Attachment 1 - Basis for Determination That Valero's Revised Fenceline Air Monitoring Plan and Quality Assurance Project Plan (Submitted February 3, 2023) Do Not Meet District Regulation 12-15-403

1. Appendix B and Appendix D to the quality assurance project plan (QAPP) both contain maintenance and audit procedures for the Unisearch LasIR tunable diode laser absorption spectroscopy ("TDLAS" or "TDL") system. The content is similar, but not identical. If a duplicate appendix was provided in error, consolidate the content into a single appendix. Otherwise, make a clearer distinction between the purpose of each one. Also, please consider all comments below, as they may apply to each appendix separately or to both appendices.

2. According to the Air Monitoring Guidelines for Petroleum Refineries (Guidelines) established pursuant to District Regulation 12-15-406 in April 2016, fenceline measurements must be continuously measured with a time resolution of five minutes, and instrumentation must meet a minimum of 75% completeness on an hourly basis, 90% of the time based on annual quarters (p. 5). In other words, because a single clock hour has twelve discrete 5-minute periods, 90% of the clock hours in a calendar quarter must include at least nine valid 5-minute average measurements in order to satisfy the completeness requirement.

   In contrast, the air monitoring plan (AMP) and QAPP contain the following content regarding data completeness:

   a. Page 13 of the AMP states that instruments are operated to meet a minimum of 75% completeness for the purpose of calculating hourly averages, and 90% completeness by annual quarter;

   b. page 39 of the AMP and page 20 of the QAPP include the following table, which the AMP (p. 38) incorrectly says reflects Air District guidance for open-path measurement data recovery requirements:

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

   c. pages 19-20 of the QAPP describe a process for calculating data completeness using various statistics that are based on 1-hour rolling averages.

   These provisions are inconsistent with the Guidelines. While the Guidelines contain a single requirement for data completeness, the AMP and QAPP mischaracterize it and appear to present it as two separate requirements. Data completeness should also not be based on rolling averages. Furthermore, although pages 19-20 of the QAPP provide various statistics that will be used to calculate completeness, the AMP and QAPP lack adequate detail (e.g., formulas) to establish exactly how completeness will be demonstrated.

   This issue is among several others identified in a notice of deficiency sent to Valero on July 15, 2022. To aid in resolving this deficiency, Attachment 3 to our December 22, 2022 letter interpreting Regulation 12-15 and the associated Guidelines (12/22/2022 letter) outlined detailed procedures Valero must use to demonstrate compliance with the data completeness requirement. The problem nevertheless remains unresolved, as the AMP and QAPP continue to mischaracterize the completeness requirement, and

contain unacceptable procedures for demonstrating compliance with it. Valero must incorporate the contents of Attachment 3 to our 12/22/2022 letter into the AMP and QAPP.

3. With regard to data completeness, page 19 of the QAPP states that planned maintenance is among exclusionary conditions, which are not counted against the refinery for data completeness calculations. This statement is inconsistent with the Guidelines and must be removed from the QAPP.

   Recognizing that open-path measurements are affected by low-visibility conditions like dense fog, the Guidelines state that data from such periods will not count against data completeness requirements, as long as appropriate meteorological measurements document time periods when those conditions exist (p. 5). However, the Guidelines do not similarly allow for the exclusion of invalid or missing data associated with maintenance activities; the Guidelines also do not allow exclusions for QA/QC activities such as instrument calibrations or bump tests. This issue is addressed in Attachment 3 to our 12/22/2022 letter, which states that the "expected" number of data points is the number of possible 5-minute average concentrations in a given hour, adjusted for periods of low visibility during adverse atmospheric or environmental conditions. Valero must address this deficiency by incorporating the contents of Attachment 3 to our 12/22/2022 letter into the AMP and QAPP.

4. With regard to quarterly reporting:
   a. page 13 of the AMP states that Valero will provide one-hour average concentration data to the Air District in a comma separated value (CSV) file; and
   b. page 52 of the AMP and page 31 of the QAPP state that Valero will provide rolling hourly and 5-minute concentration data to the Air District, along with the site code, local standard time, measurement duration, concentration value, signal strength, concentration unit, QC and OP codes, and real-time minimum detection limits (MDLs).

   Not only are the above passages inconsistent with each other, they are inconsistent with the procedures specified in our 12/22/2022 letter interpreting the Guidelines. In particular, attachments 2 and 3 to the letter:

   - stated that all fenceline monitoring concentration data should be provided as 5-minute averages (not 1-hr rolling averages);
   - identified several required data elements;
   - specified formats for the required data elements;
   - specified procedures for reporting missing data;
   - specified reporting procedures for bump tests and calibration checks;
   - specified reporting procedures for quarterly data completeness; and
   - required the use of templates provided by the Air District.

   These provisions are either missing or inadequately specified in the AMP and QAPP. The contents of attachments 2 and 3 to our 12/22/2022 letter must be included in the AMP and QAPP.

5. As stated in Attachment 3 to our 12/22/2022 letter, Valero's quarterly report must include meteorological data and a narrative explanation sufficient to justify invalidation of data for every hour of the calendar

quarter where data has been excluded due to adverse atmospheric or environmental conditions. While page 31 of the QAPP states that meteorological data will be provided to the Air District with each quarterly report, it does not also state that the accompanying narrative explanation will be provided. The AMP and QAPP are deficient in this regard. The contents of Attachment 2 to our 12/22/2022 letter must be included in the AMP and QAPP in its entirety.

6. With regard to the quarterly monitoring data provided to the Air District, pages 13 and 52 of the AMP state that the Air District may make one-hour average data available to the public through an Air District Website or a public records request. The AMP should instead state that the Air District may make publicly available any of the data routinely submitted in a quarterly report.

7. With regard to quality assurance and quality control, the Guidelines require the AMP to include a QAPP that follows EPA guidelines and specifies methodologies for ensuring appropriate levels of QA/QC, data acceptance criteria, levels of data quality, data management issues and procedures, and data review and validation procedures (p. 10).

   Tables 6 and 8 of the AMP, tables 3 and 10 of the QAPP, and Table B-1 of Appendix B identify maintenance and QA/QC activities for the hydrogen sulfide (H_2S) monitoring system. As a general matter, the AMP, QAPP, and appendix contain an insufficient level of detail regarding the methods, procedures, equations, and calculations that will be used to perform these actions. For example, tables 6, 3, and B-1 state that an "evolving checklist" of system performance indicators will be checked on a quarterly basis. It is unclear what indicators will be checked, how they will be checked, and what acceptance criteria will be used.

   As another example, Table D-1 of Appendix D states that system settings should be verified on an unspecified frequency. While Appendix D has procedures for verifying the system settings (see Section 4.7), it merely directs personnel to view the settings, compare them with historical settings, and explain any changes. Details that should be provided in the QAPP or in standard operating procedures (SOPs) attached to the QAPP include: an explanation of the settings and how they affect instrument performance, the range of options available for each setting, typical or expected values for each setting, considerations to make when adjusting the settings, and procedures for documenting adjustments that are made.

   While these examples are not exhaustive, they illustrate a fundamental lack of detail in the AMP and QAPP. To resolve this issue, Valero must do the following:

   a. attach to the QAPP detailed SOPs for all performance indicator checks, corrective actions, maintenance activities, QA/QC activities, data management activities, and reporting activities; and

   b. for each performance indicator check, corrective action, maintenance activity, QA/QC activity, data management activity, or reporting activity identified in the AMP or QAPP, provide references to the relevant SOPs.

   Note that this is among the issues discussed in our July 15, 2022 and 12/22/2022 letters that Valero has failed to address. Also note that the SOPs will become part of the publicly available QAPP; as a result, if an SOP contains confidential information, two copies must be submitted – one that has the confidential information redacted and that can be made available to the public, and another unredacted copy for internal Air District reference. Finally note that by submitting a confidential redacted version, Valero represents to the District that it includes information recognized as trade secret under California law.

8. Section 3.3 of the QAPP outlines procedures for subjecting measurements to precision and accuracy tests. Accuracy and precision are defined on page 20 of the QAPP as follows:

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

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

The term "accuracy" is generally understood in the scientific community to refer to the closeness of agreement between a measured quantity and its true value, such that a higher accuracy represents greater agreement. However, as it is defined above, higher values of "accuracy" actually reflect less agreement between the measured quantity and its true value because the formula represents error in the measurements rather than accuracy. This convention may be confusing or misleading to casual readers of the AMP and QAPP, and, because they are public documents, it is important that they be clear and understandable, and use plain language, to the extent possible. To improve clarity, Valero must modify the formulas as shown below, and revise the AMP, QAPP, and any attachments as necessary to accommodate the revised definitions (e.g., if the QAPP currently states that corrective action will be taken if the percent accuracy exceeds 15%, it should be revised to state that corrective action will be taken if the percent Error exceeds 15%).

$$\% \text{ Error} = \left| \frac{\bar{x} - x_{std}}{x_{std}} \right| \times 100\%$$

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

9. With regard to bump tests:
    1. Table 6 of the AMP, Table 3 of the QAPP, and Table B-1 of Appendix B state that a bump test will be performed using sealed cells, and that corrective action will be taken if the percent accuracy is more than 25%;
    2. Table 8 of the AMP and Table 10 of the QAPP state that the acceptance criteria for accuracy and repeatability (as %CV) during the monthly bump tests are 25%; and
    3. appendices B and D further outline procedures for performing bump tests.[1]

    The Air District has the following comments regarding these provisions:

    a. The Air District's 12/22/2022 letter stated that the H_2S TDL to have a measurement accuracy within 15% of the reference standard, and a coefficient of variation (CV) not greater than 15%.The accuracy and precision specifications must be met for each monthly bump test. The AMP and QAPP are inconsistent with these requirements. The AMP, QAPP, and any SOPs must clearly state that both accuracy (as % Error) and precision (as % CV) will be assessed during each bump test, with acceptance criteria of ≤15% for both performance indicators.

[1] Appendix B and Appendix D to the QAPP both contain maintenance and audit procedures for the Unisearch LASIR TDLAS. The content is similar but not identical. If a duplicate appendix was included in error, please consolidate the content into a single appendix. If this was not done in error, please explain.

In response to our 12/22/2022 letter, Valero stated that a determination of the lower limit at which calibration and bump testing can be routinely performed, and performance criteria reliably achieved, is ongoing. As a result, Valero suggested, the accuracy and precision requirements should be specified at 25% until it is clear commercially available TDL systems can achieve better performance on a routine basis. The Air District is in receipt of information that demonstrates a commercially available TDL system can in fact meet the previously stated specifications and we decline to set them at the levels Valero has suggested. The specifications in our 12/22/2022 letter must be incorporated into the AMP, QAPP, and all associated appendices. If Valero's current air monitoring system is unable to meet these specifications, Valero should notify the Air District and take immediate steps to procure an open path monitoring system that can perform as required.

b. The Air District's 12/22/2022 letter stated that the H_2S TDL must meet the accuracy and precision specifications for each bump test at a concentration of 50 to 100 ppb. While the procedures for single-point bump tests in section 6.1 of Appendix D provide an example calculation based on a 250 ppm-m sealed cell, the Appendix does not explicitly state what cell concentration will be used. That information must be clearly stated in the standard procedures, while ensuring the resulting path average concentration is between 50 and 100 ppb for each path.

c. As noted above, our 12/22/2022 letter stated that the H_2S TDL must meet the accuracy and precision specifications for each bump test at a concentration of 50 to 100 ppb. The procedures for performing bump tests outlined in section 5.2 of Appendix D, using flow-through cells ,call for use of a 750 ppm blend of H_2S. Such a cell concentration will result in a path average concentration outside of the specified range for all paths.

   As explained in Appendix D, the 750 ppm blend of H_2S will be delivered to the optical path through a 0.167 m flow-through cell. This will result in a 125.25 ppm-m path integrated concentration along all paths:

   Path integrated concentration (ppm-m) = [H_2S concentration in cell] x [flow cell length]

   Path integrated concentration = 750 ppm x 0.167 m = 125.25 ppm-m

   The path average concentration then equals the path integrated concentration divided by the total optical path length. The path lengths from Table 3 of the AMP and the resulting path average concentrations are shown below:

$$\text{Path average concentration} = \left(\frac{125 \text{ ppm-m}}{2 * 326 \text{ m}}\right)\left(\frac{1000 \text{ ppb}}{1 \text{ ppm}}\right) = 192 \text{ ppb}$$

Path	One-way Path Length (m)	Path Average Concentration (ppb)
1 – 1′	326	192
1 – 1″	481	130
2 – 2′	567	110
2 – 2″	609	103
3 – 3′	578	108
3 – 3″	549	114

Valero must revise the procedures in Appendix D so they utilize cell concentrations that result in average path concentrations within the required 50 to 100 ppb range.

d. Table 6 of the AMP and Table 3 of the QAPP state that bump tests will be performed using sealed cells. However, footnote b to Table 8 of the AMP and Table 10 of the QAPP state that sealed cell development is in process to enable bump tests and 3-point calibration checks, and the accuracy of tests using this equipment still needs to be determined for the TDLAS. If NIST-certified sealed cells are not available, or the procedures are still in development, flow-through cells with NIST traceable gases may be used in the alternative. However, the AMP, QAPP, and any SOPs must be clear and consistent about which procedures will be used and when.

10. With regard to 3-point calibration checks:

    - Table 6 of the AMP, Table 3 of the QAPP, and Table B-1 of Appendix B to the QAPP state that a 3-point calibration check using sealed cells will be performed on a quarterly basis. Tables 6 and B-1 additionally state that corrective action will be taken if the % Accuracy is greater than ±25% (acceptance criteria are not specified in Table 3 of the QAPP); and
    - Table 8 of the AMP and Table 10 of the QAPP state a 3-point calibration check will be performed on a quarterly basis, and both tables provide tiered acceptance criteria for the accuracy and repeatability ranging from ±10% to ±25%.

    The Air District's 12/22/2022 letter stated that the H_2S TDL must have a measurement accuracy within 15% of the reference standard, and a coefficient of variation not greater than 15%. The letter further stated that these specifications must be met at each calibration point. The AMP and QAPP do not satisfy these requirements, and are deficient in this regard. The AMP, QAPP, and any SOPs must clearly state that both accuracy (as % Error) and precision (as % CV) will be assessed during each 3-point calibration check, with acceptance criteria of ≤15% for both performance indicators at each calibration point.

11. With regard to the required 3-point calibration checks and bump tests, the 12/22/2022 letter stated that a failure to meet the stated accuracy and precision specifications must trigger repair, maintenance, and root cause analysis, followed by repeat calibration checks or bump tests, until a passing check or test is completed. The letter also stated that all steps in this process, including the results of each passing and failed calibration check and bump test, and monitor response or calibration adjustments, must be fully documented in the quarterly report submitted to the Air District.

    In response to the 12/22/2022 letter, Appendix E to Valero's QAPP states, "[t]he QAPP and SOPs can be revised to cover corrective actions in the case of a failed test." However, the District is unable to find the revisions in question. The AMP and QAPP also do not state that the quarterly reports will contain the information described above. The AMP and QAPP are therefore deficient and must be revised to include these requirements.

12. With regard to the established precision and accuracy specifications, the Air District's 12/22/2022 letter stated that a failure to meet the specifications during two or more bump tests in any quarter, or four bump tests in any 12-month period, will result in a violation of the accuracy or precision specifications (as applicable) and QAPP requirements. The letter further stated that such occurrences will invalidate all data prior to the failed bump test going back to the last passing bump test, and that invalidated data will count against data completeness requirements. These requirements and procedures cannot be found in the QAPP and must be added.

13. With regard to the detection capabilities of the H_2S monitoring equipment, our 12/22/2022 letter stated that a TDL system used to monitor H_2S must have a limit of quantitation (LOQ), which ranges from 3 to 25 ppb depending on environmental and operational conditions. In comparison to this requirement:

    - page 33 of the AMP and page 6 of the QAPP state that, under typical operating conditions, the TDL is expected to have a minimum detection limit (MDL) between 3 and 25 ppb;
    - Table 3 of the AMP (p. 35) and Table 1 of the QAPP (p. 7) state that the MDL for H_2S is 25 ppb along all paths;
    - Table 8 of the AMP and Table 10 of the QAPP state that the 5-minute MDL calculations have an acceptance criteria of less than 25 ppb;
    - pages 33-34 of the AMP states that a real-time MDL is calculated continuously using the standard deviation of the last seven 5-minute average concentration values containing no measurable analyte; and
    - Appendix E defines the MDL for the H_2S system as *3s,* and defines the LOQ as *10s*, where *s* is the standard deviation of a 5-min average blank sample.

    The AMP and QAPP are deficient with respect to this requirement as they are inconsistent with the specifications in our 12/22/2022 letter. Valero must revise the AMP and QAPP to reflect the requirement that the LOQ (not MDL) of the H_2S system be between 3 and 25 ppb.

14. Page 33 of the AMP and page 6 of the QAPP state that, under typical operating conditions, the TDL is expected to have an MDL between 3 and 25 ppb between 1% and 3% transmission. At the same time, the AMP and QAPP use a signal power of 0.4 as a quality control parameter. However, according to Appendix E to the QAPP, a signal strength greater than 0.4 mW corresponds to a transmission greater than 3% to 5%. Thus, there is an apparent discrepancy between various parts of the AMP and QAPP, which must be resolved. Furthermore, none of these provisions satisfy our October 6, 2021 and 12/22/2022 letters interpreting the Guidelines, which stated that the system must have specified detection capabilities at a light transmission of 1% or less. Valero must revise the AMP and QAPP to reflect the required performance specification.

15. Page 46 of the AMP and page 24 of the QAPP state there is an expectation that no measurements would be collected when visibility is less than 2.5 miles. This is a false expectation, and must be stricken from the AMP and QAPP. Valero must operate its fenceline monitoring systems at all times, including periods with low visibility. When such conditions preclude valid measurements, the Guidelines require Valero to provide the Air District with appropriate meteorological measurements to justify exclusion of the data when assessing data completeness. The procedures for providing this information are in Attachment 3 to our 12/22/2022 letter, and must be incorporated into the AMP and QAPP; the language described above must also be stricken from the AMP and QAPP.

    In addition, page 17 of the QAPP describes automatic screening for invalid data due to weather, and Table 9 of the QAPP indicates that data are automatically marked as invalid if visibility is less than 2.5 miles. However, page 46 of the AMP and page 24 of the QAPP state that an exact relationship between visibility and open-path measurements has not been established, and Valero has provided no actual information to demonstrate that relationship, or to support the use of a specific threshold for flagging data. If Valero is going to use an automated process to flag data based on visibility data, a more thorough justification must be provided.

16. Page 46 of the AMP states, "Final data sets are compiled quarterly, 60 days after each quarter, and provided to the BAAQMD." Page 31 of the QAPP has similar language. The AMP and QAPP must be revised to state that final data sets will be provided to the BAAQMD no later than 60 days after the end of each calendar quarter.

17. Page 21 of the QAPP states the following: "For factory calibrations, a certification of the standard gases used will be requested from the manufacturer. Standards will not be used past their expiration date. If an expired standard is used, it will be recertified by the manufacturer." The last sentence of this passage must be stricken from the QAPP, as the use of expired standards is unacceptable. As such, any system audits using expired standards will be invalidated.

18. Page 23 of the QAPP states that the data management system (DMS) provides auto-screened data to the field ops website and notification system to inform and alert staff. It additionally states that the ops website displays maps and time series plots for BTEX, SO2, and wind data. Please clarify whether the H_2S data are included in this process.

19. The AMP and QAPP are unclear and ambiguous about how data are validated, and about what data are displayed to the public. For example, page 43 of the AMP and page 31 of the QAPP state that all data values that are not associated with bump tests, other instrument maintenance, or instrument problems are displayed to the public in near-real time. The AMP goes on to say that if data are subsequently proven to be invalid, they are removed from the public display. At the same time, however, Table 7 of the AMP and Table 9 of the QAPP state that if visibility is less than 2.5 miles, data on the website are coded as invalid. It is thus unclear whether invalid data are removed from the website, or whether they are displayed on the website but flagged as invalid. To add to the confusion, the captions to Table 7 of the AMP and Table 9 of the QAPP state, "[a]ll valid and flagged data values are displayed to the public in real time. If data are invalid they are be (sic) included in the public display."

    Also concerning is a statement on page 23 of the QAPP that says automated data screening checks "screen out invalid data for public display," and another statement on page 30 of the QAPP, which says that data are invalidated "in the event of an automated screening check failure." These statements suggest that if a measurement is flagged by an automated screening check, it may be invalidated and never make it to the public website at all. This is particularly troubling given that any H_2S measurement above 30 ppb is flagged by the auto-screening process.

    To resolve these issues, Valero must:

    a. include in the QAPP a detailed process flow diagram depicting the end-to-end data handling, review, and management process, from the moment of data acquisition to the quarterly submittal of final quality-controlled data to the Air District;

    b. revise the narrative descriptions of the data handling, review, and management process in the AMP and QAPP to clearly and fully describe the step-by-step process depicted in the flow diagram;

    c. articulate all decision rules used to automatically or manually screen data;

    d. illustrate the application of all auto-screening rules using real data and screen shots depicting how the auto-screened data are depicted on the public website; and

    e. improve transparency about the data that has been invalidated by revising the website to allow members of the public to see two alternative views of the data – one view with invalid data removed, and another view showing all data (valid and invalid). Invalid data displayed on the

website must be flagged as such, and the reason for invalidation must be indicated on the website alongside the corresponding invalid data.

20. Please correct the following table reference on page 23 of the QAPP, which appears to be in error because Table 8 lists data recovery requirements rather than data screening criteria:

> be left as is. However, if the criteria listed in Table 8 result in erroneous flagging of data, the thresholds will be revised and this QAPP will be updated accordingly. The DMS auto-screening checks include:
>
> - Range. These checks verify that the instrument is not reporting values outside of reasonable minimum and maximum concentrations.

Also, with regard to quarterly reporting, page 52 of the AMP says the reported data elements will include QC and OP codes defined in Table 4-1. This appears to be an error, as Table 4-1 cannot be found in either the AMP or the QAPP.

Given the multiple erroneous references, please check all table and figure references, and correct them as necessary before resubmitting a revised plan.

21. Page 13 of the AMP states that all data will be retained by the facility for a period of five years, consistent with Regulation 12-15-302. Please change this citation to the correct citation to the rule, which is section 12-15-502.