BAY AREA AIR QUALITY MANAGEMENT DISTRICT

Sampling Study Protocol Specifications for Third-Party Verifiers

Fugitive Emissions from Petroleum Refinery Equipment in Heavy Liquid Service

Joint Study between the

Bay Area Air Quality Management District

And

Western States Petroleum Association

Representing

Chevron Richmond Refinery
Phillips 66 San Francisco Refinery (Rodeo)
Shell Martinez Refinery
Tesoro Golden Eagle Refinery
Valero Benicia Refinery

January 08, 2018

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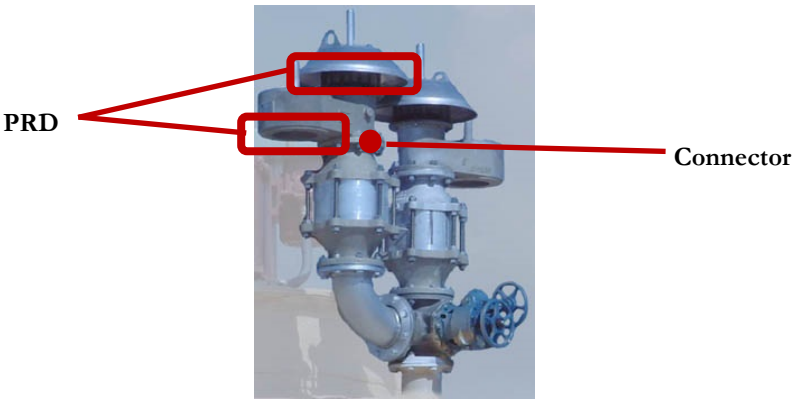
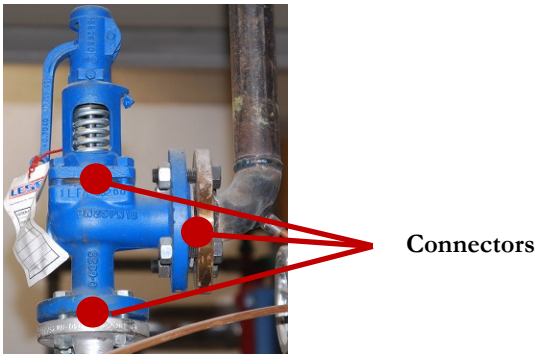
Acronyms, Definitions, and Terms

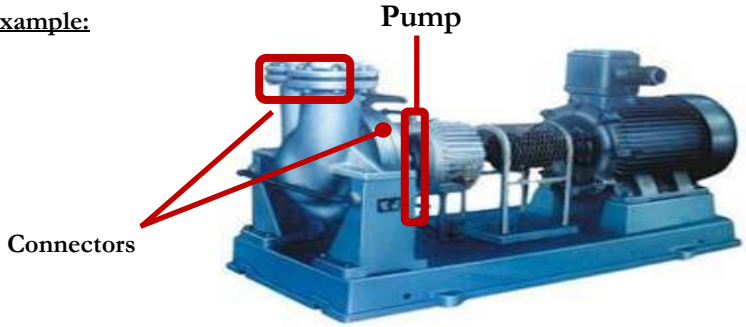
Introduction	The following acronyms, definitions, and terms are used within this protocol.
ASTM	ASTM, International (formerly American Society for Testing and Materials)
Background	The ambient concentration of total organic compounds determined at least 3 meters (10 feet) upwind from the equipment to be inspected and not influenced by any specific emission point.
Component	A part or element of a larger whole. The following are considered components: connectors, flanges, open-ended line, pump seals, valves, and others.
Connector	A flanged, screwed, or other joined fitting used to connect any piping or equipment. This includes sub-components of larger equipment.
Gas	material in gaseous state at operating conditions
Heavy Liquid	liquids with an ASTM D86 initial boiling point greater than or equal to 150 degrees Celsius (302 degrees Fahrenheit)
LDAR	Leak Detection and Repair
Leak	Any screening reading of 2.5 ppm or more above background
Light Liquid	any hydrocarbon liquid that is not a "heavy liquid"; the delineation between the two has varied slightly between different programs.
Method 21	EPA Method 21, 40 CFR Part 60 Appendix A-7
PPM	parts per million, by volume
Pressure Relief Device (PRD)	The discharge horn or vent of an automatic pressure-relieving device actuated by the static pressure upstream of the valve and that relieves to atmosphere. **<u>Examples:</u>**





Pump The rotating components of a mechanical device using suction or pressure to raise or move liquids. Non-rotating components may be considered connectors.

Example:



Screening monitoring an equipment component for fugitive hydrocarbon emissions using an instrument that measures the concentration of hydrocarbon leaks

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TVA Toxic Vapor Analyzer

Valve The rotating part of any device that regulates the flow or process material by means of an external actuator acting to permit or block passage of liquids or gases. Due to bagging concerns, for the purposes of this study, any valve bonnet flanges will be considered part of the valve.

VOC	Volatile Organic Compounds

Monitoring – Component Screening

Overview	The following practices and procedures will be used when conducting component screening.
Instruments	When possible, the District or District-approved contractor and refinery personnel shall use the same model instrument for conducting component screening.
Calibration	Prior to use, each monitoring instrument will be calibrated per the Section "Methodology – Component Screening".
Drift Check	At the end of each monitoring shift, each monitoring instrument will be checked for drift. If the instrument is found to have drifted more than ten percent from any span gas value, those components monitored with that instrument will be re-monitored after the instrument has been calibrated.
Component Identification	As components in heavy liquid service are not required to be identified and monitored as part of an LDAR program, heavy liquid service components that are monitored and found to have screening values greater than or equal to 25 ppmv will be identified in such a way that they can be found again for potential bagging.
Digital Photograph	Each monitored component found leaking shall be digitally photographed by the District or District-approved contractor for use in future locating the component as well as to document the state of the component at the time of component screening. A standard twelve-inch ruler shall be placed in the picture frame as a reference for scale. The picture shall also include a marker with the component test number so that the photograph may be linked to the monitoring data. If possible, the marked location of maximum leak shall also be digitally photographed for reference in mass emissions testing.
Leak Tagging	Each component that is found to emit 25 ppm or more above background shall be affixed with a weather-proof, heat-resistant tag that will allow this component to be easily found if selected as one of the components to be bagged with the date, time, and maximum reading value listed.
Leak Location Marking	If possible, the location of maximum leak shall be indicated, with an indelible marking, on the component for future reference.
District Verification	District personnel or District-approved contractor will screen all components. District personnel or District-approved contractor shall identify the maximum screening value of any leaks. Refinery personnel may also verify the maximum screening values of any leaks found. Whenever there is a disagreement in screening values, the value most likely to provide the most representative and accurate data, based on this protocol, will be used.
Component Screening	The methodology outlined in "*Methodology – Component Screening*" Section shall be followed to screen identified components.

Methodology – Component Screening

Overview	When screening components, the following methodologies and techniques must be used.
Method 21/ EPA Protocol	Component monitoring equipment, calibration, and component screening shall follow the procedures outlined in U.S. EPA Method 21 as listed in 40 CFR Part 60 Appendix A-7 with the exceptions listed in this guidance document. The relevant screening sections of Section 4.0 of the 1995 EPA Protocol for Emission Estimates shall be followed (including calibration gases) with the exceptions listed in this guidance document.
Screening Distance	Component screening shall occur at the interface whenever possible. If not possible, screening distance should not exceed 1 centimeter. When screening does not occur at the interface, it will be noted with the rationale for why screening could not occur at the interface.
Calibration	Each monitoring instrument will be calibrated, per U.S. EPA Method 21, daily prior to use. If monitoring occurs in both the morning and afternoon, the instrument shall be calibrated prior to use in the morning and again prior to use in the afternoon. Instrument Drift Check and Calibration shall also occur after 30 consecutive readings with no results over 25 ppm, and after high readings from which the instrument does not return to background within ten minutes after achieving the peak reading. Calibration of all monitoring equipment shall be done by the same individual.
Calibration Gas	Each instrument shall be calibrated using methane.
Zero Air	Air with less than 0.2 ppm of hydrocarbon
Calibration Span Gas	Monitoring instruments will be calibrated to five points. Calibration gas with the following values shall be used to calibrate each instrument: • 10 ppm methane • 100 ppm methane • 500 ppm methane • 3,000 ppm methane • 10,000 ppm methane
Calibration Precision	With the exception of the 10 ppm span value, calibration accuracy shall be less than ten percent of the calibration gas span value. For the 10 ppm span value, calibration accuracy shall be less than 25 percent.
Drift Check	Drift checks need to be performed to ensure that monitoring instruments remain calibrated.

Each monitoring instrument will be checked for drift at the end of each monitoring shift. If the difference between the drift check measurement and the calibration value exceeds ten percent of the span value, those components monitored with that instrument must be re-monitored.

Background

The cause of any background reading (as defined in Regulation 8, Rule 18) greater than 25 ppm shall be identified and recorded.

Monitoring Technique

The following monitoring technique will be used:

- Place the probe at the surface of the component interface where leakage could occur
- Move the probe along the interface periphery at a 90-degree angle to the interface while observing the instrument readout
- Locate the maximum reading by moving the probe around the entire interface
- Keep the probe at the location of maximum reading for at least three times the response time of the instrument

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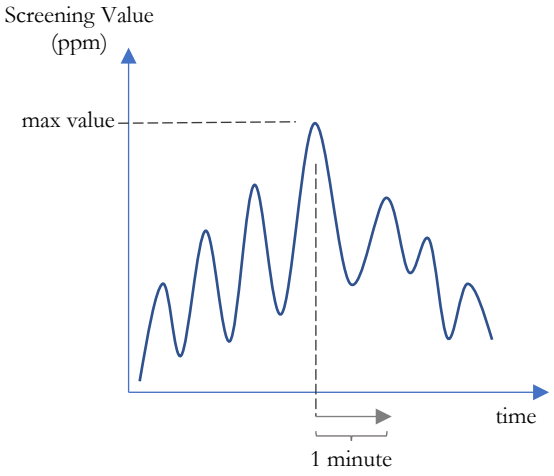
Monitoring Speed

Monitoring shall not occur faster than four seconds per inch monitored (e.g. flange four inches in circumference would require at least 16 seconds to monitor). Monitoring speed may be determined either in the field or at the end of the monitoring period.

Components will be screened until the screening value peaks and then for one additional minute or longer depending on the periodicity (as determined in the field) before recording the reading. Screening personnel will take particular consideration for pulsing leaks that increase in value (see figure).



Monitoring Pace

Unlike gas and light liquid service, fugitive leak readings from components in heavy liquid service tend to rise more slowly and decay more slowly once the probe is moved away from the component. Therefore, monitoring pace will be slower. After initial monitoring, a minimum monitoring pace may be developed and required.

Pulsing Leaks	Every effort shall be used to identify if a leak is pulsing. At any indication that a leak may be pulsing, the instrument shall remain at the location of maximum reading for at least four times the instrument response time.
Filters	Monitoring instrument filters will be changed out whenever there is a large or significant difference in subsequent monitoring readings
Safety	Refinery personnel will alert monitoring staff of any safety or access issues for the selected unit prior to arrival.
Ladders	Each refinery shall provide ladders and/or scaffolding for heavy liquid components elevated higher than eight feet.
Pumps with Steam Injection	Out of a concern for potential malfunctioning monitoring equipment, pumps that have steam injection will not be screened unless steam does not pose a concern (i.e. steam injection turned off). For these pumps, only the pump housing (a connector) will be screened unless the housing itself is also affected by steam.
Refinery Data	The refinery being screened will provide to the District the operating pressure and operating temperature of process lines being screened. This data will be provided prior to completing screening at the refinery.

Quality Control and Quality Assurance

Overview

The sampling study shall employ the quality control and quality assurance measures listed within this document.

Personnel

As much as possible, the same District and third-party personnel will be involved in sampling at all five refineries.

Training (Monitoring)

All District and third-party personnel involved in the monitoring portions of the study will attend a preliminary training session.

Training (Bagging)

All District personnel involved in the bagging portions of the study will attend a preliminary training session. All personnel involved in the bagging portions of the study will follow a District-approved bagging procedure.

Standardized Forms and/or Handheld Devices

Standardized forms and/or field sheets and/or handheld monitors will be employed to record and collect screening and monitoring data from all five refineries. Abbreviations for process unit, component type, stream service, etc. shall be standardized for all data recorded.

Screening Instruments

The Thermal Fisher, Total Vapor Analyzers (TVA) 2020 will be used by screening personnel.

All TVA 2020s used shall meet the following specifications:

Parameter	Specification
Model type	Flame-ionization detector (FID)
Accuracy	± 10 percent of reading or ± 1.0 ppmv, whichever is greater, from 1.0 to 10,000 ppmv
Repeatability	2% at 500 ppmv of methane
Minimum Detectable Limit	0.5 ppmv of methane
Resolution	0.1 ppmv
Range	0 – 30,000 ppmv (methane)
Flow Rate	1 L/min, nominal at sample probe inlet
Response Time	< 3.5 seconds for 90% of final value, using 10,000 ppmv of methane
Calibration gas	Methane
Calibration gas values	• Zero air • 10 ppmv • 100 ppmv • 500 ppmv • 3,000 ppmv • 10,000 ppmv
Response factors (to methane)	Same as ThermoFisher Scientific TVA-2020
Probe Outer Diameter	3/16”
Probe Inner Diameter	1/8”
Probe Length	Enhanced – 16” Standard – 12”
Probe Hose Inner Diameter	1/8”

Probe Hose Length	88" for Enhanced and 80" for standard (in both cases this is from the beginning of the hose to the end of the probe tip, subtract probe length if just hose length is desired)

Instrument Calibrations

All monitoring instruments will be calibrated prior to any monitoring session (once in the morning/once in the afternoon), and after an Instrument Drift Check resulting from 30 consecutive readings with no result over 25 ppm, or after high readings when the instrument does not return to background within 10 minutes of recording the peak reading.

Instrument Drift Checks

All monitoring instruments will undergo drift checks at the end of each monitoring session. If the drift for any gas exceeds ten percent (or 25 percent for the 10 ppmv gas), the screening data will be invalidated and screened components will be re-monitored.

Technician Observation

District staff or District-approved contractor will observe and verify that proper bagging technique is employed by all refinery monitoring personnel conducting monitoring. Any District concerns will be discussed between the District and the refineries.

Screening Verification

All screened components will be monitored or verified by the District or District-approved contractor. As much as possible, the same District and third-party personnel will be used at all five refineries.

Screening Time

If screening data is captured electronically, at the end of each monitoring day, the District and/or third-party screening data will be uploaded by refinery and District personnel to a computer and the following monitoring diagnostics performed by District personnel.

- Monitoring time (≥ 4 seconds per inch)
- Monitoring time (≥ 4 x response time)
- Time between measurements
- Sequential background measurements
- If screening data is captured on paper, copies of all data sheets for each monitoring day shall be provided to the District by the following work day.

Peer Review

All calculations will be peer-reviewed by the District, WSPA, and refinery staff.

Component Selection

Individual process lines to be screened will be selected by the District using PFDs and P&IDs. This should eliminate any bias that might result if components are selected in the field (i.e. components determined by observation to be leaking will not be preferentially selected over non-leaking components, or vice-versa).

Using knowledge of the process operation, the individual process lines will be distributed such that a wide range in the values of variables thought to affect the emission rate will be obtained.

EPA

All quality assurance and quality control measures will be followed as prescribed in any applicable EPA analytical or sampling method used in the study.

Data

Overview

The following best practices and policies will guide the collection, retention, and use of data obtained during the sampling study.

Confidentiality

Data deemed to be a trade secret pursuant to Section 6254.7 of the Government Code shall be designated as such by the refinery submitting the data. The refinery shall include for each trade secret item a statement signed by a responsible representative of the refinery identifying that portion of Government Code Section 6254.7(d) upon which the assertion is based and a brief statement setting forth the basis for this assertion.

Metadata

The following metadata shall be collected and reported when readily available:

Phase	Data	Metadata
II	Instrument Readings	Zero and span gas certification values
		Zero and span gas certification expiration dates
		Daily calibration sheets
		Instrument Response Times
		Technician names
		Instrument serial numbers
		Measurement date
		Daily drift sheets
		Background readings
II	Components	Unique identification number
		Digital picture of screened component if greater than 25 ppm above background
		Component type (e.g. valve, etc.)
		Component sub-type (e.g. control, gate, etc.)
		Component size (e.g. 3", 0.25", etc.)
		Wind speed (miles per hour)
		Ambient Temperature
		Stream (e.g. diesel, resid, gas oil, etc.)
		Stream Approximate Initial Boiling Point
II	Components	Stream ASTM D86 Initial Boiling Point
		Stream Operating Temperature
		Stream Operating Pressure
		Location/Elevation
		For Pumps, the Suction and Discharge Pressures
		Work Order History
III	Mass Emissions	Ambient Temperature
		Ambient Pressure
		Vacuum Pressure
		Wind speed (miles per hour)
		Total Organic Concentration
		Background (TOC) Concentration
		Instrument Serial #
		Calibration Sheets
		Technician Name
		Date and Time

Training

Overview	The following training will be conducted by the District prior to beginning the study.
Calibration	All monitoring personnel will be trained on conducting a five point calibration, as specified in the Section "Methodology – Component Screening".
Drift Check	All monitoring personnel will be trained on how to conduct an instrument drift check.
Field Sheets and/or Handheld Devices	All personnel involved in monitoring will be trained to use standardized field sheets and/or handheld devices for uniform collection of required information.
Monitoring Technique	All monitoring personnel will be trained on monitoring techniques, as specified in the Section "Methodology – Component Screening", to be used in the study.
Monitoring Speed	Personnel will be informed and tested (either in the field or at the end of the monitoring period) against proper monitoring speed.
Monitoring Pace	Personnel will be told that, unlike gas and light liquid service, fugitive leak readings from components in heavy liquid service tend to rise more slowly and decay more slowly once the probe is moved away from the component. Therefore, monitoring pace will be slower. After initial monitoring, a minimum monitoring pace may be developed and required.
Accuracy	Personnel will be informed that sampling study is not a "leak/no leak" inspection but rather that accuracy is important (a 5 ppm difference in reading is important).