December 22, 2022

Michael Marlowe
Manager, Environmental Affairs
Martinez Refining Company, LLC
3485 Pacheco Boulevard
Martinez, CA 94553

RE: Refinery Fenceline H_2S TDL Monitoring System Specifications

Dear Mr. Marlowe:

Pursuant to Bay Area Air Quality Management District (Air District) Regulation 12, Rule 15 (Refining Emissions Tracking), Martinez Refining Company (MRC) must install and operate a fenceline monitoring system in accordance with an approved air monitoring plan (AMP) and quality assurance project plan (QAPP); both the AMP and QAPP must be consistent with monitoring guidelines established by the Air District. Among other requirements, the current guidelines state that MRC must measure hydrogen sulfide (H_2S) concentrations at the refinery fenceline with open path technology capable of measuring in the parts per billion range. The purpose of this letter is to clarify the required performance criteria for any open path H_2S tuneable diode laser (TDL) systems being considered.

From 2018 to 2021, the Air District sent MRC a series of letters extending the deadline for selection of an H_2S monitoring method. The Air District afforded MRC these extensions to encourage the use of open path H_2S monitoring and allow more time for the development and validation of commercially available systems. In 2021, the Air District notified MRC that an open path TDL monitoring system for H_2S had successfully completed a 6-month proof of performance field study at a California refinery and the results indicated this technology had advanced to the point that open path monitoring could be successfully implemented. The Air District issued its last extension on October 6, 2021, giving MRC up to 15 months to begin operating a TDL system for H_2S, which met specifications and performance criteria that were outlined in the same letter.

By this letter, the Air District is revising the specifications and performance criteria based on new information we have received; the revised requirements are provided in attachment 1. Any open path H_2S monitoring system that can be shown to meet these specifications will be deemed acceptable until such time the Air District determines the system is not complying with the specifications. If existing monitoring systems can be optimized to meet the specifications detailed in this letter, MRC should submit verification that the systems are meeting the requirements upon installation and check out. Following review, any existing system deemed by the Air District to not be capable of meeting the specifications will need to be replaced with a monitoring system that does meet the specifications.

Please be advised that these revisions do not relieve MRC from adhering to the schedule for selecting, installing, and operating the H_2S monitoring system outlined in our October 6, 2021 letter. Also be advised that the H_2S monitoring data must be included in the quarterly fenceline data reports upon commencement of operation, regardless of the final AMP and QAPP approval status.

In addition to revising the performance criteria for the H_2S monitoring system, we are also taking this opportunity to standardize procedures for quarterly reporting across all of the facilities that are subject to Rule 12-15; those requirements are further explained in attachments 2 and 3, and pertain not only to the H_2S TDL system but to all fenceline monitoring systems and parameters.

Lastly, the Air District is in receipt of a revised AMP and QAPP submitted by MRC on August 29, 2022 in response to a July 15, 2022 notification of deficiency from the Air District. In light of the revised requirements discussed in this letter, the Air District will allow MRC to rescind its August 29 submittal and resubmit an updated AMP and QAPP consistent with the requirements described herein. If MRC intends to rescind its August 29 submittal, it must notify the Air District of its decision within 7 business days following the date of this letter. Upon such notification, MRC will have 45 days to resubmit a revised AMP and QAPP. In addition to satisfying the requirements outlined in this letter, the revised AMP and QAPP must address the issues discussed in our July 15 notification of deficiency; failure to do so may result in disapproval of the plans.

If you have any questions regarding this notification, please contact Chris Crowley at 415-749-5118 for compliance issues or me at 415-749-4601 for technical issues.

Sincerely,

Jerry Bovee, P.E., QSTI
Air Quality Engineering Manager

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Attachment 1

Required Specifications and Performance Criteria for TDL Systems used to Monitor H_2S at the Refinery Fence Line Pursuant to Air District Regulation 12, Rule 15

- A Limit of Quantitation (LOQ),[1] which ranges from 3 to 25 ppb H_2S, depending on environmental and operational conditions, with an average integrated path LOQ of 15 ppb H_2S. The stated LOQ limits can be converted to a path length equivalent (i.e., ppb-m) value, based on the actual installation path length, for convenience if necessary.

- An LOQ of 25 ppb at a light transmission less than or equal to 1%, or at a signal power equivalent to 1% light transmission, provided the equivalency is demonstrated and documented in the quality assurance project plan (QAPP).

- A path integrated measurement range of 3 to 5,000 ppb H_2S with a measurement accuracy within 15% of the reference standard and a coefficient of variation not greater than 15% using a concentration of 40 to 60 ppb H_2S equivalent integrated path average.

- Equipment calibration performed at least on a quarterly basis to validate monitor performance under real-world operating conditions and potential ambient concentrations.

    - Calibration checks must be performed at a minimum of three concentration points (low, mid, high), using sealed or flow-through cells and NIST traceable standards.

    - The low calibration point must be in the range of 40 to 60 ppb H_2S equivalent integrated path average. Two reasonable upscale (mid, high) calibration concentrations should be chosen to confirm the accuracy and precision of the system over the measurement range, without adjustment after each calibration point measurement; these calibration concentrations should be commensurate with ambient concentrations that may result from process upsets, leaks, or other malfunctions.

    - The accuracy and precision specifications of 15% must be met at each calibration point. Failure to meet these specifications must trigger repair, maintenance, and root cause analysis, followed by repeat calibration checks until a passing calibration check is completed. All steps in this process, including results of each passing and failed calibration check, and monitor response or calibration adjustments, must be fully documented in the quarterly report submitted to the Air District as described in the requirements below and subsequent attachments. Standard operating procedures, which describe the calibration checks and corrective actions, must also be attached to the QAPP.

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

[1] For reference, the minimum detection limit (MDL) of a measurement process is defined as the lowest concentration of the analyte that can be reliably detected (i.e., distinguished from zero), and the LOQ is the lowest concentration at which the analyte can not only be reliably detected but at which predefined goals for accuracy and precision are met. The LOQ may be equivalent to the MDL, or it could be at a higher concentration. All LOQ specifications provided here are established with respect to the accuracy and precision requirements stated in this attachment.

Equivalent introduction of calibration gas into the light path may be considered if the stated accuracy and precision specifications can still be met.

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

- Failure to meet the monthly accuracy or precision requirements during two or more bump tests in any quarter, or four bump tests in any 12-month period, will result in a violation of the accuracy and/or precision specifications and QAPP requirements. Such occurrences will invalidate all data prior to the failed bump test going back to the last bump test passed. Invalidated data will be counted against data completeness requirements.

- Real time validation of TDL data must be performed using measurement of another common ambient air component, such as methane, water, or carbon monoxide if present in the spectra.

- LOQ quantification and verification must be performed continuously in near real time, reported in near real time on the refinery fenceline monitoring website, and included in the quarterly reports along with the measurement data as specified in the requirements below and subsequent attachments.

- Percent light transmission received at the detector, including the signal or power strength, must be measured in real time, and provided in the quarterly reports as specified in the requirements below and subsequent attachments. All data, metrics, and procedures used to exclude data due to environmental conditions must be fully documented in the QAPP and explained/supported in the quarterly reports as specified in the requirements below and subsequent attachments.

- Raw spectral data files must be saved as single files and made available to the Air District upon request. File formats must be specified in the QAPP.

- All quality assurance and quality control metrics and procedures must be clearly and completely documented in the AMP and QAPP.

- Standard operating procedures (SOPs) for all quality assurance, quality control, and maintenance activities must be attached to the AMP and QAPP. For any SOP that contains confidential information, two copies must be submitted – one that has the confidential information redacted and that can be made available to the public, and another unredacted copy for internal Air District reference.

- Quarterly reports must be submitted to the Air District consistent with the specifications outlined in attachments 2 and 3 to this letter.

- Optional - The Air District recommends that system operation and performance is based on a standardized method, such as EPA Method TO-16, or a method developed by a credible standardization body, such as ASTM International or the International Organization for Standardization (ISO).

Attachment 2

Required Procedures for Quarterly Reporting

All quarterly reports submitted following the date of this letter must meet the following specifications:

1. Quarterly reports must be submitted to the Air District within 60 days following the end of each calendar quarter

2. Assign a unique identification number to each instrument or system that generates fenceline air monitoring data; add the unique IDs to the tables in the AMP and QAPP that identify the corresponding fenceline monitoring equipment

3. Report all fenceline monitoring concentration data as 5-minue averages

4. Submit the following data for all instrument/parameter combinations to the Air District in a single comma separated value (CSV) data file using the template provided by the Air District with the following fields:

    a. facility_name – the name of the facility where the equipment is located

    b. instrument_id – the unique identification number assigned to the instrument described above

    c. instrument – a short descriptive name for the instrument associated with the reported unique ID (e.g., "H2S TDL", "OGD1", "OGD2", etc.)

    d. parameter – the name of the pollutant being measured and reported

    e. date – the date of measurement, reported in Pacific Standard Time and formatted as "yyyy-mm-dd"

    f. time – the hour of the day and the beginning of the five-minute period over which measurements were collected and averaged, reported in Pacific Standard Time (without any adjustments for daylight saving time) and formatted as "hh:mm" using 24-hour notation, where hh is the number of full hours (00 – 23) that have passed since midnight; for example, a 5-minute average concentration based on measurements collected between 1:10 pm and 1:15 pm should have a time stamp of "13:10"

    g. mean_concentration – the arithmetic mean pollutant concentration measured over the corresponding averaging period; for measurements below the LOQ, the mean concentration must be reported as a numeric value based on the actual values returned by the instrument during the corresponding averaging period

    h. units_of_measure – the units of measure corresponding to the reported mean pollutant concentration

    i. averaging_period – the averaging period (in minutes) for the reported mean pollutant concentration; this should be "5" unless otherwise approved by the Air District and specified in the QAPP

    j. observation_count – the number of values that comprise the reported mean concentration

    k. validity_indicator – an indicator ("Y" or "N") representing whether the reported mean concentration represents a valid air measurement; types of invalid data include but are not limited to data

affected by instrument malfunction, environmental conditions, or data collected during a QC verification procedure

l. error_codes – one or more error codes (as specified in the QAPP) explaining the reason for invalid or missing data; multiple codes should be separated by a semicolon without spaces, and the field should be left blank for valid data

m. max_value – the maximum concentration measured during the corresponding averaging period, reported in the same units of measure as the mean concentration

n. required_loq – the required LOQ for the corresponding instrument, reported in the same units of measure as the mean concentration

o. real_time_loq – the real-time average LOQ for the corresponding averaging period, reported in the same units of measure as the mean concentration

p. signal – the average measured light signal for the corresponding averaging period

q. signal_units - the units of measure for the corresponding light signal

5. For every instrument/parameter combination, the data file outlined above must contain a record for every 5-minute period in every hour for the entire quarter. Where pollutant measurements are missing:

    a. The following fields should be populated with their respective values:

        i. facility_name

        ii. instrument_id

        iii. instrument

        iv. parameter

        v. date

        vi. time

        vii. error_codes

    b. All other fields should be populated with a value of "NA"

6. Provide the information related to data completeness as further outlined in attachment 3

7. Identify all monthly bump tests and quarterly calibration checks performed in the quarter, including failed bump tests and calibration checks; for each bump test and calibration check, specify: the system or equipment in question, the type of test or check performed, the beginning date and time, the ending date and time, and the date and time the equipment resumed normal operation

8. Report the results of all bump tests and calibration checks, including the associated accuracy and precision measurements; for any bump test or calibration check that yields accuracy and precision measurements outside of the stated specifications, include a root cause analysis and a narrative description of the maintenance or repairs performed to return the system to proper operation

9. Describe any corrections made to any data to account for the effects of gas cells or other equipment on light transmission; such corrections must be consistent with the procedures explained in QAPP

Attachment 3

Required Procedures for Assessing and Reporting Quarterly Data Completeness

- For all instrument/parameter combinations, calculate the data completeness statistics below for each hour[2] of the calendar quarter and include the results in the respective quarterly report to the Air District; provide the information in a single CSV data file for all instruments/parameters using the template provided by the Air District.[3]

- In the cover letter that accompanies the quarterly report, include the results of the following calculation based on data for the respective quarter along with a statement as to whether MRC met the required 90% completeness threshold:

$$\text{Quarterly \% Completeness} = \frac{[\text{count of hours in the calendar quarter where hr\_complete\_pct} \geq 75\%]}{[\text{count of all hours in the calendar quarter}]} \times 100$$

- For every hour of the calendar quarter where data has been excluded due to adverse atmospheric or environmental conditions, MRC's quarterly report must include meteorological data and a narrative explanation sufficient to justify invalidation of the data. If MRC fails to adequately substantiate the exclusion of any data due to adverse atmospheric or environmental conditions, the Air District will consider the respective hour of data to be missing and will recalculate the Quarterly % Completeness statistic for purposes of determining compliance with the data completeness requirement.

- Data completeness statistics:

  - possible - The maximum number of 5-minute average concentrations that can be measured in a given hour and logged in the DMS; because data are reported in Pacific Standard Time, this should always be equal to 12

  - captured - The actual number of 5-minute average concentrations that were measured in a given hour and logged in the DMS; for each hour, this value should equal the count of reported 5-minute average concentrations where the validity_indicator field is equal to "Y" or "N" (see attachment 2)

  - missing - The number of possible 5-minute average concentrations not measured or logged in the DMS in a given hour; for each hour, this value should equal the count of reported 5-minute periods where the mean_concentration field is reported as "NA" (see attachment 2)

    missing = possible – captured

  - missing_pct - The percentage of missing 5-minute average concentrations in a given hour relative to the possible number of average concentrations

    missing_pct = (missing / possible) x 100

[2] In all cases, an "hour" refers to an individual clock hour (0 - 23) of a particular day rather than a rolling 60-minute period.

[3] Field definitions and formatting for the facility_name, instrument_id, instrument, parameter, date, and hour columns in the provided template should be consistent with the specifications in attachment 2.

- invalid_total - The number of invalid (for any reason) 5-minute average concentrations measured and logged in the DMS in a given hour; for each hour, this value should equal the count of reported 5-minute average concentrations where the validity_indicator field is equal to "N" (see attachment 2)

- invalid_total_pct - The percentage of invalid (for any reason) 5-minute average concentrations measured and logged in the DMS in a given hour

  invalid_total_pct = (invalid_total / possible) x 100

- invalid_environmental - The number of invalid 5-minute average concentrations in a given hour due to adverse atmospheric or environmental conditions; for each hour, this value should equal the count of reported 5-minute average concentrations where the validity_indicator field is equal to "N" and where the error_codes field (see attachment 2) contains one or more error codes documented in the QAPP and associated with adverse atmospheric or environmental conditions

- invalid_other - The number of invalid 5-minute average concentrations in a given hour due to anything other than adverse atmospheric or environmental conditions; this may include, but is not limited to, planned or unplanned maintenance; for each hour, this value should equal the count of reported 5-minute average concentrations where the validity_indicator field is equal to "N" and where the error_codes field (see attachment 2) contains one or more error codes documented in the QAPP and not associated with adverse atmospheric or environmental conditions

- invalid_other_pct - The percentage of invalid 5-minute average concentrations in a given hour due to anything other than adverse atmospheric or environmental conditions

  invalid_other_pct = (invalid_other / possible) x 100

- expected - The number of possible 5-minute average concentrations in a given hour, adjusted for periods of low visibility during adverse atmospheric or environmental conditions

  expected = possible – invalid_environmental

- valid - The number of valid 5-minute average concentrations measured and logged in the DMS in a given hour; for each hour, this value should equal the count of reported 5-minute average concentrations where the validity_indicator field is equal to "Y" (see attachment 2)

- valid_pct - The percentage of valid 5-minute average concentrations in a given hour relative to the possible number of 5-minute concentrations

  valid_pct = (valid / possible) x 100

- hr_complete_pct - The percentage of valid 5-minute average concentrations in a given hour relative to the expected number of data points

  hr_complete_pct = (valid / expected) x 100