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DRAFT TEST PROCEDURE

Determination of Methane, Carbon Dioxide, and
Volatile Organic Compounds from Crude Oil and Natural Gas
Separation and Storage Tank Systems

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California Environmental Protection Agency Air Resources Board

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Determination of Methane, Carbon Dioxide, and Volatile Organic Compounds from Crude Oil and Natural Gas Separation and Storage Tank Systems

1. PURPOSE AND APPLICABILITY

This procedure is used to determine methane (CH₄), carbon dioxide (CO₂), and volatile organic compound (VOC) emission rates from onshore crude oil and natural gas separation and storage tank systems. This procedure is conducted by gathering one sample of crude oil or condensate and one sample of produced water from a pressurized vessel and having the liquids analyzed by a laboratory to determine the rate and composition of gas that is released from the liquids while they change from reservoir to standard atmospheric conditions. The rate and gas composition are used in conjunction with throughput to calculate annual emission rates of the specified gaseous compounds. If a vapor recovery system is installed on the entire separation and storage tanks system, the emission rates may be calculated as above, or they may be calculated using measured vapor recovery throughput and gas composition instead of gathering and evaluating liquid samples. The results of this procedure are used to estimate or report emission rates from separation and storage tank systems. This procedure is applicable in all cases where crude oil, condensate, or produced water is handled as a result of onshore crude oil or natural gas production, processing, or storage.

2. PRINCIPLE AND SUMMARY OF TEST PROCEDURE

This procedure describes approaches on gathering and analyzing liquid samples in order to calculate emission rates from crude oil, condensate, or produced water separation and storage tank systems. As these liquids change in pressure and temperature from reservoir to storage conditions, hydrocarbons flash from the liquids as vapor. The laboratory tests specified in this procedure can provide input data for use with E&P Tank 2.0 or equivalent software to calculate emission rates from crude oil or condensate, or they can generate a Gas-Oil or Gas-Water Ratio per barrel of liquid produced. The laboratory tests are primarily based on Gas Processor Association (GPA) Standards, including modifications.

In order to evaluate a crude oil or condensate separation and storage tank system, two liquid samples are required: one sample of crude oil or condensate and one sample of produced water. If a vapor recovery system is installed on the entire separation and storage tank system, an alternative method is available in Section 9 for calculating annual emission rates using measured vapor recovery system throughput and gas composition instead of gathering and evaluating liquid samples.

3. DEFINITIONS

For the purposes of this procedure, the following definitions apply:

- 3.1 "API Gravity" means a scale used to reflect the specific gravity (SG) of a fluid such as crude oil, water, or natural gas. The API gravity is calculated as $[(141.5/SG) - 131.5]$, where SG is the specific gravity of the fluid at 60°F, and where API refers to the American Petroleum Institute.
- 3.2 "Chromatograph Extended Analysis" means a laboratory method for measuring the composition and properties of gases released from liquids, such as Gas Processor Association Standard 2186-02.
- 3.3 "Condensate" means hydrocarbon liquid, separated from crude oil or natural gas, that condenses due to changes in temperature, pressure, or both, and which remains in liquid form under storage conditions.
- 3.4 "Crude Oil" means any of the naturally occurring liquids and semi-solids found in rock formations composed of complex mixtures of hydrocarbon ranging from one to hundreds of carbon atoms in straight and branched chain rings.
- 3.5 "Double-Valve Cylinder" means a cylinder used for gathering crude oil or condensate. The cylinder is typically provided by the laboratory conducting the Chromatograph Extended Analysis and is filled with laboratory grade water. The laboratory grade water is displaced from the cylinder with sample liquid to prevent the sample from expanding and flashing during the sampling procedure.
- 3.6 "E&P Tank 2.0 or equivalent software" means Exploration and Production Tank software version 2.0, applicable for crude oil or condensate up to 68 API Gravity, that estimates flashing, working, and breathing losses of carbon dioxide and hydrocarbons including methane and VOCs.
- 3.7 "Emulsion" means a mixture of crude oil, condensate, or produced water in the primary stages of production and prior to separation.
- 3.8 "Flashing" means the release of hydrocarbons and carbon dioxide from liquid to surrounding air when the liquid changes temperature and pressure, also known as phase change.
- 3.9 "Flash Liberation Analysis" means a laboratory methodology for measuring the volume and composition of gases released from liquids, such as Gas Processor Association Standard 2174-93, that provides a Gas-Oil or Gas-Water Ratio, the molecular weight of the total gaseous

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sample, and the WT% of individual compounds required to calculate the specified emission rates as described in Section 10.

- 3.10** “Flash Vapor” means the resulting quantity of hydrocarbon vapor and carbon dioxide that is emitted from the liquid when the liquid changes temperature and pressure.
- 3.11** “Floating-Piston Cylinder” means a cylinder used for gathering produced water samples. The cylinder contains an internal floating-piston that is manually controlled by relieving inert gas pressure to introduce liquid. A Floating-Piston Cylinder is typically provided by a laboratory with the floating-piston pressurized to the closed position using inert gas pressure. As the inert gas is relieved from the cylinder, the cylinder draws in a produced water sample.
- 3.12** “Gas-Oil-Ratio (GOR)” means the ratio of gas produced from a barrel of crude oil or condensate when cooling and depressurizing these liquids to standard conditions, expressed in terms of standard cubic feet of gas per barrel of oil.
- 3.13** “Gas-Water-Ratio (GWR)” means the ratio of gas produced from a barrel of produced water when cooling and depressurizing produced water to standard conditions, expressed in terms of standard cubic feet of gas per barrel of water.
- 3.14** “Graduated Cylinder” means a measuring instrument for measuring fluid volume, such as a glass container (cup or cylinder or flask) which has sides marked with or divided into amounts.
- 3.15** “Onshore Crude Oil and Natural Gas Production” means any structure affixed temporarily or permanently to land that houses equipment to extract hydrocarbon liquid or vapor from wells, gravity separation equipment, and storage tanks, used in the production, extraction, recovery, stabilization, separation, or treatment of hydrocarbon liquid or gas. This includes petroleum and natural gas production facilities located on islands, artificial islands or structures connected by a causeway to land, an island, or artificial island.
- 3.16** “Operating Pressure” means the working pressure that characterizes the conditions of crude oil, condensate, or produced water inside a particular process, pipeline, vessel or tank.
- 3.17** “Operating Temperature” means the working temperature that characterizes the conditions of crude oil, condensate, or produced water inside a particular process, pipeline, vessel or tank.

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- 3.18** “Percent Water Cut” means the percentage of water by volume, of the total emulsion throughput. The percent water cut is expressed as a percentage.
- 3.19** “Produced Water” means the resulting water that is produced as a byproduct of onshore crude oil or natural gas production.
- 3.20** “Reid Vapor Pressure (RVP)” means the vapor pressure of crude oils at temperatures between 5 and 80°C as described in American Society for Testing and Materials (ASTM) method D 5191-01.
- 3.21** “Reservoir” means a porous and permeable underground natural formation containing hydrocarbon liquid or gas. A reservoir is characterized by a single natural pressure.
- 3.22** “Separator” means a vessel or device used to separate crude oil, condensate, or natural gas from produced water.
- 3.23** “Storage Tank” means a vessel designed to contain an accumulation of crude oil, condensate, or produced water.
- 3.24** “Throughput” means the average daily volume of emulsion processed by a vessel recorded in barrels per day. The throughput of produced water is calculated by applying the percent water cut to the emulsion throughput. The throughput of crude oil or condensate is calculated as the difference between those liquids and the produced water.
- 3.25** “Vapor Recovery System” means any equipment designed to capture, control, or treat gaseous emissions, including piping, connections, and, if necessary, flow-inducing devices for routing gas into a process as a product or fuel source.
- 3.26** “Volatile Organic Compounds (VOC)” means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.¹

4. BIASES AND INTERFERENCES

- 4.1** The sampling procedures specified in this procedure have an impact on the laboratory procedures and final results reported. All samples must be gathered in adherence with the minimum procedures and specifications identified in this procedure.
- 4.2** A representative sampling point must be selected to ensure that

¹ Code of Federal Regulations, 40: Chapter 1, Subchapter C, Part 51, Subpart F, 51100 (s).

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pressurized carbon dioxide and hydrocarbons remain suspended in liquid during sampling. Obtaining samples from a non-pressurized vessel or from a vessel connected to a vapor recovery system will produce non-representative results.

- 4.3 Un-calibrated equipment, including the use of instruments located on a vessel, may produce non-representative results. This may result in data errors when analyzing samples in a laboratory. All pressure and temperature measurements used in the field at the time of sampling must be calibrated as described in Section 5.
- 4.4 The analytical portion of this procedure must be conducted by laboratories experienced with laboratory instrumentation, analytical methods, and the GPA Standards specified in this procedure.

5. EQUIPMENT SPECIFICATIONS

All pressure and temperature measurements must be recorded using instruments calibrated to the minimum specifications listed. The use of uncalibrated instruments when taking field measurements may produce invalid results.

- 5.1 A low-pressure measuring device capable of measuring liquid pressure less than 200 pounds per square inch pressure within +/-10% accuracy.
- 5.2 A high-pressure measuring device capable of measuring liquid pressure greater than 200 pounds per square inch pressure within +/- 5% accuracy.
- 5.3 A temperature measuring device capable of reading liquid temperature to within +/- 2°F. The range of the instrument must be at least 32 to 200°F.
- 5.4 A volume meter with minimum full-scale range of 800 standard cubic feet per hour with a maximum rated back pressure less than 0.26 inches water column and accuracy less than 2% of the true volume over the entire range of flow rates for which the meter is used. Volume meters must be calibrated annually against a NIST traceable standard such as a bell type spirometer or field standard transfer meter.

6. TEST EQUIPMENT

- 6.1 A Double-Valve Cylinder filled with laboratory grade water for gathering crude oil or condensate or a Floating-Piston Cylinder for gathering light crude oil, condensate, or produced water samples.
- 6.2 A Graduated Cylinder to capture and accurately measure displaced laboratory grade water from a Double-Valve Cylinder.

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- 6.3 A waste container suitable for capturing and disposing of sample liquid.
- 6.4 High-pressure rated components and control valves that can withstand liquid pressure under the same operating conditions as the vessel sampled.
- 6.5 A low-pressure and a high-pressure measuring device with minimum specifications listed in Section 5.
- 6.6 A temperature measuring device with minimum specifications listed in Section 5.
- 6.7 A calibrated volume meter, outfitted with a temperature and pressure gauge for correcting volume, with minimum specifications listed in Section 5 for measuring vapor recovery system gas throughput per Section 9.
- 6.8 A stainless steel hand pump equipped with one-way check valves suitable for pumping low API gravity crude oil into a Double-Valve Cylinder per Section 7.3. Stainless steel material is required to prevent sample contamination.

7. SAMPLING PROCEDURE

The sampling procedure chosen depends on the liquid sampled. Crude oil is collected using the Partial Displacement Method specified in Section 7.1. Produced water or condensate is collected using the Floating-Piston Cylinder Method specified in Section 7.2. Low API gravity crude oil that will not flow into a sampling cylinder under system pressure may be collected using the method specified in Section 7.3.

Liquid samples must be taken from separated liquids (e.g., clean crude oil, condensate, or produced water). This is accomplished by taking samples from different levels in a pressurized separator. Liquid samples of emulsions cannot be evaluated by a laboratory and are therefore not applicable to this procedure. To gather a crude oil or produced water sample, the vessel from which the sample is taken must be pressurized to ensure that hydrocarbons remain entrained in the liquid. Samples must not be taken from shipping tanks or other downstream vessels that may allow vapor to flash from the liquid.

When taking a sample from a pressurized vessel, care must be taken to gather liquid without allowing gas to flash within the sample cylinder. This is accomplished by purging the sampling train and collecting liquid at a very slow and steady rate. The cylinders specified in this procedure are either filled with laboratory grade water or use a Floating-Piston Cylinder to prevent a headspace from forming within the sampling cylinder.

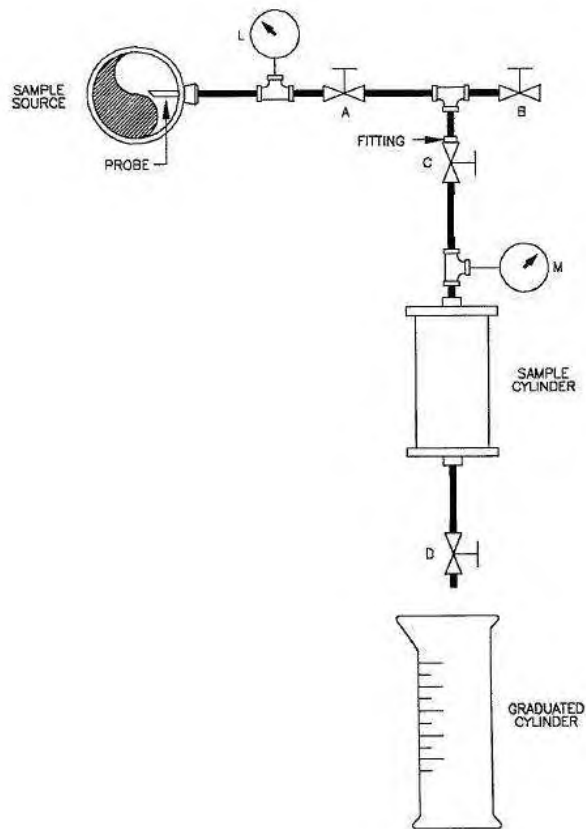
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When a pressurized liquid sample is gathered, the technician records the temperature, pressure, total emulsion throughput, and percent water cut of the vessel sampled and then ships the sample to a laboratory for analysis. The sample is then reheated and re-pressurized to the same conditions recorded at the time of sampling and the laboratory performs an analysis while the liquid is allowed to cool and depressurize to the specified atmospheric conditions.

7.1 PARTIAL DISPLACEMENT SAMPLING METHOD FOR CRUDE OIL

The Partial Displacement Method is used for crude oil or condensate less than or equal to 68 API Gravity. The Partial Displacement Method refers to displacing a specified amount of laboratory grade water with pH between 5 and 7 from a Double-Valve Cylinder. The water prevents hydrocarbons from flashing while liquid is collected. Figure 1 illustrates a Double-Valve Cylinder and sampling train. The configuration shows a Double-Valve Cylinder outfitted with high-pressure rated components that can be used for controlling the flow of liquid. Calibrated temperature (Gauge L) and pressure (Gauge M) gauges are included for conducting field measurements. Sample liquid enters the cylinder when water is slowly displaced into a graduated cylinder. The amount of sample liquid contained in the cylinder is equal to the amount of laboratory grade water measured in the graduated cylinder.

Figure 1
Double-Valve Cylinder Sampling Train



- (a) Prior to sampling, determine the volume of the Double-Valve Cylinder and calculate the amount of water to be displaced. The following example depicts the amount of water to displace from a 500 ml Double-Valve Cylinder, pre-filled with laboratory grade water: 70% of the volume ($0.7 \times 500 \text{ ml} = 350 \text{ ml}$) represents the amount of water that is displaced with sample liquid. 20% ($0.2 \times 500 \text{ ml} = 100 \text{ ml}$) represents the amount of water to displace after the sample is gathered to allow liquid to expand and contract during shipping. 10% ($0.1 \times 500 \text{ ml} = 50 \text{ ml}$) of water remains in the sample cylinder with the sample liquid.
- (b) Connect the sampling train to a sampling point on the pressurized vessel. Bushings or reducers may be required.
- (c) Purge the sample line: with Valves C and D closed, route the outlet of Valve B into a suitable waste container to purge sample liquid. Slowly open Valve B. Slowly open Valve A and allow air and liquid to purge. Continue purging until a consistent, steady stream of liquid is observed and gas pockets subside. Close Valve B.

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- (d) With Valve C and D closed, slowly open Valve A to the full-open position and then slowly open Valve C to the full-open position.
- (e) Slowly open Valve D to allow a slow discharge of water into the graduated cylinder at a rate of approximately 60 milliliters per minute (1 drip per second).
- (f) Record the temperature from Gauge L and pressure from Gauge M while the liquid is filling the cylinder. Do not take temperature or pressure measurements on stagnant liquid. Continue allowing a slow discharge of liquid until 70% of the water is displaced with sample liquid.
- (g) Close Valves D, C, and A in that order.
- (h) Purge the line pressure: slowly open Valve B and allow pressurized liquid to drain into the waste container.
- (i) Take outage: outage refers to draining a portion of liquid to allow liquid to expand within the sampling cylinder during shipping. While holding the sample cylinder in a vertical position, slowly open Valve D and drain another 20% of the pre-filled water from the sample cylinder by draining the water into the graduated cylinder and measuring the amount of water displaced. 10% of the pre-filled water remains in the sample cylinder along with the sample liquid. Close Valve D to the full-closed position.
- (j) Disconnect the Double-Valve Cylinder from the sampling train and disconnect the sampling train from the pressurized vessel.
- (k) Check Valves C and D for leaks. If either Valve C or D is leaking, drain the cylinder into a suitable waste container and use a different cylinder to obtain a new sample.
- (l) Wrap the threaded connections of the cylinder with Teflon tape and cap using threaded metal caps to protect the threads and ensure the cylinder is securely sealed for shipping.
- (m) Identify and ship the sample cylinder to the laboratory for analysis according to the procedures listed in Section 8.

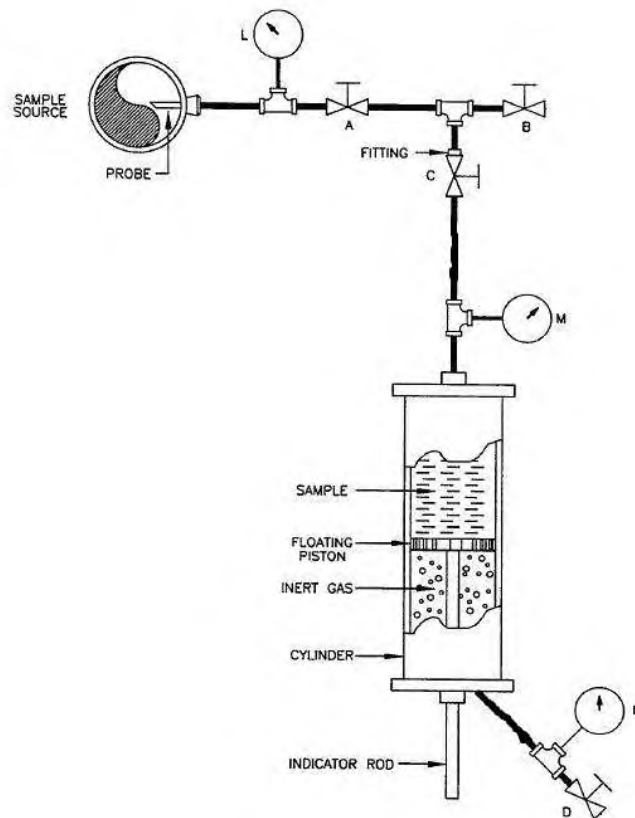
7.2 FLOATING-PISTON CYLINDER SAMPLING METHOD FOR PRODUCED WATER OR CONDENSATE

The Floating-Piston Cylinder Method is used for gathering produced water or condensate. The sampling cylinder is provided by the laboratory with the floating-piston pressurized, typically to 1,500 psig. Prior to gathering a sample, the technician first bleeds off pressure from the cylinder to at least

10 psig greater than the vessel to be sampled. Then, when collecting a sample, in a very slow and controlled manner the technician bleeds off additional pressure which allows liquid to enter the cylinder. The rate at which liquid is gathered is controlled by relieving cylinder pressure, which must not exceed 60 milliliters per minute or vapor expansion may occur within the cylinder.

Figure 2 shows a Floating-Piston Cylinder sample train outfitted with high-pressure rated components. Calibrated temperature (Gauge L) and pressure gauges (Gauge M and N) measuring devices are included for conducting field measurements. The amount of liquid contained in the cylinder is indicated on the sampling cylinder.

Figure 2
Floating-Piston Cylinder Sampling Train



- (a) Connect the sampling train to a sampling point on the pressurized vessel. Bushings or reducers may be required.
- (b) Purge the sample line: with Valves C and D closed, route the outlet of Valve B into a suitable waste container to purge sample liquid. Slowly open Valve A to the full-open position. Slowly open Valve B and allow liquid to purge. Continue purging until a consistent, steady stream of liquid is observed and gas pockets subside. Close Valve B.

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- (c) Slowly open Valve C to the full-open position.
- (d) Slowly open Valve D to release inert gas pressure until the pressure indicated on Gauge N is equal to Gauge M. When both gauges read equal pressure, close Valve D and prepare to gather sample liquid.
- (e) Slowly open Valve D and allow liquid to enter the cylinder at a slow rate of approximately 60 ml per minute to prevent liquid from flashing within the sampling cylinder. Use the measurement scale located on the sampling cylinder and a stopwatch to measure the rate at which liquid is gathered.
- (f) Record the temperature from Gauge L and pressure from Gauge M while liquid is gathered. Do not take measurements on stagnant liquid.
- (g) Continue gathering liquid until the cylinder is 80% full as indicated on the cylinder scale. The rate at which liquid enters the cylinder, and the volume of liquid in the cylinder, are indicated on the sample cylinder. No outage is required when using a Floating-Piston Cylinder.
- (h) Close valves D, C, and A in that order.
- (i) Purge the line pressure: slowly open Valve B and allow pressurized liquid to drain into the waste container.
- (j) Disconnect the Floating-Piston Cylinder from the sampling train and disconnect the sampling train from the pressurized vessel.
- (k) Check Valves C and D for leaks. If either Valve C or D is leaking, drain the cylinder into a suitable waste container and use a different cylinder to obtain a new sample.
- (l) Wrap the threaded connections of the cylinder with Teflon tape and cap using threaded metal caps to protect the threads and ensure the cylinder is securely sealed for shipping.
- (m) Identify and ship the sample cylinder to the laboratory for analysis according to the procedures listed in Section 8.

7.3 LOW API GRAVITY CRUDE OIL SAMPLING

In some cases, low API gravity crude oil may not flow into a sampling cylinder. This could be due to the viscosity, temperature, or pressure of the oil. In these cases, a stainless steel hand pump is used to assist with the collection of liquid. The pump must be outfitted with one-way check valves to ensure that liquid flows in only one direction. The difference between Section 7.1 and this method is that

the hand pump is used in place of system pressure.

- (a) Install the stainless steel hand pump equipped with one-way check valves as described in Section 6 at the inlet of the Double-Valve Cylinder Sampling Train.
- (b) Using the hand pump to slowly force the flow of liquid, collect a liquid sample following the sample procedures described in Section 7.1.

8. SAMPLE IDENTIFICATION AND SHIPPING

Prepare the sample cylinder information tag and package the sample cylinder for shipping. The sampling technician must make prior arrangements with the laboratory prior to collecting or shipping samples.

8.1 Identify the sample cylinder information tag with the following minimum information:

- (a) Date and time;
- (b) Unique sample ID number or cylinder number;
- (c) Sample type (crude oil, condensate, or produced water);
- (d) Sample pressure and temperature during sampling;
- (e) Vessel description;
- (f) Vessel throughput of emulsion or liquid in barrels per day;
- (g) Percent Water Cut of vessel;
- (h) Facility name and location of where sample was gathered; and,
- (i) Attach a completed copy of Form 1.

8.2 Package the cylinder(s) with the information tag(s) and copy(s) of Form 1 in a suitable container that meets hazardous material shipping requirements of the shipping company. Obtain a tracking number and Bill-of-Lading to track shipment progress.

9. ALTERNATIVE METHODOLOGY FOR CALCULATING EMISSION RATES USING MEASURED VAPOR RECOVERY SYSTEM PARAMETERS IN LIEU OF GATHERING AND EVALUATING LIQUID SAMPLES

The following is used to calculate the specified emission rates for separation and storage tank systems that have a vapor recovery system installed on the entire separation and storage tank system. This methodology is an alternative to gathering and evaluating liquid samples and may be used for systems that handle emulsions of crude oil, condensate, or produced water or for systems that handle one liquid only. The emission rates are not calculated using a Gas-Oil or Gas-Water Ratio so liquid throughput is not required.

The carbon dioxide, methane, and VOC_{C3+} emission rates are calculated using

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the metered vapor recovery gas volume and an annual gas composition analysis. The annual volume metered is adjusted by the capture and control efficiency of the vapor recovery system to account for fugitive losses.

- (a) Measure the annual gas volume recovered by the vapor recovery system using the calibrated meter outfitted with temperature and pressure gauges as described in Section 6.
- (b) Obtain an annual gas sample of the vapor recovery gas and evaluate it for all gaseous compounds, the molecular weight, and the WT% of carbon dioxide, methane, and VOC_{C3+}.
- (c) Calculate the annual emission rates as described in Section 10.4.

10. CALCULATING RESULTS

The following describes procedures for estimating emission rates from crude oil, condensate, or produced water using laboratory results or vapor recovery system parameters.

10.1 Crude Oil or Condensate Less Than or Equal to 68 API Gravity Using E&P Tank 2.0 or Equivalent Software

E&P Tank 2.0 is designed to work with crude oil or condensate up to 68 API Gravity. For liquids greater than 68 API Gravity, you must use the method specified in Section 10.2.

- (a) Input the results of a Chromatograph Extended Analysis into E&P Tank 2.0 or equivalent software including the MOL% of each compound, the specific gravity, the molecular weight of Decanes (C10 Plus), and Base Conditions (101.325 kPa at 68°F). In addition, E&P Tank 2.0 also requires the following input parameters that were recorded on Form 1 or measured using the specified laboratory procedures:
 - (1) Sample pressure and temperature;
 - (2) Crude oil or condensate daily throughput (barrels);
 - (3) Days per year of operation;
 - (4) API Gravity (determined using ASTM D 4052-11); and,
 - (5) RVP (determined using ASTM D 5191-01).

10.2 Crude Oil or Condensate Emission Rate Calculation Methodology Using the Results of a Flash Liberation Analysis

As an alternative to Section 10.1, or for crude oil or condensate greater than 68 API Gravity, the emission rates of the separation and storage tank system may

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be calculated using the results of a Flash Liberation Analysis which does not require E&P Tank 2.0 or equivalent software. The Flash Liberation Analysis provides the GOR, gas composition, and information required to calculate the emissions rates of carbon dioxide, methane, and VOC_{C3+}.

- (a) Calculate the annual volume of gas produced from liquid as follows:

$$Ft^3 / Year = (GOR) \left(\frac{\text{barrels}}{\text{day}} \right) \left(\frac{\text{Days}}{\text{year}} \right) \quad \text{Equation 1}$$

Where:

Ft³/Year = standard cubic feet of gas produced per year

GOR = Gas-Oil-Ratio from the laboratory analysis

barrels/day = daily throughput of crude oil or condensate, excluding produced water

Days/year = days per year system is in operation

- (b) Convert the annual cubic feet of gas to tons of emissions using the following equation:

Equation 2

$$Tons / Year = \left(\frac{Ft^3}{Year} \right) \left(\frac{X \text{ grams}}{\text{gram - mole}} \right) \left(\frac{\text{gram - mole}}{23.690 \text{ l}} \right) \left(\frac{28.317 \text{ l}}{Ft^3} \right) \left(\frac{\text{lb}}{454 \text{ grams}} \right) \left(\frac{\text{tons}}{2000 \text{ lb}} \right)$$

Where:

Tons/Year = tons of gas produced per year

Ft³/Year = total cubic feet of gas produced (result of Equation 1)

X grams/gram-mole = average gram molecular weight of the total gaseous sample from the laboratory analysis.

23.690 l/gr-mole = molar volume of ideal gas at standard conditions of 101.325 kPa at 68⁰F.^{2,3}

- (c) Calculate the carbon dioxide, methane, and VOC_{C3+} emission rates using the WT% of the specified compounds and Equations 3 through 5 as follows:

$$Tons \text{ CO}_2 / Year = \left(\frac{WT\% \text{ CO}_2}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 3}$$

$$Tons \text{ CH}_4 / Year = \left(\frac{WT\% \text{ CH}_4}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 4}$$

² Standards of Performance for New Sources", 40 CFR--Protection of the Environment, Chapter I, Part 60, Section 60.2, 1990.

³ <http://www.epa.gov/apti/bces/module1/pressure/pressure.htm>.

$$TonsVOC_{C3+} / Year = \left(\frac{WT\% VOC_{C3+}}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 5}$$

Where:

Tons CO₂, CH₄, VOC_{C3+} / Year = tons of emissions per year

WT%CO₂, WT%CH₄, WT%VOC_{C3+} = the weight percent of required compounds (from laboratory analysis)

Tons/Year = mass of gas produced per year (result of Equation 2)

- (d) If a vapor recovery system is installed on the entire separation and storage tank system, reduce the CO₂, CH₄, and VOC_{C3+} emissions rates as follows:

$$Emissions_{CO_2/CH_4/VOC_{C3+}} = (Tons/Year_{CO_2/CH_4/VOC_{C3+}})(1-0.95) \quad \text{Equation 6}$$

Where:

Emissions CO₂, CH₄, VOC_{C3+} = tons of emissions per year

Tons/Year_{CO2/CH4/VOC C3+} = emissions (results of Equations 3 through 5)

0.95 = capture and control efficiency of the vapor recovery system.

10.3 Produced Water Emission Rate Calculation Methodology Using the Results of a Flash Liberation Analysis

The following is used to calculate emission rates from produced water using the results of a laboratory Flash Liberation Analysis. The Flash Liberation Analysis provides the GWR, gas composition, and information required to calculate emissions rates of carbon dioxide, methane, and VOC_{C3+}.

- (a) Calculate the annual cubic feet of gas produced from liquid as follows:

$$Ft^3 / Year = (GWR) \left(\frac{Barrels}{day} \right) \left(\frac{Days}{Year} \right) \quad \text{Equation 7}$$

Where:

Ft³/Year = total volume of gas produced per year

GWR = Gas-Water-Ratio from the lab analysis

Barrels/day = daily throughput of produced water

Days/Year = number of days separator is in operation per year

- (b) Convert the annual cubic feet of gas to tons of emissions using the following equation:

Equation 8

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$$Tons / Year = \left(\frac{Ft^3}{Year} \right) \left(\frac{X \text{ grams}}{gram - mole} \right) \left(\frac{gram - mole}{23.690 \text{ l}} \right) \left(\frac{28.317 \text{ l}}{Ft^3} \right) \left(\frac{lb}{454 \text{ grams}} \right) \left(\frac{tons}{2000 \text{ lb}} \right)$$

Where:

Tons/Year = tons of gas produced per year

Ft³/Year = total cubic feet of gas produced (result of Equation 7)

X grams/gram-mole = average gram molecular weight of the total gaseous sample from the laboratory analysis.

23.690 l/gr-mole = molar volume of ideal gas at standard conditions of 101.325 kPa at 68⁰F.^{4, 5}

- (c) Calculate the carbon dioxide, methane, and VOC_{C3+} emission rates using the WT % of the required compounds and Equations 3 through 5 as follows:

$$Tons \text{ CO}_2 / Year = \left(\frac{WT\% \text{ CO}_2}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 9}$$

$$Tons \text{ CH}_4 / Year = \left(\frac{WT\% \text{ CH}_4}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 10}$$

$$Tons \text{ VOC}_{C3+} / Year = \left(\frac{WT\% \text{ VOC}_{C3+}}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 11}$$

Where:

Tons CO₂, CH₄, VOC_{C3+} / Year = tons of emissions per year

WT%CO₂, WT%CH₄, WT%VOC_{C3+} = the Weight % of required compounds (from laboratory analysis)

Tons/Year = mass of gas produced per year (result of Equation 8)

- (d) If a vapor recovery system is installed on the entire separation and storage tank system, reduce the CO₂, CH₄, and VOC_{C3+} emissions rates as follows:

$$Emissions_{CO_2/CH_4/VOC_{C3+}} = \left(Tons/Year_{CO_2/CH_4/VOC_{C3+}} \right) (1 - 0.95) \quad \text{Equation 12}$$

Where:

Emissions CO₂, CH₄, VOC_{C3+} = tons of emissions per year

Tons/Year_{CO2/CH4/VOC C3+} = emissions (results of Equations 9 through 11)

0.95 = capture and control efficiency of the vapor recovery system

⁴ Standards of Performance for New Sources", 40 CFR--Protection of the Environment, Chapter I, Part 60, Section 60.2, 1990.

⁵ <http://www.epa.gov/apti/bces/module1/pressure/pressure.htm>.

10.4 Emission Rate Calculation Methodology Using Vapor Recovery System Parameters

The following is used to calculate emission rates using vapor recovery system parameters from separation and storage tank systems as described in Section 9. The emission rates are calculated using the volume and composition of gas collected by the system as follows:

- (a) Convert the annual volume of vapor measured using the calibrated meter and average annual vapor temperature and pressure to standard ambient conditions as follows:

$$Ft^3 / Year = V \left(\frac{68}{T} \right) \left(\frac{P + 101.325}{101.325} \right) \quad \text{Equation 13}$$

Where:

$Ft^3/Year$ = annual cubic feet of gas corrected to standard conditions (scf)
 V = annual volume of gas measured by the calibrated meter (cubic feet)
 T = average annual vapor temperature measured at the meter (degrees F)
 P = average annual gauge pressure measured at the meter (kPa gauge)

- (b) Convert the annual cubic feet of gas measured with the volume meter to tons of emissions per year using the results of the gas analysis and the following equation:

Equation 14

$$Tons / Year = \left(\frac{Ft^3}{Year} \right) \left(\frac{X \text{ grams}}{\text{gram - mole}} \right) \left(\frac{\text{gram - mole}}{23.690 \text{ l}} \right) \left(\frac{28.317 \text{ l}}{Ft^3} \right) \left(\frac{\text{lb}}{454 \text{ grams}} \right) \left(\frac{\text{tons}}{2000 \text{ lb}} \right)$$

Where:

Tons/Year = tons of gas produced per year
 $Ft^3/Year$ = annual cubic feet of gas corrected to standard conditions (result of Equation 13)
 X grams/gram-mole = average gram molecular weight of the total gaseous sample from the laboratory analysis.
 23.690 l/gr-mole = molar volume of ideal gas at standard conditions of 101.325 kPa at 68⁰F.^{6,7}

- (c) Calculate the carbon dioxide, methane, and VOC_{C3+} emission rates using the WT% of the required compounds as follows:

⁶ Standards of Performance for New Sources", 40 CFR--Protection of the Environment, Chapter I, Part 60, Section 60.2, 1990.

⁷ <http://www.epa.gov/apti/bces/module1/pressure/pressure.htm>.

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$$Tons\ CO_2 / Year = \left(\frac{WT\% \ CO_2}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 15}$$

$$Tons\ CH_4 / Year = \left(\frac{WT\% \ CH_4}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 16}$$

$$Tons\ VOC_{C3+} / Year = \left(\frac{WT\% \ VOC_{C3+}}{100} \right) \left(\frac{Tons}{Year} \right) \quad \text{Equation 17}$$

Where:

Tons CO₂, CH₄, VOC_{C3+} / Year = tons of emissions per year

WT%CO₂, WT%CH₄, WT%VOC_{C3+} = the Weight % of required compounds (from laboratory analysis)

Tons/Year = mass of gas produced per year (result of Equation 14)

- (d) Adjust the annual emission rates by the capture and control efficiency of the vapor recovery system as follows:

$$Emissions_{CO_2/CH_4/VOC_{C3+}} = \left(Tons/Year_{CO_2/CH_4/VOC_{C3+}} \right) \left(\frac{1}{0.95} \right) \quad \text{Equation 18}$$

Where:

Emissions CO₂, CH₄, VOC_{C3+} = tons of emissions per year

Tons/Year_{CO2/CH4/VOC C3+} = emissions (results of Equations 15 through 17)

0.95 = capture efficiency of the vapor recovery system

11. REPORTING RESULTS

The results of this procedure are used to estimate or report emission rates of the specified gaseous compounds from separation and storage tank systems used in onshore crude oil or natural gas production, processing, or storage. All results shall be reported to at least three significant figures. All supporting information used to derive the emission estimates, including sample information, laboratory results, and calculations must be maintained by the reporting entity for a minimum of three years in order to reproduce the estimated or reported results. The following information related to each methodology listed in Section 10 must be maintained by the reporting entity:

Crude Oil or Condensate (Section 10.1 or 10.2)

- (a) Laboratory results of a Chromatograph Extended Analysis or Flash Liberation Analysis for compounds specified in Section 12.2;
- (b) E&P Tank 2.0 or equivalent software results;
- (c) A completed copy of Form 1; and,
- (d) Annual emission rates of carbon dioxide, methane, and VOC_{C3+}.

Produced Water (Section 10.3)

- (a) Laboratory results of a Flash Liberation Analysis for compounds specified in Section 12.2;
- (b) All calculations and calculated results;
- (c) A completed copy of Form 1; and,
- (d) Annual emission rates of carbon dioxide, methane, and VOC_{C3+}.

Emulsion or Liquids Under Vapor Recovery (Section 10.4)

- (a) Laboratory results of an annual gas composition analysis;
- (b) Measured annual vapor recovery system gas throughput;
- (c) All calculations and calculated results; and,
- (d) Annual emission rates of carbon dioxide, methane, and VOC_{C3+}.

12. ANALYTICAL LABORATORY PROCEDURES

12.1 LABORATORY PROCEDURES

The laboratory procedures referenced in this section are approved for conducting the analyses of crude oil, condensate, or produced water. As a requirement of this procedure, a copy of the original laboratory analysis and reference to the GPA Standard(s) used to evaluate samples must be provided. The following methods are approved for use with this procedure:

GPA 2174 *Obtaining Liquid Hydrocarbon Samples for Analysis by Gas Chromatography*

GPA 2177 *Analysis of Natural Gas Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography*

GPA 2186 *(Including Modifications) - Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography*

GPA 2261 *Regular gas analysis utilizing a Thermal Conductivity Detector*

GPA 2286 *Extended gas analysis utilizing a Flame Ionization Detector*

Other Relevant Standards, Procedures, and References:

ASTM D-86 *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure*

ASTM D-2001 *Standard Test Method for Depentanization of Gasolines and Naphthas*

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ASTM D-4052-11 *Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter*

ASTM D 5191-01 *Standard Test Method for Vapor Pressure of Petroleum Products (Mini Method)*

American Petroleum Institute 4697:2000 E&P Tank 2.0 software

12.2 LABORATORY REPORTS

Any chromatograph system that allows for the collection, storage, interpretation, adjustment, or quantification of chromatograph detector output signals representing relative component concentrations may be used to conduct this procedure. However, the laboratory results must be submitted as specified in Section 10. The following minimum data, needed to calculate results specified in Section 9, and report results specified in Section 10, must include:

- (a) The composition of all compounds including the C1 through C10+ classification, with Weight % and molecular weight of the compound;
- (b) For compound classifications of C10 or greater, the Weight %, and molecular weight of the class;
- (c) API Gravity of the crude oil or condensate under both sample and storage conditions;
- (d) Reid Vapor Pressure of the crude oil or condensate under both sample and storage conditions;
- (e) Specific Gravity of the gas liberated (from crude oil, condensate, and produced water);
- (f) Molecular Weight of the gas liberated (from crude oil, condensate, and produced water);
- (g) Volumetric Gas-Water-Ratio for produced water;
- (h) Volumetric Gas-Oil-Ratio for crude oil or condensate;
- (i) Separator throughput, temperature, pressure, and percent water cut (if applicable);
- (j) Average annual storage tank temperature and pressure;
- (k) The presence of a vapor recovery system on the storage tank where the liquid is diverted and stored; and,
- (l) The type of vapor recovery system (flare, incinerator, or other).

Form 1
Crude Oil, Condensate, and Produced Water Sampling Field Data Sheet
(report measured results to at least three significant figures)

Facility Contact Information:

Facility Name: _____
Address: _____
City: _____ State: _____
Zip: _____ Phone: _____
Facility Contact: _____

Sampling Company:

Company Name: _____
Address: _____
City: _____ State: _____
Zip: _____ Phone: _____
Sampling Technician: _____

Sample Information:

Sample Type: _____ (crude oil, condensate, produced water)
Date: _____
Time: _____ Sample Temperature: _____ Deg. F
Cylinder Number: _____ Sample Pressure: _____ PSI
Field Name: _____ (field from where sample was taken)

Vessel Information:

Vessel Type: _____ (e.g., separator, heater/treater)
Vessel Throughput: _____ (barrels/day)
Percentage Water Cut _____ % Days in Operation/Year: _____

Vapor Recovery System:

Vapor Recovery System: Yes No
Type: _____ (flare, engine, boiler, etc.)

Shipping Information:

Shipping Date: _____
Shipping Company: _____
Tracking Number: _____