Fenceline Air Monitoring Plan

For BAAQMD Rule 12-15

Chevron Richmond Refinery

Revision 3

September 5, 2023

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Document Control

Document No.	Rev. No.	Rev. Date	Effective Date	Distribution	Description
AMP	0	12/7/2018	12/7/2018	Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Original submission.
AMP	1	6/1/2022		Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Addressing BAAQMD comments, including addition of Tunable Diode Laser measurements of hydrogen sulfide.
AMP	2	2/16/2023		Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Addressing BAAQMD comments on Revision 1. The original submission of Rev. 2 on 11/2/2022 was rescinded and modified.
AMP	3	9/5/2023		Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Revised in response to July 19, 2023 comments from BAAQMD

List of Acronyms

BAAQMD – Bay Area Air Quality Management District

BTEX – Benzene, Toluene, Ethylbenzene, Xylenes

CFR – Code of Federal Regulations

CHS – Contra Costa County Health Services

COES – California Governor's Office of Emergency Services

CWS – Contra Costa County Community Warning System

DMS – Data Management System

EBV – Emergency Block Valves

EPA – Environmental Protection Agency

FTIR – Fourier Transform Infrared

GC-PID – Gas Chromatograph followed by Photoionization Detector

GLM – Ground Level Monitor required by Rules 9-1 and 9-2

H$_2$S – Hydrogen Sulfide

IR – Infrared Light

LFL/LEL – Lower Flammability Limit/Lower Explosive Limit

LOQ – Limit of Quantitation

OEHHA – California Office of Environmental Health Hazard Assessment

PMT - Photomultiplier Tube

ppb – Parts Per Billion

ppm – Parts Per Million

QA/QC – Quality Assurance / Quality Control

QAPP – Quality Assurance Project Plan

RCAMP – Richmond Community Air Monitoring Program

REL – Reference Exposure Level; RELs used are from OEHHA (http://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary)

RLOP – Richmond Lube Oil Project

SO$_2$ – Sulfur Dioxide

TDL – Tunable Diode Laser

TRI – Toxic Release Inventory

UV-DOAS – Ultraviolet Differential Optical Absorption Spectroscopy

UV – Ultraviolet

Section 1.   Overview

On April 20, 2016, the Bay Area Air Quality Management District (BAAQMD) published guidelines containing criteria for an approvable Air Monitoring Plan, required by BAAQMD Rule 12-15 Section 403. On October 6, 2021, the BAAQMD provided updated requirements for refineries to conduct additional monitoring of hydrogen sulfide (H_2S) concentrations along refinery fenceline paths, and to implement this enhanced monitoring by January 1, 2023. On December 22, 2022, the BAAQMD revised the requirements for H_2S monitoring. The additional H_2S monitoring was operational on January 1, 2023. BAAQMD issued updated specifications on December 22, 2022, and Chevron's response to the updated specifications was submitted on February 17, 2023. This revision addresses feedback from BAAQMD received July 19, 2023

The Chevron Richmond Refinery (Chevron) has followed these guidelines to generate the Air Monitoring Plan (this document) in November of 2020, and have updated the Air Monitoring Plan and the Quality Assurance Project Plan (QAPP, located in Appendix B) to account for the H_2S requirements. As presented in "Air Monitoring Guidelines for Petroleum Refineries, AIR DISTRICT REGULATION 12, RULE 15: PETROLEUM REFINING EMISSIONS TRACKING," the key elements of the BAAQMD guidelines (Guidelines) are as follows (Bay Area Air Quality Management District, 2016):

Element #1 – Gases Requiring Monitoring

Refinery operators must measure benzene, toluene, ethylbenzene, and xylenes (BTEX) and H_2S concentrations at refinery fencelines with technology capable of measuring in the parts per billion (ppb) range.

Element #2 – Other Gases to Be Considered for Measurements

Measurement of sulfur dioxide (SO_2), alkanes, or other organic compound indicators, 1,3-butadiene, and ammonia concentrations are to be considered in the Air Monitoring Plan. Refinery operators must provide a rationale in the Air Monitoring Plan for not measuring all the above compounds. The rationale must address the following questions:

- Why these compounds are not contained in the compositional matrix of emissions
- Why these compounds are not at expected concentrations measured by available equipment
  - Address the technical or other considerations that make specific measurements inappropriate or unavailable.

Element #3 – Fenceline Coverage

For refineries that do not have open-path monitoring capability in place, measurements must cover populated areas within 1 mile of the refinery fenceline likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time, or greater, based on the most representative meteorological measurements for sources likely to emit the compounds listed above at the refinery. In addition, the monitoring plan should take into consideration seasonal and short-term meteorological events. Refineries that already have open-path monitoring capabilities in place need only provide verification that those current systems adequately address population requirements.

Element #4 – Sample Time Resolution and Data Completeness

Open-path fenceline measurements must be continuously measured with a time resolution of five minutes. If this is not the case, refinery operators must provide rationale in the Air Monitoring Plan for lesser time resolutions based on equipment or other operational limitations. Instrumentation are operated to meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters. Atmospheric conditions beyond the control of the refinery that affect accurate measurements, such as dense fog, shall not be counted against data completeness calculations.

Element #5 – Data Presentation to the Public

Measurements must be provided to the public on a real-time basis, with appropriate Quality Assurance/Quality Control (QA/QC) measures taken to provide assurance of data accuracy.

Element #6 – Develop a Quality Assurance Project Plan

A QAPP that follows U.S. Environmental Protection Agency (EPA) guidelines must be developed that outlines the QA/QC parameters.

Chevron's policy is to comply with all local and federal environmental regulations including the fenceline monitoring provisions of BAAQMD Rule 12-15. In accordance with Rule 12-15-403, Chevron's goal is to provide the BAAQMD with an approvable Air Monitoring Plan (Plan) and QAPP and then operate and install systems in accordance with the plans.

Section 2.   Chevron's Existing Fenceline and Community Monitoring

As of the establishment of Rule 12-15, the Richmond Refinery was operating three open-path fenceline monitors and three community monitors as part of the Richmond Community Air Monitoring Program (RCAMP). The fenceline monitors have been in operation since 2013. The community monitors have been in operation since 2014. Siting of the fenceline and community monitors and the compounds to be monitored were subject to City of Richmond approval. Site locations for the fenceline equipment were selected to strategically position the fenceline monitors using the predominant and variable meteorological conditions and topographical terrain features within and near the refinery.

The fenceline and community monitoring sites were selected with the following considerations, consistent with guidance from EPA and CARB. Environmental requirements were considered in the monitors' placement with respect to on-site and off-site sources. The existing fenceline monitors do not have any large-scale sources between the monitor and the fenceline. The monitors were placed with consideration toward proximity to off-site emissions sources. Sampling requirements were considered. Chevron aimed to make the horizontal distance from a point sampler to an obstacle, such as a building, at least twice the vertical distance that the obstacle protrudes above the sampler. Chevron aimed to make the horizontal distance from 90% of the open-path to obstacles at least twice the vertical distance that the obstacles protrude above the path. For open-path monitors, a direct line of sight between light source and receiver must be available for the monitors to function. Logistical requirements were considered such as proximity to power, capability to access the internet for real-time data reporting and on-line troubleshooting, and adequate security.

Chevron also met on multiple occasions with Shields-Reid, Point Richmond, and Atchison Village Neighborhood Councils, who provided input on the locations of the air monitors between September 2011

and November 2012. These are all the neighborhoods that border the refinery. The compounds to be monitored were selected with input from the City of Richmond, Chevron consultants, and community representatives. The compounds monitored by the fenceline system are considered to be common for refinery operations. The specific chemicals that require monitoring were evaluated for each source from emissions estimates based on available TRI (Toxic Release Report) information. The compounds monitored by the community monitors represent a larger spectrum of compounds that can be attributed to many sources present in the Richmond community. The final siting locations and compounds to be monitored were approved by the City of Richmond in 2013. The fenceline and community monitoring data are made available to the public online at https://www.richmondairmonitoring.org/index.html. The following sections provide a summary of Chevron's Air Monitoring Plan in accordance with Rule 12-15 Section 403.

Section 3.   Evaluation

Element #1 – Gases Requiring Measurements

In 2013, Chevron installed and began operating open-path air monitoring systems in cooperation with the City of Richmond. Chevron compared the BAAQMD Air Monitoring Guidelines with Chevron's existing monitoring system, which quantifies benzene, carbon disulfide, H_2S, ozone, SO_2, toluene, and xylene. Chevron has added capability to our Open-path Ultraviolet Differential Optical Absorption Spectroscopy (UV-DOAS) system to measure ethylbenzene. Benzene, toluene, and xylene will continue to be detected and quantified by UV-DOAS. H_2S will continue to be detected and quantified using an open-path Tunable Diode Laser (TDL) air monitoring system and the Castro Street ground level point monitor, which is used to demonstrate compliance with BAAQMD Rule 9-2-301. Relevant equipment specifications are provided in Section 4 of this Plan.

Element #2 – Other Gases to Be Considered for Open-Path Measurements

Chevron considered the measurement of SO_2, alkanes, or other organic compound indicators, 1,3-butadiene, and ammonia for inclusion in the Air Monitoring Plan. Chevron continues to perform fenceline monitoring for SO_2 and has added fenceline monitoring of alkanes. Chevron does not plan to add fenceline monitors for 1,3-butadiene and ammonia.

SO_2

SO_2 will continue to be monitored by the existing UV-DOAS monitoring system and the Castro Street ground level monitor.

Alkanes or other organic compound indicators

Chevron has added monitoring for alkanes at the BAAQMD's suggestion for measuring refinery fugitive leak emissions from process units that do not emit BTEX compounds detectable on the UV-DOAS monitors. Chevron does not expect refinery alkane emissions to be regularly detected and rare detections will contain some ambient alkanes (Stephens and Burleson, 1969).The installed analyzers provide indication of emissions from process units that do not emit BTEX compounds, namely the Alkylation Unit, Liquid Petroleum Gas spheres and loading racks, and hydrogen plant.

The alkanes being monitored include methane, ethane, propane, butane, and pentane. Methane and alkane (C2 through C5) concentrations are reported on the website. C6 and greater are not measured, because process streams such as gasoline, naphtha, and crude containing C6 and greater also contain BTEX compounds, which are measured on the UV-DOAS monitors. Chevron has installed open-path Fourier Transform Infrared (FTIR) monitors for monitoring alkanes to accommodate the public's preference for open-path monitors. Chevron appreciates that open-path monitors span long distances around a refinery and are more likely than point monitors to capture a possible plume that may cross the fenceline. Chevron received a manufacturer's guarantee based on results of a study conducted in Atlanta, Georgia in December 2017 that an open-path FTIR with 500 meters path length will measure alkanes C2 through C4 at 200 ppb concentration with 75% accuracy at 2 vol% water vapor in ambient air. In the Atlanta study, at 800 meters path length and 1.1 vol% water in ambient air, water vapor did not cause interference in alkane measurements. Interpolation of data justifies the manufacturer's guarantee.

The FTIR monitoring technology has the ability to detect ambient methane and part per billion detection limits for C2 through C5 alkanes. Relevant equipment specifications are provided in Section 4 of this plan.

Existing measures for monitoring alkane and organic compound leaks

The systems do not serve as a first alert to Chevron of an alkane leak because Chevron has numerous systems in place for detecting an alkane leak. On most days, seven contracted individuals are monitoring background hydrocarbon concentrations and components in the refinery using Method 21. Method 21 is described in 40 Code of Federal Regulations Subpart 60 Appendix A-7. In accordance with Rule 8-18, Chevron repairs any source of a leak causing background concentration higher than 50 ppmv. Chevron Method 21 monitors light liquid pumps monthly, valves and pressure relief devices quarterly, and connectors annually. Leaks are typically repaired within 24 hours of discovery. Tank floating roof seals are inspected on a quarterly, semiannual, or annual basis per the requirements of BAAQMD Regulation 8, Rule 5. The liquid petroleum gas sphere area has five lower flammability limit (LFL) analyzers that alarm operators inside and outside the console when 5% of the LFL is detected. Chevron employees also wear personal LFL monitors while inside the process units that alarm at 5% of the LFL. All contractors entering Chevron process units are required to wear personal LFL monitors that sound an alarm at 5% of the LFL.

1,3-Butadiene

1,3-Butadiene is not produced as an intermediate or end product and is only present in trace quantities at the refinery. Chevron reports about 100 lb. per year of 1,3 butadiene emissions to the EPA in its annual Toxic Release Inventory Report. Chevron does not expect 1,3-butadiene to be present in measurable concentrations at the fenceline.

Ammonia

Chevron excludes ammonia from fenceline monitoring because it is not emitted in measurable amounts at the fenceline as anhydrous ammonia, which is BAAQMD's primary toxicity concern. Sources of ammonia leaks are not as prevalent as alkanes. Ammonia is produced at Refinery plants 8 and 18; however, it is otherwise isolated to three anhydrous ammonia vessels for storage/loading or use in small streams in process units, primarily for pollution control devices. Anhydrous ammonia is sold as a by-product. Anhydrous ammonia loading points are tightly sealed and closely monitored by operators as

explained below. Chevron's aqueous ammonia emission rates are already monitored through direct measurement in source tests submitted to BAAQMD. Aqueous ammonia reduces nitrogen oxide emissions from furnace stacks and filterable particulate emissions from the fluidized catalytic cracking unit (FCCU). Ammonia slip emissions from the FCCU have dramatically decreased following Regulation 6-5 compliance implementation.

Additionally, Chevron already has numerous systems in place, developed in cooperation with the City of Richmond, for preventing, detecting, and mitigating an anhydrous ammonia leak. The bulk of the refinery's anhydrous ammonia is kept in storage vessels near the ammonia loading rack and rail cars. Anhydrous ammonia is produced at 8 and 18 plants and consumed at the cogeneration units, FCC, hydrogen plant, and Richmond Lube Oil Project (RLOP). The ammonia storage vessels are elevated above normal vehicle height and surrounded by steel barricades to prevent a motor vehicle from puncturing a vessel. Chevron also documented in its Risk Management Plan that the ammonia storage vessels will not be filled more than 45 percent. Redundant high-level alarms sound at 41 percent and emergency alarms sound at 43 percent to ensure operators do not fill the ammonia storage vessels past 45 percent. Ammonia pumps are protected from cavitation by ensuring the ammonia storage vessels are at least 10 percent filled. Redundant low-level alarms sound at 15 percent and emergency low level alarms sound at 10 percent. As shown in Appendix A, anhydrous ammonia storage is located away from the refinery perimeter to minimize the effect on the public in the event of a release.

The ammonia storage area is equipped with excess flow valves and emergency block valves (EBV) to prevent or limit the severity of a release. EBVs are installed at the train loading racks' liquid and vapor lines, suction lines on the ammonia storage vessels, and on the common header. EBVs close with emergency shutdown switches, hand activation, and fusible plugs. When an EBV closes, the associated pumps are interlocked to shut down as well. Operators routinely test the EBVs.

In the event of a fire, each storage vessel is equipped with a firewater deluge system to scrub vapor from the atmosphere and cool the vessel. The fusible plugs on the EBVs cause the EBVs to close in the event of a fire. The ammonia storage area is encircled by a firewater-monitor fog system. One large water fog spray can be remotely operated. In the case of a leak, operators wearing air-supplying respirators, immediately begin mitigation by isolating the line where the leak is located, applying water spray, and/or shutting down the process unit.

Any significant release of ammonia would be detected by the refinery, and if off-site impacts are possible, this would be communicated by Chevron to the community via the Contra Costa County Community Warning System (CWS). Numerous ammonia sensors located throughout the refinery would alert operators if a leak would occur. If more than 100 lb. of ammonia are released in a 24-hr period, Chevron would immediately notify the Contra Costa County Health Services (CHS) Department on-call pager via the CWS as Level 1 and would call the Bay Area Air Quality Management District, the National Response Center, and the California Governor's Office of Emergency Services (COES). In the case of possible off-site health impacts, CHS would alert the community with sirens.

Lastly, Chevron voluntarily measures ammonia on three community monitors. The monitors collect 5-min average concentration data similar to fenceline monitors and post the 5-min average concentrations to a website. Since measurement began in 2014, ammonia concentration data through December 31, 2016, has been consistently well below the California health standards at all three community locations. **Figure 3.1** compares the community monitor data with health standards. Figure 3.1 shows that the maximum 1-hr

average concentration was less than four percent of the acute health standard. To determine the maximum 1-hr average concentrations for comparison with the acute health standard, 60-min averages were calculated for every five minutes of data from the community monitor's start of operation in 2014 through December 31, 2016. During periods that a chemical was not detected, one ppb was substituted for calculating the average concentration. The average concentration measured at each community monitoring station was less than two percent of the chronic health standard. The California Office of Environmental Health Hazard Assessment (OEHHA) publishes reference exposure levels (REL), which are health standards at https://oehha.ca.gov/air/general-info/oehha-acute-8-hour-and-chronic-reference-exposure-level-rel-summary. Lastly, as described in Section 2, compounds expected to be commonly emitted by refinery operations were required to be monitored at the existing fenceline monitors, of which ammonia was not selected.

Figure 3.1 – Comparison of Richmond Community Monitors 1-Hr Average Concentrations with Acute (1-Hr Average) OEHHA Health Standard
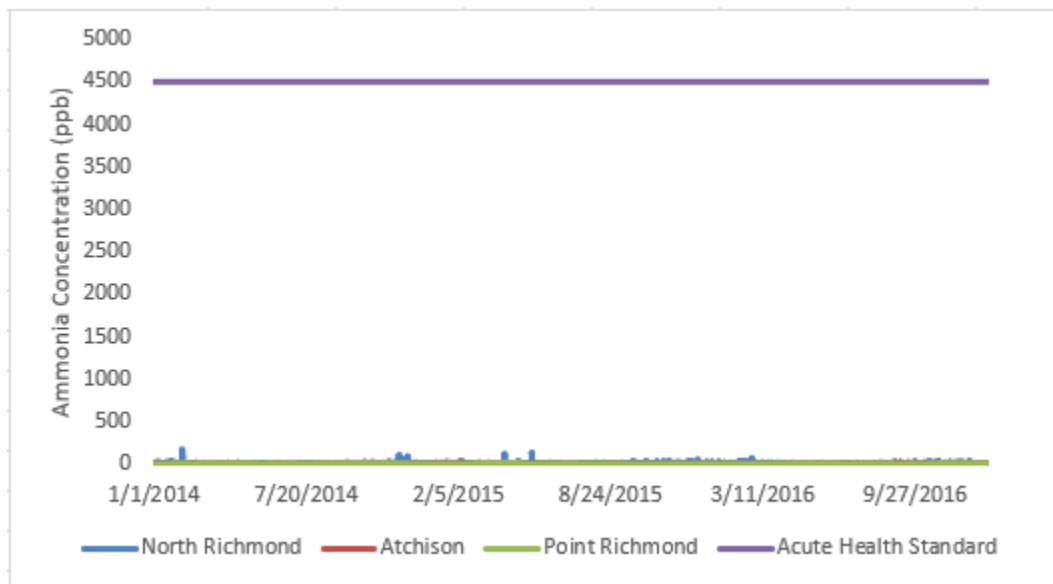

Table 3.1 summarizes the gases included in the Rule 12-15 fenceline air monitoring program and the equipment to be used to detect them.

Table 3.1 – Gases Included in the Fenceline Air Monitoring Plan

Gas	Equipment
Alkanes (C2 through C5)	Five open-path FTIRs
Benzene	Three open-path UV-DOAS instruments North Richmond community monitor Sorbent tubes at sample stations 6 and 7*
Ethylbenzene	Three open-path UV-DOAS instruments North Richmond community monitor
Hydrogen Sulfide	Five open-path TDLs Castro Street ground level monitor
Methane	Five Open-path FTIRs
Sulfur Dioxide	Three open-path UV-DOAS instruments Castro Street ground level monitor
Toluene	Three open-path UV-DOAS instruments North Richmond community monitor
Xylene	Three open-path UV-DOAS instruments North Richmond community monitor

*Sampled and analyzed in accordance with 40 CFR 63.658

Element #3 – Fenceline Coverage

This section describes the process used to determine where fenceline air monitoring equipment are installed and/or made part of the Rule 12-15 fenceline monitoring compliance program. In accordance with the Guidelines, wind rose analyses were completed to determine the monitor locations needed to cover populated areas within 1 mile of the refinery fenceline likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time or greater, given site topography.

Meteorological data collected from January 1, 2012, through December 31, 2016, from the Gertrude Meteorological Station, associated with the Rules 9-1 and 9-2 ground level monitors, were used to generate the wind roses in **Figures 3.2 and 3.3** and summary in **Table 3.2**. Figure 3.2 compares the 2016 wind rose with the five-year wind rose to show a consistent wind pattern with wind primarily blowing from the south. Wind occurred greater than 10% of the time from 0 degrees north and from 135 degrees to 225 degrees. Thus, the Guidelines suggest monitoring for Rule 12-15 in the arc from 292.5 degrees to 67.5 degrees and in the arc from 157.5 degrees to 202.5 degrees if there are receptors downwind of sources within 1 mile of the refinery fenceline, depending upon site topography.

Figure 3.2 – Wind Rose (1/1/12 – 12/31/16) Consistent Wind Pattern Primarily from South
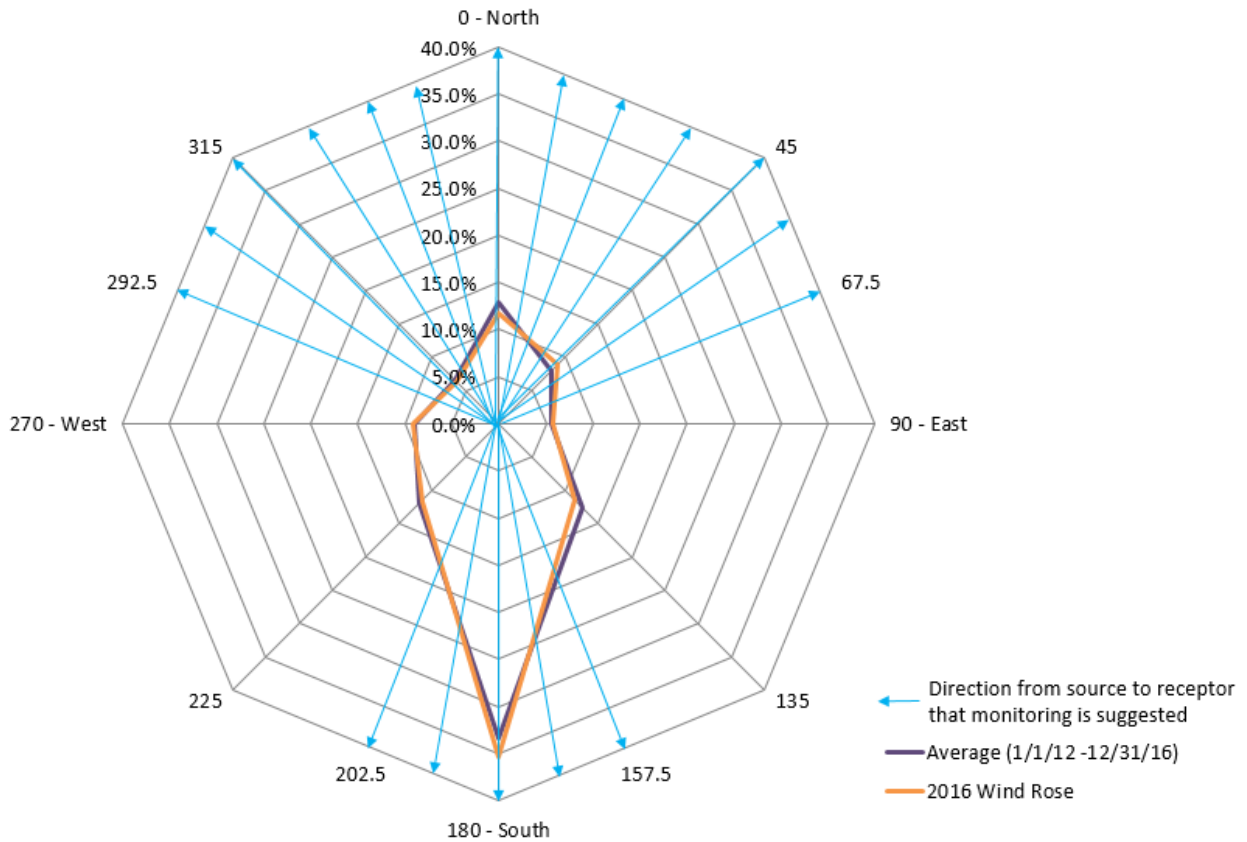
Figure 3.3 contains a wind rose of winter winds from November 1 through February 15 in the years 2012 through 2016. This figure shows winds blowing primarily from the north and northeast during winter months. The wind direction is from 0 degrees north through 90 degrees east more than 10% of the time during winter months. Per the guidelines, fenceline monitoring coverage should be considered in the arc between 157.5 and 292.5 degrees if there are receptors downwind from sources within one mile of a receptor, depending upon site topography.

Figure 3.3 – Winter Wind Rose (2012-2016): Wind Primarily from North/Northeast
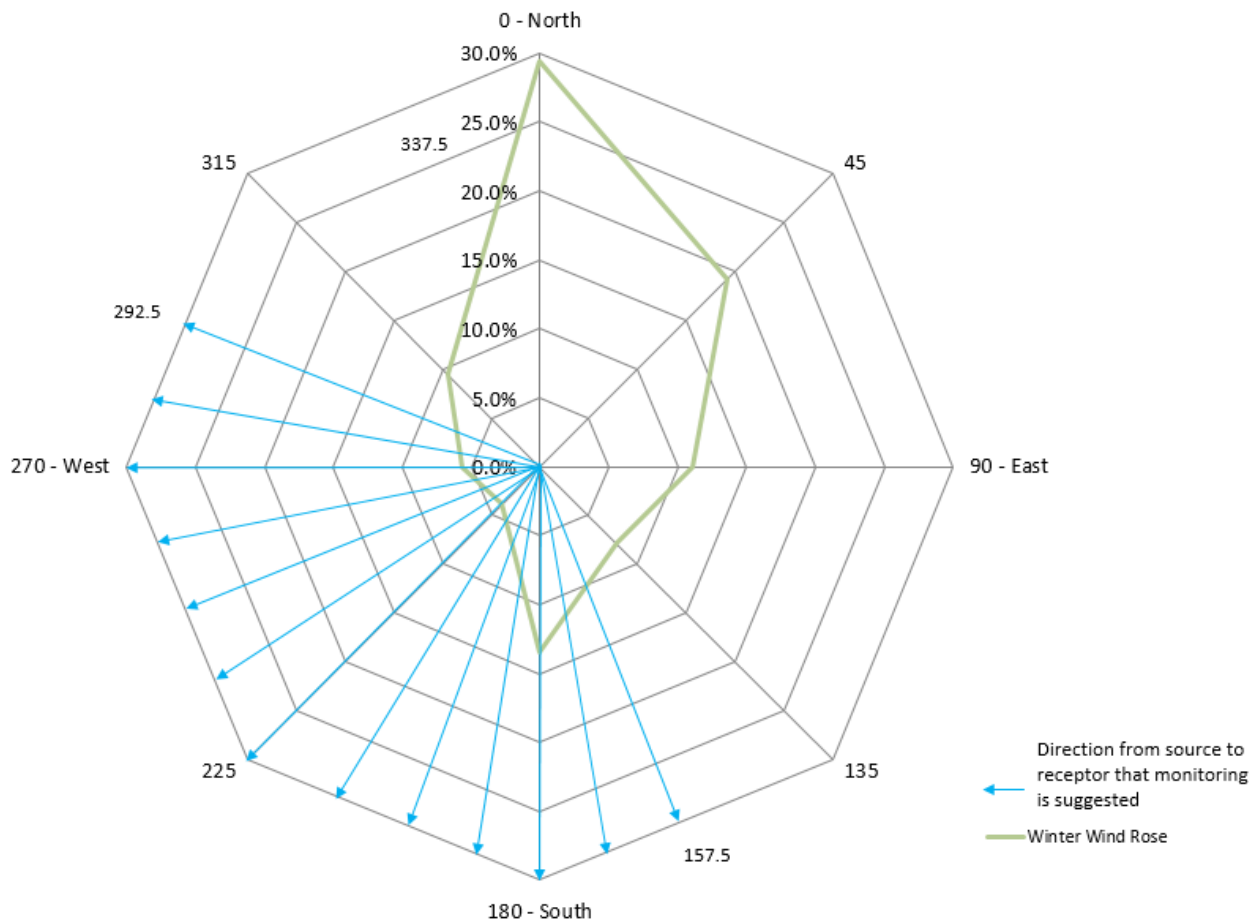
Based on the wind rose analyses, the Guidelines suggest some additional fenceline monitor coverage beyond the pre-existing RCAMP fenceline monitors. As described in Section 2, the existing fenceline monitor open-path locations were already agreed upon with the City of Richmond and developed in cooperation with local neighborhood councils. In adhering to this agreement, Chevron aims to either keep the monitors in the same locations or expand the path to capture more sources. **Table 3.2** shows the percentage of time that wind blew from each wind rose sector. Sectors where wind blows in that quadrant greater than 10% of the time are highlighted in blue.

Table 3.2 – Additional Monitors Based on Wind Rose Analyses

Direction From	Range (Degrees)	Percent	Coverage on Existing Public Website
North	337.5-22.5	12.61%	Partial coverage by Point Richmond open-path UV-DOAS, FTIR, and TDL
Northeast	22.5-67.5	7.68%	Southwest refinery perimeter is not populated
East	67.5-112.5	5.49%	West refinery perimeter is not populated
Southeast	112.5-157.5	12.68%	Northwest refinery perimeter is not populated
South	157.5-202.5	33.74%	North refinery perimeter is not populated
Southwest	202.5-247.5	12.18%	• Atchison Village and North Richmond open-path UV-DOAS, FTIR, and TDL • North Richmond community monitor • Benzene sorbent tube sample at stations 6 and 7 • Castro Street ground level monitor
West	247.5-292.5	9.04%	• Atchison Village and North Richmond open-path UV-DOAS, FTIR, and TDL • North Richmond community monitor • Benzene sorbent tube sample at stations 6, 6D, and 7 • Castro Street ground level monitor
Northwest	292.5-337.5	6.59%	Atchison Village and Point Richmond UV-DOAS, FTIR, and TDL open-path monitors

Based on the 2012 through 2016 wind rose analysis, the monitors cover populated areas within 1 mile of the refinery fenceline likely to be affected when the annual mean wind direction lies in an arc within 22.5 degrees of a direct line from source to receptors 10% of the time or greater, given site topography. Refinery emission sources, and existing air monitoring equipment, are shown on a map of the refinery in Appendix A. The open-path monitors are located south, east, and northeast of refinery processes in between the processes and populated areas. The North Richmond open-path monitors are located northeast of the refinery. The Atchison Village open-path monitors are located east of the refinery. The Point Richmond open-path monitors are located south/southeast of the refinery. The map shows that the refinery is surrounded on the north, west, and southwest parts of the refinery by large water bodies, which are not populated.

Chevron has installed open-path FTIR, UV-DOAS, and TDL analyzers and retroreflectors along the North Richmond, Point Richmond, and Atchison paths. The path lengths for the UV-DOAS, TDL, and FTIR paths are provided in **Table 3.3**. Because intermediate paths (e.g., F1 and F2) are close to but not exactly the same as the overall path (e.g., path F), the distances may not be exactly the same.

Table 3.3 – Fenceline Open-Path Lengths

Fenceline[1]	Path Designation	Open-Path Equipment	Approximate Path Length (meters)
North Richmond	D	UV-DOAS, TDL, FTIR	692
Atchison	E	UV-DOAS	791
Atchison (North)	E1	FTIR, TDL	415
Atchison (South)	E2	FTIR, TDL	376
Point Richmond	F	UV-DOAS	899
Point Richmond (East)	F1	FTIR, TDL	497
Point Richmond (West)	F2	FTIR, TDL	400

Chevron has included measurements from benzene sample stations 6 and 7, the Castro Street ground level monitors, and the North Richmond community monitor BTEX measurements in the Rule 12-15 program. **Figure 3.4** provides a visual summary of the monitoring locations that are part of Rule 12-15 compliance.

Figure 3.4 – Locations of Rule 12-15 Monitors
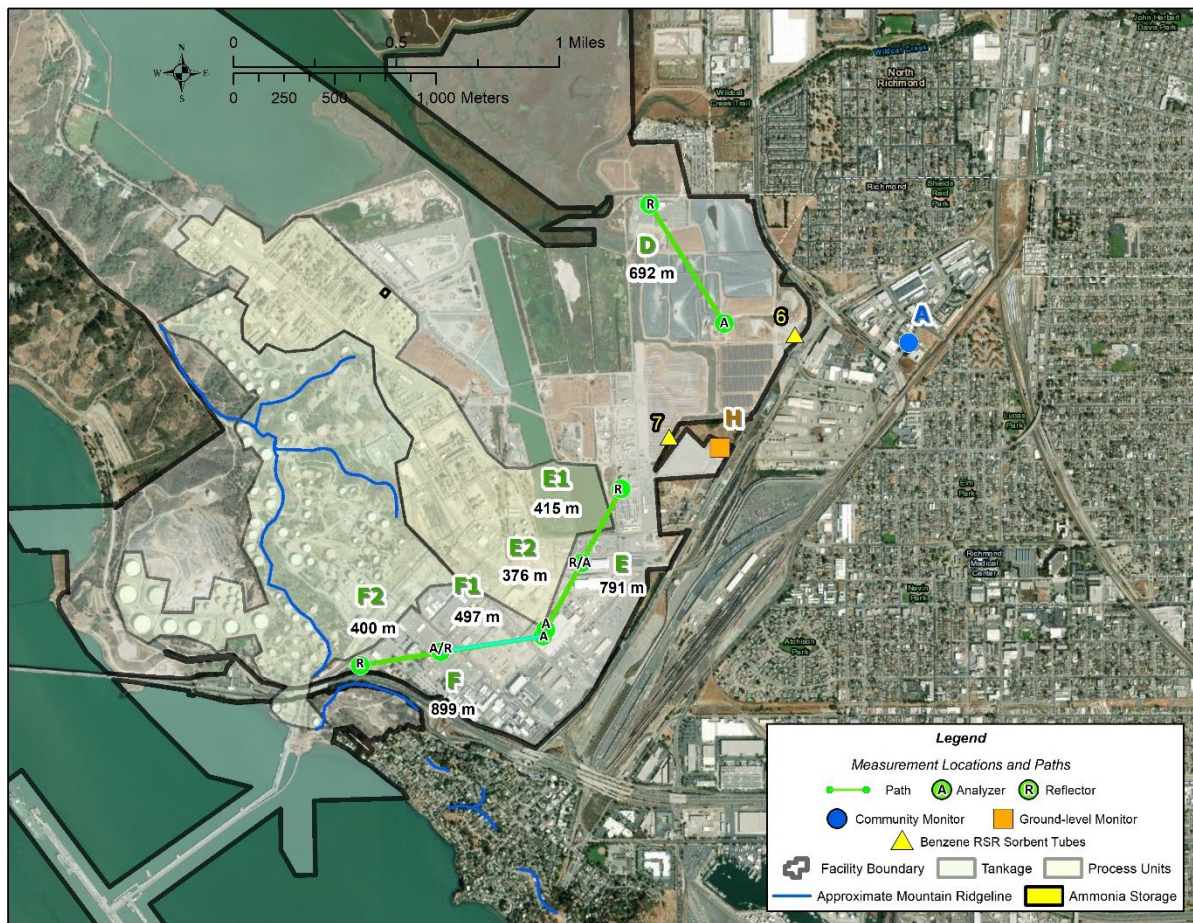
The City of Richmond was interested in capturing emissions from as many refinery sources as possible, including elevated sources, such as flares and furnaces. At BAAQMD's suggestion, Chevron moved the

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[1] FTIR and TDL instruments cover path E and F via subpaths E1, E2, F1, and F2

Point Richmond open-path monitors to a lower elevation so that fugitive emissions are primarily measured. The manufacturers of the open-path analyzers (Cerex for the UV-DOAS and FTIR, and Unisearch for the TDL), who are experienced with operating and maintaining the monitors, indicated that the current minimum detection limits for BTEX, SO_2, and H_2S should be achievable at the path lengths installed. Flare and furnace stack emissions are already measured continuously with sampling systems, flow meters, and stack analyzers. Most fugitive emissions are measured at each component periodically using Method 21, but site-wide fugitive emissions can only be measured continuously with fenceline monitors. Thus, the BAAQMD is primarily interested in using the fenceline monitors to measure fugitive emissions, which occur near ground level.

During winter winds from the north, the Point Richmond and Atchison Village open-path monitors provide the suggested monitoring coverage when terrain is considered. Due to the mountainous terrain and presence of the Interstate 580 freeway, it is not practicable to install an open-path monitor west of the Point Richmond monitor. Appendix A shows a mountain ridge line southwest of the Point Richmond open-path monitor that is expected to direct wind from refinery tanks away from receptors. It is expected that for the tanks located northwest of the Point Richmond open-path monitor and to the west of the mountain ridge that runs north-south, the mountains would cause wind across the tanks to move westward away from the community. It is expected that for the tanks located northwest of the Point Richmond open-path monitor and to the east of the mountain ridge that runs north-south, the mountains would cause wind across the tanks to pass through the Point Richmond open-path fenceline monitor. Also, the tanks are compliant with Rule 8-5 storage-vessel requirements, which limit organic compound emissions. The seals are inspected at least semiannually to verify proper function of the emission control technology. It is expected that a potential seal leak from a tank located northwest of the Point Richmond open-path monitor would be detected on the Point Richmond open-path monitor, because wind direction varies throughout the day.

Monitoring coverage is not needed for wind directions from the northeast, east, southeast, and south because the downwind areas are not populated.

Monitoring coverage between the North Richmond and Atchison open-path monitors are fulfilled with point monitors. The following point monitors are part of the Rule 12-15 compliance program.

- Castro Street ground level monitor fulfills H_2S and SO_2 monitoring
- One sorbent tube at each sample station 6 and 7 fulfills suggested benzene monitoring
- North Richmond community monitor fulfills benzene, ethylbenzene, toluene, and xylene monitoring

The two sorbent tube samples will continue to be analyzed for benzene at frequencies specified in 40 CFR 63 Subpart CC. In April 2019, the EPA began reporting benzene sorbent tube data over a public website on a quarterly basis. The link to the EPA website is: https://cfpub.epa.gov/webfire/reports/eSearchResults.cfm. To access the Chevron Richmond data, enter or select the following search criteria:

- Report Type: All, then Submit
- Facility Name: Chevron
- Facility Location: California, Contra Costa County, Richmond
- Regulatory Part and Subpart:

- o CFR Part: 63-NESHAP
- o CFR Subpart: NESHAP-CC: Petroleum Refineries

Next, submit the search. Once the search results appear, select the row with the submission date of interest and download the file in the document column.

5-min average Castro Street GLM data and 5-min average North Richmond community monitor data are posted to the public website.

The only sources located within one mile upwind of a receptor greater than 10% of the time that are between the North Richmond and Atchison monitors are the bioreactor and two recovered oil storage tanks. We expect that the Atchison open-path monitor, which crosses the bioreactor, or North Richmond open-path monitor typically catches any possible plumes from these sources. However, in the rare instance when wind direction is between the North Richmond and Atchison open-path monitors, it is expected that the previously mentioned point monitors will measure possible emissions.

A review of ten years of GLM reports showed that Chevron has not caused exceedance of the sulfur dioxide ground level concentration limits in Rule 9-1-301 or the H_2S limits in Rule 9-2-301 at the Castro Street GLM. Additionally, the GLM has much lower detection limits than open-path monitors. The GLM's detection limit for H_2S is about 0.5 ppb, while the Unisearch TDL open-path monitor's detection limit or limit of quantitation (LOQ)[2, 3] for H_2S is 3-25 ppb. The GLM's detection limit for SO_2 is also about 0.5 ppb, while the Unisearch TDL open-path monitor's detection limit for SO_2 is about 0.5 ppb.

Analyses of sorbent tubes installed in preparation for compliance with 40 CFR 63.658 indicate that benzene concentrations at sample stations 6 and 7 along the fenceline between the North Richmond and Atchison open-path monitors are much lower than the OEHHA chronic health standard of 3 $\mu g/m^3$. Sorbent tubes were replaced and analyzed for benzene approximately every 14 days. Sorbent tube data available to date for sample points 5 through 8 located between and nearby the North Richmond and Atchison open-path monitors are provided in **Table 3.4**. The refinery map in Appendix A shows the sorbent tube locations. Sample point 5A located on refinery property near the heavy traffic intersection of Gertrude, Castro, and Richmond Parkway had the highest readings of all the sample points in the refinery. The benzene concentrations decreased when the sample station was moved closer to the refinery processes around March 7, 2017. The current location is labeled as sample point 5. The elevated results at sample point 5A were attributed to off-site sources, likely traffic congestion at the Gertrude intersection or nearby off-site excavation of contaminated soil.

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[2] December 22, 2022, letter from BAAQMD, the LOQ is taken to be equivalent to the MDL. For the TDL, the MDL is calculated as twice the standard deviation of a blank sample
[3] Bovee, J. "Refinery Fenceline H_2S TDL Monitoring System Specifications," Communication to Chevron, December 22, 2022.

Table 3.4 – **Benzene Sorbent Tube Results Are Within OEHHA Chronic Health Standard**

Sample Start Date	Sample End Date	Sample Point / Benzene Concentration* (ug/m³)				
		5A	**5**	**6**	**7**	**8**
7/27/2016	8/10/2016	0.19		Not Detectable	0.18	Not Detectable
8/10/2016	8/24/2016	0.18		0.24	0.25	0.20
8/24/2016	9/7/2016	0.36		0.38	0.29	0.40
9/7/2016	9/21/2016	0.52		0.34	0.38	0.29
9/21/2016	10/5/2016	0.69		0.52	0.51	0.52
10/5/2016	10/19/2016	0.68		0.44	0.46	0.41
10/19/2016	11/2/2016	0.97		0.57	0.60	0.55
11/2/2016	11/16/2016	2.41		0.96	0.75	0.77
11/16/2016	11/30/2016	1.34		0.67	0.79	0.76
11/30/2016	12/14/2016	1.44		0.65	0.64	0.71
12/14/2016	12/28/2016	0.94		0.63	0.63	0.58
12/28/2016	1/11/2017	1.03		0.85	0.48	0.50
1/11/2017	1/25/2017	1.09		0.62	0.64	0.60
1/25/2017	2/8/2017	1.07		0.65	0.58	0.59
2/8/2017	2/22/2017	0.86		0.49	0.44	0.55
2/22/2017	3/8/2017	1.04		0.51	0.49	0.55
3/8/2017	3/22/2017		0.44	0.46	0.40	0.41
3/22/2017	4/5/2017		0.38	0.34	0.31	0.44
4/5/2017	4/19/2017		0.34	0.33	0.30	0.38
4/19/2017	5/3/2017		0.26	0.28	0.28	0.29
5/3/2017	5/17/2017		0.21	0.20	0.21	0.23
5/17/2017	5/31/2017		0.17	0.21	0.18	0.22
5/31/2017	6/14/2017		0.20	0.18	0.19	0.25

* Values less than 0.37 are less than the analytical reporting limit, but greater than the method detection limit.

Lastly, Chevron continues to operate the existing North Richmond community monitor, located at Richmond Fire Station 62 on 7th Street, to deliver BTEX data to meet Rule 12-15 needs. The North Richmond community monitor is located downwind of the refinery when wind is from the west or southwest. The monitor also measures H_2S, ammonia, several alkanes, trimethylbenzenes, 3-methylpentane, 2,2,4-trimethylpentanes, $PM_{2.5}$, and black carbon. All data from the North Richmond community monitoring station is posted at https://www.richmondairmonitoring.org/index.html.

Table 3.5 shows that BTEX concentrations measured at the North Richmond community monitor for any wind direction are far below OEHHA acute health standards. The North Richmond community monitor collects 5-min average concentration data and posts the 5-min averages to the website similar to fenceline monitors. To determine the maximum 1-hr average concentrations for comparison with the acute health standard, 60-min averages were calculated for every five minutes of data from January 1, 2014, through December 31, 2016. During periods that a chemical was not detected, one half the detection limit of 0.25 ppb was substituted for calculating the average concentration. The table shows that the maximum 1-hr average concentration was equal to 34% (2.75 ppb 1-hr average/8 ppb acute health standard) of a health standard.

Table 3.5 shows that BTEX concentrations measured at the North Richmond community monitor for any wind direction are far below OEHHA chronic health standards. To determine the average concentration for comparison with the chronic health standard, all 5-min average data was averaged from January 1, 2014, through December 31, 2016. During periods that a chemical was not detected, one half the detection limit of 0.25 ppb was substituted for calculating the average concentration. The table shows that for the worst-case chemical (benzene), the average concentration was about 25% (0.25 ppb average/1 ppb benzene of the chronic health standard) of a chronic health standard.

Given the data in Table 3.5, Chevron does not expect BTEX to be regularly detectable by an open-path fenceline monitor between the North Richmond and Atchison open-path monitors and does not expect any exceedance of a health standard. The community monitor is more sensitive than open-path fenceline monitors, and only half a mile downwind (westerly wind) from the North Richmond fenceline.

Table 3.5 – North Richmond Community Monitor Data Are Within Health Standards
**(1/1/2014 – 12/31/2016)**

Chemicals	Maximum 1-Hr Average Concentration (ppb)	Acute OEHHA REL (ppb)	Average Concentration (ppb)	Chronic OEHHA REL (ppb)
Benzene	2.75	8.6	0.25	1
Ethylbenzene	12	None published	0.25	400
Toluene	111	1,328	0.30	70
Xylenes	65	5,000	0.57	200

Element #4 – Sample Time Resolution and Data Completeness

Fenceline continuous monitoring equipment specified for the Chevron fenceline system collects data on 5-min averages and report the 5-min averages. Instruments are operated to meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters. Atmospheric conditions beyond the control of the refinery that affects accurate measurements, such as dense fog, are not counted against data completeness requirements. In addition to rain and fog, other types of environmental conditions beyond the control of the refinery can occur. These environmental factors include but are not limited to strong winds, dust, and earthquakes, which can impact the ability of open-path instruments' ability to provide accurate measurements.

Element #5 – Data Presentation to the Public

Data from the fenceline monitors are transmitted to an Internet website where near-real-time results can be viewed by the public. **Figure 3.5** shows the home page of the fenceline webpage, located at
https://www.richmondairmonitoring.org/index.html.

Figure 3.5 – Sample Real-Time Fenceline and Community Air Monitoring Webpage
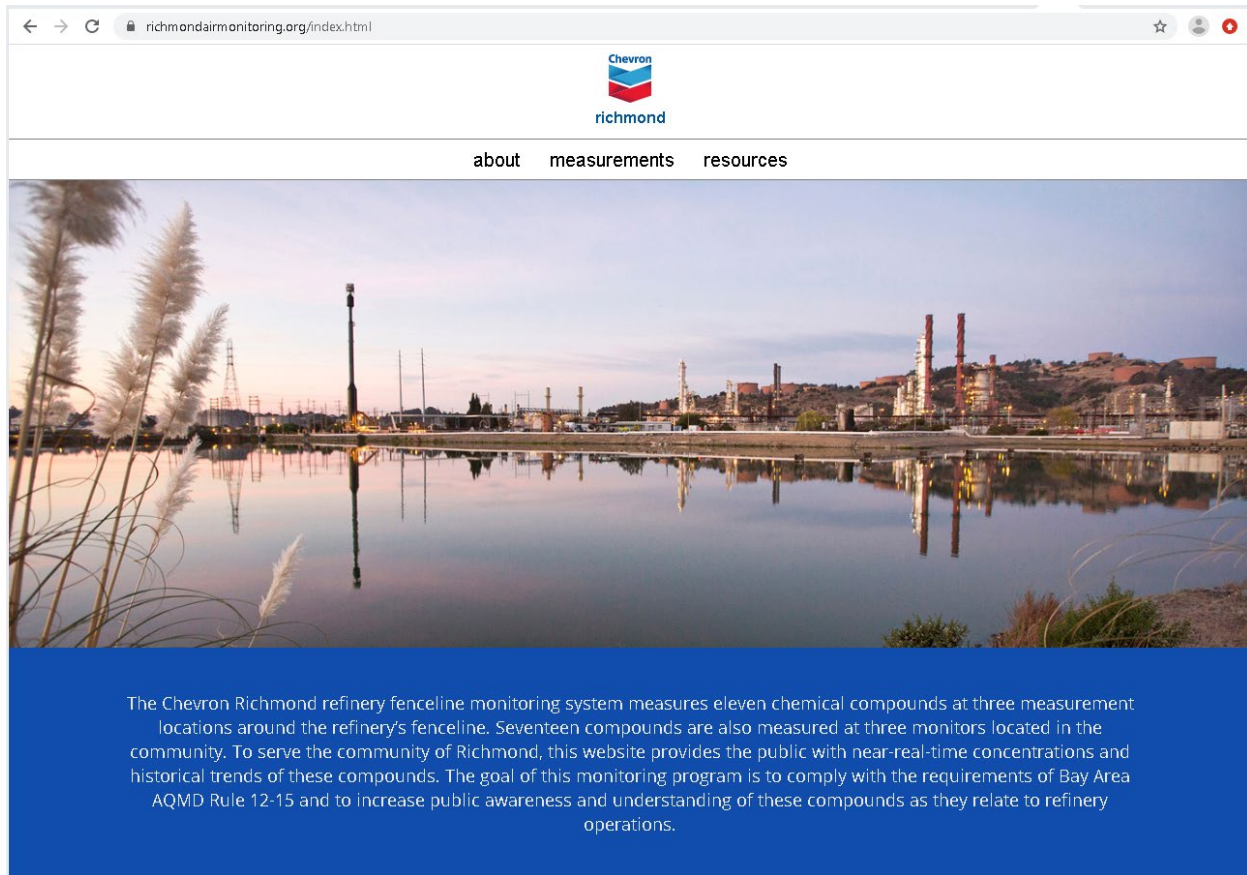
Data generated by the fenceline monitoring equipment undergoes review throughout the measurement and reporting process. Included in this process are automated QA/QC checks that occur before data are reported on the real-time website. Under normal circumstances a 5-min average measurement appears on the website within 10 minutes of the end of the measurement period. However, the data uploaded may be impacted by Internet traffic. An automated system conducts the Quality Assurance checks listed in **Table 3.6** before the data are reported to the website. The website also makes available a rolling 1-hr trend of the 5-min data for each gas reported.

Final data sets are compiled quarterly and will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter. Data deliveries are consistent with BAAQMD guidance and additional details are provided in Section 5 of the QAPP. The BAAQMD may make data available to the public through a BAAQMD website or through public records request. The refinery will make data available to BAAQMD upon request prior to the report submittal. All data are retained by Chevron for a period of five years, consistent with Regulation 12-15-502.

Table 3.6 – Response to Potential Monitor Problems

Potential Problem	Response
Analyzer has low signal (integration time >250 ms for UV, <2% for IR, or <0.1 mW [<1% transmission] for TDL)	Website updated with low signal message for specific analyzer. If the low signal is not due to weather conditions, a Field Technician corrects the issue.
Analyzer off-line	Website updated with analyzer off-line message. Field Technician corrects issue.
Workstation fails	Website updated with analyzer off-line message. Technician corrects the issue.
Internet communication failure	Backup Internet connection activated

Figure 3.6 shows an example page from the website that appears when a person clicks the Compounds page of the Resources section of the website. The web page describes the chemical's properties, common sources of the chemical, and links to the OEHHA health standards.

Figure 3.6 – **Example Website Display of Compound Descriptions and Resources**

Additional information is available on the website to help the public understand how the fenceline monitoring system works and to help explain the data. Fenceline monitor locations, how the locations were selected, and descriptions of equipment used are included. Context of what fenceline measurements

represent as compared to other regional air quality measurements, as outlined by BAAQMD, are provided on the website.

To facilitate public feedback, a feedback button is provided on the resources page of the website. When a user clicks on the button, an email form pops up for the user to submit comments about the website. The email is delivered to a Chevron contact or a designated consultant responsible for deciding how to respond to the public comments. The emails received through the website are archived. Although not all comments have to be addressed, all comments are made available to BAAQMD upon request. Some of the comments will aid in the creation of frequently asked questions to be published on the website.

Element #6 – Quality Assurance Project Plan

An updated QAPP is included with this monitoring plan as Appendix B.

Section 4.   Monitoring Equipment Description

The fenceline monitoring program for Rule 12-15 integrates the equipment currently used as part of RCAMP along with additional equipment to monitor additional target gases, namely alkanes, and extend spatial coverage. This equipment used to meet the monitoring requirements for Rule 12-15 are described below.

Section 4.1 – Fundamentals of Operation

The following paragraphs describe how the equipment measures compound concentrations. Open-path monitors report average concentration over the path length. Point monitors measure the concentration at the point of the monitor's intake line.

Castro Street Sulfur Dioxide and Hydrogen Sulfide Pulsed Fluorescence GLMs

The sulfur dioxide and H_2S GLMs comply with the BAAQMD Manual of Procedures Volume VI. The sulfur dioxide GLM is a trace level pulsed fluorescence sulfur dioxide analyzer. The analyzer operates by measuring the emitted fluorescence of SO_2 produced by the absorption of ultraviolet (UV) light. Pulsating UV light is focused through a narrow band-pass filter mirror allowing only
light wavelengths of 190 to 230 nm to pass into the fluorescence chamber. SO_2 absorbs light in this region without any quenching by air or most other molecules found in ambient air. The SO_2 molecules are excited by UV light and emit fluorescence light at a longer wavelength (lower energy). A second filter allows only this fluorescent light to contact a photomultiplier tube (PMT). The PMT converts the optical signal from the fluorescent light into a voltage that is recorded and turned into a concentration value.

The H_2S GLM operates using similar technology as the GLM SO_2 analyzer. Continuous H_2S monitoring is accomplished by conversion of the H_2S in the sample to SO_2 and its subsequent detection by the SO_2 analyzer.

North Richmond Community Monitor Auto Gas Chromatograph

Automated Gas Chromatographs are point sampling technologies. The systems work by inserting a sample of ambient air into a narrow tube known as the column. A carrier gas flows through the column and carries the sample through the column; depending on the chemical composition, the various sample gases exit the column at different times. As the chemicals exit the end of the column, they are detected

using a photoionization detector. The major advantage of the Auto GC air monitoring system is its sensitivity in that it can measure gases such as BTEX at very low concentrations in the air.

Open-Path FTIRs

Open-path FTIR air monitoring systems use a beam of infrared (IR) light to detect and measure alkanes in the air. A beam of light passes across ambient air to a reflector that sends the light beam back to the light detector. If a gas is present that absorbs IR light, it can be identified by the specific wavelengths of light that were absorbed. The concentration of a gas can be determined by measuring the amount of each specific wavelength of light that was absorbed. The primary interferents associated with FTIR air monitoring systems are water vapor and carbon dioxide (CO_2) gas. The two gases absorb light in the same region as alkanes and can be mistaken for the target gas. Also, due to the similarity in chemical structure, the C1 through C5 alkanes absorb light in a similar region and may interfere with measurements of total alkanes. However, the presence of potentially interfering gases can be accounted for through the analytical software of the system.

Open-path FTIRs can theoretically achieve lower detection limits than extractive FTIRs because the beam path is much longer. The primary limitations for these systems are that the light signal cannot penetrate heavy fog or rain. Thus, they may not be effective during situations where dense fog or heavy rain are present.

Open-Path TDLs

Open-path TDLs are similar to open-path FTIR air monitoring systems in that they use beams of infrared light to measure gases. The primary difference between the two systems is the TDL system uses a laser as its light source whereas a FTIR uses a broad band beam of light as its source. TDL systems are designed to measure a limited number of gases, which, for this application, are H_2S, CO_2, and water vapor. The primary interferents for the H_2S measurement are water vapor and CO_2 because both absorb light in the same region as H_2S. The primary limitation for the system is that the light signal cannot penetrate heavy fog or rain.

Open-Path UVs

The open-path UV system differs from the open-path FTIR and TDL systems in two major ways. First the system has a light source at one end of the path that sends a beam directly to the light detector at the other end of the light beam. The other difference is that the system uses ultraviolet light as a light source. The open-path UV air monitoring system is used to detect BTEX and sulfur dioxide. The primary interferents associated with the UV air monitoring systems are ozone and oxygen gas because both absorb light in the same region as the target gases. However, the presence of these gases can be accounted for with the system's analytical software. The primary limitation for the systems is that the light signal cannot penetrate heavy fog or rain.

Sorbent Tubes

Sorbent tubes placed approximately six feet above ground level absorb benzene, if present, from the ambient air during the sampling period, which is about 14 days. The sorbent tubes are installed at locations along the refinery perimeter specified in 40 CFR 63 Appendix A Method 325A Section 8.2. The tubes are analyzed in a laboratory at the end of the sampling period in accordance with 40 CFR 63

Appendix A Method 325B. The sorbent tubes are placed in shelters similar to **Figure 4.1** to protect them from rain. Thus, the tubes can provide average benzene concentrations in the ambient air during nearly all weather conditions including fog, the exception for periods of extremely high winds with rain. The sorbent tube method also achieves benzene concentration measurements at concentrations lower than open-path monitor minimum detection levels.

Figure 4.1 – Benzene Sorbent Tube and Shelter
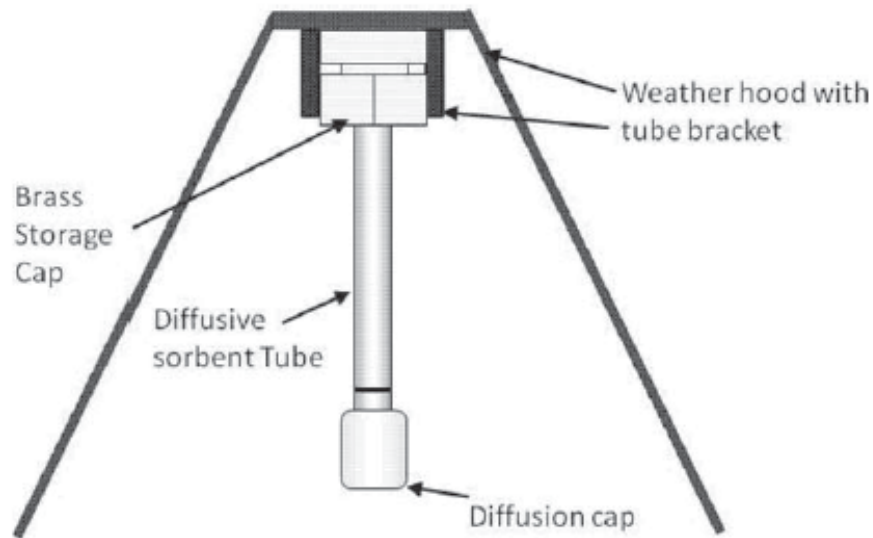
Section 4.2 – Monitoring Equipment Capabilities

Table 4.1 summarizes monitoring equipment capabilities, interferences, limitations, and measurement errors.

Table 4.1 – Monitoring Technology Capabilities, Interferences, Limitations, Measurement Errors

Equipment	Capabilities	Interferences	Limitations	Measurement Errors
Sorbent tubes	Absorbs benzene from ambient air, if present, at a point over approximately 14-day periods; Lower detection limit than open-path monitors	Sorbent artifacts, Water (rain)	Heavy rains with high winds; Continuous reporting not possible	Within 30% (Per 40 CFR 63 Appendix A Method 325B Section 9.7)
North Richmond Community Monitor Auto Gas Chromatograph	Measures BTEX continuously at a point with lower detection limit than open-path monitors	--	Measures at point vs. open-path	Within 25%
Open-path FTIR	Measures alkanes across an open path continuously; Likely lower detection limit than extractive FTIR	Water (humidity), CO_2, and C2-C5 alkanes may interfere with each other	Heavy Fog and Rain	Within 25%; Uses Single Regression Analysis to quantify data
Open-path UV-DOAS	Measures BTEX and SO_2 across an open path continuously	Ozone and oxygen	Heavy Fog and Rain	Within 25%; Uses Single Regression Analysis to quantify data
Open-path TDL	Measures H_2S continuously across an open path	H_2O and CO_2	Heavy Fog and Rain	Within 15%[a]
Castro St. GLM H_2S and SO_2 Pulsed Florescence Analyzers	Measures H_2S and SO_2 at a point continuously; Lower detection limit than open-path monitors	High concentrations of hydrocarbons; Mercaptans interfere with H_2S measurement	Measures at a point vs. open path	Within 10% for SO_2, within 15% for H_2S (BAAQMD MOP Volume VI)

[a] For the TDL, accuracy (measurement error) specifications will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions.

Section 4.3 – Detection Range

Table 4-4 in Appendix B summarizes the expected detection ranges of the open-path monitors. Alkane detection ranges are based on an initial study conducted in Atlanta, Georgia, in December 2017. The alkane detection ranges shown are accurate when multiple alkanes are present. The detection ranges are much wider if only an individual alkane is present. As mentioned previously, the FTIR should always show methane readings greater than 1,800 ppb due to the inherent presence of methane in the ambient air.

Table 4.2 lists the messages displayed on the public website that outline the conditions and detection limits for the pollutants measured in this program.

Table 4.2 – Messages Displayed on the Website with Each Compound and Data Value
(Hover Over the Data Point to View the Message)

Condition	Message
Valid	X parts per billion of Compound Y were measured at this location
Below detection	The concentration of the compound is so low that the instrument cannot accurately detect it.
Questionable	No additional information available. Pending further review.
Missing	A problem (such as power failure, calibration, etc.) prevented the instrument from collecting or reporting the data.
Invalid	No additional information available. Pending further review.
Not Measured	There is no instrumentation at the given site to measure this chemical.

The minimum detection limit of the sorbent tubes is dependent upon several analytical factors, including the presence of moisture. The minimum detection limit for benzene is typically 0.07 ug/m^3, equivalent to 0.02 ppb, while the minimum reporting limit, which is the lowest end of the calibration range is typically 0.37 ug/m^3, equivalent to 0.12 ppb. The minimum detection limit of the Castro Street GLMs and North Richmond BTEX community monitor is 0.5 ppb for each compound.

Section 4.4 – Monitoring Equipment Locations

Table 4.3 lists the locations of the fenceline monitoring equipment.

Table 4.3 – Monitoring Equipment Locations

ID	Fenceline Name	Equipment	Approx. Elevation (ft agl)	Location
D	North Richmond	UV analyzer; TDL & FTIR analyzers (D)	28.5	Next to Gertrude GLM
D	North Richmond	UV source; TDL & FTIR reflectors (D)	23	Near Maintenance Building
6	North Richmond	Sorbent tube site 6	5	Reclamation Yard Gate to Castro St.
6D	North Richmond	Sorbent tube site 6D	5	Reclamation Yard Gate to Castro St.
A	North Richmond Community Monitor	Auto-gas chromatograph	13	Fire Station #62
7	Atchison Village	Sorbent tube site 7	5	Solar-panel field
H	Atchison Village - Castro GLM	Pulsed fluorescence analyzers	8	Gate 91
E	Atchison Village	UV source (E)	38.5	Parking lot south of RARE Plant

ID	Fenceline Name	Equipment	Approx. Elevation (ft agl)	Location
E1	Atchison Village	FTIR & TDL reflectors (E1)	38.5	Parking lot south of RARE Plant
E1/E2	Atchison Village	FTIR & TDL analyzers (E1); FTIR & TDL reflectors (E2)	37	Next to Warehouse 8
E2	Atchison Village	FTIR & TDL analyzers (E2)	64.5	Top Level Roof of Lube Plant
E	Atchison Village	UV analyzer (E)	64.5	Top Level Roof of Lube Plant
F	Point Richmond	UV analyzer (F)	31.5	Near SW Corner of Lube Plant Roof
F1	Point Richmond	FTIR & TDL analyzers (F1)	31.5	Near SW Corner of Lube Plant Roof
F1/F2	Point Richmond	FTIR & TDL reflectors (F1); FTIR & TDL analyzers (F2)	37.5	Next to Permits Office
F2	Point Richmond	FTIR & TDL reflectors (F2)	23.5	Hill SW of Chevron Fire Department
F	Point Richmond	UV source (F)	23.5	Hill SW of Chevron Fire Department

Section 5. Timing

Chevron reports near real-time data over a website from open-path TDL, UV-DOAS, and FTIR monitors. The operation of these instruments will be conducted in accordance with this Plan pursuant to the timing requirements in Rule 12-15.

Section 6.   References

Bay Area Air Quality Management District (2016) Air monitoring guidelines for petroleum refineries: Air District Regulation 12, Rule 15: Petroleum Refining Emissions Tracking; April. Available at http://www.baaqmd.gov/~/media/files/planning-and-research/public-hearings/2016/9-14-and-12-15/042016-hearing/1215-amg-041416-pdf.pdf?la=en.

Edgar R. Stephens & Frank R. Burleson (1969) Distribution of Light Hydrocarbons in Ambient Air, *Journal of the Air Pollution Control Association, 19:12, 929-936*, doi: 10.1080/00022470.1969.10469359, https://doi.org/10.1080/00022470.1969.10469359

APPENDIX A

Wind Roses and Refinery Map of Fenceline Monitoring Equipment

Figure 3.2 – Wind Rose (1/1/12 – 12/31/16) Consistent Wind Pattern Primarily from South
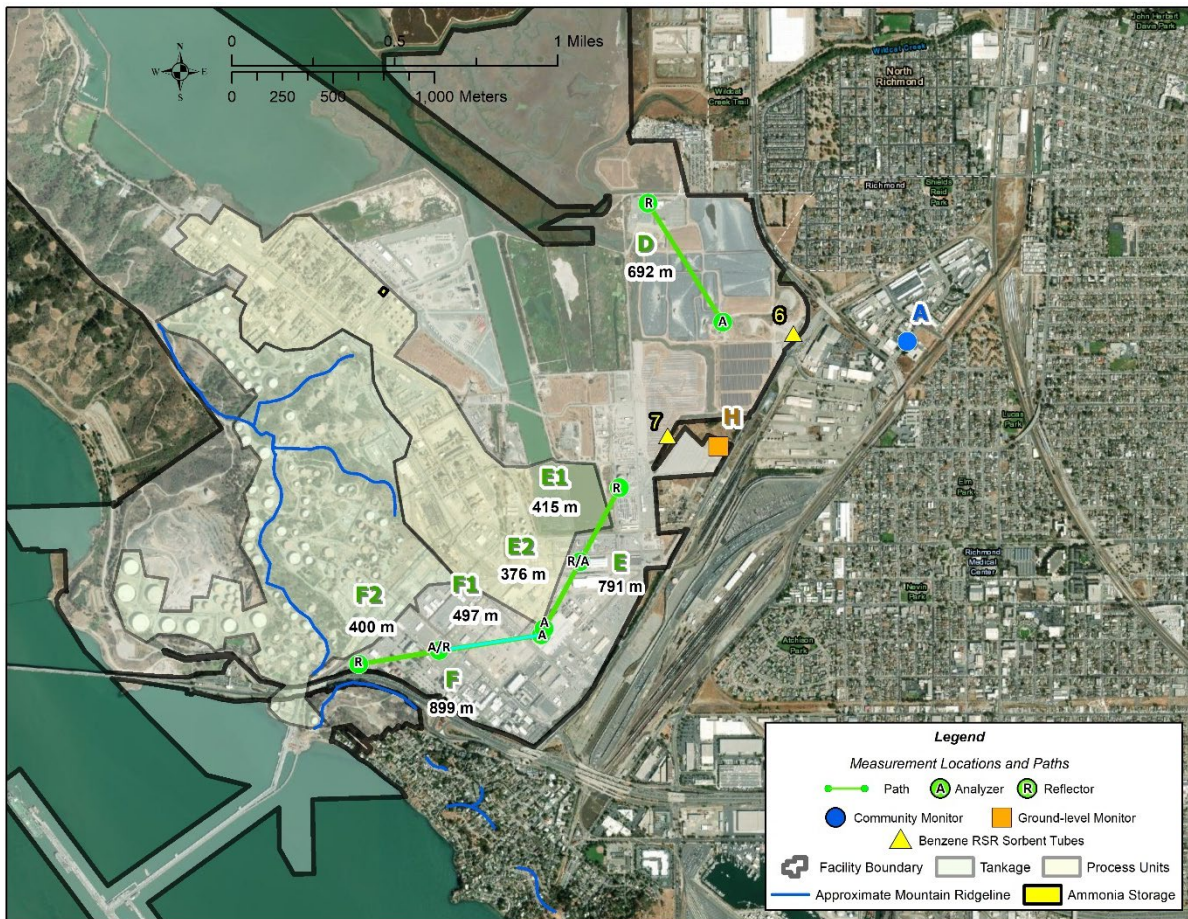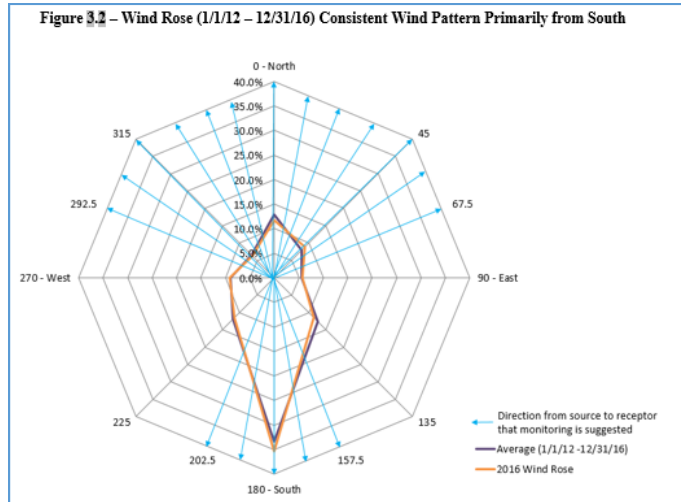
APPENDIX B

**Quality Assurance Project Plan for the
Chevron Richmond Refinery Fenceline Air Monitoring Program**

Quality Assurance Project Plan for the Chevron Richmond Refinery Fenceline Air Monitoring Program

October 20, 2020

Revised September 5, 2023

Revision 6

Approvals

Quality Assurance Project Plan
Fenceline Monitoring for the Chevron Refinery in Richmond, California

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Signature   Date

Name   Title
Chevron Products Company

Signature   Date

Name   Title
Chevron Products Company

Signature   Date

Name   Title
Bay Area Air Quality Management District

[signature]   9/5/2023
Signature   Date

Ryan Moffet   Department Manager, Data Services

Name   Title
Sonoma Technology

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1 Introduction

1.1 Background

On April 20, 2016, the Bay Area Air Quality Management District (BAAQMD) adopted Rule 12-15-403, which requires development of a Fenceline Air Monitoring Plan (Plan). The Plan must include procedures for implementing data quality assurance and quality control (QA/QC). The purpose of this QAPP is to fulfill the QA/QC requirements in Rule 12-15-403. In April 2016, the BAAQMD also published Air Monitoring Guidelines for Petroleum Refineries. On October 6, 2021, the BAAQMD provided updated requirements for refineries to conduct additional Hydrogen sulfide (H_2S) monitoring along refinery fenceline paths and to implement the enhanced monitoring by January 1, 2023; implementation of this additional monitoring was completed on schedule. BAAQMD issued updated specifications on December 22, 2022, and Chevron's response to the updated specifications was submitted on February 17, 2023. This revision addresses feedback from BAAQMD received July 19, 2023. Chevron's policy is to comply with all local and federal environmental regulations including the fenceline monitoring provisions of BAAQMD Rule 12-15.

This QAPP focuses on quality assurance of equipment that is subject to Rule 12-15 and that are not already subject to quality assurance measures by another regulatory program. Sorbent tube analysis for benzene and Ground Level Monitors (GLMs) are mentioned for informational purposes, but QA/QC of this equipment is considered outside the scope of this QAPP. Sorbent tube analyses are subject to QA/QC requirements in 40 CFR 63 Appendix A Methods 325A and 325B. GLMs are subject to QA/QC requirements in BAAQMD Manual of Procedures Volume VI.

1.2 Fenceline Monitor Geographical Locations and Coverage Paths

The Chevron Richmond Refinery Fenceline Air Monitoring Program consists of eight field equipment installation platforms as detailed in **Table 1-1**.

Table 1-1. Fenceline monitor geographical locations and coverage paths. See Table 4.3 of the fenceline monitoring plan for an inventory list for each endpoint. Because intermediate paths (e.g. F1 and F2) are close to but not exactly the same as the overall path (e.g. path F), the distances may not be exactly the same.

Endpoint	Coordinate (Decimal Degrees)	UV-DOAS	FTIR and TDLAS
North end of North Richmond fenceline monitor	37.953652, -122.379626	Path D, 692 m	Path D, 692 m
South end of North Richmond fenceline monitor	37.948302, -122.375505		
North end of Atchison fenceline monitor	37.940985, -122.381348	Path E, 791 m	Path E1, 415 m
Intermediate point of Atchison Fenceline Monitor	37.937706, -122.383615		Path E2, 376 m
South end of Atchison fenceline monitor	37.934659, -122.385536		
North end of Point Richmond fenceline monitor	37.934345, -122.385961	Path F, 899 m	Path F1, 497 m
Intermediate point of Point Richmond fenceline Monitor	37.933810, -122.391573		Path F2, 400 m
South end of Point Richmond fenceline monitor	37.933217, -122.396070		

1.3   Fenceline Monitoring Key Personnel

The Chevron Richmond Refinery Fenceline Air Monitoring Program (Program) is operated by the following key personnel.

Program Manager – The Program Manager (PM) is responsible for maintaining and updating the Fenceline Air Monitoring Program and associated Quality Assurance Project Plan (QAPP). The Program Manager acts as the central point of contact with the BAAQMD. The PM provides an initial copy of the Plans and updates to key personnel. The Program Manager finds additional resources needed to support the fenceline air monitoring program when needed. Since the field work, the website, and the project quality assurance are operated by contractors, the Program Manager supports the contractors.

Project Manager – The Project Manager is responsible for overseeing the day-to-day operation of the fenceline monitoring system. The Project Manager coordinates logistics and procurement, ensures maintenance is completed according to schedule, and ensures any outstanding system issues are addressed in a timely manner.

Data Manager – The Data Manager is responsible for data review, verification, and validation. The Data Manager is responsible for ensuring the quality of the data collected in this program. The Data Manager oversees data collection and review, provides QA oversight, and reports on QA activities to the Refinery PM. The Data Manager oversees daily data review and data management, works with the Field Technician Supervisor to ensure that any data issues are addressed promptly by the Field

Technicians, and works with the Information Technology Manager to ensure that data provided to the public are credible and meet the requirements of Rule 12-15.

Data Reviewer(s) – Daily data review and data validation are conducted by experienced air quality analysts. 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.

Field Technician(s) – The Field Technician is responsible for the day-to-day operation of the fenceline monitoring system, including following an equipment operation verification and maintenance schedule to assure data quality. Duties include performing work in a safe manner, completing training in a timely manner, and following all standard operating procedures associated with the Program.

Field Technician Supervisor – The Field Technician Supervisor is responsible for ensuring Standard Operating Procedures are updated, are maintained, and meet regulatory requirements. The Field Technician Supervisor coordinates staff coverage and serves as a technical resource for site measurements.

Information Technology Manager – The Information Technology Manager supports the website and information technology infrastructure that enables the fenceline monitoring data to be made available real time to the public. The Information Technology Manager also supports the system that sends alerts when monitor operating parameters are abnormal.

1.4   Personnel Qualification and Training

Field Technicians and the Field Technician Supervisor are trained in the operation, maintenance, and operation verification of the equipment and have resources to troubleshoot any technical issues. Training is provided by an instructor who has undergone vendor-specific training for each analyzer. It is expected that once the Field Technicians and Field Technician Supervisor gain about three years of experience with the analyzers, they will have developed expertise so that they can become trainers of new Field Technicians.

1.5   Equipment Functionality

The following sections summarize equipment functionality.

1.5.1   Open-Path UV-DOAS

Benzene, toluene, o-xylene, m-xylene, p-xylene, and SO_2 are measured with a Cerex UV Sentry bistatic Ultraviolet-Differential Optical Absorption Spectrometer (UV-DOAS). The UV-DOAS operates in the bistatic configuration where the Xenon source is at one end of the path and the analyzer (detector) is at the other end. 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. The approach is analogous to that used in U.S. Environmental Protection Agency's (EPA) TO-16. Closeness of fit is indicated by the correlation coefficient (R^2) of agreement between the measured spectra and the reference spectra. The R^2 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.

1.5.2 Open-Path Tunable Diode Laser

H_2S is measured with the Unisearch LasIR Tunable Diode Laser (TDLAS) air monitoring system. The system measures (1) sample path absorbance in a region of the spectra where H_2S absorbs infrared light, and (2) absorbance through an internal reference cell containing a known concentration of H_2S. The two resultant spectra are compared to each other using analytic software that determines the concentration of H_2S in the sample path. In addition, the software reports a correlation coefficient (r) between the two measurements, with larger r values reflecting higher confidence for analyte detection.

The signal power for the TDLAS is measured with a photodiode detector and reported in the data file. Together with an independent visibility measurement, the signal power can be used to evaluate the impact of atmospheric conditions or instrument misalignment on data quality. During normal operations, the photodiode detector has an auto-gain feature that resets at ~ 20% on the low end and ~80% at the high end.

Because the Unisearch TDLAS operates in a wavelength range that also contains an absorbance feature for water vapor and carbon dioxide (CO_2), the correlation coefficient of these gases can be used as a performance metric. If the water vapor correlation drops below a threshold value, CO_2 correlation is examined. If that also drops below a threshold value, data are flagged as invalid. This logic reflects that water vapor and CO_2 are always present in the atmosphere.

Per the December 22, 2022, letter from BAAQMD,[1] the TDLAS level of quantitation (LOQ) is taken to be equivalent to the minimum detection limit (MDL), and is calculated as twice the standard deviation of a blank sample. Under acceptable operating conditions, the expected LOQ of the Unisearch TDLAS is expected to be between 3 to 25 ppb below 1% transmission. The LOQ may be higher than 25 ppb if there is poor atmospheric visibility (e.g., heavy fog, rain, smoke, or dust), the instrument is misaligned, there are hardware problems, or an interferant is present. LOQs at the lower end of the specified range are expected under the opposite conditions. Real-time LOQs for the TDLAS are calculated and reported along with each 5-min concentration value and provided on the public-facing website. Additional information regarding real-time MDLs/LOQs for TDLAS is provided in Section 4.2

1.5.3 FTIR

Straight chain alkanes 2 to 5 carbons long and methane are measured using a Cerex AirSentry Fourier Transform Infrared (FTIR) spectrometer. 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 configuration using gold thin film corner-cube retroreflectors), where the absorption due to target gases is measured and recorded. The analyzer uses a classical Least Squares Regression analysis to compare the measured absorption spectrum to calibrated reference absorption spectra files consistent with 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 minimize interference from both water vapor and interference

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

gases, including spectral subtraction, path length adjustments, and selecting isolated absorbance peaks for the gases of interest. Proprietary methods include multi-peak analytics.

1.5.4 GC-PID

The North Richmond community monitor uses a gas chromatograph with a photoionization detector to measure BTEX compounds in ambient air. Sample gas flows through the gas chromatograph column and separates at different rates depending on the various chemical and physical properties. The photoionization detector causes ionization of the sample using ultraviolet light. The ionization chamber exposed to the light source contains a pair of electrodes. When a positive potential is applied to one electrode, an electro-magnetic field is created in the chamber. Ions formed by the adsorption of photons are driven to a collector electrode. The current produced correlates with concentration.

1.5.5 Pulsed Fluorescence

The Castro St. ground-level monitor uses two ultraviolet pulse analyzers to measure H_2S and SO_2 in ambient air. The H_2S analyzer draws sample gas through an H_2S-to-SO_2 converter coupled to a pulsed fluorescence SO_2 analyzer. Continuous H_2S monitoring is accomplished by conversion of the H_2S in the sample to SO_2 and its subsequent detection by the SO_2 analyzer. The SO_2 fluorescence analyzer has a similar principle of measurement as the H_2S analyzer: sample flows into the fluorescence chamber, where pulsating UV light excites the SO_2 molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective mirrors that reflect only the wavelengths that excite SO_2 molecules. As the excited SO_2 molecules decay to lower energy states, they emit UV light that is proportional to the SO_2 concentration.

1.6 Instrument Performance

The entire fenceline monitoring system is continually monitored for system performance. This includes the instruments, workstations, internet communication hardware, and network operations. If at any time an element of the system fails to meet performance criteria, a message is generated to key personnel, who will begin activities to correct the problem. **Table 1-2** lists potential problems and responses; additional checks are listed in Section 1.7, Emergency Maintenance Procedures, and in Section 1.8, Routine Maintenance. If the Field Technician cannot correct an issue, the Field Technician Supervisor and/or specific instrument experts will be called.

Table 1-2. Response to potential monitor problems.

Potential Problem	Response
Analyzer has low signal (integration time >250 ms for UV, <2% for IR, <0.1 mW [<1% transmission] for TDLAS)	Website updated with low signal message for specific analyzer. If the low signal is not due to weather conditions, a Field Technician corrects the issue.
Analyzer off-line	Website updated with analyzer off-line message. Field Technician corrects issue.
Workstation fails	Website updated with analyzer off-line message. Technician corrects the issue.
Internet communication failure	Backup Internet connection activated

Corrective action will be taken to ensure that data quality objectives are met. Table 1-2 lists the potential 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 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. Twice daily, analysts 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 Data Manager, Field Technician Supervisor, 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.

1.7   Emergency Maintenance Procedures

When a problem is discovered with the fenceline monitoring system, corrective actions and maintenance procedures are required; specific problems are listed in **Tables 1-3 and 1-4**. 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 Sonoma Technology on-call field operations team (field ops team, supported by Terra Applied Systems), and (2) the Sonoma Technology IT operations team (the IT ops team). The overall field ops team consists of one field technician; the IT ops team consists of one IS engineer and one IT specialist. Sonoma Technology manually checks the website daily, and automated checks are enabled. If the automated checks identify a problem, the automated system will immediately send an alert to the field ops team and/or the IT ops team. This approach helps to guarantee that problems are identified and addressed in a timely manner. The on-call teams are required to acknowledge alerts within 30 minutes of their receipt. Refinery personnel will be notified if a solution for issues affecting data availability cannot be resolved within an hour.

The rotating field ops team 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 to the website
2. Data out of expected range (for details, see Table 4-2 in Section 4 and the attached SOPs)
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 remotely monitors the status of the website and associated equipment using automated system checks such as those listed in Table 1-3 to determine actions. Automated alerts are triggered when any of the parameters surpasses their limit or threshold.

**Table 1-3. Parameters monitored by automated system checks, their
monitoring frequency, and threshold for alerting.**

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

The IT ops team is expected to acknowledge alerts within 30 minutes of their receipt. If an issue needs to be escalated for project-specific reasons, the IT ops team will notify the project's primary and secondary point persons at Sonoma Technology. If deemed necessary, Sonoma Technology will notify the 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. 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 1-4 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 review data daily to identify issues, and work with the field technicians and instrument contractors to resolve issues that need to be addressed on site. Twice daily, Analysts 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 Data 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.

Table 1-4. Potential sampling and data reporting problems and corrective actions.

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	IT Manager
Server	Not working properly	Contact Website/Data System Manager	Notify QA Manager	IT Manager
Network	Network is down	Contact Website/Data System Manager	Notify QA Manager	IT Manager
Data Flow	Data flow interruption	Contact Website/Data System Manager	Notify QA Manager	IT Manager
Data Flow	Errors in Processing	Contact Website/Data System Manager	Notify QA Manager	IT Manager

1.8   Required Routine Maintenance

Routine maintenance for the UV-DOAS, TDLAS, FTIR, and North Richmond GC is summarized in **Tables 1-5, 1-6, 1-7, and 1-8** below; additional details on the actions to be taken and when they will be taken are provided in the instrument SOPs (attached). Maintenance for the visibility sensors located at the analyzer sites for paths D (North Richmond) and E1 (Atchison) is included at the end of this section. The Castro Street GLM is maintained in accordance with BAAQMD Manual of Procedures Volume VI. In addition, maintenance checks will be performed if Data Quality Checks fail or data availability targets are not met.

Chevron's contractor will keep a small supply of critical consumable parts on site for the UV-DOAS, FTIR and other instruments (TDLAS, etc.) as needed. Critical consumables will be replaced as they are used such that a supply is always on hand. Beyond the supply of critical consumables, the

maintenance contractor will be responsible for supplying any additional parts or materials needed to maintain the fenceline monitoring system

Table 1-5. Schedule of maintenance activities and performance indicator checks for the UV-DOAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system (an evolving check list is maintained).	✓		
Inspect optics on detector and retro-reflector. Clean if necessary.	✓		
Inspect and clean system filters.	✓		
Confirm the alignment to verify there has not been significant physical movement. This is accomplished by noting the integration time and signal strength – both should be less than 250 ms and greater than 90%, respectively.	✓		
Download data older than 12 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure 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.	✓		
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency. Measure stray light. Realign system if integration time exceeds 250 ms.	✓		
Change out the UV source if the intensity has dropped below acceptable range (service hours >2000 hours and intensity at 250 nm <3% with 40 ms dwell time under high visibility conditions).		✓	
Replace ventilation exit and intake filters.		✓	
Clean and inspect optics on detector and retro-reflector.		✓	
Realign system after service. Ensure integration time is less than 250 ms and intensity is greater than 90% under high visibility conditions.		✓	
Check other system performance indicators, if necessary.		✓	
Perform bump test.	✓		
Verify system settings.			✓

Table 1-6. Schedule of maintenance activities and performance indicator checks for the TDLAS.

Activity	Monthly	Quarterly	Annually
Visually inspect the system.	✓		
Inspect optics on detector. Clean if necessary.	✓		
Check the alignment to verify there has not been significant physical movement and confirm signal levels.	✓		
Download data older than 12 months from the analyzer hard drive, move to a permanent archive, and delete the old files from the analyzer.	✓		
Ensure there are no obstructions between the detector and the retro-reflector (such as equipment, vegetation, or vehicles).	✓		
Inspect all electrical and optical cables for wear. Replace as needed.	✓		
Perform bump test	✓		
Review and test light and signal levels.[a]		✓	
Perform a 3-point calibration check		✓	
Verify system settings.			✓

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

Table 1-7. Schedule of maintenance activities and performance indicator checks for the FTIR.

Activity	Monthly	Quarterly	Annually	18-24 months	Five Years
Visually inspect the system.	✓				
Inspect optics on detector and retro-reflector. Clean if necessary.	✓				
Confirm the alignment to maximize signal intensity.	✓				
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).	✓				
Perform bump test.	✓				
Check system performance indicators (an evolving checklist will be maintained).		✓			
Inspect and clean AC system exterior heat sink.		✓			
Review and test light and signal levels. Check average light intensity to establish baseline for IR Source change frequency and retro-reflector wear.			✓		
Replace cryocooler or swap detector module assembly.				✓	
Change out the IR source.					✓

**Table 1-8. Schedule of maintenance activities for the
North Richmond community monitor GC-PID.**

Activity	Quarterly	Annually	Two Years
Replace micro dust filter for sample.	✓		
Remove dust from ventilator.	✓	✓	
Clean the lamp.		✓	
Clean the PID.		✓	
Change the carrier gas filters.		✓	
Clean the diaphragm.		✓	
Renew external sample tubing.		✓	
Replace preconcentration tenax tube.		✓	
Replace cooled preconcentration trap.		✓	
Optimize hard disk.		✓	
Clean internal gas tubing.			✓
Clean lamp housing.			✓

Quarterly maintenance will be performed on the Campbell Scientific CS120A visibility sensors. Quarterly checks for the visibility sensors are as follows:

1. Inspect the sensor for dirt, spiderwebs, birds' nests, or other obstructions. Clean the glass windows.
2. Check that the cable connections are secure.
3. Inspect the hardware holding the sensors to the tower, and tighten the bolts if necessary.

The calibration of the visibility sensors will be checked annually.

2 Data and Measurement Quality Objectives

Data completeness is assessed after reviewing the data flags assigned for each 5-min binned average data point. BAAQMD guidance for open-path measurement data recovery is that instrumentation must meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters. Completeness is therefore calculated as follows:

$$Quarterly\ \%\ Completeness = \left(\frac{Count\ of\ hours\ in\ the\ calendar\ quarter\ where\ hourly\ completeness > 75\%}{Count\ of\ all\ hours\ in\ the\ calendar\ quarter}\right) x\ 100$$

Additional data completeness definitions are included below.

- Possible – Maximum number of 5-min average concentrations that can be measured in a given hour and logged in the DMS
- Captured – Actual number of 5-min average concentrations that were measured in a given hour and logged in the DMS
- Missing – Number of 5-min average concentrations not measured or logged in the DMS in a given hour

- o   Missing = Possible – Captured
- **% Missing** – Percentage of missing 5-min average concentrations in a given hour relative to the possible number 5-min average concentrations
    - o   % Missing = (Missing / Possible) x 100
- **Invalid Total** – Number of invalid 5-min average concentrations measured and logged in the DMS in a given hour
- **% Invalid Total** – Percentage of invalid 5-min average concentrations in a given hour relative to the possible number of 5-min average concentrations
    - o   % Invalid Total = (Invalid Total / Possible) x 100
- **Invalid Environmental** – Number of invalid 5-min average concentrations in a given hour due to adverse atmospheric or environmental conditions
- **Invalid Other** – Number of invalid 5-min average concentrations in a given hour due to anything other than adverse atmospheric or environmental conditions
- **% Invalid Other** – Percentage of invalid 5-min average concentrations in a given hour due to anything other than adverse atmospheric or environmental conditions relative to the possible number of 5-min average concentrations
    - o   % Invalid Other = (Invalid Other / Possible) x 100
- **Expected** – Number of possible 5-min average concentrations in a given hour, adjusted for periods of low visibility during adverse atmospheric or environmental conditions
    - o   Expected = Possible – Invalid Environmental
- **Valid** – Number of valid 5-min average concentrations in a given hour
- **% Valid** – the percentage of valid 5-min average concentrations in a given hour relative to the possible number of 5-min average concentrations
    - o   % Valid = (Valid / Possible) x 100
- **% Hourly Completeness** – Percentage of valid 5-min average concentrations in a given hour relative to the expected number of 5-min average concentrations
    - o   % Hourly Completeness = (Valid / Expected) x 100

2.1   Data Representativeness

Site locations for the fenceline monitoring system were selected to ensure data representativeness by strategically positioning monitors using the predominant and variable meteorological conditions as well as topographical terrain features within the refinery.

The fenceline monitoring sites were selected to be consistent with guidance from EPA and CARB. Environmental requirements were considered in the monitors' placement with respect to on-site and off-site sources. The existing fenceline monitors do not have any large-scale sources between the monitor and the fenceline. The monitors were placed with consideration given to the proximity of off-site emissions sources. Sampling requirements were also considered in the siting of monitors. Chevron's goal was for the horizontal distance from a point sampler to an obstacle, such as a building, to be at least twice the vertical distance that the obstacle protrudes above the sampler. To keep paths away from buildings and other obstacles, Chevron's goal was that 90% of the open path was not within a distance of two times the height the obstacle above the path. For open-path monitors, a direct line of sight between light source and receiver must be available for the monitors to function.

Chevron met on multiple occasions between September 2011 and November 2012 with Shields-Reid, Point Richmond, and Atchison Village Neighborhood Councils, who provided input on the locations of the air monitors. These are all the neighborhoods that border the refinery. The compounds to be

monitored were selected with input from the City of Richmond, Chevron's consultant, and community representatives. The compounds monitored by the fenceline system are considered representative of refinery operations. The specific chemicals that require monitoring were evaluated for each source from emissions estimates based on available TRI (Toxic Release Inventory) information. The compounds monitored by the community monitors represent a larger spectrum of compounds that can be attributed to many sources present in the Richmond community. The final siting locations and compounds to be monitored were approved by the City of Richmond in 2013.

3   Quality Control

All monitoring equipment is and will be operated using quality assurance protocols outlined in this QAPP. This includes continuous monitoring of instrument parameters for data quality (error flags/messages from the analyzers, low signal measurements), quarterly validations, and annual servicing of the analyzers. Accuracy is measured using the protocols outlined in the SOPs included in this QAPP.

Whenever equipment is replaced or added, a Factory Acceptance Test (FAT) will be made at the manufacturer's location using these methods; a Site Acceptance Test (SAT) using the same methods will be made in the field during the startup phase, both tests will be done with the system in its standard operational configuration. Chevron will obtain a report of the FAT and SAT tests conducted. FAT and SAT tests determine precision and percent error using certified standard gas concentrations, with an expected precision of greater than 90% and an expected percent error of less than 25% for the UV-DOAS and FTIR and 15% for the TDLAS,[2] using the certified concentration and the procedures outlined in the SOPs. Adjustments and improvements will be made in the field until performance is acceptable (±25% of expected concentrations for the UV-DOAS and FTIR and ±15% for the TDLAS).[3] For the UV-DOAS system, bump test will be performed quarterly, as recommended by the manufacturer. In the field, a bump test is used to verify that the system can detect at or below a set level of concern; performance should meet the same criteria as for the FAT tests. A bump test will also be performed if major changes are made to the instrument during troubleshooting or if there is a recently measured value that is still in question after investigations are performed (e.g., if there are multiple 5-min measured values at a very high level [for example, a value over 20 times the MDL for that compound]; MDLs are given in Table 4-4 in Section 4).

For an open-path FTIR, a bump test will be performed quarterly, as recommended by the manufacturer. In the field, a bump test is used to verify that the system can detect at or below a set level of concern; performance should meet the same criteria as for the FAT tests. A bump test will also be performed if major changes are made to the instrument during troubleshooting or there is a recently measured value that is still in question after investigations are performed (e.g., if there are multiple 5-min measured values at a very high level (for example, a value over 20 times the MDL for that compound); MDLs are given in Table 4-4).

The TDLAS system for measuring H_2S will be bump tested monthly, as required by the BAAQMD in updated guidance. In addition, quarterly three-point calibration checks will be performed. Both bump tests and three-point calibrations will be performed with either sealed cells or flow-through cells capable of incorporating the atmospheric path. Sealed cells will be used for tests requiring greater

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[2] For the TDLAS, accuracy and repeatability specifications will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions.
[3] For the TDLAS, accuracy and repeatability specifications will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions.

than 750 ppm gases due to safety concerns. The concentration of the bump test will differ from the concentrations used for the three-point calibration check. A bump test will also be performed if major changes are made to the instrument during troubleshooting or if there is a recently measured value that is still in question after investigations are performed (e.g., if there are multiple 5-min measured values at a very high level, for example, a value over 20 times the MDL for that compound. MDLs are given in Table 4-4).

For factory calibrations, a certification of the standard gases used will be requested from the manufacturer. In addition, the spectra background file version number used for signal processing will be documented.

For the North Richmond community monitor GC-PID, zero and span checks will be conducted monthly. The analyzer will be calibrated if the target zero value reads greater than or equal to two ppb or if the span value is greater than equal to 25%. Calibrations are scheduled quarterly, and instrument bias is checked annually.

For the Castro Street GLM a zero and span check will be completed every two weeks.

Benzene sorbent tube will be used for EPA 40 CFR 63 compliance. Sorbent tubes and subsequent laboratory analyzers are calibrated in accordance with 40 CFR 63, Appendix A, Method 325B requirements.

3.1 Precision and Accuracy

For the open-path systems, precision can be measured by evaluating the variance of pollutant concentrations during a period of low variability, when atmospheric influence on variability is assumed to be minimal. For example, measurements should not be performed in the rain, fog, or when ambient concentrations of analytes/interfering species are changing rapidly (e.g., ozone). On a monthly basis, 5-min data will be selected during periods of low variability, but when concentrations are well above the MDL. The precision can then be evaluated by calculating the coefficient of variation (CV) during the period of low variability, as shown in the equations below. If there are no periods of low variability with concentrations above the MDL, bump test data will be used to calculate precision.

During these tests, a number (N) of replicated measurements (x_i) of a standard reference material of known magnitude (x_{std}) will be measured. Here, an acceptable number of trials will be defined as $7 \leq N \leq 15$, and a subset of test data will be used for subsequent calculations. The average value of these measurements is calculated as

$$\bar{x} = \frac{\sum_i x_i}{N} \qquad (1)$$

and the standard deviation (σ) as:

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

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

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

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

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

4 Data Management

Data quality criteria are evaluated through (1) automatic data checks conducted through a data management system and (2) data review by trained analysts.

4.1 Data Acquisition and Communications

Data are stored onsite on instrument computers, and are also transferred through a data acquisition system (DAS) to a Data Management System (DMS) in real time. Raw data are not yet intended for the public website.

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/alert project and facility staff. The automatically QC'd air quality data will be fed to the public website typically within 10 minutes of data measurement.

4.2 Automated Data Review

Automated data review is conducted within the DMS upon data ingest. Automated checks screen out invalid data from the public display, and the quality control (QC) codes and operational (OP) codes used in this process are summarized in **Table 4-1**. The QC and OP codes in this table are verified or changed as appropriate during later (manual) stages of data review. Initial quality review checks, along with actions to be taken, are summarized in **Table 4-2**. The review concentration criteria used to select the values in Table 4-2 are based on an analysis of expected instrument performance, concentration levels of concern by compound, and typical ambient concentrations by compound. All review criteria (flags and rates of change) are preliminary and will be refined during the project, based on actual observations. The DMS auto-review 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; from a value equal to negative three times the MDL, to values greater than three times the notification threshold for that 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. 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. Missing data alerting will be set for six missing 5-min intervals (30 minutes).

Table 4-1. Overview of data quality control (QC) and operational (OP) codes.

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

Additional parameters that may be monitored as indicators of data quality include spectral matches for each concentration as reported by the instrument (i.e., correlation between measured and reference spectra), and signal strength. Data points collected with a signal strength percentage outside of an acceptable range, based on the criteria in Table 4-5 (see Section 4.4, Data Validation), will be flagged as invalid. For UV-DOAS, this is also paired with integration time since elevated integration times are indicators of difficulty achieving a sufficient signal level.

For the Unisearch TDLAS, a real-time MDL is calculated continuously in real time using the standard deviation of the last seven 5-min average concentration values containing no measurable analyte (as determined by the correlation coefficient). The MDL is defined at three times this standard deviation and is reported alongside every 5-min average concentration value. Data with real-time MDL values that are greater than 25 ppb are flagged for additional review, and, in the absence of marginal operating conditions or an instrument malfunction, will be considered to not meet the performance criteria.

For all open-path data, when the spectral match is below the threshold, interference, and noise from the lack of signal are believed to have impacted measurements, so data are then flagged as poor spectral match. Data with good spectral match that are below the MDL are flagged as below MDL. A visual review of peaks can be conducted using manufacturer-supplied data processing software. This visual inspection will be used to determine the validity of 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 (for example, fewer false positives and false negatives).

Table 4-2. The following checks are used for post-process data review. If visibility is less than 2.5 miles and data are invalid due to low signal strength, data are flagged as invalid due to environmental conditions.

Compound	MDL	Range	Checks		
			Sticking	Missing	Sensor Alarm
Benzene (ppb)	If below MDL, flag as below MDL	If above 5 ppb, flag for review	If value is above MDL and the same value is observed for four or more intervals, flag for review	If data are missing, flag as missing	If sensor indicates malfunction or maintenance, flag as appropriate
Toluene (ppb)		If above 70 ppb, flag for review			
Ethylbenzene (ppb)		If above 320 ppb, flag for review			
Total Xylene (ppb)		If above 200 ppb, flag for review			
H$_2$S (ppb)		If above 25 ppb, flag for review			
SO$_2$ (ppb)		If above 40 ppb, flag for review			
Methane (ppm)		If below 1,440 ppm, flag for review			
Alkanes, C2-C5 (ppb)		If above 1 ppm, flag for review			

Data flags identified through auto-review will be reviewed during data validation (i.e., not in real time), and QC flags will be updated with quarterly actions. Data quality analysts will review data daily in the beginning of operations. This may reduce to several times a week as the analysts become more familiar with the data and expected data trends are established. Analysts use the administrator website and the analyzer signal processing software to ensure that data flags are being applied correctly. If it is found that data were incorrectly flagged during this process, the analyst will manually change the flag. Data changes will be tracked. Raw data are preserved as well as all changes.

Messages are provided for every compound and time period; these messages are listed in **Table 4-3**.

Table 4-3. Messages displayed on the website with each compound and data value (hover over the data point to view the message).

Condition	Message
Valid	X parts per billion of Compound Y were measured at this location
Below detection	The concentration of the compound is so low that the instrument cannot accurately detect it.
Questionable	No additional information available. Pending further review.
Missing	A problem (such as power failure, calibration, etc.) prevented the instrument from collecting or reporting the data.
Invalid	No additional information available. Pending further review.
Not Measured	There is no instrumentation at the given site to measure this chemical.

Table 4-4 shows the expected detection ranges for the open-path monitors at North Richmond, Atchison, and Point Richmond. The operation of these instruments will be conducted in accordance with the Fenceline Monitoring Plan pursuant to the timing requirements in Rule 12-15. MDLs change depending on atmospheric conditions. Real-time MDLs/LOQs for the TDLAS are provided on the public-facing website.

Table 4-4. Approximate minimum detection limits (MDLs) and upper detection limits (UDLs) by compound and path.

		Path Integrated Values		North Richmond (D)		Atchison (E)		Atchison (E1)		Atchison (E2)		Point Richmond (F)		Point Richmond (F1)		Point Richmond (F2)	
	Path Length	N/A*	N/A*	692 m		791 m		415 m		376 m		899 m		497 m		400 m	
		MDL (ppmm)	UDL (ppmm)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)	MDL (ppb)	UDL (ppb)
FTIR	**Methane**	7	4,200	5.1	3,000	-	-	8.4	5,000	9.2	5,500	-	-	7.1	4,200	8.8	5,200
	Ethane	3.2	1,100	2.3	810	-	-	3.8	1,300	4.2	1,500	-	-	3.2	1,100	4	1,400
	Propane	3.8	1,100	2.7	810	-	-	4.5	1,300	5	1,500	-	-	3.8	1,100	4.7	1,400
	Butane	4.2	1,100	3	810	-	-	5	1,300	5.5	1,500	-	-	4.2	1,100	5.2	1,400
	Pentane	1.6	1,100	1.2	810	-	-	1.9	1,300	2.1	1,500	-	-	1.6	1,100	2	1,400
TDLAS**	**Hydrogen Sulfide**	3-25	7,500	3-25	5,400	-	-	3-25	8,900	3-25	9,900	-	-	3-25	7,500	3-25	9,300
UV-DOAS	**Benzene**	0.27	16,000	0.19	23,000	0.17	20,000	-	-	-	-	0.15	18,000	-	-	-	-
	Toluene	0.84	22,000	0.61	32,000	0.53	28,000	-	-	-	-	0.47	25,000	-	-	-	-
	Ethylbenzene	0.3	11,000	0.22	16,000	0.19	14,000	-	-	-	-	0.17	12,000	-	-	-	-
	o-xylene	3.8	2,100	2.7	3,100	2.4	2,700	-	-	-	-	2.1	2,400	-	-	-	-
	m-xylene	0.35	920	0.25	1,300	0.22	1,200	-	-	-	-	0.2	1,000	-	-	-	-
	p-xylene	0.24	360	0.17	510	0.15	450	-	-	-	-	0.13	400	-	-	-	-
	Sulfur Dioxide	0.68	21,000	0.49	30,000	0.43	26,000	-	-	-	-	0.38	23,000	-	-	-	-

*Path lengths are given as N/A because path-integrated concentrations given in ppmm are independent of pathlength.
**Per the December 22, 2022, letter from BAAQMD,[4] the LOQ is taken to be equivalent to the MDL. For the TDLAS, the MDL is calculated as twice the standard deviation of a blank sample.

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

4.3 Data Verification

In addition to the automated system, which conducts initial data review checks, data analysts will examine both public-facing and internal websites twice daily to assess data quality and availability. If issues are noted, the analyst will further investigate and work with the QA Manager, the 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 it appears that an instrument is not operating, or the data are missing, the field operator will conduct further investigation and corrective action.

The 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-min values (i.e., 30 minutes).

4.4 Data Validation

On a frequency of at least once every quarter, an experienced air quality analyst will validate data by building on the automated screening results. This process starts with an in-depth review of the data, a review that includes evaluation 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:

- Reviewing spectral features in flagged data to verify the measurement.

- Ensuring there are not several continuous 5-min averages of the same number.

- Evaluating monthly summaries of the minimum, maximum, and average values.

- Ensuring data reasonableness by comparing concentrations 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.

- Inspecting several sampling intervals before and after data issues or instrument 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 the site operator.

- Assessing instrument metadata to confirm reasonableness.

- Assessing weather-related downtime based on two or more analyzers in the same proximity experiencing a drop in signal simultaneously.

Additional QC checks for the instruments are summarized in **Table 4-5**. Data that fail checks will be flagged in the DMS and brought to the attention of the reviewer by color coding 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, we will evaluate, refine, and update the screening to improve the data quality and minimize false

positives and false negatives. If these analyses suggest that a reduction in frequency is prudent, then a request will be submitted to the BAAQMD for approval. Screening checks are typically specific to the site, instrument, time of day, and season and are adjusted over time as more data are collected.

Table 4-5. Instrument QA/QC checks.

Instrument Checks	Frequency	Acceptance Criteria
UV-DOAS		
Bump test accuracy (as % Error) with benzene and SO$_2$	Monthly and after major service	±25%
Measurement quality – R^2	Continuous	0.8 to 1.0
Integration time	Continuous	≤250 ms
Spectral Match	Continuous	≥80%
TDLAS		
Bump test[a] accuracy and repeatability (as %CV); H$_2$S at a concentration between 50 and 100 ppb which differs from 3-point calibration points.	Monthly	±15%
3-point calibration accuracy (as % error) and precision (as %CV) [a, b, c] The lowest calibration concentration must be in the range of 40 to 60 ppb.	Quarterly	±15% for each calibration point H$_2$S
5-min LOQ[d]	Continuous	3-25 ppb
H$_2$S correlation coefficient (r)	Continuous	0.72 to 1.0
Power	Continuous	0.1 mW (corresponds to <1% transmission)
H$_2$O correlation coefficient (r)	Continuous	≥0.95
FTIR		
Bump test accuracy (as % Error) with propane	Monthly	±25%[a]
Signal intensity	Continuous	≥2%[b]
Spectral Match	Continuous	≥80%
Visibility Sensor		
Accuracy (as % Error)	Annually	±25%

[a] For the TDLAS, accuracy and repeatability specifications will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions.

[b] NIST TN 1297: Appendix D1. Terminology.

[c] For test concentrations requiring greater than 750 ppm H$_2$S, safety considerations necessitate certified sealed cells be used. For test concentrations requiring lower than 750 ppm, certified flow-through cells may be used.

[d] Per the December 22, 2022, letter from BAAQMD[5], the LOQ is taken to be equivalent to the MDL. For the TDLAS, the MDL is calculated as twice the standard deviation of a blank sample.

Data are invalidated only if a reason can be found for the anomaly or automated screening check failure. If the data are anomalous or fail screening, but no reason can be found to invalidate the

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

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.

On at least a quarterly basis, analysts will subject the data to final QC by filling in missing records with null values, and adding Null Codes:

- Invalid data will have an operational code, or in other words, a reason for being invalid.

- If a record is not created for a particular site/date/time/parameter combination, a data flag will be created for data completeness purposes.

- Data completeness for the quarter will be reviewed.

All actions will be documented so that raw data are retained and all actions that result in the final data are traceable.

On an annual basis, the refinery or its designated contractor will review the performance of the network by reviewing the data completeness by monitoring path, instrument, and species; by reviewing results of QA/QC tests; by analyzing the reported values in context of refinery operations; and by analyzing the data in context of the meteorology. The refinery or its designated contractor 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 provided to the BAAQMD upon request.

Chevron or its contractor will monitor and investigate any portion of the fenceline system that fails to meet data quality objectives, measurement quality objectives, or on-stream efficiency requirements under Rule 12-15. The investigation team will include members of the fenceline management team, contractors, and appropriate equipment vendors. They will assess the problem and initiate corrective action. Corrective actions will be undertaken in a timely manner with the understanding that all work will be done with safety as a primary focus. If monthly bump test accuracy and precision specifications are not met, repair, maintenance, and a root-cause analysis will be triggered, with repeat bump tests performed until a passing test is completed. All steps in this process will be recorded. In addition, improvement opportunities identified will be considered to minimize the chance for similar problems in the future.

4.5   Data Uncertainty and Limitations of Use

Table 4.6 describes data uncertainty and limitations by instrument type in terms of monitoring technology capabilities, interferences, and measurement errors.

It is important to note that monitoring data at the fenceline show higher concentrations than would be expected in the community due to dispersion. The Chevron fenceline monitoring website provides links to health standards for reference; however, when comparing fenceline monitor readings with health standards, it should be understood that concentrations in the community are expected to be less than the fenceline monitor readings. Additionally, due to higher minimum detection limits of some fenceline instruments, a comparison with health standards is not possible. In cases where a chemical is not detected, the fenceline monitoring website may show concentrations below the minimum detection limit, but accuracy is

significantly poorer for these values. Information will be posted on the monitoring website advising users about limitations on data use.

Table 4-6. Data uncertainty and limitations of use.

Equipment	Capabilities	Interferences	Limitations	Measurement Errors
Sorbent tubes	Absorbs benzene from ambient air, if present, at a point over approximately 14-day periods; lower detection limit than open-path monitors	Sorbent artifacts, Water (rain)	Heavy rains with high winds; continuous reporting not possible	Within 30% (Per 40 CFR 63 Appendix A Method 325B Section 9.7)
North Richmond Community Monitor Auto Gas Chromatograph	Measures BTEX continuously at a point with lower detection limit than open-path monitors	--	Measures at point vs. open-path	Within 25%
Open-path FTIR	Measures alkanes across an open-path continuously; likely lower detection limit than extractive FTIR	Water (humidity), CO_2, and C2-C5 alkanes may interfere with each other	Heavy fog and rain	Within 25%
Open-path UV-DOAS	Measures BTEX and SO_2 across an open path continuously	Ozone and oxygen	Heavy fog and rain	Within 25%
Open-path TDLAS	Measures H_2S continuously across an open path	H_2O and CO_2	Heavy fog and rain	$\pm15\%$ for $[H_2S]$[a]
Castro St. GLM H_2S and SO_2 Pulsed Fluorescence Analyzers	Measures H_2S and SO_2 at a point continuously; lower detection limit than open-path monitors	High concentrations of hydrocarbons; mercaptans interfere with H_2S measurement	Measures at a point vs. open-path	Within 10% for SO_2, within 15% for H_2S (BAAQMD MOP Volume VI)

[a]For the TDLAS, accuracy and repeatability specifications will be treated as objectives to become requirements once it is proven they can be reliably met for all seasons and atmospheric conditions.

5   Data Delivery

Final data sets are compiled quarterly and will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter. Outside of the normal quarterly delivery, data will be made available to the BAAQMD upon request; data will be delivered within 30 days of the request. Consistent with BAAQMD guidance, quarterly data deliveries will include the following.

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

    - The name of the facility where the equipment is located

    - A unique identification number assigned to each instrument or system

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

    - The name of the compound being measured

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

    - The hour of the day and the beginning of the 5-min period over which measurements were collected and averaged, reported in Pacific Standard Time (PST) and formatted as "hh:mm" using 24-hr notation

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

    - The unit of measure corresponding to the reported mean concentration

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

    - The number of values that comprise the reported mean concentration

    - An indicator representing whether the reported mean concentration represents a legitimate air measurement ("Y") or one that has been affected ("N") by an instrument malfunction, adverse environmental conditions, maintenance events, etc.

    - Error codes explaining the reason for invalid or missing data, with multiple codes separated by a semicolon without spaces and the field left blank for valid data

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

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

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

    - The average measured light signal for the corresponding averaging period

    - The units of measure for the corresponding light signal

- A record for each 5-min period of the quarter for all instrument and parameter combinations. Records corresponding to missing data will include the facility name, instrument ID, instrument descriptor, parameter, date, time, and error codes with their respective values, and remaining fields will be populated with a value of "NA."

- An assessment of data completeness, as described in Section 2.

- A summary of bump tests and calibration checks performed according to the QAPP, including the instrument or system, the type of test or check, the start and end date and

time of the test or check, and the date and time that the instrument or system resumed normal operations. Potential failed bump tests or calibration checks will be included.

- The results of bump tests and calibration checks performed according to the QAPP, including accuracy and precision. Root cause analysis and a narrative description of maintenance or repairs performed to return the system to proper operations will be included for potential bump tests or calibration checks with accuracy and precision results that are not within the acceptance criteria.

- Data corrections accounting for the effects of gas cells or other equipment on instrument signal.

- Meteorological data and a narrative explanation sufficient to justify where data has been excluded due to adverse atmospheric or environmental conditions.

Supporting documentation, such as SOPs and raw/spectral data, will be made available to BAAQMD upon request and not on a routine basis.

5.1 Fenceline Monitoring Plan and QAPP Distribution

The Program Manager will be responsible for providing initial copies and updates of the Plan including the QAPP to key personnel identified previously. The Plan and QAPP will be updated periodically and distributed to address a deficiency, improve procedural accuracy, or to make procedures more robust. The QAPP will be updated when changes are made to SOPs, testing criteria, etc.; new version numbers and dates will be assigned and submitted to the Air District for review and approval.

5.2 QA/QC Records

The Program Manager will retain QA/QC reports from equipment manufacturers. The Field Technician Supervisor will retain field QA/QC records.

5.3 Training Records

The Field Technician Supervisor is responsible for maintaining documentation of required training.

5.4   Document Control

Document No.	Rev No.	Rev Date	Effective Date	Distribution	Description
QAPP	0	12/7/2018	12/7/2018	Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Original Submission.
QAPP	1	08/23/2019	08/23/2019	Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Addressed BAAQMD comments, including revised emergency maintenance procedures and description of key personnel.
QAPP	2	01/08/2020	01/08/2020	Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Addressed BAAQMD comments, including modifications to FTIR, data completeness, and other open-path-related items.
QAPP	3	10/20/2020	10/20/2020	Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Modified descriptions of UV and FTIR systems. Added detail on visibility measurements. Added description of QC and OP Codes.
QAPP	4	6/1/2022		Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Addressed BAAQMD comments, including addition of Tunable Diode Laser measurements of hydrogen sulfide.
QAPP	5	2/15/2023		Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Addressed BAAQMD comments on Revision 4.
QAPP	6	9/5/2023		Program Manager, Project Manager, Data Manager, Field Technician Supervisor, Information Technology Manager, BAAQMD	Revised in response to BAAQMD comments

6 Standard Operating Procedures

Standard Operating Procedures for maintenance and quality assurance checks of the Cerex UV-DOAS instrument, the Cerex FTIR instrument, the Synspec GC, and the Unisearch TDLAS are provided in Appendices A through D of this QAPP.

Appendix A

Standard Operating Procedures for the CEREX UV Sentry UV-DOAS

Contents

1. Scope and Application

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

2. Introduction and Overview

The CEREX UV Sentry ultraviolet differential absorption spectrometer (UV-DOAS, shown in **Figure 1**) is an instrument that is used to detect BTEX, SO_2, NO_2, and a number of other gases in the ultraviolet (UV) region of the electromagnetic spectrum. The instrument consists of a Xenon light source, several optical elements, including a spectrometer. UV-DOAS instruments may be configured so that the spectrometer and source are in one location (monostatic) or at opposite ends of the path (bistatic). For a monostatic configuration, the light from the light source is collimated with the primary mirror and directed along a path length of about 500 m. At the other end of the path is an array of corner-cube reflectors called retroreflectors that direct the light directly back into the analyzer where the light is dispersed and measured using a spectrometer. The working range of the spectrometer is from about 200 to 400 nm. This document addresses the routine operations and maintenance procedures for the Cerex Monitoring Solutions UV Sentry units. The procedure is intended to guide the field technician in ensuring and verifying that the equipment is performing to expectations. As required, hard copies of this procedure and the associated test forms will be kept on site and a copy of the test form showing the results will be sent to the Refinery Project Manager upon completion of the test procedure.
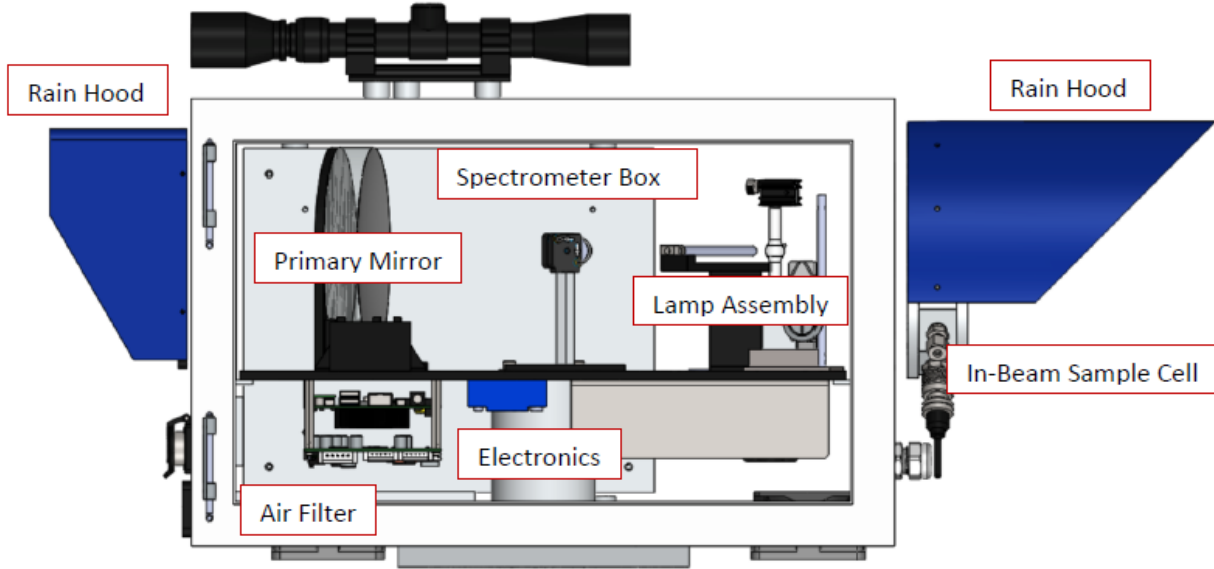
Figure 1. Schematic of the monostatic UV Sentry UV-DOAS analyzer.

The purpose of field maintenance is to ensure that the instrument is operated within specification and for field verification of the factory calibration of the UV Sentry. The QA Test process challenges the instrument using known concentrations of select BTEX reference gases and/or Sulfur Dioxide to verify proper detection and quantification under field conditions.

3. Definitions

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

Term/Acronym	Definition
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes (Xylenes are composed of ortho, meta and para isomers)
Bump Test	Also known as QA Audit; test where gas of a known concentration is introduced to the analyzer to check for response accuracy and precision
CMS	Continuous Monitoring Software
Integration Time	The amount of time the spectrometer detector collects light for (typically 20 to 300 ms)
Intensity	A measure of how much light was collected
PPE	Personal Protective Equipment

Term/Acronym	Definition
QA	Quality Assurance
QC	Quality Control
QAPP	Quality Assurance Project Plan
SOP	Standard Operating Procedure
UV-DOAS	Ultraviolet Differential Absorption Spectroscopy

4. Safe Work, Hazard Identification, and Precautions

The following information is intended to provide guidance in ensuring a safe work environment.

Operator Qualifications

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

Work should conform to the manufacturer guidance and site health and safety practices.

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

WARNING – Eye hazard. Risk of eye injury. CEREX UV-DOAS Analyzers contain an ultra-violet light source that may cause eye injury after prolonged exposure. Always wear UVA/B/C eye protection when working on or near the operating equipment.

Procedure Warnings

The procedure contained within this document requires the handling of toxic substances including but not limited to benzene, aromatic hydrocarbons, and sulfur dioxide gas, and it requires the operation of equipment designed for toxic gas containment and dispensation. Improper handling of materials or hardware may result in serious injury, destruction of property, or damage to the UV Sentry. Only qualified individuals should attempt or perform analyzer operation or testing activities.

Safe Operating Precautions

Ensure that a clear escape path is identified.

Standard site personal protective equipment (PPE) is appropriate. If gloves are required for work on optics, nitrile or latex should be used.

NOTICE

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

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

5. Routine Operations

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

1. Start the CMS software (if not already initiated). You should see a window similar to the one shown below in **Figure 2**.
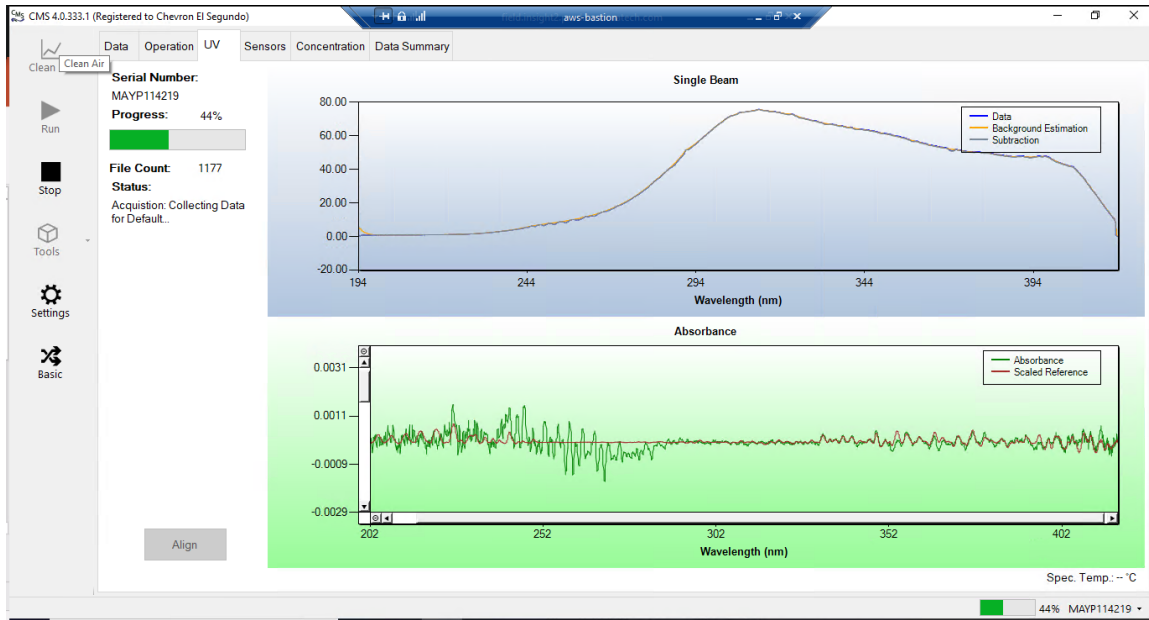
Figure 2. Screenshot showing the **UV** tab of the CMS software. Note that the **Align** button is grayed out because the instrument is in run mode (the **Run** button is also grayed out because the instrument is in run mode).

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

Figure 3. Screenshot for **Align** mode. The integration time can be entered in the upper right of the screen. In this particular screenshot, the integration time is 38 ms.

3. Enter an integration time of 25 ms and optimize the signal intensity by adjusting the pan-tilt head of the UV-DOAS unit to adjust the position of the UV beam on the retroreflector.

NOTE: Make sure not to saturate the peak of the spectrum when at 25 ms integration time. An example of a saturated spectrum is shown in **Figure 4**; note that the spectrum is flattened out starting at about 290 nm. Also, ensure there is sufficient intensity at 250 nm compared to the stray light intensity. If there is more than 10% stray light, advanced optical adjustment or bulb change may be necessary. To measure stray light, block the beam from exiting the analyzer with an opaque object (such as a black cloth) and measure the intensity at the wavelength of interest.
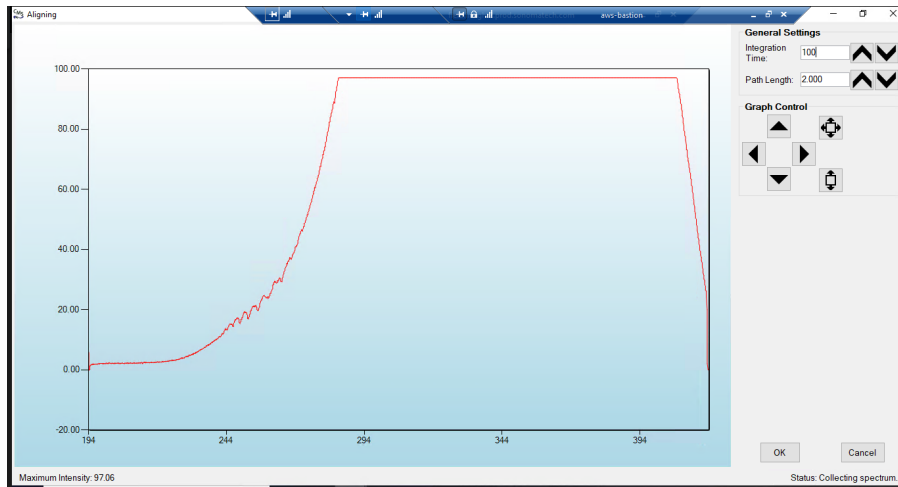
Figure 4. An example of a saturated spectrum when in **Align** mode. Note the "flat top" profile of the spectrum. The spectrum flattens out because the detector has saturated at those wavelengths and cannot quantitatively measure additional light.

4. Once sufficient alignment is obtained, exit the align mode by pressing **Cancel**.

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

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

- RunTime
    - General
        - Operator Name: **Default** (these will change based on the path and site you are working on)
        - Sitename: **Cerex** (these will change based on the path and site you are working on)
        - Auto Run: `ON`
        - Auto Run Delay (s): **15**
    - File

7

- File Type: **.CSV**
- Primary Data Logging File: **ON**
  - C:\Users\CMS-USER\Documents\Cerex\Data
- Secondary Data File Logging: **ON**
  - \\OPT1-PC1\VLOData\OPT1_Path1\UVSentry_POC1
    - Note this path will change based on the different computer and path you are working on. This is just a basic file writing path to show you what it should look like.
- Single Data Folder: **OFF**
- Primary Summary File Logging: **ON**
  - C:\Users\CMS-USER\Documents\Cerex\Data
- Secondary Summary File Logging: **ON**
  - \\OPT1-PC1\VLOData\OPT1_Path1\UVSentry_POC1
    - Note this path will change based on the different computer and path you are working on. This is just a basic file writing path to show you what it should look like
- Single Summary File: **OFF**
  - Library
    - Library File: C:\Users\CMS-USER\Documents\Cerex\Library\
  - UI
    - Sort Column: Compound Name
    - Data Summary Chart: **OFF**
    - Concentration Chart: **OFF**
    - Password Protection Settings: **ON**
    - Pump Control: **OFF**
    - Status Control: **OFF**
    - Testing Control: **OFF**
- <u>Analysis</u>
  - General
    - Moving Average Interval: **12**
    - Display Units: **PPM**
  - Concentration
    - Zero Readings on Non-Detect: **OFF**
    - Zero Readings on Negative concentrations: **OFF**
    - Display BDL: **OFF**
    - Quick Analysis MDL Wave length Range: **276 -280 (The range doesn't matter)**
    - Temperature/ Pressure Concentration: **OFF**
  - Filters
    - Absorbance Savitzhy-Golay: **ON**
    - Baseline Correction Savitzky-Golay: **OFF**

- <u>Instruments</u>
  - o UV
    - ▪ Operation
      - • UV: **ON**
      - • Acquisition Time (s): **30 (this is the "averaging time" of the instrument)**
      - • Integration Time (ms): **Always will change if Auto integration is turned on**. This is the amount of time that the instrument will collect light.
      - • Path Length (m): **2 (2 for monostatic, 1 for bistatic)**
      - • Trigger Mode: **Norma**l
    - ▪ Auto Routine
      - • Auto Integration: **ON** **(the software will determine the integration time)**
      - • Intervals (s): **300**
      - • Wavenumber Range: **300-310 (This is the range where the intensity will be measured for autointegration determination. This is different on all instruments due to Spectral Background and Intensity Range)**
      - • Intensity Range **75-85 (This is the target intensity range for the autointegration routine)**
      - • Maximum Integration: **300**
      - • Auto Background: **ON**
      - • Interval (Acquisitions): **5**
      - • Wavenumber Range: **266-270**
    - ▪ Verification
      - • Verification: **OFF** **(This inactivates all inputs)**
- <u>Controller</u>
  - o General
    - ▪ Serial Port: **n/a**
    - ▪ Sensor Refresh Interval (s): **15**
  - o Sensors
    - ▪ **Don't Touch Anything**
  - o Alarms
    - ▪ **Don't Touch Anything**
- <u>Email</u>
  - o General
    - ▪ Data Recipient: **Blank**
    - ▪ Email Sender: **Blank**
    - ▪ Email Periods (s): **60 (doesn't matter the time, we don't use this setting)**
    - ▪ Send Data: **OFF**
  - o SMTP

- Server: **smtp.gmail.com**
- Port: **587**
- Username: **Blank**
- Password: **Blank**
- Timeout (s): **100**
- SSL Authentication: **ON**
- Auxiliary Coms
  - Modbus
    - Modbus: **ON**
    - System Type: **Ethernet**
    - TCP Port: **502**
    - Unit ID: **2**
    - 16-bit unsigned int to: **OFF**

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

6. Equipment and Supplies

1. Field notebook

2. Tool kit, especially including: 7/64 hex driver, complete set of combination wrenches, adjustable wrenches, screwdrivers, etc.

3. Cleaning supplies designated to be safe for use on a Cerex UV-DOAS – especially lens paper.

4. All relevant PPE, hardware, and procedural guidance per SOP, Safety Plan, and Safe Work Permit

5. Local or remote network link device (as required).

6. External laptop computer with network interface device to the Sentry unit (as required)

7. Cerex UV Sentry Unit equipped with CMS software

8. Cerex UV-DOAS 8" x 8" x 1" pleated filter

9. Isopropyl Alcohol (≥80%)

10. Distilled water

11. Pressurized sprayers

12. Cerex UV-DOAS UV source bulb

13. Nitrile gloves

14. Cell bump test apparatus (including panels, regulators, valves, meters, etc.)

15. Tubing as required: 1/4" PTFE tubing for gas supply from the bottle to the QA cell

16. Tubing as required: 3/8" PTFE tubing with inline flow indicator from the QA cell to the scrubber

17. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less

18. Gas scrubber appropriate for gas used. Activated carbon may be used for benzene.

19. Reference standard traceable zero compressed air purge gas

20. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher

21. Cerex UV Sentry Unit equipped with CMS software

22. Spare reflector for alignment

7. Maintenance Activities

The following sections outline the routine performance indicator checks and maintenance activities to be carried out for each analyzer and sensor, followed by maintenance forms (see Section 9) used to indicate when the checks are completed and document any corrective actions taken. These activities are also expected, based upon the project plan, to be logged in a site logbook either in hard copy or electronic form and can reference this SOP and associated forms.

The following UV-DOAS maintenance activities and performance checks are recommended by the manufacturer:

- Visually inspect the system.

- Inspect optics on detector and retroreflector; clean if necessary.

- Inspect system filters on the optics and retroreflectors.

- Confirm the alignment to verify there has not been significant physical movement. Note: this is automatically monitored as well.

- Download data from detector hard drive and delete old files to free space, if needed. Ensure data are backed up on external drive.

- Ensure there are no obstructions between the detector and the retroreflector (such as equipment, vegetation, vehicles).

- Change out the UV source.

- Replace ventilation exit and intake filters.

- Clean optics on detector and retroreflector.

- Realign system after service.

- Perform bump test (simulates system-observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit.

- Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency.

- Verify system software settings.

- Deliver previous years data to client and remove from brick and analyzer

7.1 Visual Inspections

1. Ensure that the instrument is running and the data look reasonable.

2. Clean and correct any obvious problems with the system (cobwebs, rodent nests, broken optics, etc.).

3. Inspect all electrical cables for wear; replace as needed.

4. Indicate these visual checks are complete on the form included at the end of this document.

5. Document any changes to the system in the course of these checks in the site logbook.

7.2 Filter Inspection and Replacement

Filters are present on both the instrument and the retroreflector fans. Some DOAS units may have two filters on the analyzer to mitigate salt intrusion and subsequent corrosion. Ensure all system filters are visually inspected and replaced if dirty.

Remove and inspect instrument filters following the procedure described here. Replace if necessary. Ensure fans are running (they should make an audible sound) when the system is turned back on.

NOTICE

The UV Sentry should be powered down prior to changing the filter. When powering down, adhere to the recommended shut-down procedure, which includes properly shutting down all applications, and then shut down the instrument PC.

When the PC has been successfully shut down, remove the power cord from the unit.

The UV Sentry contains a filter which must be changed on a periodic basis. Good airflow through the filter is directly related to the ability of the instrument to properly regulate internal temperature. If

the filter is allowed to become clogged (through lack of maintenance), the system can overheat, and go into thermal shutdown. In extreme cases, damage may occur to the internal electronics.

The main filter is a custom size 8" x 8" x 1" pleated filter, which is stocked at the Cerex factory. If a large number of replacement filters are ordered, the lead time could be several weeks.

7.2.1 Filter Installation Procedure

1. Power down the instrument—you cannot replace the filter with the instrument running. First, close the software and shut down the onboard PC. Next, disconnect the power.

2. The filter is accessible by removing the black plate located beneath the instrument touchscreen. The plate has the words "Filter Access" imprinted on it (**Figure 5**).

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

Figure 5. Location of filter access plate.

4. Once the access plate is removed, the filter can be accessed for removal and replacement. Old filters should be discarded and not re-used. Insert the new filter with the "Airflow" arrow pointing in the "UP" direction (**Figures 6 and 7**).

5. When inserting the new filter, do not force the filter into the slot. If you encounter any unusual resistance, open the side door, and ensure no wires have fallen into the filter slot.

6. When fully inserted, the filter should be flush with the instrument case.
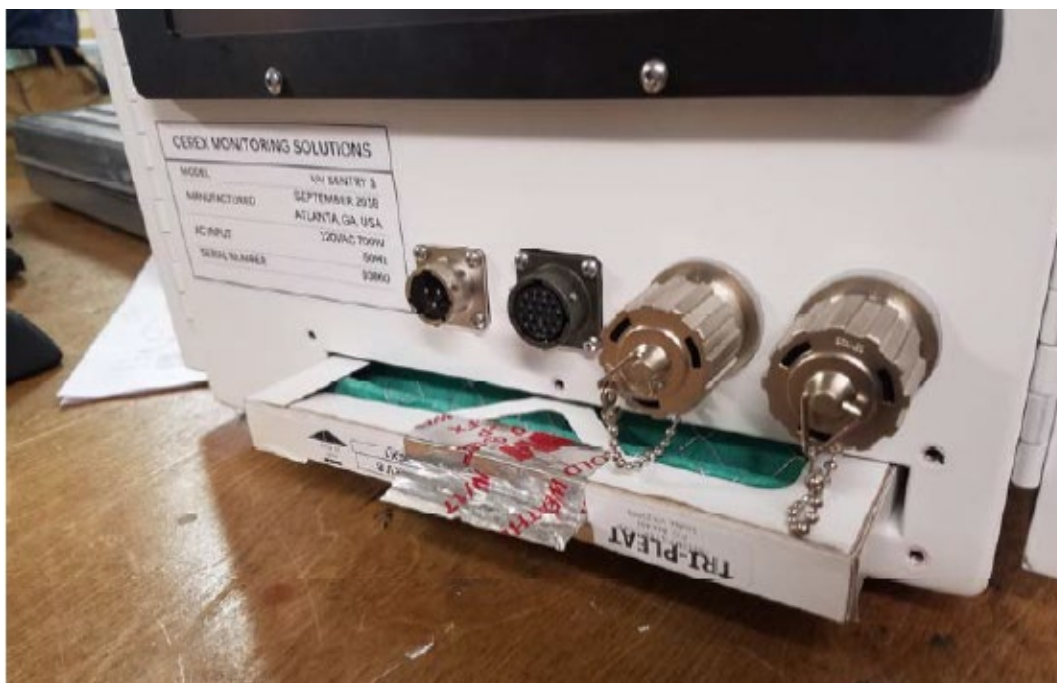
Figure 6. Filter access plate removed and filter partially removed.

Figure 7. Filter completely removed.

7. Re-attach the black filter access panel, using the same driver and six screws.

8. Power up the instrument, make sure CMS software has started, and realign the instrument.

7.3 Light Level Check

For good visibility conditions, signal strength is normally >90% and integration time is normally <50 ms. If it is determined that these values are out of range, re-alignment may be needed.

Check and record signal strength at 250 nm. With an integration time of less than 125 ms, minimum signal intensity at 250 nm should be greater than 5%.

7.3.1 Check for Stray Light

Ensure there is sufficient intensity at 250 nm compared to the stray light intensity. If there is more than 10 - 20% stray light, advanced optical cleaning, replacement, alignment, or bulb change may be necessary. To measure stray light, block the beam from exiting the analyzer with an opaque object (such as a black cloth) and measure the intensity at the wavelength of interest. Calculate stray light by dividing the intensity of the beam while blocked by the intensity of the unblocked beam and multiplying by 100:

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

Note the result of this stray light calculation in the form at the end of this document.

7.4 Data Management

7.4.1 Archiving and Deleting Older Data

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

Raw instrument data are stored on the analyzer computer, the site PC, and the hard drive attached to the site PC. Data consists of spectral data containing two columns: one for wavelength and the other for intensity. There are also two types of "summary" files that contain data resulting from the classical least squares analysis of the spectral data as a function of time. These file formats are described in the CMS Software User Manual.[1] Spectral data and summary files are automatically written to the site PC and moved to the external hard drive after a regular interval. Deliver the external hard drive to the client with the frequency indicated in the QAPP.

As noted above, data on the instrument must be deleted at monthly intervals. Details on the proper procedure for deleting data files from the instrument are as follows.

1. Confirm that the data files have been successfully written to the external hard drive attached to a separate PC also located in the instrument shelter.

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[1] CMS Software User Manual Rev 4. CMS Version 4.0.298.1, CEREX Monitoring Solutions, December 5, 2017.

2. Make a note of the amount of available space on the instrument's internal drive on the maintenance form.

3. Locate files older than 12 months on the instrument file directory here: C:\Users\CMS-USER\Documents\Cerex\Data\.

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

4. Log into the brick PC located in the instrument shelter and locate the data files written from the instrument onto the external hard drive.

5. Confirm all Complete Data Summary files and Simple Data Summary files for the desired month have been transferred over completely to the external hard drive attached to the brick PC.

6. Once you have confirmed that those files have transferred over to the external hard drive, delete those exact Complete Data Summary and Simple Data Summary files from the instrument data folders.

7. For each individual day of single beam folders, ensure that the amount of single beam files are the same on both the external hard drive located on the brick pc and the internal hard of the instrument.

8. If both folder locations match and you have ensured proper file download, you may permanently delete the Single Beam folders from the instrument computer.

9. After all data older than 12 months have been deleted, note how much free space is now available on the instrument's internal drive. If removal of the files does not result in enough free disk space, the disk drive may need to be reindexed (see Section 7.4.2).

7.4.2 Rebuilding the Instruments Indexing Preferences

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

1. Under the **Control Panel Menu**, use the search function in the lower left-hand corner of the task bar to search for "Indexing Options".

2. Click on the **Advanced** tab with the shield logo.

3. Click **Rebuild**.

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

7.5 Clean Optics on Detector and Retroreflector

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

Optic Cleaning

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

1. Wear powder-free gloves to avoid transferring skin oils onto the optics.

2. Use compressed air/canned air to remove particles from the surface of the optic. If the optic is sufficiently clean after this step, stop here

3. Use a solvent (isopropyl alcohol or methanol/acetone in a 60/40 ratio) and lens tissue to wipe the optic clean. If using acetone, make sure to use acetone-impenetrable gloves. Wipe slowly from the edges first with a solvent-soaked lens tissue. One technique is to drop solvent on the unfolded lens tissue and drag from one end to the other.

7.5.1 Retroreflector Cleaning

1. Power down any equipment to prevent electrical shock or damage to the system.

2. Use a gentle stream of distilled water, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust built up on the retroreflector.

3. Use a gentle stream of 80% isopropyl alcohol, usually from a weed sprayer or other type of gentle delivery method, to remove any remaining salt or dust built up on the retroreflector.

4. Once the retroreflector has been cleaned and is dry, repower any electrical equipment you powered down and clean any spills you created while cleaning.

7.6 Inspect and Change Out UV Source If Intensity Spectrum Has Dropped Below Acceptable Range

NOTICE

Never power the UV Sentry without a properly installed Xenon UV Source obtained from Cerex.

Powering the system without a UV source may cause an electrical short, which will permanently damage the instrument.

Always remove the Xenon UV Source and secure the analyzer heat sink anode prior to transporting or shipping the UV Sentry.

Failure to remove the Xenon Source and secure the Heat Sink anode prior to transporting or shipping the UV Sentry may cause destruction of the source as well as the anode.

Always check the polarity of the Xenon UV Source for proper installation prior to powering the analyzer.

Installing the UV source with reverse polarity will permanently damage the UV Source and cause immediate failure. The Xenon UV Source is shipped from Cerex with Heat Shrink and labeling over the Anode (+) end of the Source. The UV Source must be installed so the Anode (+) end of the bulb mounts to the Anode Heat Sink. The UV Source will be oriented with the (+) end at the top.

7.6.1 Xenon UV Source Handling

The UV Sentry Xenon Source is shipped from Cerex in a protective plastic enclosure (see **Figure 8**). The (+) Anode end of the UV Source is labeled "UP." The UV Source must be installed with the (+) side UP. Always wear clean powder-free nitrile gloves when handling the UV Source. Oils from hands deposited on the UV Source glass bulb will cause damage in operation. Remove the "UP +" label from the UV Source prior to installation. If the glass bulb is touched with bare hands, clean the glass bulb with isopropyl alcohol or acetone prior to installation.

Figure 8. The ANODE end of the UV Source is marked (+). The CATHODE end of the UV Source is marked (-).

7.6.2 UV Sentry Xenon Source Removal

Prior to shipping or transporting the UV Sentry, remove the Xenon UV Source and secure the anode heat sink assembly.

1. Power off the analyzer and disconnect from power. Allow the analyzer to cool completely.

2. Use the provided key to remove the Source Access Panel (see **Figure 9**).

Figure 9. Opening the source access panel.

3. Wearing clean nitrile gloves, loosen the retaining thumbscrew on the Anode Heatsink at the top of the UV Source (see **Figure 10**).
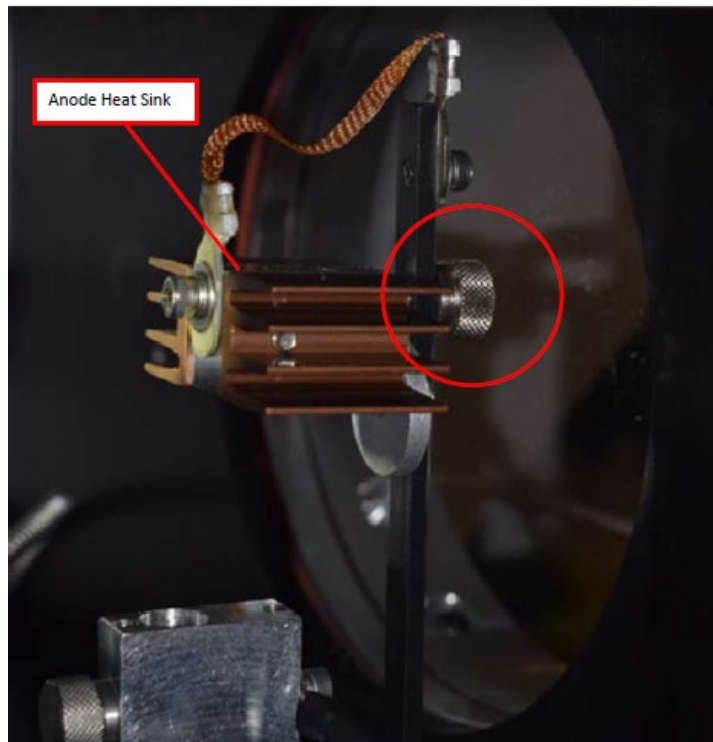
Figure 10. Anode heatsink at the top of the UV source.

4. Lift the Anode Heat Sink off the top of the UV Source. It is connected to the post by a cable. Gently let the heat sink dangle.

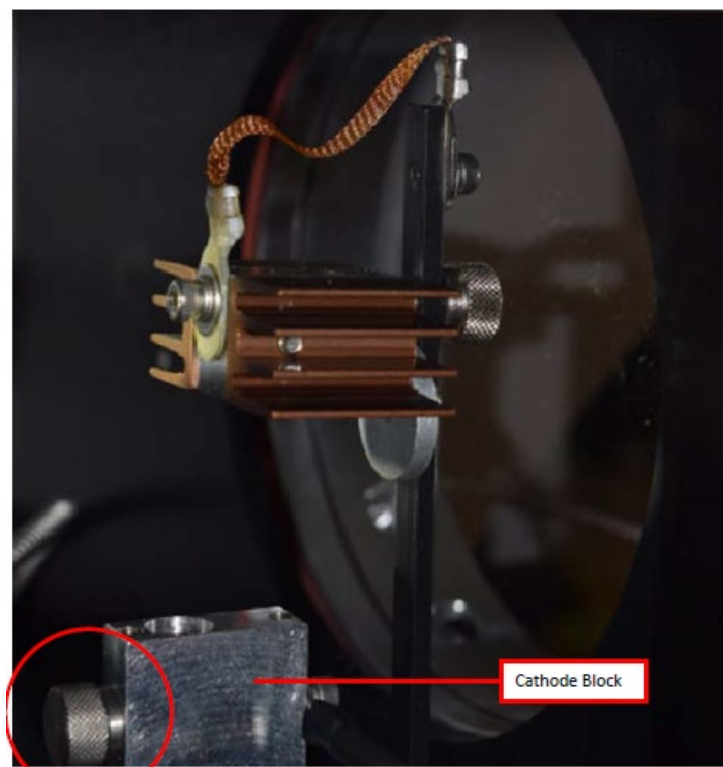5. Loosen the retaining thumbscrew on the Cathode block at the bottom of the source (**Figure 11**).

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

6. Lift the source lamp straight up and out of the mount.

7.6.3 UV Sentry Xenon UV Source Installation

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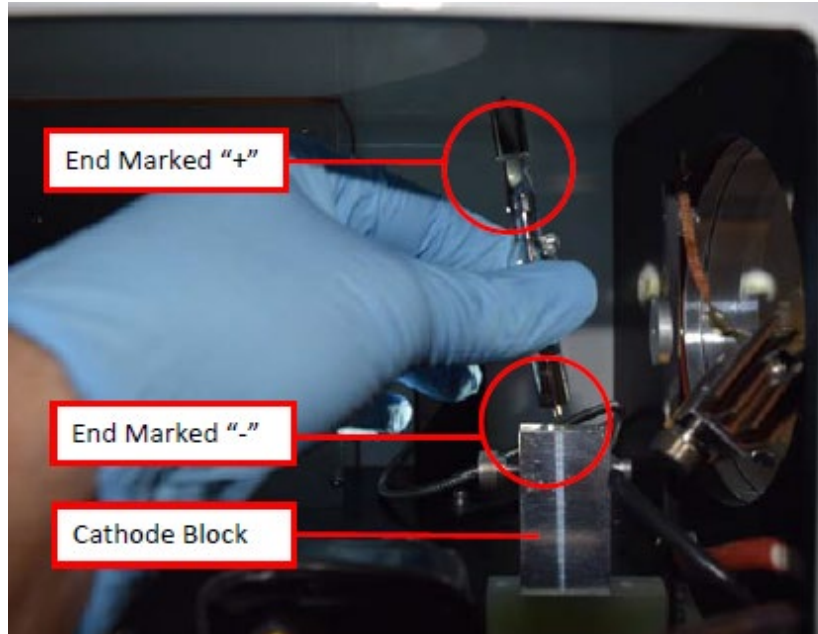
Figure 12. Inserting the Xenon UV Source into the Cathode block.

2. Rotate the UV Source so the nipple on the glass envelope faces the aluminum disc on the mounting post.

3. Tighten the Cathode block thumbscrew gently. Gently pull up on the Xenon UV Source to verify the thumbscrew has made contact with the nipple on the UV Source cathode.

4. Slide the Anode Heat Sink (+) over the top of the UV Source Anode. The Anode end of the UV Source is marked (+). Gently tighten the Anode Heat Sink thumbscrew to secure. Gently pull up on the heat sink to ensure the thumbscrew has made contact with the nipple on the UV Source anode.

5. Reinstall the Source Access Panel prior to powering on the analyzer.

6. Confirm signal strength through remote desktop connection before leaving path.

7.6.4 Secondary Optic Alignment

If there is lower intensity than what was previously observed after the UV Source been replaced, an internal alignment of the secondary optic might be required. This should only be performed by a technician who has been properly trained to perform internal alignments.

Note: Proper PPE must be worn (glasses, sunblock) while performing a secondary alignment to prevent over-exposure to high intensity UV light from the UV Source within the instrument. Also, use an opaque object (such as cardboard or paper) to block as much of the light from the bulb as possible while still maintaining a view of the secondary mirror and fiber (if required).

1. Stop CMS and navigate to the **Alignment** menu.

2. Properly align the instrument at 20 to 25 ms integration time, as shown in **Figure 3**. Make a note of the intensity at 254 nm and the overall shape of the UV signal return.

3. Open the side of the instrument to gain access to the secondary optic.

4. Ensure alignment achieves maximum signal return and is fully aligned to the retroreflector. This is achieved by maximizing signal intensity in align mode at an 8 ms integration time. If signal cannot be confirmed in align mode, this can be done visually by maximizing the visual return brightness on the retroreflector either by looking through the telescope or by placing your head next to the instrument and observing the returned reflection from the retroreflector.

5. If the entire spectrum is visible in the alignment menu, take note of the deep UV intensity at 254 nm. If the instrument is over saturation, as seen in **Figure 4**, take note of the wavelength at which the oversaturation starts.

6. Once the instrument is aligned, take care not to bump the instrument.

7. Adjust the first secondary mirror mount thumb screw to maximize the overall intensity.

8. Move on to the second mirror mount thumb screw and repeat the same process of adjustment to maximize the signal return.

9. In an iterative process, continue to adjust the optical mount screws to maximize intensity, one at a time, until no further gain in signal intensity is achieved.

Note: Only adjust the two thumb screws of the secondary optic.

10. Set the integration time back to 20-25 ms and make sure the instrument is able to achieve a proper UV spectrum, as shown in Figure 3**.** If you are not able to achieve the proper UV spectrum, repeat steps 6-8.

11. Take note of the overall shape of the UV intensity and adjust secondary mirror to maximize intensity at 254 nm**.**

12. Close the access door of the instrument enclosure. Observe if having the access door closed changed the internal alignment.

13. Return the instrument to its normal operation and observe the first few scans to ensure the UV spectra are acquired.

7.7 Perform Bump Test

7.7.1 Apparatus Setup

Audits of open-path analyzers require high concentration (~100 ppm) calibration gases. Standard refinery personal protective equipment (PPE) should be worn at all times, including safety glasses. This procedure requires the use of pressurized gas cylinders; training on proper handling of

pressurized systems is required. The operator-supplied Standard Operating Procedure (SOP), approved by the End User and in compliance with End User's Health and Safety Plan, is also required.

Verify the system is set up (minus the instrument connections) as depicted in **Figure 13**.
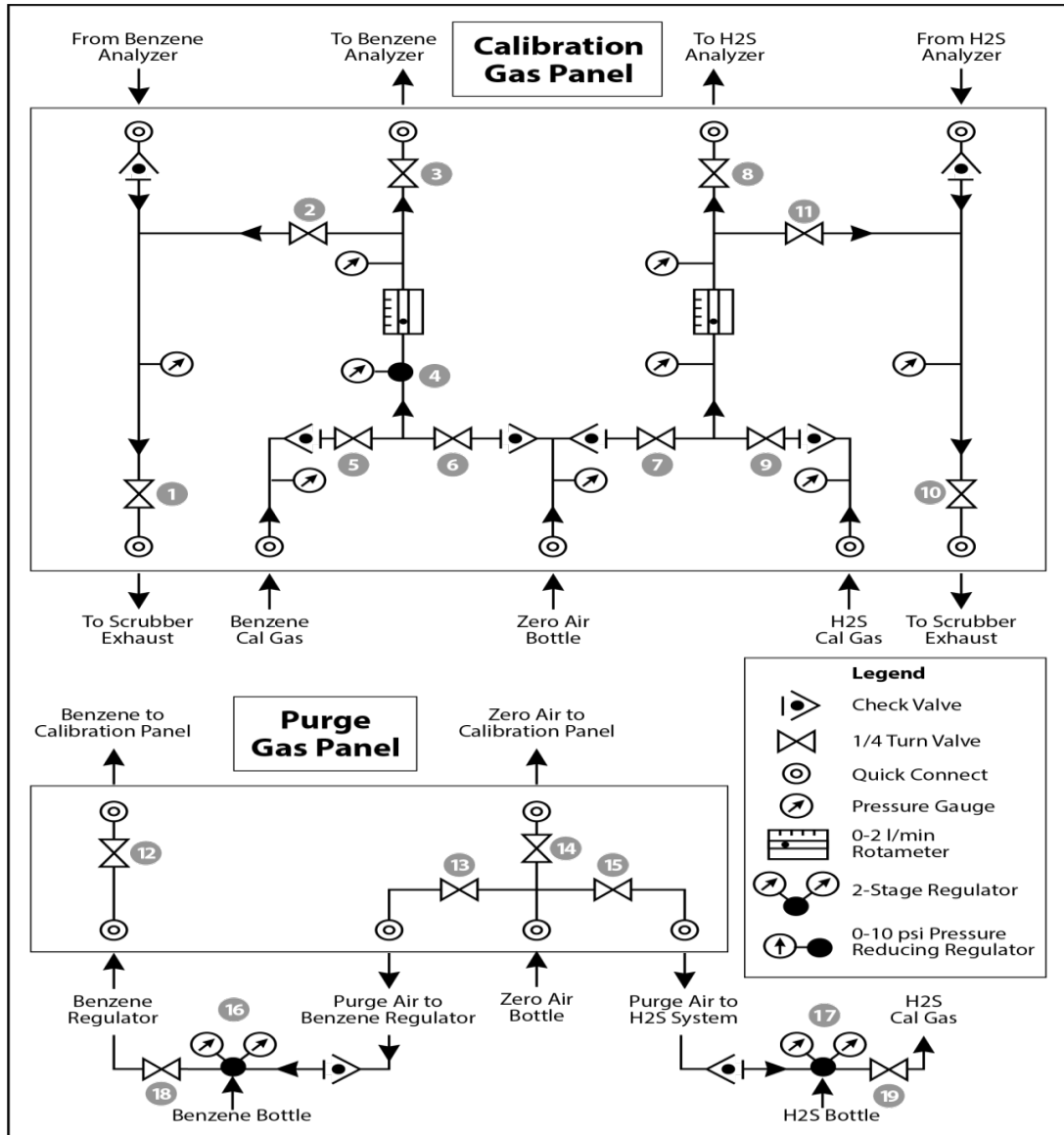

Figure 13. Diagram of the calibration gas panel (top) and purge gas panel (bottom) used for gas delivery.

7.7.2 Prepare CMS for Gas Testing

Note: There is a summary of system settings in Section 5 that can help you when you are changing any setting in the Cerex UV-DOAS instrument.

7.7.3 Configure CMS for Test (This may be concurrent with Gas Purge System setup)

1. The analyzer should be powered and running for **at least 30 minutes**.

2. Stop CMS data collection by pressing the **STOP** button.

7.7.4 Configure Test Files

1. Click **Advanced** on the left side of the CMS software window; password is *advanced*.

2. Under **Advanced** -> **Settings** -> **Runtime -> File**, note the current file path so that it can be restored at the end of the test.

3. Under **Advanced** -> **Settings** -> **Runtime -> File**, turn off **Secondary Logging**.

4. Change the primary file logging paths (both of them) to: C:\Users\CMS-USER\Documents\Cerex\Data\bumptest. Then select **File** and select **Save**.

7.7.5 Leak Check

1. Ensure all the tubing from the purging panel is connected to the calibration panel in the mobile van. Ensure gas cylinders are connected to the purge panel as depicted in Figure 13. Then attach the calibration panel to the analyzer connection in the analyzer shelter.

2. Connect the PTFE tubing containing the activated carbon scrubber to the analyzer exhaust.

3. Close all valves on the calibration and purging panel.

4. Verify that the regulators on the zero air and benzene cylinders are completely closed (all the way to the LEFT!!) to prevent any pressure buildup at the regulator.

5. Open high-pressure valves on both the benzene and zero air bottles.

6. Open valve (14) and slowly open the regulator on the zero air cylinder to a pressure of 5-10 psi, observed on the calibration panel zero gas pressure gauge. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

7. Open valve (12) and slowly open the regulator on the benzene cylinder to a pressure of 5-10 psi on the pressure gauge on the benzene calibration gas channel of the panel. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

8. Open the bypass valve (2).

9. Open zero air valve (6) and slowly open the regulator to a final pressure of about 2 psi (as read on cell and exhaust pressure gauges). **DO NOT pressurize above 3 psi**.

10. Now pressurize cell: slowly open the valve going to the cell (valve 3) and close the bypass valve (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, just open the bypass valve (2) to relieve the pressure on the cell. Wait until the same pressure is reached on the pressure gauge of the exhaust side of the calibration panel.

11. Close the zero air valve (6) going to the benzene regulator on the panel so the system is now fully closed off to external pressure.

12. Watch the system for a minimum of 5 minutes to ensure there is no pressure drop and the system is leak free.

13. Open the leak check valve (1) to release the pressure from the system, and then close all the valves on both panels.

14. Record leak check.

15. Click the **ALIGN** button at the bottom left of the plot display.

16. Adjust the alignment until the signal intensity is optimized.

    a. **Target intensity is 70 – 90%.**

    b. **Target integration time is between 20 ms and 25 ms.**

17. **Record** the intensity and integration time.

7.7.6 Bump Test

This procedure was written assuming that the benzene and zero (purge) air side of the calibration panel has been pressurized according to the procedure above. At this point it is prudent to set up the instrument to start taking test measurements according to the UV-DOAS test procedure.

Background Measurement Using Zero (Purge) Gas

1. Close the secondary pressure regulator (4) on the panel by turning all the way to the left.

2. Open the leak check (1) and bypass valve (2)

3. Open Zero Air Valve (6)

4. Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

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

6. Press **RUN** to start background acquisitions

7. Flow compressed zero air purge gas at total flow of 1 L/min for 10 30-second acquisitions.

8. Monitor until a stable zero reading is reached and then allow the analyzer to run until an acceptable background is reached.

9. Close the zero gas valve (6).

10. Close all valves.

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

7.7.7 Span Test

1. Open the leak check (1) and bypass valve (2).

2. Open the benzene valve (5).

3. Adjust the flow of benzene going through the bypass and scrubber until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves (1) and (2)) is typically less than 1 psi.

4. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, just open the bypass valve (2) to relieve the pressure on the cell. Ensure the desired flow rate has stayed the same and adjust as needed.

5. Wait 5 minutes to fill and condition lines and cell.

6. After 5 minutes of Check Gas flow, press **Start** in CMS.

7. Collect Check Gas data.

    a. Observe the concentration reported on the **DATA** tab.

    b. After the concentration becomes stable, allow the analyzer **to run until 7 - 15 stable measurements are made.**

    c. **Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).**

7.7.8 Completion of Test and Purge of Benzene Regulator

1. Close the benzene cylinder. You will see benzene pressure increase and/or fluctuate as the pressure on the bottle regulator drops. This is normal - be patient and wait for the benzene pressure to zero out.

2. When pressure on cylinder and panel read zero, open the benzene purge valve (13)

3. **Verify that the target gas(es) concentration has returned to 0 ppm** with non-detect R2.

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

4. Once zero reading is indicated on the UV-DOAS, close all valves.

5. Close the zero air cylinder and allow for all the pressure to be released from the system.

6. Close all valves and ensure there is zero pressure on the system.

7. Disconnect tubing to the analyzer and activated carbon scrubber.

7.7.9 Restore Normal Operation

1. **Restore** Normal Operation.

   Note: When restoring normal operation, you will change the file writing path in the settings menu back to the normal file writing path (this is slightly different for each unit, so make a note when first setting up the instrument for the QA test). Once you restart CMS, you will see the file number located on the UV main menu of CMS. If the file count restarts and starts at file 1, you have the incorrect file writing path because it is starting a new folder for the entire day. Also, once you restart CMS, look at the single beam graph also located on the CMS UV main menu to ensure a good alignment and intensity in the lower UV wavelengths.

2. **STOP** CMS.

3. Click **Advanced** on the left side of the CMS software window; password is *advanced*.

4. Under **Advanced** -> **Settings** -> **Runtime** -> **File**, turn On **Secondary Logging**. Change both of the primary file logging paths to: C:\Users\CMS-USER\Documents\Cerex\Data. Then select **File** and click **Save**.

5. Check the system alignment as previously described.

6. Press **RUN** to begin monitoring.

7.7.10 Test Suspension

In the event of a leak or plant alarm requiring suspension of work, the process should be safely suspended.

1. If a plant or site alarm sounds during the validation, stop the test immediately as follows.

2. Close the reference gas bottle valve completely.

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

7.7.11 Data Evaluation, Reporting and Corrective Action

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

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

and the sample standard deviation (σ) as:

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

From these definitions, % error is defined as:

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

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

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

1. Concentration

    a. Average the concentration of 15 consecutive stable measurements.

    b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

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

2. Calculate the Limits of Detection and Quantitation.

    a. Calculate the mean (average), sample standard deviation, and % error (sometimes also referred to as % difference) of the selected results.

    b. Report the Detection Limit as three times the standard deviation.

    c. Report the Quantitation Limit as five times the standard deviation.

3. Compile all configuration files, spectra files, and log files into a single folder.

    a. The folder should be named "CUS LOC QATest UV# YearMonDy" where CUS is a three-letter designator for the customer and LOC is a three-letter designator for the facility location.

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

Note:
- **If the test produces an error or precision greater than the warning level**: corrective action should be taken so that the precision and error are below the warning levels.

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

If the measurements do not meet the data quality objectives listed in the QAPP, repeat the

procedure without adjustment. If the instrument still fails to meet the QA criteria, retest the following day with no adjustment. If these repeated tests continue to fail, initiate corrective actions such as:

- Reviewing data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features.

- Consulting with the project technical lead to identify abnormal changes to the background

- Check wavelength calibration

- Checking for large changes in stray light since the last test and adjusting calibration factors as necessary

- Reviewing gas testing apparatus for leaks or other similar problems

- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

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

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

8. Data Validation and Quality Control

Data for the fenceline monitoring network appears on both public and internal sites. The internal website allows for detailed quality control and flagging of the data. Data are checked daily and finalized quarterly as outlined in the QAPP. This section outlines how to perform daily and quarterly data validation.

8.1 Daily Checks

Both the public website and the admin website need to be checked twice daily (for example, before 10 AM and 10 PM).

1. Ensure that the site is operating properly by pointing your browser to the public website.

2. View the data display on the public website. Take note of any outages by selecting **All Compounds**" from the pollutant dropdown menu.

3. View the time series graphs for each compound by selecting each compound in the pollutant dropdown menu. Verify that pollutant concentrations are reasonable by using the guidance in Table 2. Notify the field operations team if anything seems erroneous.

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

Parameter	Observational Notes
Visibility	~30 miles is the maximum measured by the sensor. Values are typically less than 30 miles due to smog and fog.
Integration Time	Should generally be <250 ms. Report values stuck at 300 ms to PM and fieldopsalerts. Should be anticorrelated with visibility for fog events.
Winds	Typically there is a sea breeze during the day, land breeze at night. Winds are stronger near the coast at met west.
Benzene	Typically below MDL (~1 ppb) – note any high values above REL or immediately visible on the public website (this is a toxic compound
Toluene	Typically below MDL (~1 ppb) – note any high values above REL.
Ethylbenzene	Typically below MDL (~1 ppb) – note any high values above REL.
o-xylene	Typically below MDL (~1 ppb)– note any high values above REL.
m-xylene	Typically below MDL (~1 ppb) – note any high values above REL.
p-xylene	Typically below MDL (~1 ppb) – note any high values above REL.
SO_2	0 to 100 ppb, usually zero. Refineries are a local source – note any high values above REL.
NO_2	Typically 0 to 200 ppb. Values typically peak at night; sunlight destroys it, traffic and combustion produce it. Some instruments may not detect NO_2 if they are saturated.

8.2 Quarterly Validation

Quarterly validation activities involve looking at the data over a longer time period (3 months) than the daily checks (typically a time range of a few days).

1. Plot time series and look for statistical anomalies. If problems are found they may be flagged using the DMS.

2. Review any instrument bump test results.

3. Verify that daily instrument checks were acceptable.

4. Review manual changes to operations/data, and verify that the changes were logged and appropriately flagged; ensure that logged information is complete and understandable.

5. Ensure that instrument checks have the appropriate (Quality Control) QC codes applied.

6. Assign invalid data a Null Code, providing a reason for data being invalid.

7. If a record is not created for a particular site/date/time/parameter combination, create a null record for data completeness.

8. Inspect data consistency.

9. Review collected data ranges for consistency – ranges should remain within expected values over months of monitoring.

10. Check bump test values for completeness; ensure they meet acceptance criteria.

11. Review quarterly data completeness.

9. Maintenance Forms

Path:_____

Technician:_____

Date:_____

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

❒ Notify the client and project manager of maintenance tasks.

❒ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.

❒ Confirm that the data is invalidated on the public website before proceeding with maintenance.

❒ When maintenance is complete check the public site <u>for at least 15 min</u> to ensure proper reporting (no missing data, no high values, etc.).

❒ Take out of maintenance mode

❒ Notify the project manager and client when maintenance is complete.

Upon completion sign and date:_____

Checklist of maintenance activities and performance indicator checks for the UV-DOAS.

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

Activity / Check	Completed (Y/N)
Visually inspect the system.	
Inspect optics on detector and retroreflector; clean if necessary.	
Inspect system filters on the optics and retroreflectors.	
Confirm the alignment to verify there has not been significant physical movement. Note: this is automatically monitored as well.	
Download data from detector hard drive and delete old files to free space, if needed. Ensure data are backed up on external drive.	
Ensure there are no obstructions between the detector and the retroreflector (such as equipment, vegetation, vehicles).	
Change out the UV source.[a]	
Replace ventilation exit and intake filters.	
Clean optics on detector and retroreflector.	
Realign system after service.	
Perform bump test (simulates system-observed gas content at the required path average concentration) to verify the system can detect at or below a lower alarm limit.	
Review and test light and signal levels. Check average light intensity to establish baseline for bulb change frequency.	
Verify system software settings.	
Deliver previous years data to client and remove from brick and analyzer	

[a] UV bulbs will be changed depending on deep UV performance.

Corrective Actions for UV-DOAS:

UV Sentry Fenceline Detection System

DATE: _____   Location: _____

Test Technician 1:_____   2:_____

Physical one-way path length_____ m   Instrument Configuration (mono/bistatic)_____

Sentry Alignment and Light Levels

Integration time	_____	Target 20-24 ms
300 nm Intensity	_____	Target 80-120%
254 nm Intensity	_____	Target >5%

Blocked Beam Intensity at 254 nm _____

% Stray Light   _____

Gas Purge System

Flow purge gas   Start Time _____

Prepare CMS

Path length in the CMS Configuration (typically 1 m for monostatic and 2 m for bistatic)_____ m

Configure Test Files

Site File (i.e., QA Audit UV# YearMoDy)   _____

Baseline Check   _____ init

Reference Gas

Concentration	_____	ppm
Source	_____	
Date	_____	
Cylinder Pressure	_____	

NOTES:

QA Audit Record - UV Sentry Detection System - Page 2

Purge Flow Conditions

Start Time _____

Purge Gas flow _____ L/min

NOTES: Around 1 LPM

Check Gas Test

Initial Gas flow _____ L/min

Around 1 LPM

Start Time _____

Collect Check Gas Data Start Time _____

Data Record:

TIME	PPM	R2
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Verify Client _____ Init

Stop Time _____ Init

Open the **PURGE** gas Time _____

Reference Concentration _____ ppm

Average Concentration _____ ppm

% error _____ %

Std Deviation _____ ppm

% CV _____ ppm

Restore Normal Operation

Restore running data file _____ Init

Press **RUN** to begin monitoring. _____ Init

Appendix B

Standard Operating Procedures for the CEREX AirSentry FTIR

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Contents

1. Scope and Application

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

2. Introduction and Overview

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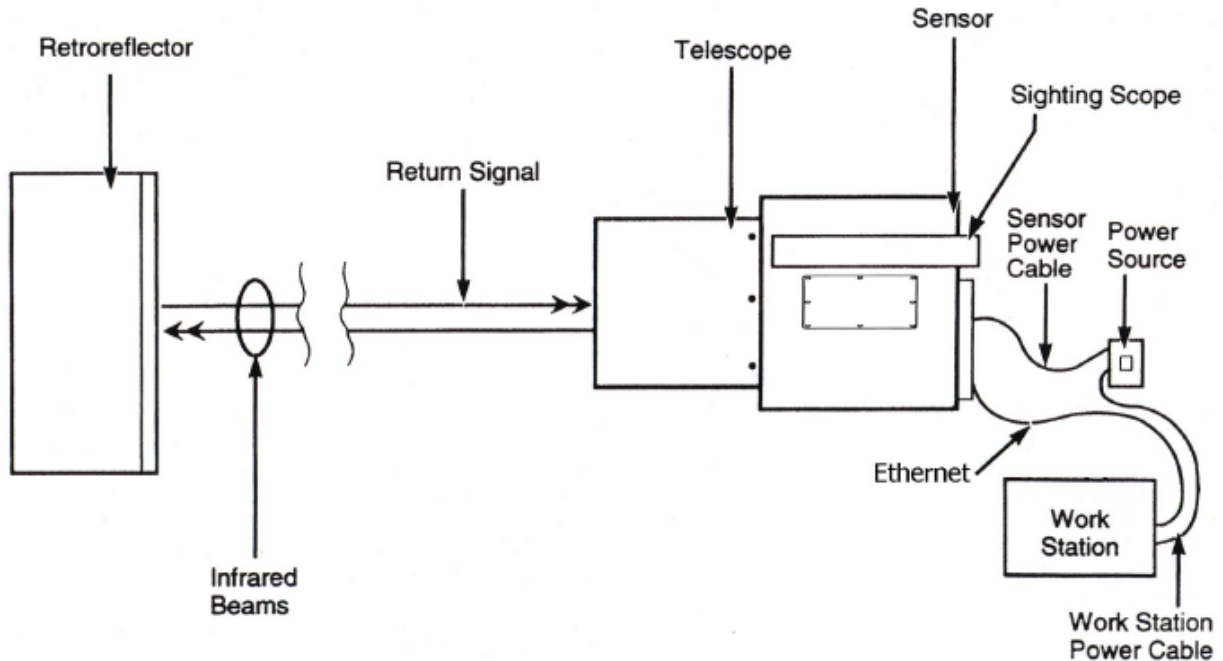
Figure 1. Schematic of the instrument.

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

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

3. Definitions

Table 1. List of definitions.

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

4. Safe Work and Hazard Identification

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

Safe Operating Precautions

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

Operator Qualifications

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

Safe Work and Hazardous Environment Operation

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

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

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

Procedure Warnings

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

NOTICE

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

❒ Notify the client and project manager of maintenance tasks.

❒ Using the field tech tool at ftt.sonomatechmonitor.com, place the equipment into planned or unplanned maintenance mode.

❒ Confirm that the data is invalidated on the public website before proceeding with maintenance.

❒ When maintenance is complete check the public site <u>for at least 15 min</u> to ensure proper reporting (no missing data, no high values, etc.).

❒ Take out of maintenance mode.

❒ Notify the project manager and client when maintenance is complete.

5. Routine Operations

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

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

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

2. Under the **FTIR** tab, left-click on the **Align** button. This action brings up a new screen showing the instantaneous single beam plot (intensity versus wavelength). If the **Align** button is not active, you may need to press **Stop**. The **Align** mode is shown in **Figure 3**.
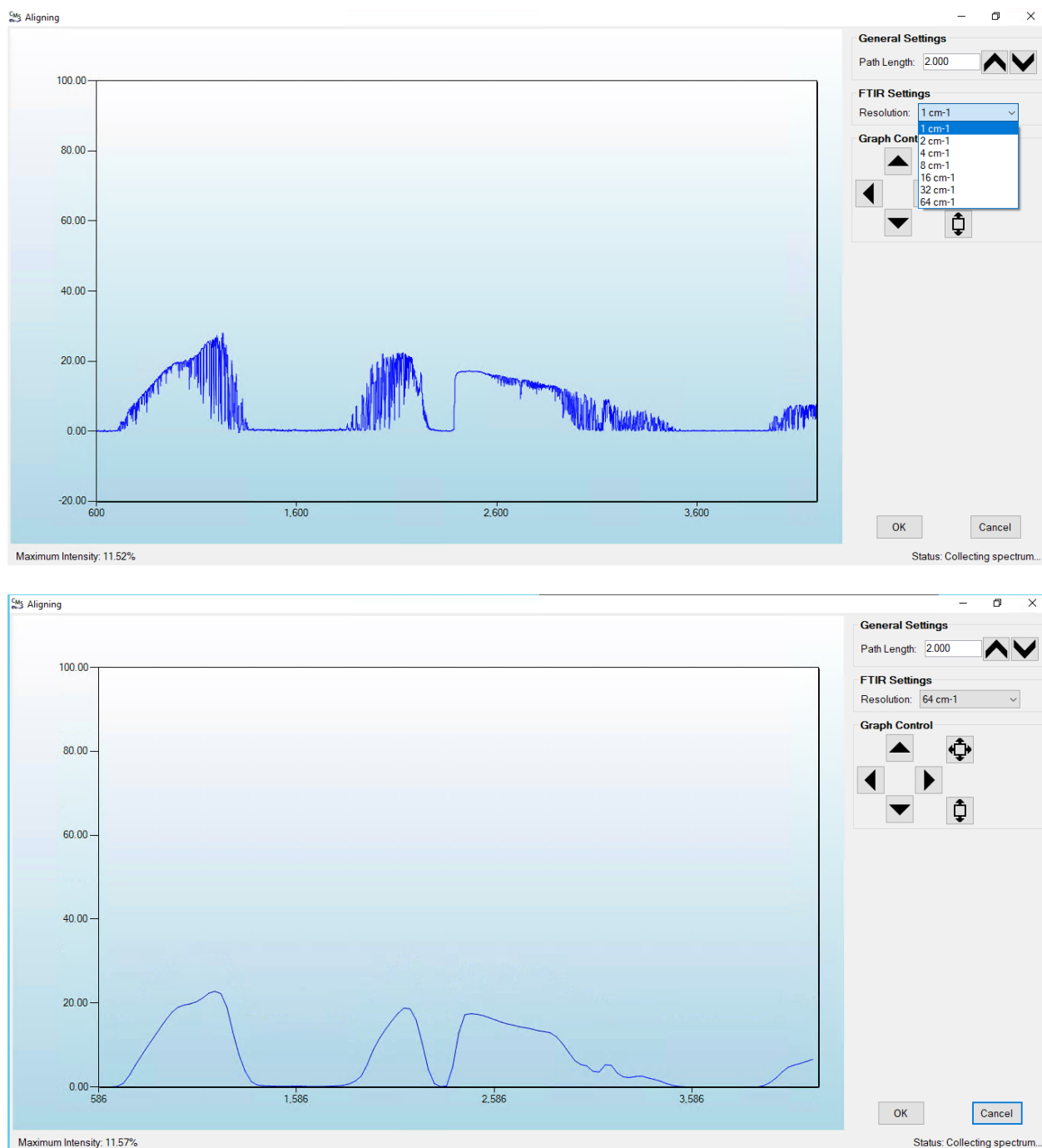
Figure 3. Screenshots of Align mode. The spectral resolution can be selected from the dropdown menu. In these particular screenshots, resolutions of 1 cm^{-1} (top) and 64 cm^{-1} (bottom) are selected.

3. Select a spectral resolution of 64 cm^{-1} and optimize the signal intensity by adjusting the pan-tilt head of the FTIR unit to adjust the position of the IR beam on the retroreflector.

4. Once sufficient alignment is obtained, exit the align mode by pressing **Cancel**.

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

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

- RunTime
  - General
    - Operator Name: **Default** (these will change based on the path and site you are working on)
    - Sitename: **Cerex** (these will change based on the path and site you are working on)
    - Auto Run: `ON` (ON means the instrument will turn on automatically if the computer is running)
    - Auto Run Delay (s): **15** (time delay for CMS autostart)
  - File
    - File Type: **.CSV**
    - Primary Data Logging File: `ON`
      - C:\Users\CMS-USER\Documents\Cerex\Data (file path will vary by facility)
    - Secondary Data File Logging: `ON`

      - \\XXX\XXX\... (file path will vary by facility)
        - Note this path will change based on the computer and path you are working on. This is just a basic file writing path to show you what it should look like.
    - Single Data Folder: `OFF`
    - Primary Summary File Logging: `ON`
      - C:\Users\CMS-USER\Documents\Cerex\Data
    - Secondary Summary File Logging: `ON`
      - \\OPT1-PC1\VLOData\OPT1_Path1\UVSentry_POC1
        - Note this path will change based on the computer and path you are working on. This is just a basic file writing path to show you what it should look like.
    - Single Summary File: `OFF`
  - Library
    - Library File: C:\Users\CMS-USER\Documents\Cerex\Library\
  - UI
    - Sort Column: Compound Name
    - Data Summary Chart: `OFF`
    - Concentration Chart: `OFF`

- Password Protection Settings: **ON**
- Pump Control: **OFF**
- Status Control: **OFF**
- Testing Control: **OFF**

- Analysis
  - General
    - Moving Average Interval: **12**
    - Display Units: **PPM**
  - Concentration
    - Zero Readings on Non-Detect: **OFF** (zeros reading below threshold % match
    - Zero Readings on Negative concentrations: **OFF** (zeros reading less than zero)
    - Display BDL: **OFF**
    - Quick Analysis MDL Wave length Range: **276 -280** (not typically used)
    - Temperature/ Pressure Concentration: **OFF**
  - Filters
    - Absorbance Savitzky-Golay: **OFF**
    - Baseline Correction Savitzky-Golay: **OFF**
  - Background
    - Auto Background: **ON** (typically ON for fenceline monitoring projects reporting concentration above background)
    - Interval (Acquisitions): **5** (How far back the routine will search for a background)
    - Depth: **4**

- Instruments
  - FTIR
    - Operational;
      - FTIR: **ON** (sets instrument type)
      - Averages/Co-adds: **28** (how many spectra will be averaged together)
      - Path Length (m): **2** (2 for monostatic units)
      - Resolution: **1 cm-1** (spectral resolution)
    - Verification
      - Verification: **OFF** **(This inactivates all inputs)**
- Controller
  - General
    - Serial Port: **n/a**
    - Sensor Refresh Interval (s): **10**
  - Sensors
    - **Don't Touch Anything**
  - Alarms
    - **Don't Touch Anything**

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

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

6. Equipment and Supplies

1. Field notebook

2. Tool kit, especially including: 7/64 hex driver, complete set of combination wrenches, adjustable wrenches, screwdrivers, etc.

3. Cleaning supplies designated to be safe for use on a Cerex FTIR

4. All relevant PPE, hardware, and procedural guidance per SOP, Safety Plan, and Safe Work Permit

5. Local or remote network link device (as required)

6. External laptop computer with network interface device to the Sentry unit (as required)

7. Cerex FTIR Sentry Unit equipped with CMS software

8. Isopropyl Alcohol (≥80%)

9. Distilled water

10. Pressurized sprayers

11. Powder-free nitrile gloves

12. Cell bump test apparatus (including panels, regulators, valves, meters, etc.)

13. Tubing as required: 1/4" metal jacketed PTFE tubing for gas supply from the bottle to the QA cell

14. Tubing as required: 3/8" metal jacketed PTFE tubing with inline flow indicator from the QA cell to the scrubber

15. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less

16. Gas scrubber appropriate for gas used. Activated carbon treated with phosphoric acid may be used for benzene

17. Reference standard traceable zero compressed air purge gas

18. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher

7. Maintenance Activities

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

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

- Visually inspect the system.

- Confirm the alignment to verify there has been no significant physical movement. Note: this is automatically monitored as well.

- Download data older than 6 months from detector hard drive and if needed delete old files to free space.

- Ensure there are no obstructions between the detector and the retro-reflector.

- Replace air conditioner fans.

- Change out the IR source.

- Realign system after service.

- Check system response (bump test). Take corrective action if % Error exceeds level specified in the QAPP.

- Review and test light and signal levels.

- Verify system settings.

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

7.1 Monthly Visual Inspections

1. Ensure that the instrument is running and the data look reasonable.

2. Clean and correct any obvious problems with the system (cobwebs, rodent nests, broken optics, etc.).

3. Inspect all electrical cables for wear; replace as needed.

4. Indicate these visual checks are complete on the form included at the end of this document.

5. Document any changes to the system in the course of these checks in the site logbook.

7.2 Light Level Check

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

Check for Stray Light

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

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

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

7.3 Data Management

7.3.1 Archiving and Deleting Older Data

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

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

1. Confirm that the data files have been successfully written to the external hard drive attached to a separate PC also located in the instrument shelter.

2. Make a note of the amount of available space on the instrument internal drive on the maintenance form.

3. Locate files older than 12 months on the instrument file directory here: C:\Users\CMS-USER\Documents\Cerex\Data\.

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

4. Log into the brick PC located in the instrument shelter and locate the data files written from the instrument onto the external hard drive.

5. Confirm all Complete Data Summary files and Simple Data Summary files for the desired month have transferred over completely to the external hard drive attached to the brick PC.

6. Once you have confirmed that those files have been transferred over to the external hard drive, delete those exact Complete Data Summary and Simple Data Summary files from the instrument data folders.

7. For each individual day of single beam folders, ensure that the amount of single beam files are the same on both the external hard drive located on the brick pc and the internal hard of the instrument.

8. If both folder locations match and you have ensured proper file download, you may permanently delete the Single Beam folders from the instrument computer.

9. After all data older than 12 months have been deleted, note how much free space is now available on the instrument's internal drive. If removal of the files does not result in enough free disk space, the disk drive may need to be reindexed (see Section 7.3.2).

7.3.2 Rebuilding the Instruments Indexing Preferences

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

---

[1] CMS Software User Manual Rev 4. CMS Version 4.0.298.1, CEREX Monitoring Solutions, December 5, 2017.

1. Navigate to the **Control Panel Menu** by using the search function in the lower left-hand corner of the task bar.

2. Once in the control panel menu, click **Indexing Option.**

3. Click on the **Advanced** tab with the shield logo.

4. Click **Rebuild**.

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

7.4 Clean Optics on Detector and Retroreflector

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

7.4.1 Retroreflector Cleaning

1. Power down any equipment to prevent electrical shock or damage to the system.

2. Use a gentle stream of distilled water, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust build-up on the retroreflector.

3. Use a gentle stream of 80% isopropyl alcohol, usually from a weed sprayer or other type of gentle delivery method, to remove any salt or dust build-up on the retroreflector.

4. Once the retroreflector has been cleaned and dried, repower the any electrical equipment you have powered down, and clean any spills you have created while cleaning.

7.4.2 Optic Cleaning

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

1. Wear powder-free gloves to avoid transferring skin oils onto the optics.

2. Use compressed air/canned air to remove particles from the surface of the optic. If the optic is sufficiently clean after this step stop here.

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

7.4.3 Replace AC Fans

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

1. Turn off MDAs and place unit into Planned Maintenance.

2. Close CMS, Shut down operating system.

3. Unplug power to unit.

4. Open FTIR lid.

    a. Note: (place barrier to prevent screws from falling into the FTIR assembly).

5. Remove shroud fan cover on the underside of the FTIR lid.

6. Make note of fan orientation before removal (i.e. front facing).

    a. Unplug each fan, then remove the four screws holding each fan for removal.

7. Install new fans with screws, then plug fans into power source.

8. Close FTIR lid.

9. Plug in the FTIR power source and begin operations.

10. Start CMS and align FTIR if needed.

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

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

<div align="center">

***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.

</div>

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

7.5.1 Apparatus Setup

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

Verify system is set up (minus the instrument connections) as depicted in **Figure 4**.
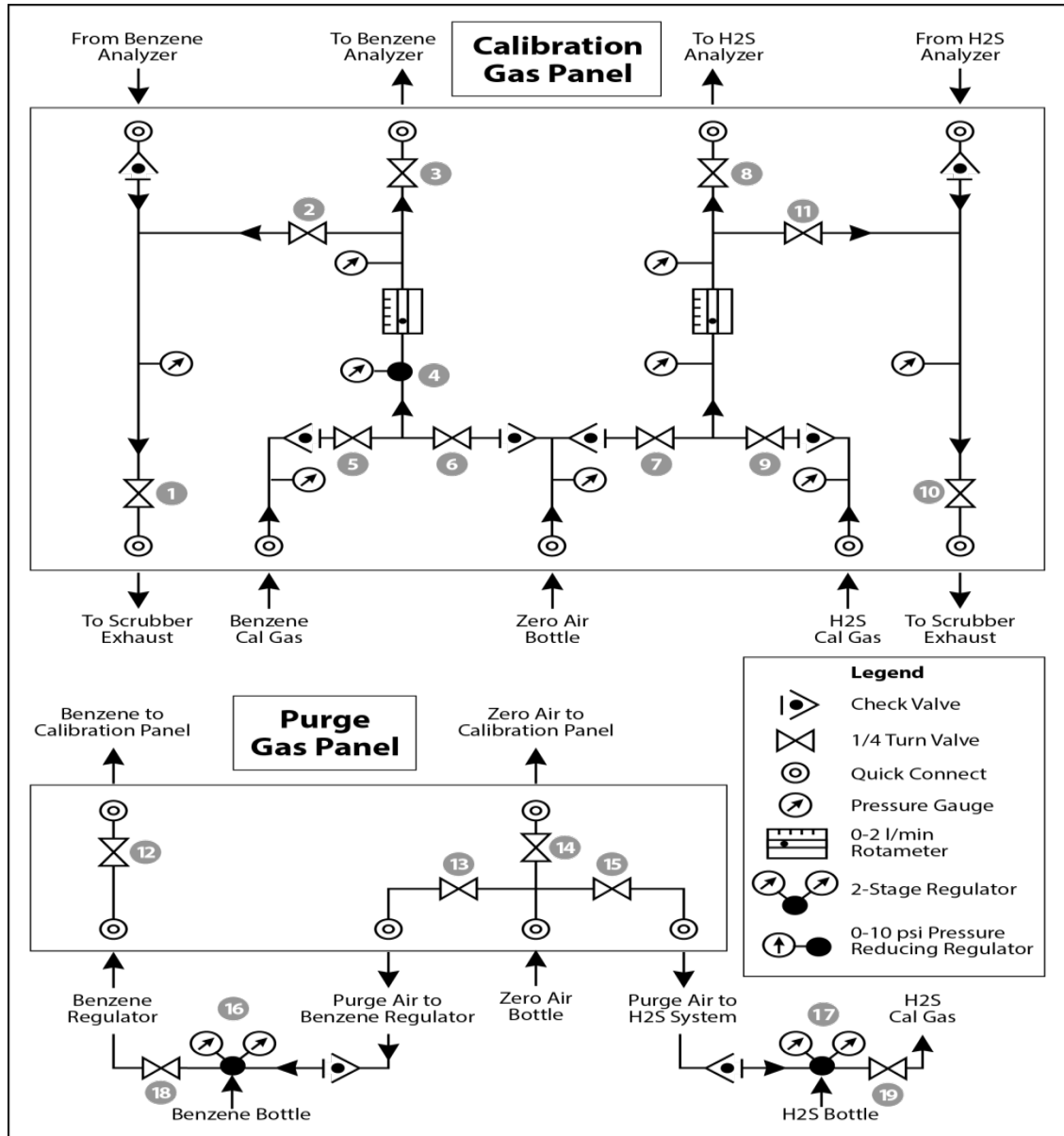
Figure 4. Diagram of the calibration gas panel (top) and purge gas panel (bottom) used for gas delivery. Note that the gas used will change depending on the instrument.

Materials Required

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

2. Cell bump test purge apparatus, including:

   a. Tubing as required: 1/4" PTFE tubing for gas supply from the calibration gas panel to the QA cell.

   b. Tubing as required: 3/8" PTFE tubing for gas supply from the QA cell to the calibration gas panel.

   c. All necessary tubing for supplying calibration and zero reference gas to calibration gas panel.

   d. Flow regulation system capable of delivering gas 0.1 to 5 L/min at a total system pressure of 3 psig or less.

3. Purge gas; typically, Zero Air.

4. Reference standard traceable gas blend in nitrogen for detection at about 5X instrument theoretical detection limit or higher.

5. All relevant PPE, hardware and procedural guidance per SOP, Safety Plan, and Safe Work Permit.

6. Local or remote network link device (as required).

7. External laptop computer with network interface device to the AirSentry FTIR unit (as required).

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

1. The analyzer should be powered on and running for <u>at least 30 minutes prior to testing</u>.

2. Stop CMS data collection by pressing the **STOP** button.

7.5.3 Gas Test System Setup

1. Connect the ¼" reference cell line coming from the calibration panel to the ¼" reference cell connection on the Cerex MS Air Sentry FTIR.

2. Connect the 3/8" reference cell line coming from the calibration panel to the 3/8" reference cell connection on the Cerex MS Air Sentry FTIR located just below the ¼" refence cell inlet.

3. Ensure all valves on the calibration gas panel are in the closed position.

4. Make all necessary connections from Zero Air and calibration gas standard cylinders to the Gas Calibration Panel.

7.5.4 Verify Proper AirSentry Alignment

1. Open the CMS window.

2. Click on the **FTIR** tab.

3. If **Run** is active, press **STOP**.

4. Click the **ALIGN** button at the bottom left of the plot display.

5. Select 32 cm^{-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. **The target intensity should be the highest achievable intensity, which varies based on instrument, but should be above 5% at minimum. Once a stable signal is obtained, select the desired operating resolution (1 cm^{-1} is required unless otherwise directed by Cerex).**

7. **Record** the signal intensity.

   a. **Optional – at this point you may wish to record the current field pathlength and create a backup of the existing configuration file.**

8. Press **OK** and **SAVE** or **ACCEPT** (when prompted) to exit the CMS Alignment window.

7.5.5 Leak Check

1. Ensure that all tubing from the purging panel is connected to the calibration panel in the mobile van. Ensure gas cylinders are connected to the purge panel as depicted in Figure 4. Then attach the calibration panel to the analyzer connection in the analyzer shelter.

2. Connect the PTFE tubing containing the activated carbon scrubber to the analyzer exhaust.

3. Close all valves on the calibration and purging panel.

4. Verify that the regulators on the zero air and benzene cylinders are completely closed (**all the way to the left**!) to prevent any pressure buildup at the regulator.

5. Open high-pressure valves on both the calibration gas and zero air bottles.

6. Open valve (14) and slowly open the regulator on the zero-air cylinder to a pressure of 5-10 psi, observed on the calibration panel zero gas pressure gauge. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

7. Open valve (12) and slowly open the regulator on the calibration gas cylinder to a pressure of 5-10 psi on the pressure gauge on the benzene calibration gas channel of the panel. Do this by making small adjustments at the cylinder regulator and watching the pressure on the calibration panel.

8. Open the bypass valve (2).

9. Open the zero-air valve (6) and slowly open the regulator (4) to a final pressure of about 2 psi (as read on cell and exhaust pressure gauges). **DO NOT pressurize above 3 psi**.

10. Now pressurize the cell. Slowly open the valve going to the cell (valve 3). Close the bypass valve (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve pressure on the cell. Wait until the same pressure is reached on the exhaust-side calibration panel pressure gauge.

11. Close the zero-air valve (6) going to the benzene regulator on the panel so the system is now fully closed off to external pressure.

12. Watch the system for a minimum of five minutes to ensure there is no drop in pressure and the system is leak free.

13. Open the leak check valve (1) to release the pressure from the system, and then close all the valves on both panels.

14. Record leak check.

7.5.6 Configure Test Files

1. Click **Advanced** on the left side of the CMS software window. The password is *advanced*.

2. Under **Advanced** -> **Settings** -> **Runtime** -> **File**, turn off **Secondary Logging**. Note current file logging paths.

3. Change both of the primary file logging paths to: C:\Users\CMS-USER\Documents\Cerex\Data\bumptest. Then select **File** and **Save**.

7.5.7 Gas System Purge

1. Close the secondary pressure regulator (4) on the panel by turning all the way to the left.

2. Open the leak check (1) and bypass valve (2).

3. Open the zero-air valve (6).

4. Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

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

6. Press **RUN** to start background acquisitions.

7. Allow the analyzer to complete **three** or more acquisitions.

    a. If after two acquisitions the absorbance graph shows negative features greater than 3X the peak-to-peak baseline noise level, take another clean air background.

8. Repeat this process until the sequential absorbance acquisition seen in the absorbance graph remains near zero (straight baseline with only normal noise peaks).

9. Once the instrument has performed ten or more acquisitions, close the zero-gas valve (6).

10. Close all valves.

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

7.5.8 Gas Span and QA Test

1. Open the leak check (1) and the bypass valve (2).

2. Open the calibration gas valve (5).

3. Adjust the flow of calibration gas going through the bypass and scrubber until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

4. Open the valve going to the cell (3) and close the valve on the bypass (2) while carefully watching the cell pressure gauge after the regulator (4). If you note any sudden pressure increase, open the bypass valve (2) to relieve the pressure on the cell. Ensure the desired flow rate has stayed the same and adjust as needed.

5. Wait 10 minutes to fill and condition lines and cell.

6. After 10 minutes of calibration span gas flow, press **Start** in CMS.

7. Collect span gas data.

    a. Observe the concentration reported on the **DATA** tab.

    b. After the concentration becomes stable, allow the analyzer **to run until at least seven stable measurements are made.**

    c. **Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).**

    d. **Verify client system** is receiving and displaying instrument information correctly.

    e. After seven stable measurements are observed, **close the reference gas cylinder valve (6)**. Allow the pressure to fall to zero and the flow to stop.

7.5.9 Completion of Test and Purge of Instrument Calibration Cell

1. Close the calibration gas cylinder. You will see calibration gas pressure increase and/or fluctuate as the pressure on the bottle regulator drops. This is normal - be patient and wait for the benzene pressure to zero out.

2. Close all valves on the calibration and purging panel.

3. Open the zero-air valve (6).

4. Adjust the flow of purge air going through the bypass until the desired flow rate (1 lpm) and pressure are achieved by slowly increasing the pressure on the secondary pressure regulator (4). The backpressure on the scrubber (measured between valves [1] and [2]) is typically less than 1 psi.

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

6. **Verify that the target gas(es) concentration has returned to 0 ppm** with non-detect R^2.

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

7. Once a zero reading is indicated on the FTIR, close all valves.

8. Close the zero-air cylinder and allow all the pressure to be released from the system.

9. Close all valves and ensure there is zero pressure on the system.

10. Disconnect tubing to the analyzer and the activated carbon scrubber.

11. Remove the hoses and cap the connectors.

7.5.10 Restore Normal Operation

1. **Restore** Normal Operation.

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

    a. **STOP** CMS.

    b. Click **Advanced** on the left side of the CMS software window; password is *advanced*.

    c. Under **Advanced** -> **Settings** -> **Runtime** -> **File**, turn On **Secondary Logging**. Change the primary file logging paths (both of them) to: C:\Users\CMS-USER\Documents\Cerex\Data. Then select **File** and select **Save**.

2. **Check the system alignment** as previously described.

3. Press **RUN** to begin monitoring.

Test Suspension

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

1. Close the reference gas bottle valve completely.

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

7.5.11 Data Evaluation, Reporting, and Corrective Action

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

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

and the sample standard deviation (σ) as:

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

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

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

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

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

1. Concentration

    a. Average the concentration of 7 - 15 consecutive stable measurements.

    b. Report the % error between the average and the certified value. The acceptable % error is listed in the QAPP.

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

2. Calculate the Limits of Detection and Quantitation

    a. Calculate the mean (average), sample standard deviation, and %error (sometimes also referred to as % difference) of the selected results.

    b. Report the Detection Limit as three times the standard deviation.

    c. Report the Quantitation Limit as five times the standard deviation.

3. Compile all configuration files, spectra files, and log files into a single folder.

    a. The folder should be named "CUS LOC QATest IR# YearMoDy" where CUS is a three-letter designator for the customer, and LOC is a three-letter designator for the facility location.

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

Note:

- **If the test produces an error or precision greater than the warning level:** corrective action should be taken so that the precision and error are below the warning levels.

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

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

- Reviewing data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features

- Consulting with the project technical lead to identify abnormal changes to the background

- Check wavelength calibration

- Checking for large changes in stray light since the last test and adjusting calibration factors as necessary

- Reviewing gas testing apparatus for leaks or other similar problems

- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

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

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

7.6 Cryocooler Replacement and Calibration

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

b. Unplug the power connector (two-pin Molex with gray cable) from the cryocooler engine (**Figure 5**).
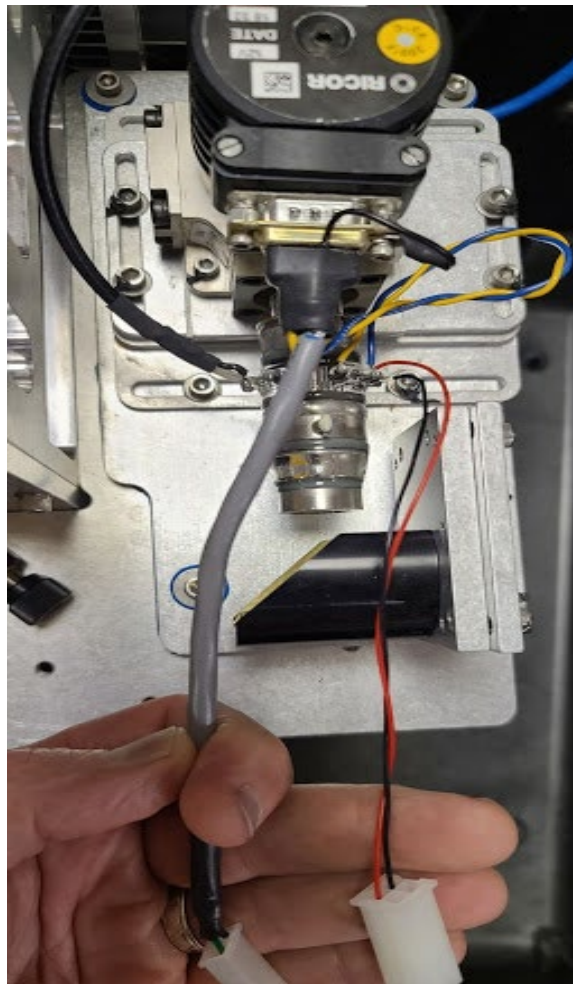
Figure 5. Detector assembly showing RICOR cryocooler, glass detector, DB9 connector, two white Molex connectors, and mirror.

c. Unplug the black and red cable molex connector coming from the glass detector assembly.

d. In some installations there is a ground cable coming from connector and going to the chassis. Remove the ground cable by unscrewing it from the chassis.

e. Take out the 3 #8 screws that hold the detector assembly to the baseplate - these will have blue grommets in the holes (See image below). Only remove 3 screws to release the entire assembly (**Figure 6**).

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

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

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

g. Disconnect power to the preamp - this is a 4-pin molex connector that can be pulled apart. The connector has purple, orange, and black wires.

h. Follow the second black coax cable from the preamp over the 4" x 6" heatsink assembly. Remove the BNC connection to this heatsink by hand twisting 1/4 turn counterclockwise and pulling it off.

i. The detector assembly and the preamp will come out together as they are attached to each other by a coax cable.

j. Pack the detector assembly and the preamp in the same box. But wrap both items separately so they can not touch. Immobilize all items in the box. Use protective case to transport entire assembly securely.

2. Re-install cryocooler

    a. The installation process is the opposite of removal.

    b. Make sure all screws and connectors are secured and tightened.

3. Optics Calibration

    a. After replacing or installing a new detector and optics optimization is required using a small test retroreflector array.

        i. Place the test retroreflector array about 2 feet from the front of the FTIR scope. Alternatively, use a small "bike reflector" in the outgoing beam path, just before the light enters the bump test cell.

        ii. With the instrument powered on and using the Align window, set the resolution to 64 ms and align the scope to obtain the maximum signal strength possible.

        iii. Open the instrument and carefully use the beam splitter adjustment screws to maximize signal strength. This means making small adjustments to each screw until you reach the maximum signal strength (**Figure 8**).
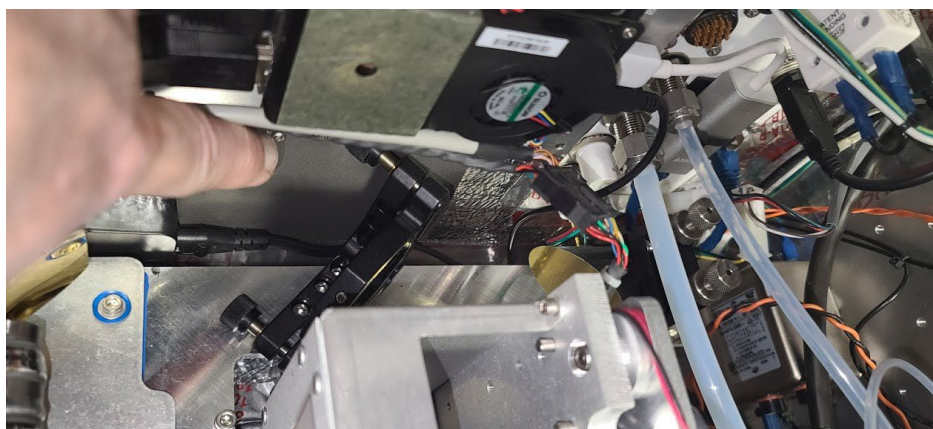
Figure 8. Beamsplitter (black object at 45-degree angle) with adjustment screws.

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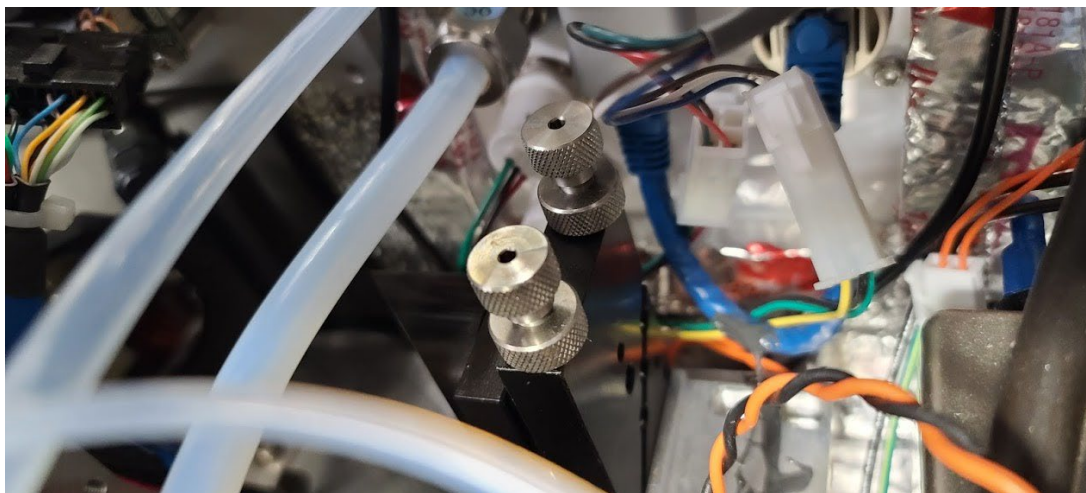
Figure 9. Beam steering mirror with sliver adjustment screws.

8. Monthly Maintenance Forms

Path:_____

Technician:_____

Date:_____

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

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

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

Upon completion, sign and date:_____

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

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

Corrective Actions for FTIR:

Cerex FTIR Air Sentry Gas Test Summary

DATE: _____   Location: _____

Test Technician 1:_____ 2:_____

Sentry Alignment

    Signal Intensity (average)   _____

    Signal Intensity at 966 cm^{-1} _____

    Blocked Beam Intensity at 966 cm^{-1} _____

    % Stray Light   _____

Gas Purge System

    Flow purge Start Time _____

Prepare CMS

    Path length in the CMS Configuration   _____ m

Configure Test Files

    Site File (i.e., QA Audit UV# YearMoDy) _____

    Baseline Check   _____ init

Reference Gas

    Concentration   _____ ppm

    Source   _____

    Date   _____

NOTES:

Gas Test Summary – Cerex FTIR - Page 2

Purge Flow Conditions

    Start Time   _____

    NOTES:

Check Gas Test

    Initial Gas Flow   _____ L/min

    Start Time   _____

    Collect Check Gas Data Start Time   _____

    Data Record:

TIME	PPM	R2
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

    Verify Client   _____ Init

    Stop Time   _____ Init

    Open the PURGE Gas   Time   _____

    Reference Concentration   _____ ppm

    Average Concentration   _____ ppm

    % error   _____ %

    % Spectral Match   _____ %

    Standard Deviation   _____ ppm

    Estimated MDL (3X Standard Dev)   _____ ppm

Restore Normal Operation

    Restore running data file   _____ Init

    Press **RUN** to begin monitoring.   _____ Init

Appendix C

SOP for Synspec GC955 Hydrocarbon Analyzer

May 31, 2022   STI-7984
Steven Schill, PhD, and Chelsie Winborg
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Contents

1.   Scope and Application

This appendix refers to the use of the Synspec GC955 analyzer for the continuous measurement of volatile organic compounds (VOCs) at community air monitoring stations. It includes procedures on the operation, quality checking, and calibration of the unit.

2.   Summary of Method

An automatic gas chromatograph (AutoGC) collects air samples via vacuum pump (ambient) or pressurized source (span/calibration) and separates compounds according to their retention time in an internal separation column. Following separation, compounds are measured with a photoionization detector (PID). This combination of separation and detection allows for identification and quantification of a range of VOCs. **Figure 1** from the GC955 manual shows the unit configuration.
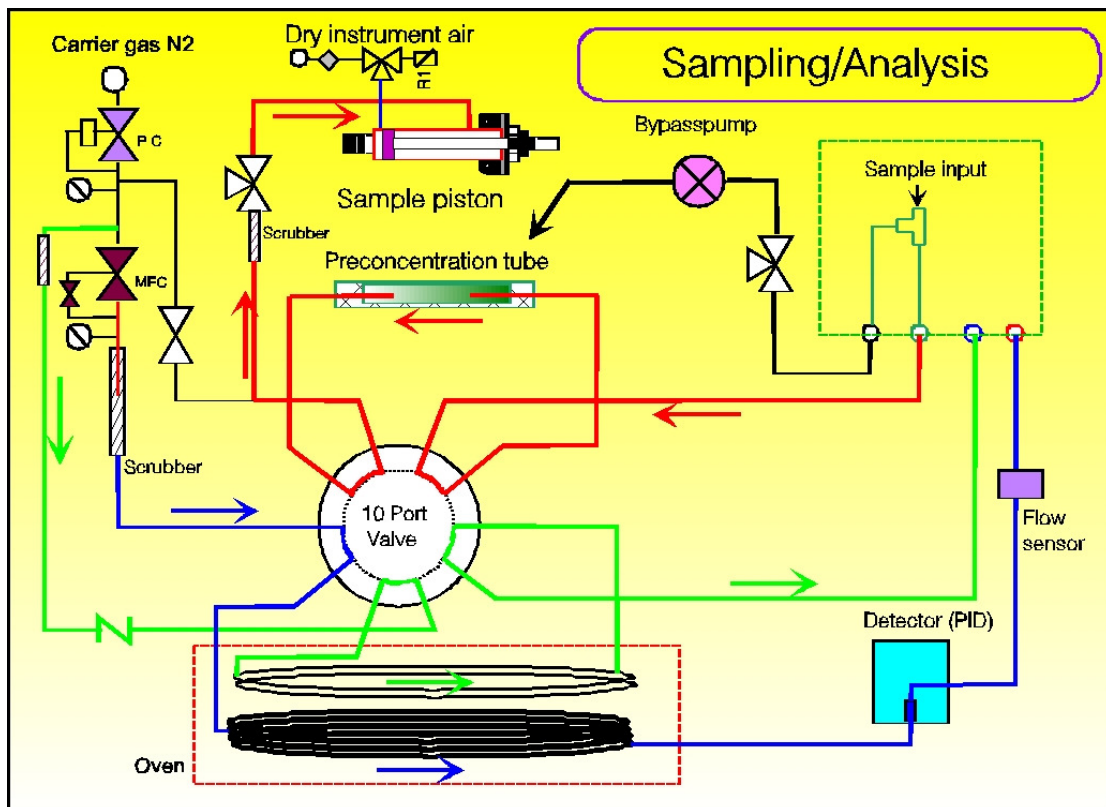
Figure 1. Instrument configuration in analyzing/sampling mode from the GC955 manual.

The major processes in getting from a sample to a concentration value are described in Section 3 of the GC955 manual. They include:

- **Sampling**: collecting a sample of ambient air.
- **Pre-concentration**: accumulating enough sample for analysis.
- **Desorption and Stripping**: moving sample from the pre-concentrator into the separation column.

- **Separation**: separating compounds based on their interaction with the separation column.
- **Detection**: measuring separated compounds with a PID to allow identification and quantification.

3.   Definitions

Abbreviation	Meaning
AC	Alternating current
BAM	Beta attenuation monitor
BC	Black carbon
C14	Carbon 14
CFR	Code of Federal Regulations
CO_2	Carbon dioxide
CPU	Central processing unit
CV	Coefficient of variance
DAS	Data acquisition system
DOT	Department of Transportation
DQO	Data quality objective
DRV	Documented reference value
EC	Elemental carbon
FEM	Federal equivalent method
GC	Gas chromatograph
H_2O	Water
H_2S	Hydrogen sulfide
IO	Input/output
IR	Infrared
IZS	Internal zero/span device
kV	Kilo volts
LPM	Liters per minute
MFC	Mass flow control/controller
MSDS	Material safety datasheet
N/A	Not applicable
NH_3	Ammonia
NH_3_CE_FACTOR1	The ammonia converter efficiency factor
NO	Nitrogen oxide

Abbreviation	Meaning
NO$_2$	Nitrogen dioxide
NO$_2$_CE_FACTOR1	Nitrogen oxide efficiency factor
NO$_x$	Oxides of nitrogen
O$_2$	Oxygen
PC	Personal computer
PID	Photoionization detector
PM	Particulate matter
PM$_{10}$	Particulate matter with aerodynamic diameter less than 10um
PM$_{2.5}$	Particulate matter with aerodynamic diameter less than 2.5um
ppb	Part per billion
ppm	Parts per million
psi	Pounds per square inch
QA	Quality assurance
QC	Quality control
QS	Quality standard
RH	Relative humidity
RS-232	Analyzer digital communication port
SO$_2$	Sulfur dioxide
SOP	Standard operating procedure
TM	Trademark
TNX	The sum of the ammonia and the oxides of nitrogen concentrations
UPS	Uninterrupted power supply
U.S. EPA	United States Environmental Protection Agency
UV	Ultraviolet
VAC	Volts alternating current
VSCC	Very sharp cut cyclone
Z/S	Zero/span

4. Health and Safety Warnings

The following is a summary of risks and qualifications relevant to analyzer operation. See the GC955 manual for additional information.

- Compressed gas at pressures from 0.5 to 5 bar will be connected to the analyzer. Personnel must be qualified to work safely with pressurized systems.

- The analyzer contains a high-voltage power supply in a protective housing. Personnel must be qualified to work safely with high-voltage power supplies.

- The pre-concentrator operates at temperatures of 100°C to 260°C. Personnel must be qualified to work safely with heated systems.

5. Interferences

Individual analyses can be affected by the peaks from other compounds in the gas mixture. These can be mitigated by the following actions.

- Ensuring peak breadth is as expected, following recommendations of the instrument manufacturer.

- Performing monthly zero and span checks with a known concentration of reference gas (Section 7.5).

- Performing quarterly checks for analyzer linearity and precision (Section 7.5).

6. Equipment and Supplies

Monitoring Apparatus: GC955 with PID detector.

Instrument Shelter: A shelter is required to (1) protect the analyzer from precipitation and adverse weather conditions, (2) maintain operating temperature within analyzer specifications, (3) provide sufficient and consistent electrical power, and (4) securely operate the analyzer.

Spare Parts and Incidental Supplies: See Section 6 in the GC955 manual for a list of recommended spare parts.

Calibration System: A system that generates known concentrations of high-quality reference gas is required for monthly and quarterly services (Section 7.5).

DAS: A data acquisition system (DAS) is required for collection, telemetry, and storage of data from the GC955.

7. Sampling Procedures

7.1 Sample Collection

Sample collection for hydrocarbons is performed by drawing ambient air through a sample manifold into the analyzer using a vacuum pump. The inlet is constructed of Teflon™ and

borosilicate glass. The siting of the community monitoring station containing the GC955 was completed according to the U.S. EPA Quality Assurance Handbook Volume II.

7.2   Sample Handling and Preservation

The sample is pre-concentrated in the analyzer before being desorbed, delivered into the separation column, and sent to the PID. Nitrogen is used as a carrier gas.

7.3   Sample Preparation and Analysis

This section does not apply to the Synspec GC955 analyzer.

7.4   Instrument Startup/Shutdown, Operation and Maintenance

This section describes the operation and maintenance of the GC955. The operator of the instrument should be familiar with the GC955 manual before attempting to operate the unit.

7.4.1   Startup

The following are excerpts from Sections 2 and 4 of the GC955 manual. See the user manual for additional information.

1. The instrument can be switched on once the gases are connected and the filter is in place. The GC must be connected to a mouse and a keyboard, the oven cover must be closed, and the L-shaped cover must be put on.

2. After starting the GC, the Windows system starts and the GC955 graphical user interface (GUI) appears. A self-test is performed on electronics and the PID lamp, and the oven is heated to the base temperature of the default application program. The PID lamp is subsequently turned on.

3. Carrier gas flows through the capillary and packed columns at programed flow rates maintained by mass flow controller(s). Checking for leaks or obstructions is advised after long transports or after working without adequate filters.

4. A pressure sensor monitors the switching of the internal diaphragm valve.

5. The program contains seven different functions: actual run, data file, program edit, calibration, graphs, auto-linearization, and IO-state diaphragm. See Section 3 of the GC955 manual for additional information.

6. The default mode is actual run. After an automatic check of the settings, the program is on standby to run. The oven must reach the desired starting temperature before the first cycle can be started by clicking **Start run**. Once the background zero adjust signal is set, the program begins. The detector needs to stabilize, which can cause the first reset to take longer. In automatic mode, the analyzer will either start immediately or once synchronization is reached. The measured values can be seen on the chromatogram. You can find clock time, cycle time, measured value for the detectors, ambient temperature, and oven temperature in the status lines below the chromatogram. Additional diagnostics include pressure of valve switching air and flow of carrier gas. Note that the ambient temperature is measured on the underside of the instrument. The baseline is normally set about 10 mm above the edge of the chromatogram window, but can be changed under **Actual run\Options\Adjust detector Y-offset** as needed.

7.4.2   Shutdown

There are three ways to shut down the analyzer.

1. The preferred method is to click **Stop Run**, which stops the program at the end of the present run.

2. If the program must be stopped between runs, click **Abort Run**. The program will stop immediately and the analyzer can be powered off. The next run of the GC may be contaminated by the aborted run.

    Although not recommended, in the case of an emergency the analyzer can be powered off without stopping the instrument software. The last run will not be saved and the analyzer has no way of saving open files.

Regardless of how the analyzer is powered down, a reset of all set parameters is completed before starting the next run. This also happens in the event of any unexpected power loss.

7.4.3   Diagnostic Checks/Manual Checks

Field operators will perform diagnostic checks to ensure analyzer operation. **Table 1** is an excerpt of checks from the GC955 manual.

Table 1. An excerpt of checks from the GC955 manual.

No.	Action	Dialog to Use	Optional
1	Switch on power.	--	--
2	Complete first run by clicking **Start Run.**	ViewMode \ actual run	Check temperatures, PID lamp functioning, attenuation.
3	Check peak windows.	ViewMode \ data file \ edit screen elements and edit peak windows	Wait for second run after start to get actual chromatogram.
4	Stop program.	ViewMode \ actual run – stop run	Click **Abort run** in emergencies, close the program GC955 by clicking the left top pulldown menu.

7.4.4 Preventative Maintenance

Table 2 below summarizes the maintenance tasks for the unit.

Table 2. A schedule of maintenance tasks required for this instrument.

Activity	Quarterly	Annually	Two Years
Replace micro dust filter for sample	✓		
Remove dust from ventilator	✓	✓	
Clean the lamp		✓	
Clean the PID		✓	
Change the carrier gas filters		✓	
Clean the diaphragm		✓	
Renew external sample tubing		✓	
Replace pre-concentration tenax tube		✓	
Replace cooled pre-concentration trap		✓	
Optimize hard disk		✓	
Clean internal gas tubing			✓
Clean lamp housing			✓

7.4.5 Troubleshooting

See Section 6.02 of the GC955 manual for the troubleshooting scheme.

7.5 Calibration and Standardization

The following data quality objectives (DQOs) are used to assess data quality based on recommendations from the instrument manufacturer. These DQOs may be adjusted on an as-needed basis.

- Monthly zero and span checks will compare analyzer response to a known reference gas concentration.
  - The zero value must agree to within ±2 ppb.
  - The span value must agree to within ±15% of the known reference concentration.
- Quarterly multipoint calibrations will check the linear response of the analyzer. These will include a zero, a maximum concentration value of 80% of full scale, and three evenly-spaced additional concentrations (e.g. for 500 ppb full-scale: 0 ppb, 100 ppb, 200 ppb, 300 ppb, and 400 ppb).
  - This five-point multipoint calibration must be linear, with an R^2 value >0.96 and a y-intercept within ±2 ppb of zero.
  - The zero value must agree to within ±2 ppb.
  - The maximum concentration of the multipoint calibration must agree to within ±2% of the known reference concentration.

   o Additional values must agree to within ±2% of the known reference concentration, and must not differ by more than 5 ppb.

   o If any of these conditions are not achieved, the analyzer will be adjusted.

  • Quarterly checks will confirm the precision of the analyzer.

   o Analyzer precision will be confirmed by calculating the coefficient of variation (CV) for at least triplicate measurements. The CV must be less than 10%.

   o If this condition is not achieved, the analyzer will be adjusted.

7.5.1 Adjustment to Zero Air

See Section 4 of the GC955 manual for additional information.

7.5.2 Adjustment to Calibration Gas

An overview of the calibration process is shown below. See Section 4.3 of the GC955 manual for additional information.

1. Go to DAS and put into Cal mode from View screen.
2. Use explorer and copy actcalib.dat from GC955 root directory into last valid calibration file folder – newest data in calibdat folder as shown below.

Name	Date modified	Type	Size
C_101129	10/12/2012 4:34 AM	File folder	
D_1108	10/12/2012 4:34 AM	File folder	
FollowMe	10/12/2012 4:34 AM	File folder	
GraphDat	10/12/2012 4:34 AM	File folder	
VALIDATE	10/12/2012 4:34 AM	File folder	
ACT_LIN.DAT	11/12/2002 1:44 PM	DAT File	7 KB
ACT_RUN.PRG	12/24/2010 6:49 AM	PRG File	3 KB
ActCalib.DAT	4/18/2005 1:19 PM	DAT File	61 KB
ALARM LOG	4/5/2013 8:45 AM	Text Document	3 KB
AUTLINDS3.DAT	6/3/2009 3:15 PM	DAT File	314 KB
DEFAULT.PRG	12/4/2001 5:17 AM	PRG File	1 KB
Erased	6/2/2009 2:59 PM	Text Document	0 KB
ERROR	1/24/2002 8:27 AM	Text Document	1 KB
GC_955_1	8/28/2007 3:47 PM	Application	1,254 KB
GC855.CFG	6/2/2009 2:54 PM	CFG File	3 KB
GC855.DYN	4/18/2005 1:19 PM	DYN File	1 KB
GC855	11/27/2003 12:37 ...	Text Document	1 KB
Gc855_id	11/7/2006 8:18 AM	Text Document	2 KB
GC855_SS.CFG	12/20/2000 7:09 AM	CFG File	3 KB
GC955	4/5/2013 8:45 AM	Text Document	29 KB
GC955.PRP	6/3/2009 2:55 PM	PRP File	4 KB
Gc955_id	7/12/2011 11:17 AM	Text Document	3 KB
GC955_TXT_DE	9/9/2003 9:40 AM	Text Document	20 KB
GC955_TXT_EN	9/9/2003 9:39 AM	Text Document	20 KB
GC955_TXT_ES	8/20/2003 10:52 AM	Text Document	22 KB
GC955_TXT_FR	7/21/2003 11:29 AM	Text Document	20 KB
GC955_TXT_NL	9/9/2003 9:41 AM	Text Document	20 KB
RD200406	6/29/2004 12:00 PM	Text Document	200 KB
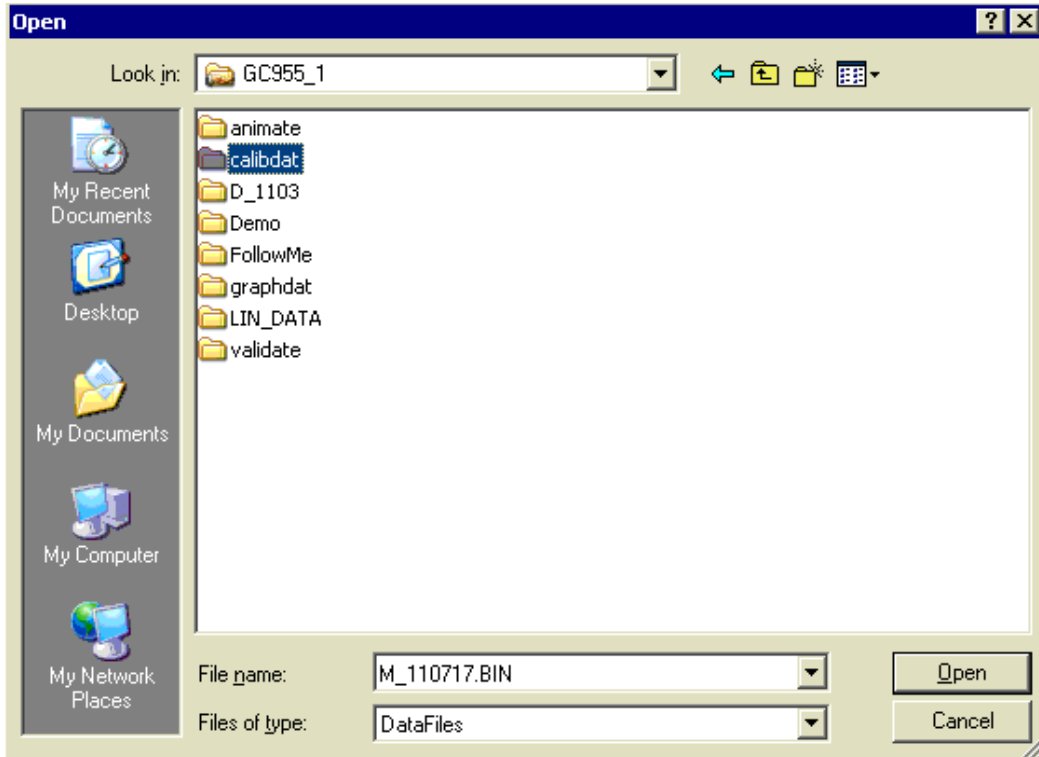
3. On GC955 go to **ViewMode** and select **Act Run PID**.
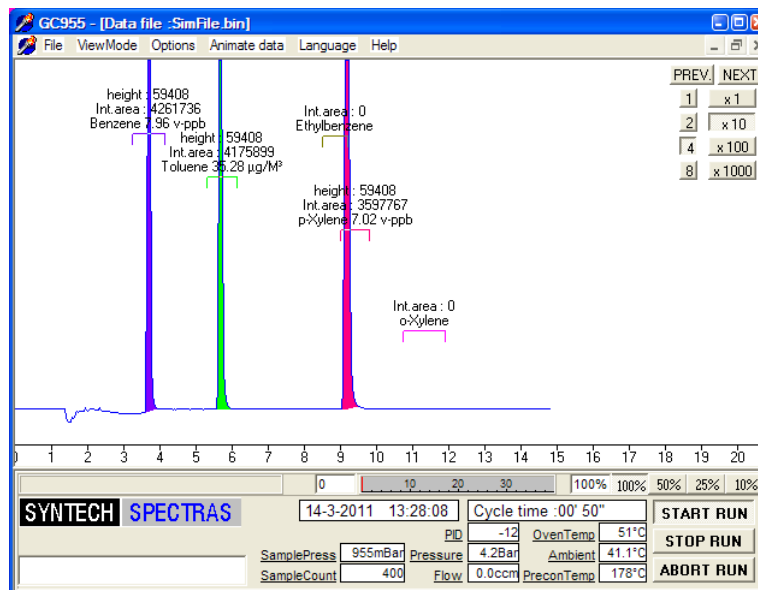
4. Connect span gas to span port on switchbox. Purge gas at the analyzer inlet so that calibration gas is available for measurement.
5. Under **Options**, click on **Open validation gas valve**.
6. Let run for four to five samples and observe peaks.
7. Go to ViewMode data file and open recent files. Adjust peak windows if necessary.
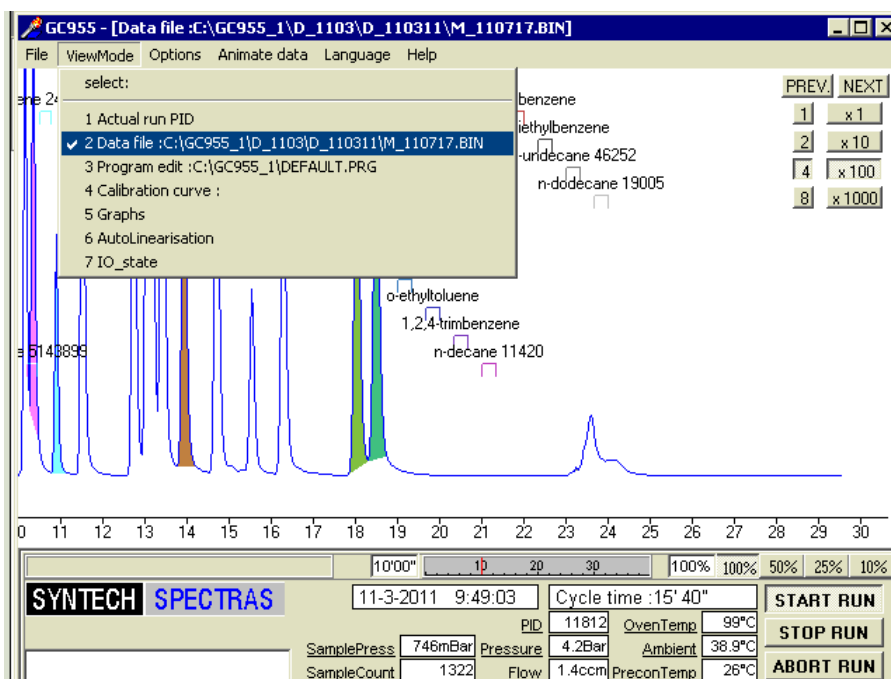
8. Go to **ViewMode act run PID** and put unit into calibration mode – have gas flowing to span valve inlet on switch box.

9. Select **Start New Calibration**.
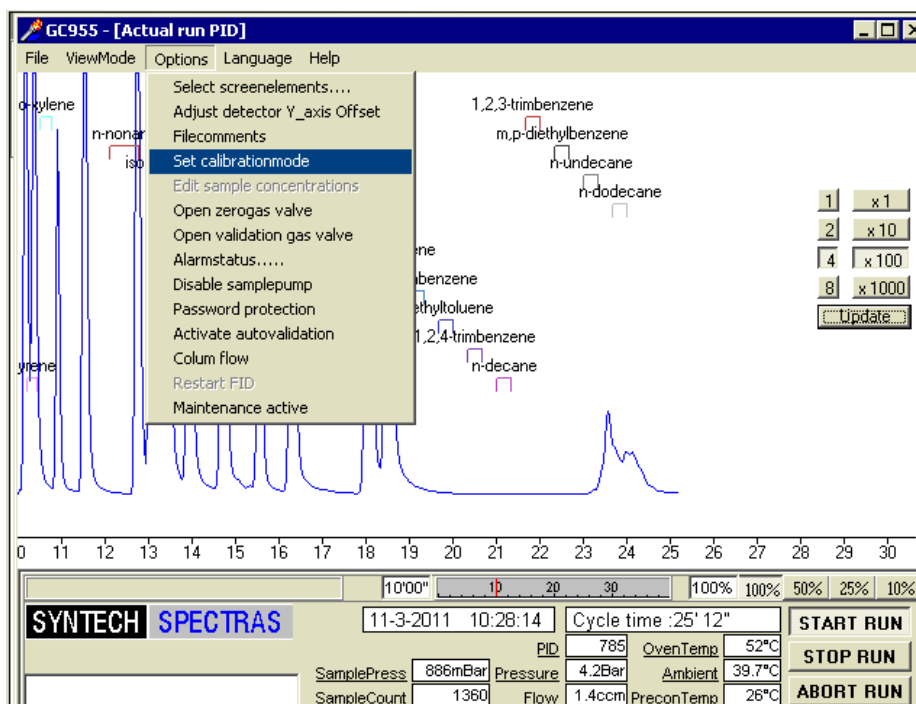
10. Enter in known reference concentration values.
    a. Recall that m- and p-xylene co-elute, so those two values should be added together.

11. Click the **USE – Yes** radio buttons as appropriate.

Make sure you have the ACTCALIB.DAT backed up per instructions above.

12. Let system run for two files or until data is stable.
13. Go to **ViewMode calibration mode**.
14. Go to **Data selection calibration files**.
15. Choose component to calibrate.
16. Select data files from the calibdat folder (YR/month/day) of data files collected – add to the display.
17. Select **Calculate calibration line** – select linear regression with fixed basepoint.
18. Calculate calibration line.
19. Repeat for all parameters.
20. Let DAS stay in calibration flag mode for ½ hour after the system finishes collecting calibration data so it is flagged in DAS.
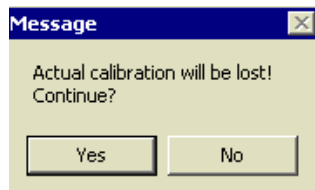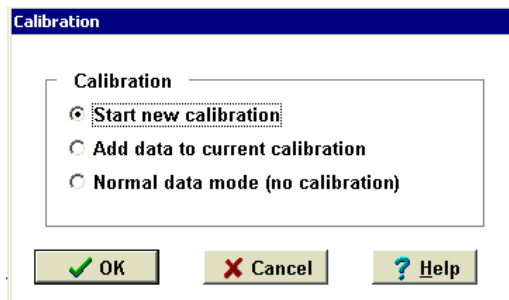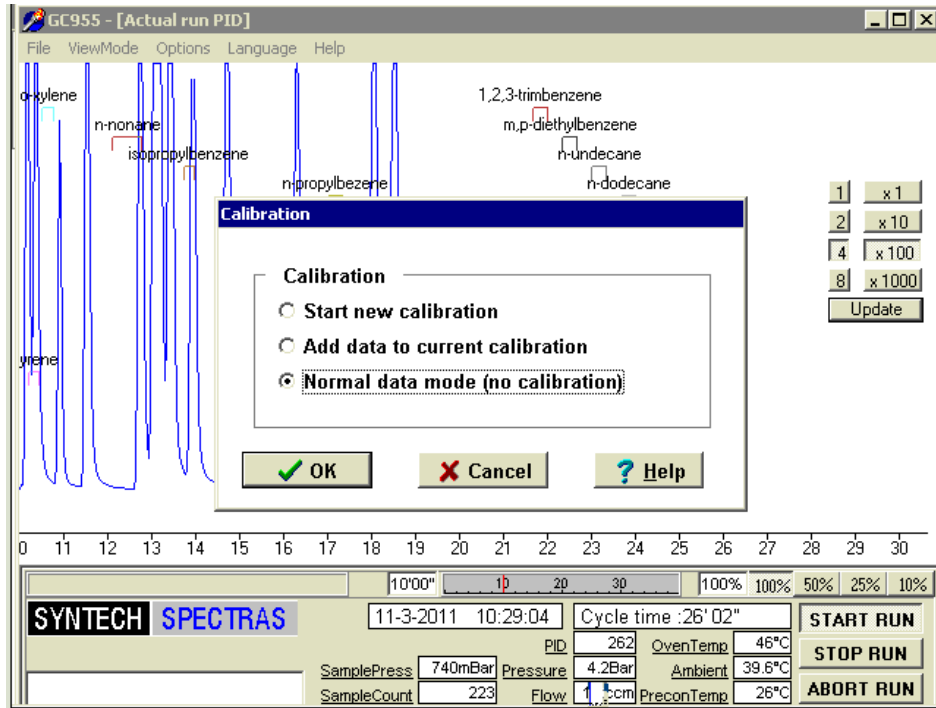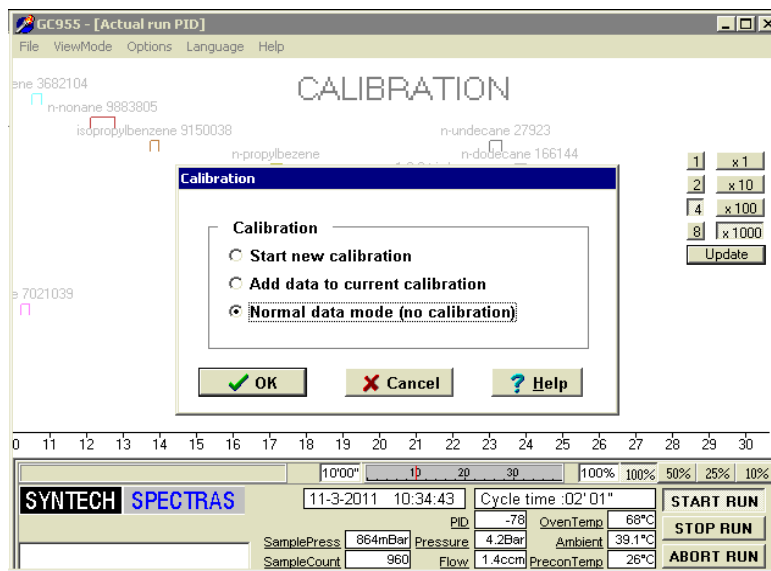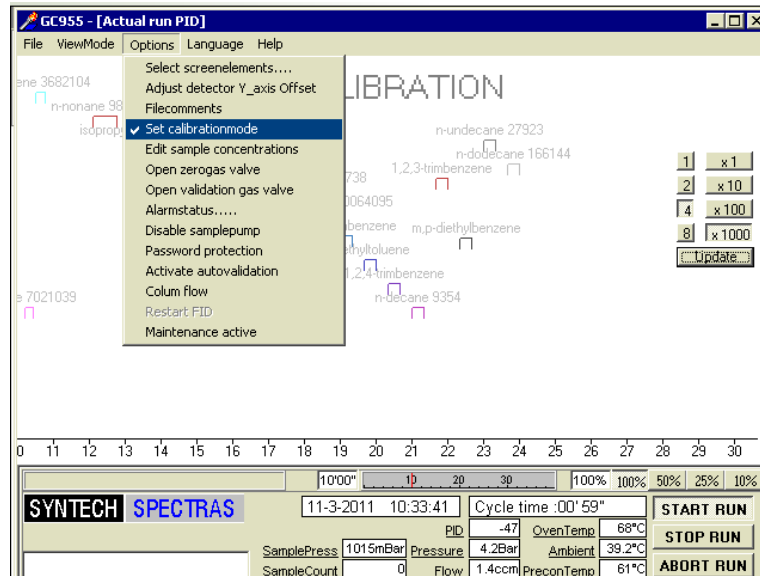
Constructing a calibration curve

1) Click in the **ViewMode** on **Calibration curve**.
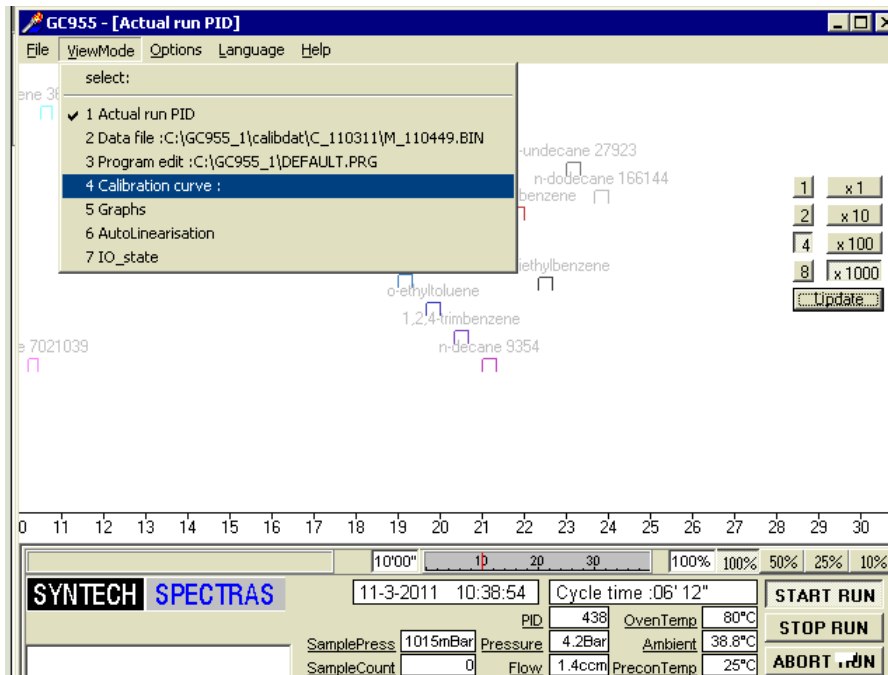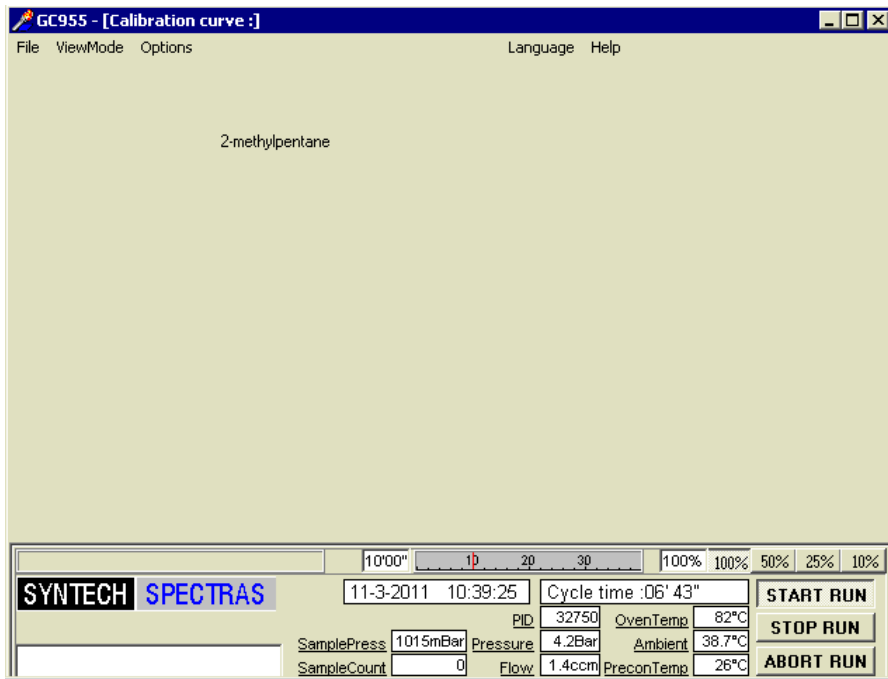
2) You will see:

Click on:

- **Options**
- **Data selection calibration file**

3) You will see:
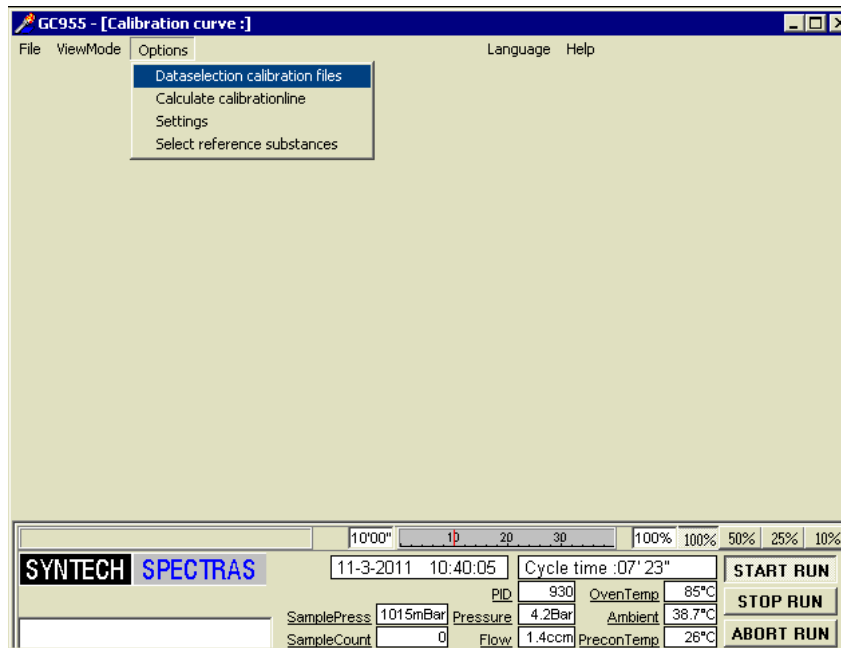
4) You will see:
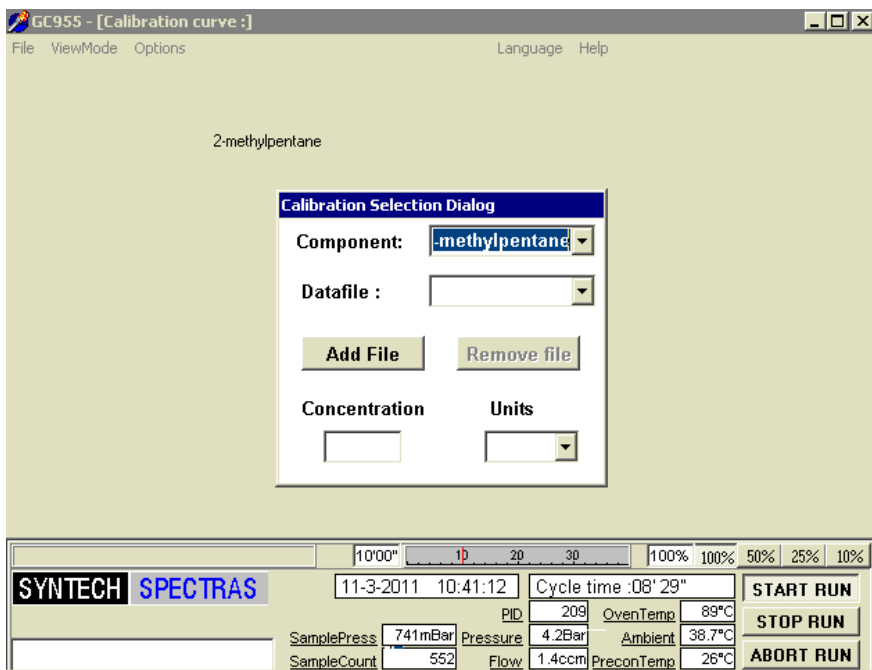
Click on:

- **Add File**

5) You will see:
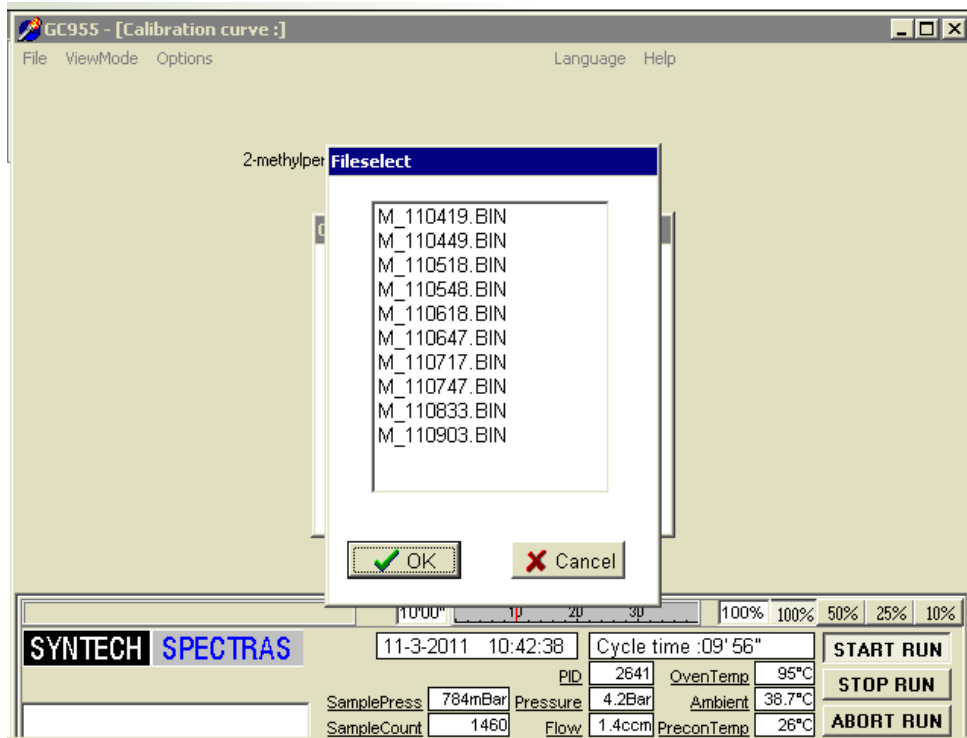
6) You should select:
   - **All Files**, in this case M_110419 to M_110903
   - **OK**
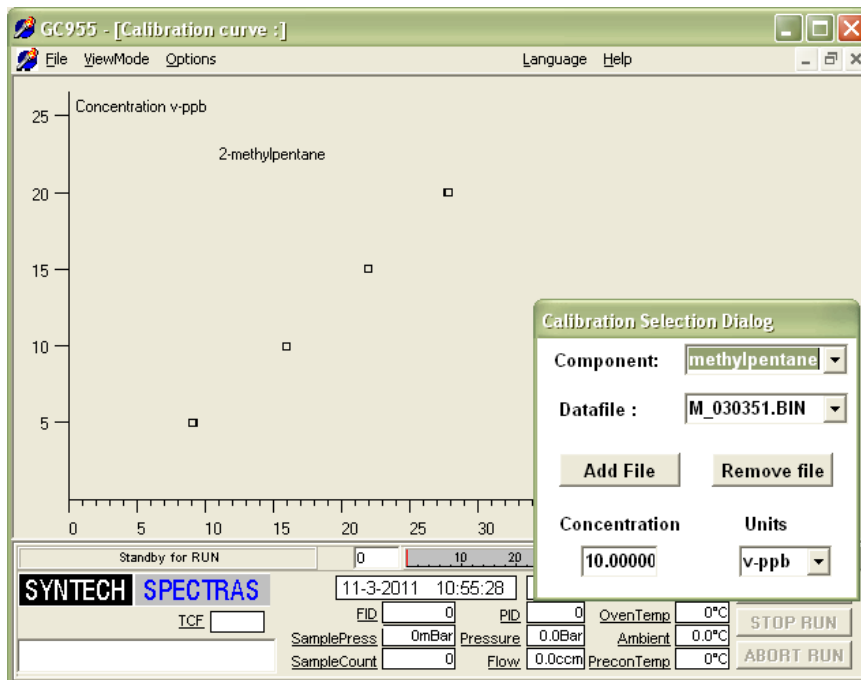
You will see that there is no calibration curve but only points, so you have to make a calibration curve.

1) Click on:
   • **Options**
   • **Calculate calibration line**
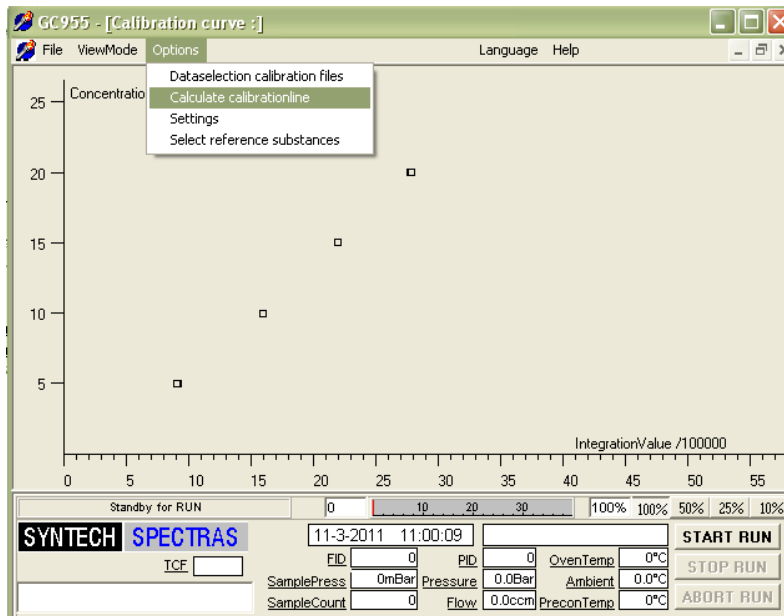
2) You will see:
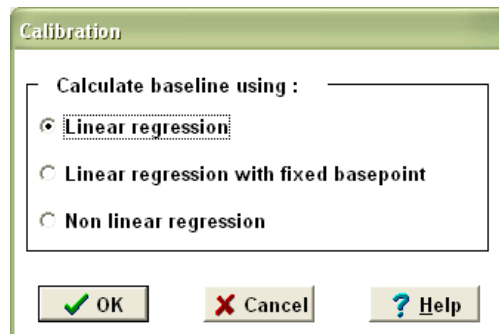
3) Click on:
   • **Linear regression with fixed basepoint**
   • **Ok**
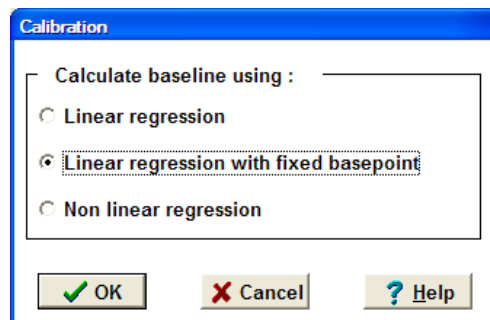
A calibration line like example below should now appear.
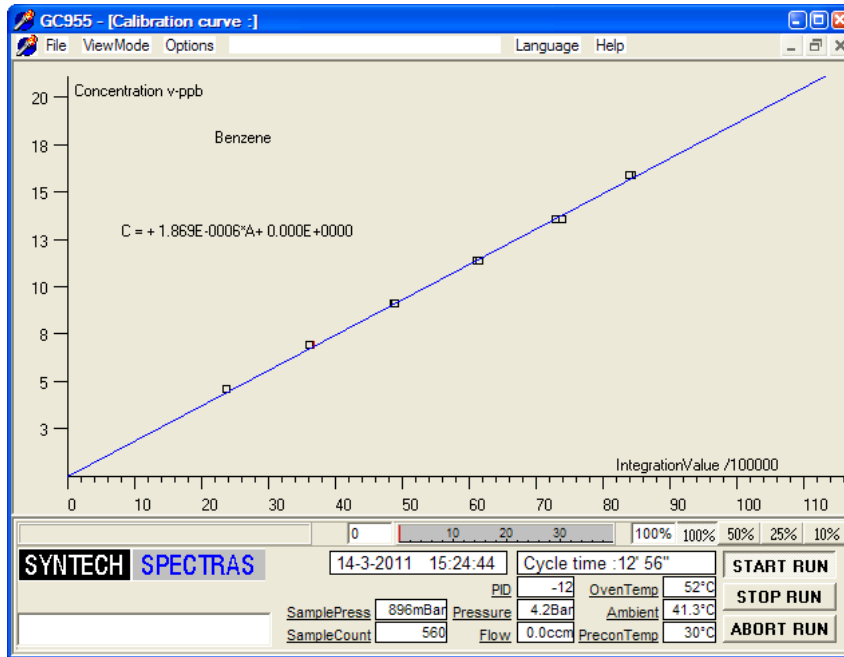
This may be repeated for additional compounds, if applicable. To do this, click **ViewMode** and then **Calibration curve.**
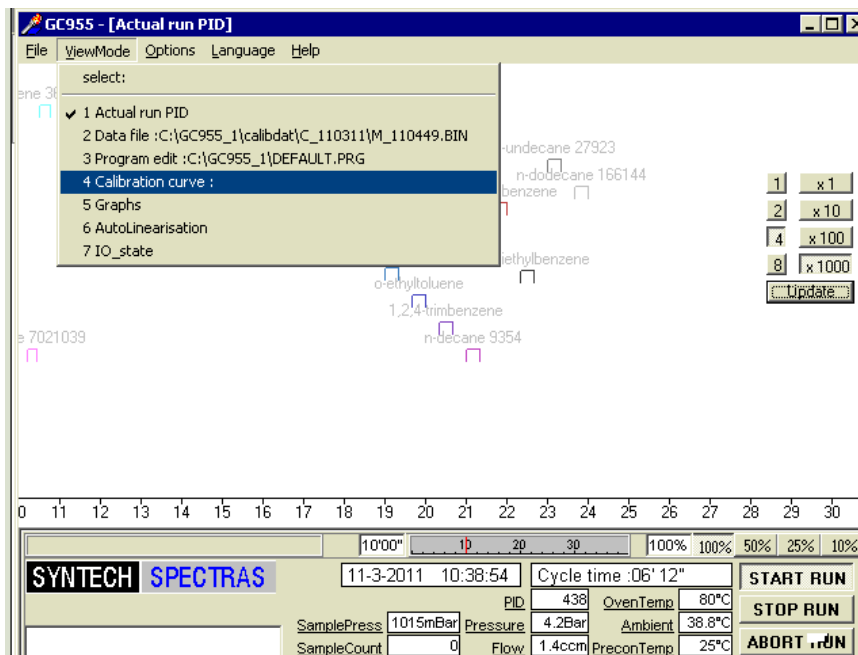
1) You will see:
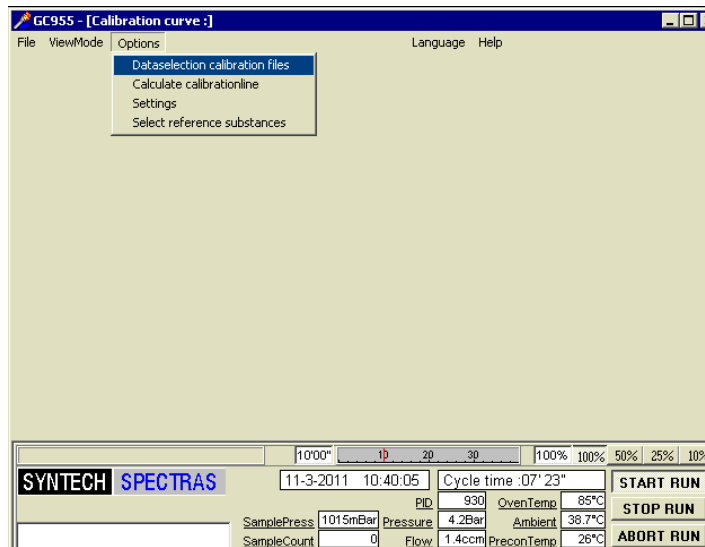
Click on:

- **Options**
- **Data selection calibration files**

2) You will see:
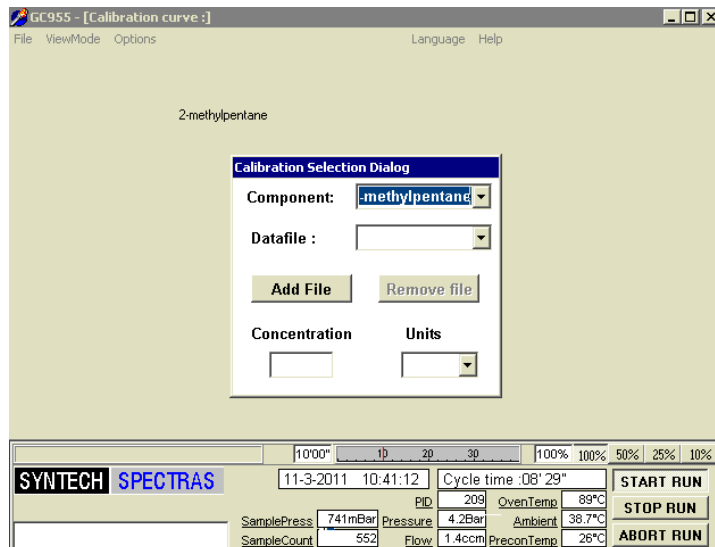
Click on the arrow down by component.

You will see:
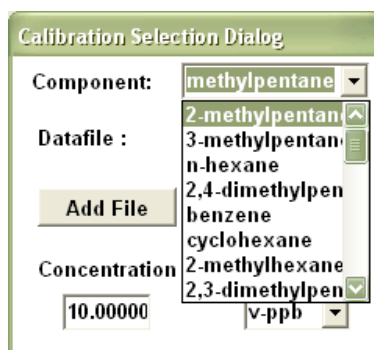
Click on **Next compound** and start again with add file and so on.

Chromatograms with the concentrations, but not areas, are now visible in calibdat.
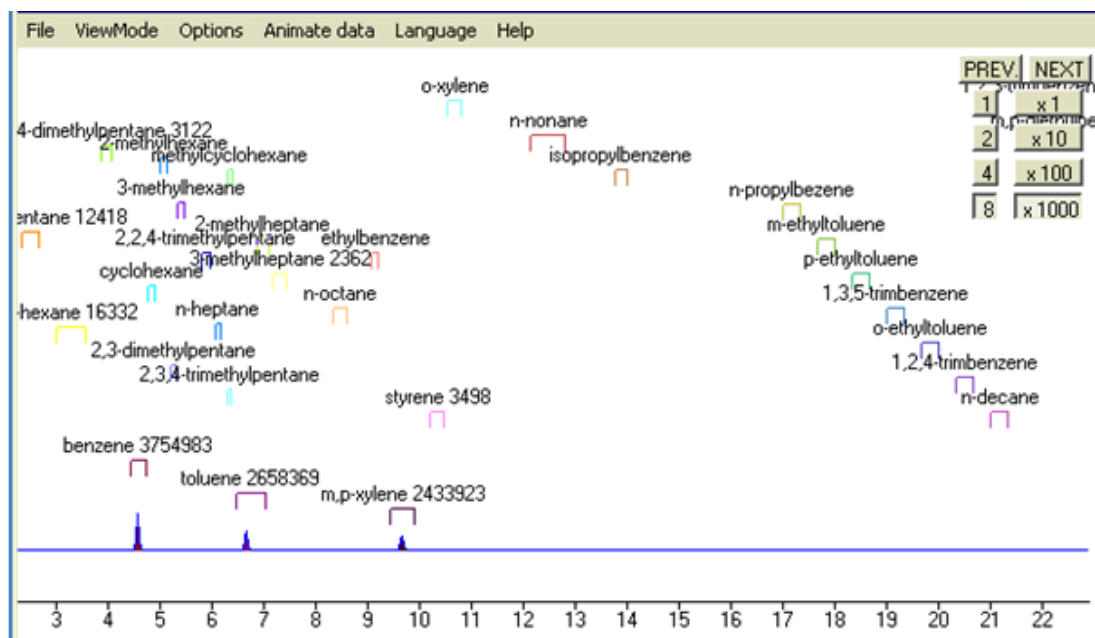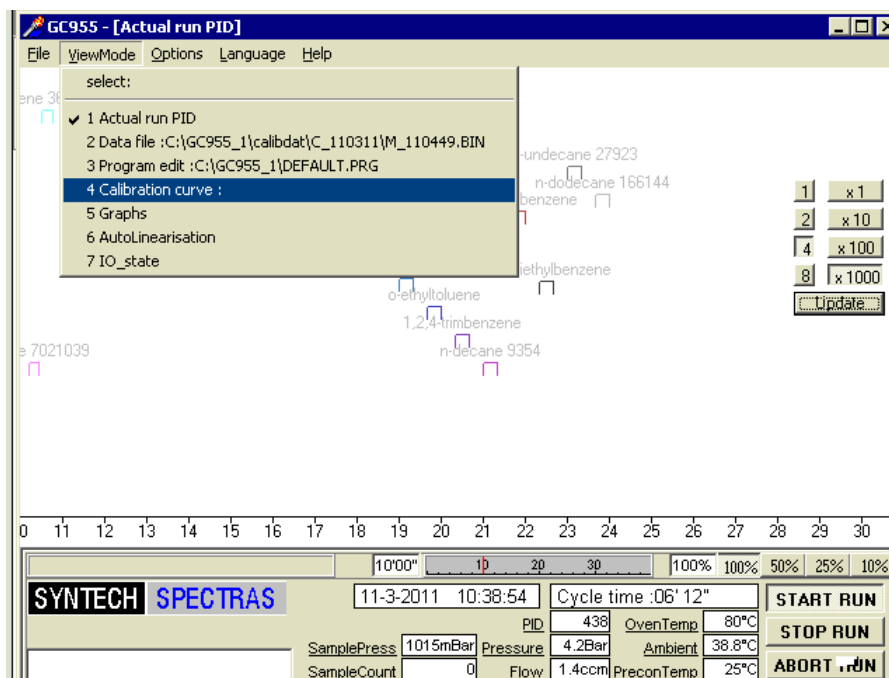
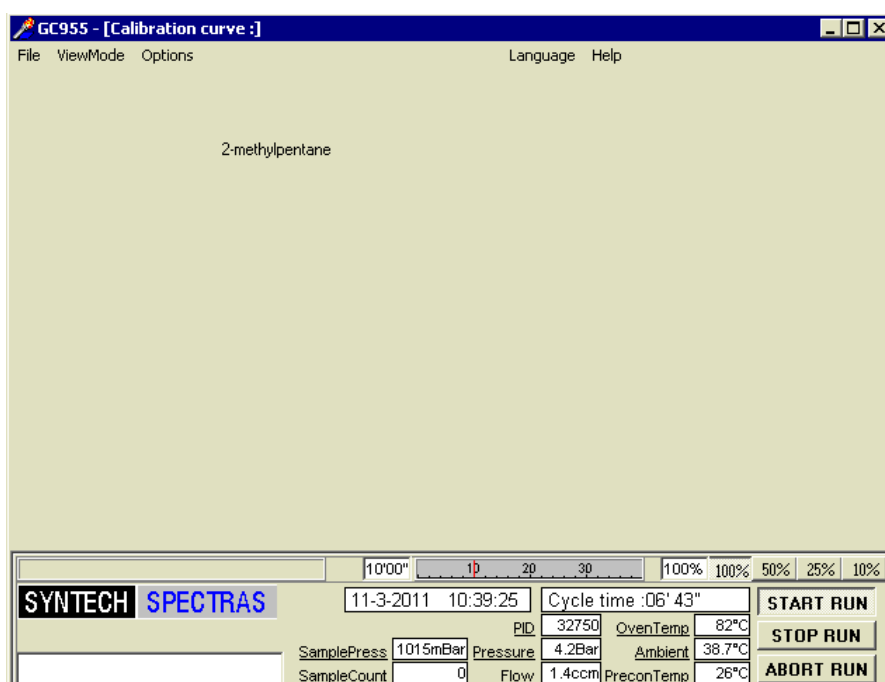After calibration, the concentrations are visible in ppb:
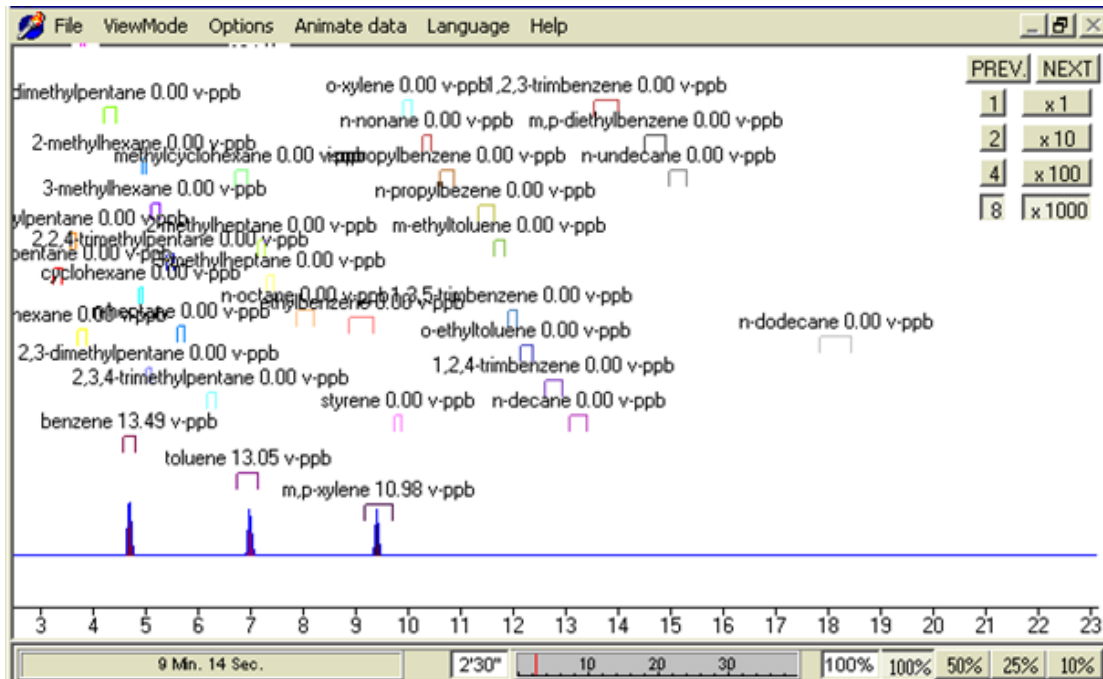
Using the calibration setting
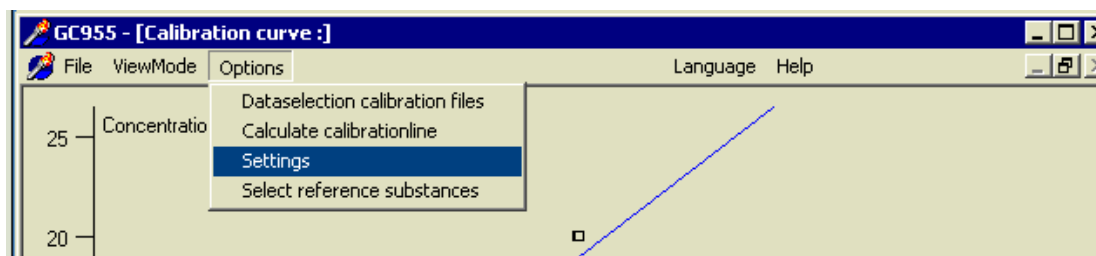
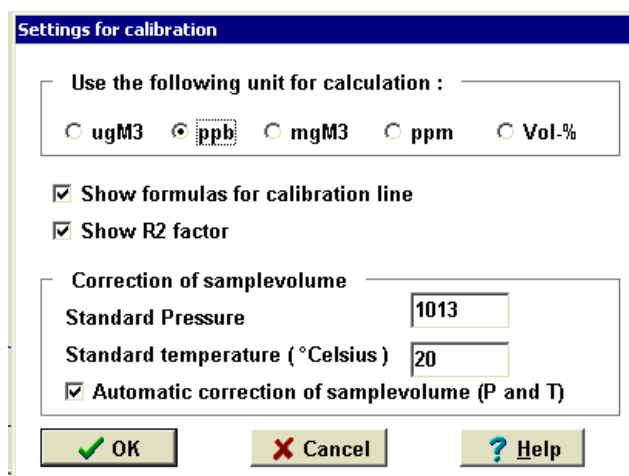1) Click in the **ViewMode** on **Calibration curve**:

2) You will see:

Click:

- **Options**
- **Settings**

3) You will see:

You can choose the unit for calculation.

7.6   Data Acquisition, Calculations, and Data Reduction

Data analysis for this analyzer is detailed in the Monitoring Plan and Quality Assurance Project Plan (QAPP) for the project.

8.   Quality Control and Quality Assurance

GC-PID		
Zero and Span	Monthly	Zero ±2 ppb Span ±15%
Linearity	Quarterly	Linear regression correlation (R^2) >0.96
Precision	Quarterly	Coefficient of Variation <10%

8.1   Corrective Action

Corrective actions are to be carried out according to the Monitoring Plan and QAPP for the project.

9.   References

Manual for the Syntech Spectras GC955-series Version 4, Synspec b.v, March 2009.

Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II, U.S. EPA Ambient Air Quality Monitoring Program, December 2008.

10. Analyzer Checklist

Criteria	Value	Notes
SN		
Power on functional		
Column flow		
Pressure		
Ambient temp.		
Oven start temp.		
Pre-concentrator start temp.		
Syringe sample strokes		
Peak windows		
Zero check (if applicable)		
Span check (if applicable)		

Appendix D

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

September 5, 2023   STI-7801
Ryan Moffet, PhD, Randy Gibbons, Ross Mohs
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Contents

1.   Summary

This document addresses the maintenance, commissioning, and performance audit procedure for Unisearch Tunable Diode Laser System (TDLAS) open-path analyzers. The document describes maintenance procedures that enable technicians to verify that equipment is performing to expectations and detection and communication links are functioning correctly.

***NOTE ***

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

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

A number of these maintenance procedures closely follow the manuals provided by Unisearch.[1] Field staff should obtain access to and read these. The Quality Assurance (QA) Audit procedure ensures field verification and calibration of the TDLAS by challenging the instrument with a known concentration of hydrogen sulfide (H_2S) and verifying proper detection and quantification under field conditions.

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[1] Unisearch Associates: A. Preinstallation Manual, B. Installation Manual, C. Networking Manual, D. Remote Sensing Optics Manual, E. Operations Manual, H. Troubleshooting Manual, I. Laser Safety Manual, J. Maintenance Manual, LasIRView 2015 Manual, 2018.

2. Safe Work and Hazard Identification

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

2.1 Laser Safety
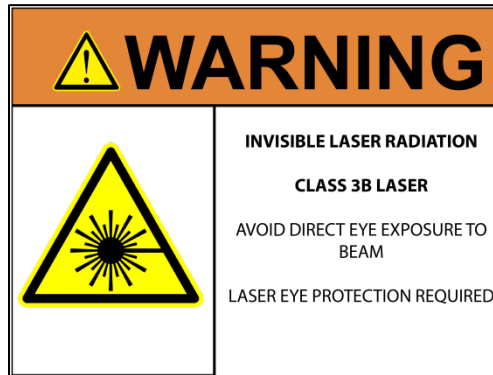
The Unisearch TDLAS produces a class IIIB LASER EMISSION that is INVISIBLE. The laser can cause eye damage if the laser is viewed directly. Unisearch recommends the use of safety procedures consistent with Class II and IIIA lasers. **PROTECTIVE EYEWEAR SHOULD BE WORN WHEN WORKING WITH THE SYSTEM**. Always avoid looking directly into any part of the instrument that can produce laser light, including the transceiver head. Make sure to read the laser safety manual and all other manuals provided with the Unisearch TDLAS instrument.

2.2 Operator Qualifications

Installing, operating, and servicing Unisearch analyzers should only be performed by personnel who are trained in the operation of the system components and are familiar with handling gas delivery and testing equipment. These procedures should not be performed by personnel who do not understand the system, technology, or hazards of the materials involved.

2.3 Safe Work and Hazardous Environment Operation

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

The Unisearch TDLAS are not rated for safe operation in hazardous or explosive environments. Using the TDLAS in an area that may contain flammable mixtures or highly corrosive vapors requires special preparation to ensure human safety and safe operation of the equipment.

WARNING – Toxic Gas and Eye Hazard. H_2S is a highly toxic gas that can cause death and other adverse health effects at concentrations above 100 ppm. This procedure requires the use of concentrations as high as 750 ppm H_2S for the span check. This procedure must be conducted in a well-ventilated area and requires gas monitors, respirators, and the use of fume scrubbers. Make sure you and others fully understand the safety procedures and gas-handling systems required. Always wear proper eye protection having OD>4 above 900 nm. Improper handling of materials or hardware may result in death, serious injury, destruction of property, or damage to the TDLAS. Only qualified individuals should perform analyzer quality assurance audit activities.

3. Overview and Operating Principle

The Unisearch LasIR open-path H_2S monitoring system (**Figure 1**) is a monostatic open-path remote sensor that uses direct absorption technique. The LasIR sensor consists of an analyzer, transmitter/receiver and retro-reflector array. The tunable infrared (IR) laser for the LasIR system is housed in the analyzer box and scanned over a small range of wavelengths at high frequency. The laser light is guided to the transmitter/receiver telescope via fiber optic cable where it is collimated and sent across the atmospheric path. The retroreflector array at the other end of the path returns the signal to the off-axis parabolic mirror that focuses the light onto a photodiode detector. The electrical signal from the photodiode detector is amplified and returned to the analyzer box where the absorption spectrum is analyzed to produce concentration data.

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

The purpose of this procedure is to check the system for expected H_2S response under the installed operating conditions. H_2S standard reference gas is introduced into the optical path by means of a flow-through or sealed cell, meaning the entire sample path is included at the time of testing.
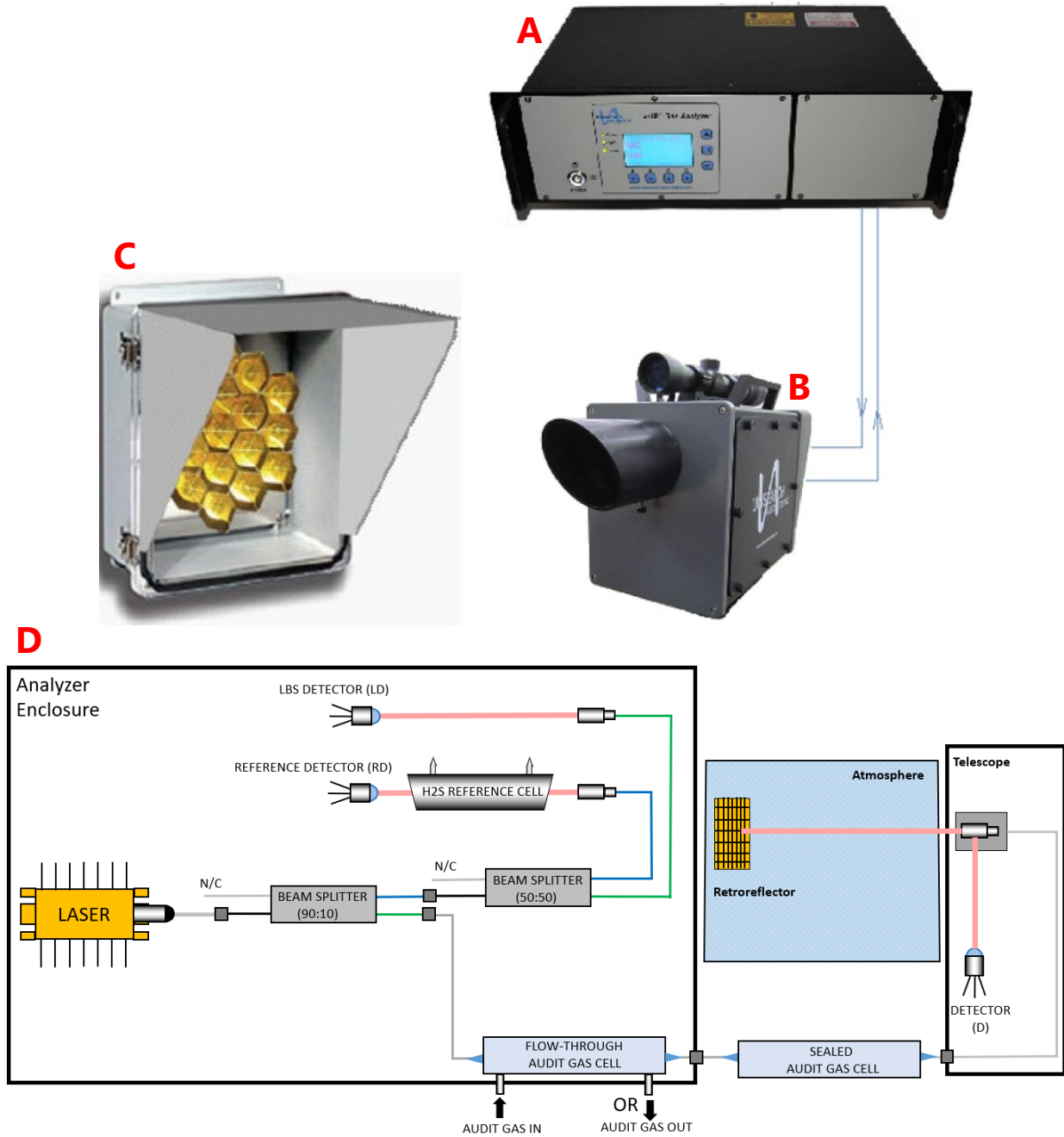
Figure 1. (a) Unisearch TDLAS Analyzer box, (b) telescope, (c) retroreflector, and (d) schematic diagram showing the optical fiber paths and detection points.

3.1 Safety

3.1.1 Exposure Control

H_2S is a colorless gas that has an odor of rotten eggs. It is hazardous at low concentrations (Immediately dangerous to life or health [IDLH] is 100 ppm, National Institute for Occupational Safety & Health [NIOSH] 10-min Reference Exposure Level [REL] is 10 ppm, California Office of Environmental Health Hazard Assessment [OEHHA] 1-hr REL is 30 ppb). The odor is not a reliable indicator of the presence of hazardous concentrations of H_2S, because olfactory senses may be deadened by exposure to concentrations below safe exposure levels. A system for scrubbing H_2S gas from a test apparatus vent is used to prevent release and worker exposure.

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

3.1.2 Personal Protection

Standard refinery personal protective equipment (PPE) should be worn at all times, including laser safety glasses with side shields, a hard hat, goggles, steel-toed boots, hearing protection, fire-retardant clothing (FRC), an H_2S monitor, and appropriate gloves that are adequate for this procedure. For testing with the flow-through cell using H_2S concentrations in excess of 100 ppm, a second person should always be present as a safety monitor. H_2S levels should be monitored inside the enclosure. Two self-contained breathing apparatuses should be on standby.

4. Routine Maintenance

The TDLAS system is designed to require only modest service and maintenance. Table 1 summarizes TDLAS maintenance activities, as recommended by the manufacturer. The frequency of activities may vary from site to site, so always check the QAPP for facility-specific maintenance schedules and acceptance criteria.

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

Activity	Section(s)
Visually inspect the system. Inspect electrical and optical cables for wear.	4.1
Inspect optics and clean if necessary	4.2, 4.3
Check the alignment to verify there has not been significant physical movement; note that this is automatically monitored as well	4.4
Download data from detector hard drive and delete old files to free space, if needed	4.5
Ensure there are no obstructions in the beam path	4.6
Review and test light and signal levels	4.6
Verify system settings	4.7
Perform bump test and take corrective action as needed	5.2 (flow-through) 6.1 (sealed cell)
3-point calibration check	6.2

4.1   Visual Inspection

During visual inspection of the analyzer, note and clean any excessive dust buildup on the equipment or analyzers. Eliminate any pests from the sample site, including birds, spiders, rodents, etc. Note the condition of the analyzer cabinet internals. Inspect wiring and note and correct any corrosion or cracking insulation.

In summary, ensure you correct and note the following: HVAC operation, corrosion, condensation, door operation, excessive dust, rodents/pests, and anything that may result in eventual degradation of the LasIR system.

4.2   Cleaning the Transmitter/Receiver Optics

Only the front surface of the window on the telescope assembly may need to be cleaned on a monthly basis. Use a clean cloth to lightly wipe the front surface of the window. Normal lens cleaner solution can be used if necessary, but dust can usually be wiped away with a dry cloth. Be careful not to scratch the window surface by pressing too hard. The shroud protecting the window from the elements may be removed for this purpose. If necessary, loosen the locking screw on the bottom of the shroud and pull the shroud away from the window housing. On telescopes designed for permanent installation, a "purge air" port is provided so that clean, dry air may be flushed over the window to help minimize any dust build-up or condensation.

If the inside of the window gets dirty, it is best to remove the window from the housing and clean it rather than open the telescope side covers, as access from these points is limited. You may either remove the shroud and unscrew the locking ring that holds the window in place or remove the entire front cover by loosening the four screws in the corners. In either case be careful to keep the O-ring seals properly seated. Improper seating may result in leaks if rain falls on the telescope, which could possibly damage sensitive electronic components inside.

4.3   Cleaning Retroreflector Array

Only the front surface of the acrylic protective window for the retro-reflector needs to be cleaned on a monthly basis. Use a clean cloth to lightly wipe the front surface of the window. A lens cleaner solution can be used if necessary, but dust can usually be wiped away with a dry cloth. Be careful not to scratch the window surface by pressing too hard. If, for some reason, the inside of the window gets dirty, this can be cleaned by opening the enclosure front cover. Reflector elements may also be cleaned if necessary, but this should be done with extreme care to prevent damage to their gold-coated surfaces.

4.4   Optical Alignment

Adjust the vertical and horizontal adjustment knobs to maximize the power as reported on the OPM-15 power meter. Lock the adjustment knobs (**Figure 2**) in place. Once aligned, it should be possible to push on the telescope top and side without disturbing the alignment. The spot size at the retro-reflector should be 2-3 times the diameter of the retro-reflector for this to be true. It may be necessary to adjust the collimator to obtain the best beam size and return power. If the beam is smaller than this, variation in the power will be observed, which may affect the alignment over time due to flexing of the mounting structure. When the vertical alignment is correct, tighten the locking thumbscrew. For the horizontal sweep, loosen the 5/8" locking nut located underneath the mount base and use the thumbscrew on the right hand side of the mount base (looking from the back) to adjust the horizontal position. When adjustment is complete, tighten the locking nut. Slight adjustment of the vertical alignment may be required after tightening the horizontal alignment-locking nut as this tightens the rear end of the telescope to the mount, which affects the tilt.
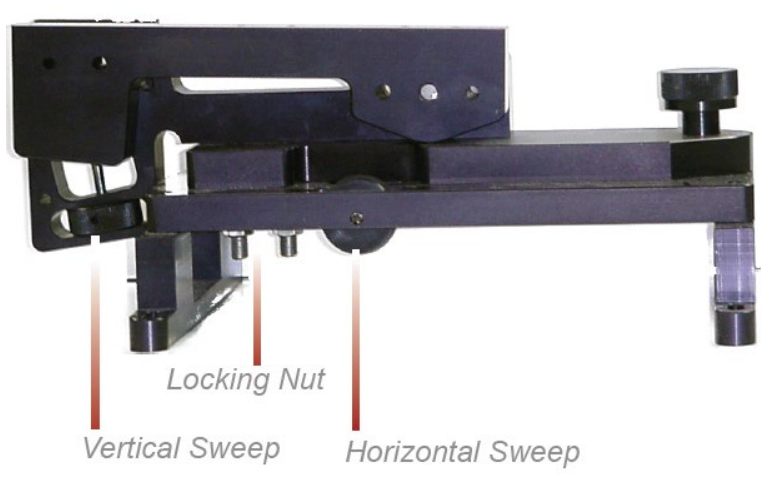
Figure 2. Location of adjustment knobs used for alignment of the Unisearch TDLAS.

4.5   Data Management

Under normal operations, the LasIR system works together with a separate program called the TASDAcc to acquire and process raw TDL data, and reports 5-min data to the Sonoma Technology-operated data system. The TASDAcc software is developed and maintained by Terra Applied Systems (TAS), the integrator of the Unisearch TDL. As depicted in **Figure 3**, the LasIR, TASDAcc, and the cellular modem are all connected through a network switch, which is located in the same cabinet as the Unisearch analyzer box. The TASDAcc software handles three main data types: (1) raw data tables from the LasIR Analyzer, (2) spectral data from the LasIR Analyzer, and (3) 5-min data for ingestion to the Sonoma Technology data system and display on the public-facing website.
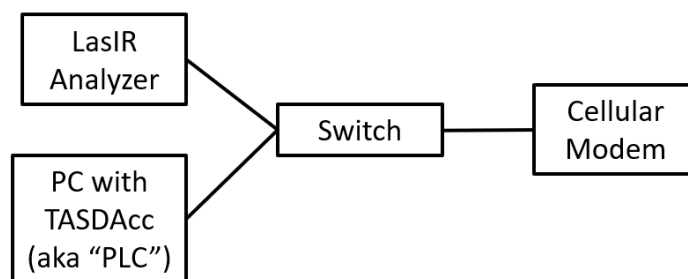
Figure 3. Diagram of local network configuration for the LasIR system.

On a routine basis, data from the PC running the TASDAcc software should be backed up and, eventually, removed from the local hard drive to prevent it from reaching capacity, which would stop proper functioning of the TASDAcc software. In the future, removable hard disk drives together with automated scripts will be used to automate some aspects of this data management and to ensure a redundant copy of data exists for the current year before delivery.

To perform data backup, transfer spectral data and raw data tables provided by the TASDAcc to a removable storage device. This enables the storage of two copies of the data. After data delivery at the beginning of the year, remove the previous year's data from the PC by deleting it.

On a routine basis, according to the maintenance schedule in the QAPP, check the hard drive space to ensure there is enough space for the following measuring period. If enough free space cannot be created on the drive, take corrective action with support from the IT department.

4.6 Test Light Levels

Although the return light level is monitored continuously and reported with the 5-min data, it is important to verify and document observations of light level during routine maintenance. Testing light levels on site allows for the determination of root-cause for problems involving low signal return. The effect of cleaning on light levels should be noted. Testing of light levels at various points in the system can be used to troubleshoot damaged optical components, such as fibers.

To check the light levels, observe the power bar (S) in the scope display or the bar at the bottom of the "Main Running" display (**Figure 4**) on the analyzer. In the host trend display it should be green. If it is yellow it indicates the power is low. If it is purple, the power is very low and the instrument will have stopped recording data. On the analyzer, the bar is normally between 25% and 75%. You may also check the percent (P) values on the analyzer display (**Figure 4**) by cycling to the "Species Information Screen." It should be greater than 5% for proper operation. Low power generally indicates a need for maintenance, such as cleaning the optics, or a problem with the process that is releasing dust into the duct and cutting down the power.
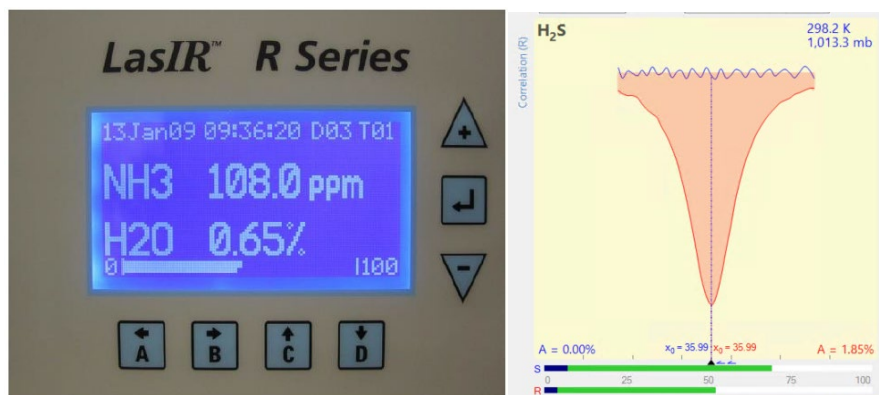

Figure 4. Main running window on instrument front panel (left) and scope display in LasIR View software (right).

4.6.1   Signal Strength Measurements

Measurement of light power at the detector can occur at several points in the system. There are two gains associated with these measurement points, as indicated in **Table 2**. The "signal gain" is the

amplification placed on the signal itself through electronic hardware, and the "IO gain" is a multiplicative modification of the input-output data streams. Using this table together with the method-appropriate use case, the actual light power at the detector can be determined.

For example, if the signal gain is 2 (signal multiplier of 2), the IO gain stage is 3 (multiplier of 5), and the peak power at the detector is 0.12 mW, then the power displayed via RS232 data stream is:

RS232 **SignalPower** = Signal Multiplier x IO Multiplier x Peak Power = (2)(5)(0.12 mW) = 1.2

The ratio of MODBUS to RS232 signal powers is always 2.5, so in this case the **SignalPower** transmitted via MODBUS is: (1.2) (2.5) = 3

Following this example, by ratioing the power at the detector to the power of the laser (say, 18 mW for this example, can be obtained from instrument data sheets), a %transmission may be calculated.

%transmission = (0.12 mW / 18 mW) 100% = 0.67%

However, if the gains are set to "auto," as they are during normal operations, it is impossible to know what gain settings are applied and, therefore, what the actual power at the detector is. Therefore, %transmission can only be assessed during routine maintenance.

Table 2. Multiplicative factors associated with gain stages and how they are translated to the Unisearch data files (SignalPower) and through the MODBUS data connection. Note that the ratio of MODBUS to RS232 is 2.5. The ratio of RMS power to peak power is 0.83.

Signal Gain	Signal Multiplier	IO Gain Stage	IO Multiplier	Power at Detector (mA or mW)	Peak Power at Detector (mA or mW)	MODBUS/ Display Power	RS232/TXT Signal Power
1	1	2	1	1	1.2	3	1.2
2	2	2	1	0.5	0.6	3	1.2
2	2	3	5	0.1	0.12	3	1.2
2	2	4	25	0.02	0.024	3	1.2
1	1	3	5	0.32	0.4	5	2
2	2	3	5	0.2	0.24	6	2.4
3	4	3	5	0.25	0.3	15 (or 1.0 if not in Fast gain with error)	6 (or 2.5 if not in Fast gain with error)
4	8	3	5	0.1	0.12	12 (or 1.0 if not in Fast gain with error)	4.8 (or 2.5 if not in Fast gain with error)
2	2	4	25	0.05	0.06	7.5 (or 1.0 if not in Fast gain with error)	3 (or 2.5 if not in Fast gain with error)
3	4	4	25	0.015	0.018	4.5	1.8

Using the OPM-15 Power Meter: When working with the laser power meter (OPM-15, provided with the analyzer, shown in Figure 5) plugged into the back of the telescope "coax out" port, the units the meter provides are in mA, which has a 1:1 conversion to laser power in mW. If a triangle appears on the screen, units will be in µA or µW. If the IO Gain is configured, the power reading will need to be adjusted by that amount, according to Table 2.

Figure 5. Measuring laser power with the OPM-15 meter provided.

Power reported in Unisearch files: The units for "Signal Power" reported in the raw data files downloaded from the LasIR analyzer are in units of mW. If the signal gain is configured to have a multiplier, the reading will need to be divided with that multiplier (Table 2) in order to get the signal power in mW.

Power reported in TASDAcc files: The power reported in the TASDAcc files are pulled from the MODBUS data stream provided by the instrument. Table 2 shows how this power is related to laser power elsewhere in the system.

4.7   System Settings

In the LasIR instrument software, select File > Configure Analyzer. Select "Expert" on the upper right corner of the Configure Analyzer window. View settings for H_2S, CO_2, and H_2O. Compare these settings with historical settings and provide any explanation for change. For a complete description of the settings and their typical ranges, consult the LasIRView software manual[2]. If you change any settings, document how the settings were changed in the instrument logbook present at the site. Note that all instrument settings are saved on the analyzer on a daily basis.

5. Flow-Through Response Test

The Unisearch analyzer enclosure comes equipped with a flow-through cell for use in response testing the LasIR units. This setup requires high-concentration compressed gases to be flowed

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[2] Mackay, K., Chanda, A., Mackay, G. Software Manual: LasIRView2015, Application Software for LasIR Analyzers. Rev. 2015-10-01

through in order to affect a response from the analyzer. An alternate way to response-test the analyzers is to use sealed cells; this procedure is described in Section 6.

5.1 Supplies

1. Nitrogen gas

2. H_2S reference gas blend

    - Note that the H_2S reference gas tank and as much of the gas lines as possible should be outside the shelter in the open air; all gas lines should be tested for leaks while filled with nitrogen gas

3. 1/8" PTFE tubing for the reference and purge gas lines into the quality assurance (QA) cell

4. 1/8" PTFE Swagelok tee union to couple the reference and purge gas feed lines into the QA cell

5. 1/4" PTFE tubing for gas flow lines on the outlet of the QA cell

6. Unisearch external 0.167-m flow cell

7. Length of PTFE 1/4" tubing with PTFE Swagelok nuts on both ends

8. Length of PTFE tubing to go from external flow cell to scrubbing system

9. A scrubbing system consisting of ½" ID PTFE tubing, 6" long, filled with GC Sulfursorb Plus activated carbon absorbent, or equivalent; this volume of absorbent has a minimum capacity of 38 grams of H_2S, which is approximately 1,000 times the amount of H_2S existing in 750 ppm H_2S gas flowing at 0.3 l/min for 100 minutes.

10. A max 5 l/min rotameter attached at the exhaust line to view that flow is occurring

5.2 Test Preparation

Depending on the requirements of the QAPP, the path-average concentration will need to be determined using the flow-through cell length, the concentration of standard gas, and the pathlength of the open-path. Note that because this is a monostatic system, the total optical pathlength is twice the distance between the telescope and the retroreflector. For example, a 750-ppm blend of H_2S (in nitrogen or air) delivered to the optical path through the 0.167-m flow-through cell and a total path length of 1000 m provide approximately 125-ppb path average H_2S. An example calculation of this is as follows:

(H_2S concentration in cylinder) (flow cell length) = Path Integrated Concentration ppm-m

(750 ppm) (0.167 m) = 125.25 ppm-m

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

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

5.3 Gas Testing Procedure

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

5.3.1 Clean-Up

1. Dispose of the waste PTFE tube filled with GC Sulfursorb Plus appropriately.
2. Download .cfg and .spectrum files and save along with the form at the end of this document.

6. Sealed-Cell Response Testing

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

6.1   Test Preparation

To meet the testing requirements, you must determine path average concentrations using the certified cell concentration and the pathlength. An example calculation of expected path average concentration for a 250 ppm-m sealed cell together with a 500 m one-way path is as follows:

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

Prior to testing, you will need to ensure that the cells you have will satisfy the testing requirements of the QAPP.

6.2   Single-Point Bump Test

1. Disable alerts on Sonoma Technology Field Tech Tool (FTT) and put instrument into planned maintenance mode.

2. Disconnect optical fiber from instrument "Fiber In" port.

3. Connect optical fiber from Step 2 to inlet of sealed cell.

4. Connect optical fiber from outlet of sealed cell to instrument "Fiber In" port.

5. Wait for response to stabilize before collecting data.

6. Collect between 7 and 15 data measurements for averaging, or the number of samples required by the QAPP.

7. Calculate the average, % error, standard deviation, % CV, and average detection r. Record these values in the test form (Section 7).

8. **Verify that the values meet the QA criteria. If the test fails QA criteria, follow the corrective actions listed at the end of this section (see: Data Evaluation, Reporting, and Corrective Action).**

9. Disconnect sealed cell outlet optical fiber from instrument and reconnect optical fiber from Step 2 to instrument "Fiber In" port.

10. Verify baseline of instrument and turn alerts back on in FTT; take out of planned maintenance mode.

11. Download .cfg and .spectrum files and save along with the form at the end of this document.

6.3   Three-Point Calibration

1. For the three-point calibration test, repeat the measurements described in Section 6.1 for the remaining concentrations using additional sealed cells.

    c.   Report the Quantitation Limit as equal to the detection limit.[3]

3. Compile all configuration files, spectra files, and log files into a single folder.

    a.   The folder should be named "CUS LOC QATest TDL# YearMonDy" where CUS is a 3-letter designator for the customer and LOC is a three-letter designator for the facility location.

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

Note:

- **If the test produces an error or precision greater than the warning level**: corrective action should be taken so that the precision and error are below the warning levels.

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

If the measurements do not meet the data quality objectives listed in the QAPP, repeat the procedure without adjustment. If the instrument still fails to meet the QA criteria, retest the following day with no adjustment. Confirm that atmospheric conditions were acceptable for bump testing. If these repeated tests continue to fail under acceptable atmospheric conditions, initiate corrective action to include the following:

- Review data for potential interferants, including a detailed check of absorbance spectra in the analysis regions configured for the analyte, noting any excessive noise or unexpected absorbance features

- Consult with the project technical lead to identify abnormal changes to the background

- Examine wavelength calibration

- Investigate any large changes in stray light since the last test and adjust calibration factors as necessary

- Review gas testing apparatus for leaks or other similar problems

- Review and confirm specifications of standard calibration equipment and gases (expiration dates, concentrations, etc.)

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

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[3] In accordance with guidance from BAAQMD in their letters to refineries dated Dec 22, 2022, and subsequent statements that the December 2022 specification (requiring LOQ of 3-25 ppb) was not a significant change from – and was no more stringent than – the October 2021 specification (which required a detection limit of 3-25 ppb).

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

8. LasIR Response Test Form

Date: _____ Location: _____

Test Technician 1:_____ 2:_____

Alignment

Signal Intensity as found(MODBUS)_____ (Target: >0.4)

Response Tests

	Trial 1	Trial 2	Trial 3
Reference ID			
Reference Concentration			
Start Time			
Stop Time			
Average			
% error			
Standard Deviation			
% CV			
Average Detection r			

Three-point Calibration Summary

	Value
Slope	
Intercept	
r^2	

Notes: