein UV# > <i>I</i>	Apply.			
RUN > complete one acquisit	ion > STOP	A englation		20
verily Acrolein Background Press RLIN to begin monitorin	na	Acrolein	ppm	KZ Init
Data Files (CUS LOC OATest UV# Yea	irMonDv)			1111
				-

••• Appendix A: CEREX UV-DOAS Audit Procedures

NOTES:

Instrument ID	Location
Technician	Date
Time	ppm R2

Results Record

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

NOTES:

Appendix B

CEREX AirSentry FTIR QA Audit Procedure

STI-918045-7036-

January 2, 2020 SOP Contact: Ryan Moffet Sonoma Technology, Inc. rmoffet@sonomatech.com 707-665-9900

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QA Audit Procedure Summary

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

***NOTE ***

THIS IS A WORKING DRAFT FOR INITIAL SYSTEM VALIDATION. IT SHOULD BE REVIEWED FOR COMPLIANCE WITH LOCAL SAFETY AND QUALITY ASSURANCE PRACTICES.

This procedure should only be used by personnel with experience in the safe use of the analyzer and test equipment.

The purpose of the QA Audit procedure is field verification of the factory calibration of the AirSentry. The QA Audit process challenges the instrument using known concentrations of Ammonia 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 AirSentry FTIR analyzers should only be performed by personnel trained in the operation of the system components and familiar with the handling of gas delivery and testing equipment. This includes troubleshooting, cleaning, replacement of parts, IR light source installation, etc.

Safe Work and Hazardous Environment Operation

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

The Cerex Monitoring Solutions AirSentry Series Analyzers are not rated for safe operation in hazardous or explosive environments. Any 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.



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

Procedure Warnings

This QA Audit procedure requires the handling of hazardous Ammonia 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 AirSentry FTIR. 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. Locate the closest safety showers and eyewash stations and ensure they are operational.
- 2. Field at least 2 people for the validations.
- 3. Ensure that a clear escape path is identified.
- 4. Standard site PPE is appropriate. If gloves are required, nitrile or latex should be used.
- 5. Operator should be fully trained and experienced in the use of compressed gas cylinders, 1 and 2 stage regulators used in conjunction with the cylinders, flow controllers, tubing connections (Swagelok, for example). Operator should be experienced with the parameters of flow and pressure, and how these relate to compressed gas and its use with calibrating gas analysis equipment.

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 AirSentry FTIR QA Cell

- 3. Cell bump test purge apparatus including:
 - a. Tubing as required: 1/4" 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 10X instrument theoretical detection limit.
- 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 AirSentry FTIR unit (as required).

Verify Proper AirSentry Alignment

- 1. Open the CMS window.
- 2. Click on the FTIR tab.
- 3. If Run is active, press STOP.
- 4. Click the ALIGN button at the bottom left of the plot display.
- 5. Select 32 cm⁻¹ and wait for resolution change.
- 6. Aim the AirSentry FTIR at the retroreflector and adjust the alignment until the signal intensity is optimized.
 - a. Target intensity should be between 20% and 80%. Once stable signal is obtained, select desired operating resolution – 1 cm⁻¹ is required unless otherwise directed by Cerex.
- 7. **Record** the signal intensity.
- 8. Optional at this point you may wish to record the current field pathlength, and create a backup of the existing configuration file, in the event that you need a restore-point
- 9. Set the QA Cell's path length 0.15 m is the required value.
- 10. Press OK and SAVE or ACCEPT (when prompted) settings to exit the CMS Alignment window.
- 11. Press **RUN** to resume operation. If the FTIR analyzer is accidentally bumped or moved in any way, then stop the procedure, and return to the Align to verify and correct if necessary.

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. A precision 2 stage regulator is attached to the cylinder (both target gas, and N₂ purge gas) at all times. Before connecting verify that the output pressure is set to less than 1 psi. Verify the flow rate is preset to 1 liter per minute prior to connecting to the FTIR. Failure to follow this step will result in permanent and costly damage to the QA cell.
- 3. Connect the purge gas cylinder tubing to the AirSentry FTIR Gas Inlet and tighten.
- Slowly open the valve (flow previously adjusted to 1 L/min). Ensure the cell vent is open and unobstructed to atmosphere by monitoring vent flow. Cell pressure must remain below 1 psi.
- 5. Flow purge gas at vent flow of 1 L/min for 1 minute to purge the system.
- 6. Take a clean air background after a minimum of three volume exchanges have completed. Ensure the background is "saved" in the software, and that the software is using this updated, new background. Further instructions can be found in the CMS manual if required.
- 7. 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 FTIR# YearMoDy" where # is the FTIR 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.
 - a. If after 2 acquisitions the absorbance graph shows negative features greater than 3X the peak-to-peak baseline noise level, take another clean air background.
- 3. Repeat this process until sequential absorbance acquisitions (as seen in the absorbance graph) remain near zero (a straight baseline with only normal noise peaks).
- 4. Click the **FTIR** Tab and inspect the absorbance plot for background target gas detection. If none is present, proceed to the next step.
- 5. Click the **RUN** button and allow the analyzer to continue operation.

Gas Check and QA Audit

Span Gas Test

- 1. Start Span Gas flow.
 - a. Close the purge gas to stop flow and remove purge gas tubing from the Gas Inlet.
 - b. Allow residual pressure to vent (approximately 10 seconds).
 - c. Prior to connecting to the analyzer, ensure the span gas regulator is set to flow 1 L/min, and is at a pressure of less than 1 psi.
 - d. Connect Span gas's tubing to Gas Inlet and open the Span gas flow control slowly.

NOTE Cell pressure must remain below 1 psi, or optical windows may break.

- e. Set vent flow to 1 L/min.
- f. After 1 min, reduce flow to 0.3 L/min.
- 2. Collect Span Gas data.
 - a. Observe the concentration reported on the DATA tab.
 - b. After the concentration becomes stable, allow the analyzer **to run until at least 15 stable measurements are made**.
 - c. Verify that the value is near the expected concentration (±20% 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.

*****NOTE*****If 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 "FTIR# 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. Be sure to set the pathlength back to the field value (i.e., not 0.15). Restore the field background file, or let auto-background perform this function (if enabled).
- 7. 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 FTIR# 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

AirSentry FTIR Fenceline	Detection System	
DATE: Locat	tion:	
Test Technician 1 :		
Test Technician 2 :		
AirSentry Alignment		
Intensity	Target 20% to 80%	
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 director	гу	initials
Configure Test Files		
Site File (QA Audit FTIR# YearMoDy)		
Optical Ringing Check	initials	
NOTES:		

QA Audit Record - AirSentry FTIR Vapor Detection System - Page 2

Purge Flow Conditions			
Initial Gas flow	L/min		
Start Time			
Reduced Gas flow	L/min		
Check Gas Test			
Initial Gas flow	L/min		
Start Time			
Reduced Gas flow time			
Start Time			
Collect Check Gas data	Start Time		
	Concentration		ppm
	Verify Client		Initial
	Stop Time		Initial
Open the PURGE gas			_
TIME	PPM	R2	
Restore Normal Operation Settings > Configuration > Fil Configuration'	e > Load > C:\User\Documents\	\Cerex\CMS\ > '	Run
Operation > Ammonia FTIR# >	Apply.		
RUN > complete one acquisition	on > STOP		
Verify Ammonia Background Press RUN to begin monitoring	Ammonia J	ppm	R2 Init
Data Files (CUS LOC QATest FTIR# Year	MonDy)		

NOTES:

Appendix C

Belfort Model 6400 Visibility Sensor Maintenance and Audit Procedures

February 20, 2019
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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.

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.
- 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 Offs	set:	
New Zero Offset: _		

Stop Time:

Notes:

Span Calibration

Start Time: _____

Scatter Plate ExCo: _____

Span Factor: _____

New Span Factor: _____

Stop Time: ______

Notes: