Final Report

OIL AND GAS MEASUREMENT AND ANALYSIS

Pressurized Hydrocarbon Liquids Sampling and Analysis Study

Data Assessment and Analysis Report

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Table of Contents

List of Tables

List of Figures

Acronyms, Abbreviations, and Symbols

α	significance level
Δ	change
Σ	sum
ρ	density
ρ_{oil}	oil density
%	percent
°C	degrees Celsius
°F	degrees Fahrenheit
~	about or approximately
+/-	plus or minus
ABS	absolute value
act	actual
APCD	Air Pollution Control Division
API	American Petroleum Institute
°API	degrees API gravity
ASTM	American Society for Testing and Materials
bbl	barrel
bbl/day	barrels per day
BTEX	benzene, toluene, ethyl benzene, and xylenes
C1	methane
C2	ethane
C3	propane
C4	butanes
C5	pentanes
C1–C5	methane to pentanes hydrocarbons
C6	hexanes
C6+	hexanes and higher hydrocarbons
C7+	heptanes and higher hydrocarbons
C8+	octanes and higher hydrocarbons
C10+	decanes and higher hydrocarbons

C11	undecane
C11+	undecanes and higher hydrocarbons
C14	tetradecane
C100+	hectanes and higher hydrocarbons
C30+	triacontanes and higher hydrocarbons
CARB	California Air Resources Board
cc	cubic centimeters
CDPHE	Colorado Department of Public Health and Environment
cf	cubic foot
CH4	methane
CI	confidence interval
CO_2	carbon dioxide
COGCC	Colorado Oil and Gas Conservation Commission
CM	Coriolis meter
CP	constant pressure
CRM	certified reference material
CV	constant volume
d	difference for paired samples
DJ	Denver Julesburg
EOS	equation of state
FG	flash gas
FGOR	flash gas-to-oil ratio
FGWR	flash gas-to-water ratio
FID	flame ionization detector
GC	gas chromatograph
GESD	Generalized Extreme Studentized Deviate
gm/g-mole	gram per gram mole
gm/ml	gram per milliliter
GOR	gas-to-oil ratio
GPA	Gas Processors Association
GUM	Guide to the Expression of Uncertainty in Measurement

HC	hydrocarbon
He	helium
HP	high-pressure
hr	hour
IPT	initial pressure test
IPT P_{BP}	bubble point pressure determined by initial pressure test
ISO	International Organization of Standards
kg	kilogram
L	liquid
lb	pound
lb/bbl	pound per barrel
LP	low-pressure
m^3	cubic meter
$m^{3/}hr$	cubic meters per hour
M	attached to an analytical method indicates lab-specific modifications
MB	mass balance
MC	Monte Carlo
MCFD	thousand cubic feet per day
min	minute
ml	milliliter
ml/min	milliliter per minute
ml/sec	milliliter per second
mol %	mole percent
MP	mid-pressure
MPMS	Manual of Petroleum Measurement Standards
Mscfd	thousand standard cubic feet per day
MW	molecular weight
N_2	nitrogen
NIST	National Institute of Standards and Technology
O_2	oxygen
OPC	operational performance check

O&G	oil and gas
oz	ounce (ounce per square inch)
oz/in^2	ounce per square inch
P	pressure
P_{BP}	bubble point pressure (at the sample collection temperature) for a pressurized HC liquids sample
P_{BP}/P_{SC}	ratio of bubble point pressure (at the sample collection temperature) for a pressurized HC liquids sample to the separator pressure during sample collection. Unless otherwise indicated, bubble point pressure is calculated using PSM/EOS software and the measured HC liquids composition
Pr	probe
P_{sep}	separator pressure
P_{SC}	separator pressure during sample collection
P_{tank}	tank pressure
$P_{tank\ bottom}$	tank bottom pressure (at the downcomer outlet)
PFD	process flow diagram
PHLSA	pressurized HC liquids sampling and analysis
PIT	pressure transducer
PPIVFR	potential peak instantaneous vapor flow rate
PRV	pressure relief valve
psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gauge
PSM/EOS	Process Simulation Model/Equation of State
QAPP	Quality Assurance Project Plan
R^2	coefficient of determination
RTD	resistance temperature detector
S-	prefix for a Summer testing well cycle
SCADA	supervisory control and data acquisition
scf	standard cubic foot
scf/bbl	standard cubic feet per barrel
scf/sec	standard cubic feet per second

sec	second
SG	specific gravity
SiG	sight glass
SOP	standard operating procedure
SPH	siphon prevention hole (in storage tank downcomer)
SPL	Southern Petroleum Laboratories
std	standard
$t_{critical}$	critical t-value
T	temperature
T_{Lab}	laboratory temperature
T_{sc}	sample collection temperature
T_{sep}	separator temperature (liquid hydrocarbon layer)
$T_{sep\ gas}$	separator headspace gas temperature
T_{tank}	tank temperature
$T_{tank\ bottom}$	tank bottom temperature (at the downcomer outlet)
$T_{tank\ gas}$	tank headspace gas temperature
TAP	Technical Advisory Panel
TCD	thermal conductivity detector
TCEQ	Texas Commission on Environmental Quality
U	uncertainty
VOC	volatile organic compound
W-	prefix for a Winter testing well cycle
WC	well cycle
WSRT	Wilconxan Sign-Rank Test
wt%	weight percent

Glossary

Accuracy	The closeness of agreement between a test result and the accepted reference value.
Breathing losses	Breathing losses occur when a storage tank temperature increases and/or the barometric pressure decreases. Volatile liquid compounds evaporate and tank headspace gases expand causing gases to be expelled from the tank.
Bubble point pressure	The bubble point pressure is the pressure (at a given temperature) at which the first bubble of gas comes out of solution in hydrocarbon liquid. For pressurized hydrocarbon liquids sampling and analysis, the bubble point pressure is typically determined at the pressurized sample collection temperature.
CDPHE	CDPHE is the Colorado Department of Public Health and Environment, and its Air Pollution Control Division (APCD).
Condensate	Condensate is hydrocarbon liquids that remain liquid at standard conditions (68 degrees Fahrenheit and 29.92 inches mercury) and are formed by condensation from, or produced with, natural gas, and which have an American Petroleum Institute gravity (API gravity) of 40 degrees or greater.
Coriolis meter	Coriolis mass flowmeters measure liquid flowrate. Coriolis mass flowmeters measure the force resulting from the acceleration caused by mass moving toward (or away from) a center of rotation. The meter utilizes a vibrating tube in which Coriolis acceleration of a fluid in a flow loop can be created and measured. The measuring tubes are forced to oscillate such that a sine wave is produced. At zero flow, the two tubes vibrate in phase with each other. When flow is introduced, the Coriolis forces cause the tubes to twist, which results in a phase shift. The time difference between the waves is measured and is directly proportional to the mass flow rate.
Downcomer	A downcomer is an extension of the separator-to-tank pipeline installed inside the tank. The line typically ends near the tank bottom. Introducing separator fluids using a downcomer line, rather than a side-fill configuration (i.e., separator fluids enter the tank headspace), prevents the splatter effect of incoming hydrocarbon liquids striking the tank liquid surface and may reduce the rapid volatilization of light hydrocarbons.
EPA	EPA is the United States Environmental Protection Agency and any of its successor departments or agencies.

Flash gas generation	Gas that is rapidly generated when a volume of hydrocarbon liquids undergoes a rapid pressure drop through a dump valve from a separator to an atmospheric hydrocarbon liquids (e.g., condensate) storage tank.
Flash gas to oil ratio	Flash gas to oil ratio (FGOR) is the volume of flash gas generation divided by the post-flash oil volume. FGOR can depend on the pressurized oil composition; the separator temperature and pressure; the tank temperature (liquid and headspace gas), pressure, and liquid height; the tank fluid inlet configuration (e.g., downcomer or side-fill); and other parameters. FGOR is reported as scf of flash gas per barrel of post-flash oil.
Hydrocarbon liquids	Hydrocarbons and mixtures of hydrocarbons that are liquid at atmospheric or higher pressures. Hydrocarbon liquids can be identified as condensate or oil (i.e., liquids that are heavier than condensate, (e.g., have an API gravity less than 40 degrees)).
Oil dump valve	A snap-acting float-activated valve that controls or limits the hydrocarbon liquids level in a separator.
Potential peak instantaneous vapor flow rate	The maximum instantaneous amount of vapors routed to a vapor control system during normal operations, including flashing, working, and breathing losses, as determined using a tank emissions model. For the purposes of the Pressurized Hydrocarbon Liquids Sampling and Analysis study, the potential peak instantaneous vapor flow rate (PPIVFR) was calculated by assuming that the entire gas volume generated during a separator well cycle exits the tank at a steady rate for a time period equal to the duration of the separator dumps during the well cycle (e.g., in engineering units of kg/sec).
Precision	The closeness of agreement between independent test results obtained under stipulated conditions.
Pressure relief valve (PRV)	Valve used to control or limit the pressure in a storage tank. Pressure is relieved by allowing pressurized headspace gas to flow to the atmosphere.
Pressurized liquids	Pressurized liquids are hydrocarbon liquids separated from, condensed from, or produced with natural gas while still under pressure and upstream of the storage tanks servicing the well.
Produced water	Water that is produced as a byproduct during oil and gas production
Pyranometer	Pyranometers measure solar radiation flux density on a surface.
Reproducibility	Reproducibility is precision under reproducibility conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

Separator	A separator is a pressurized vessel used for separating a well stream into gaseous and liquid components.
Shrinkage	Shrinkage is the reduction in the volume of a pressurized hydrocarbon liquids sample when the sample temperature and pressure change from separator conditions to tank conditions.
Sight glass	A glass tube on a separator oil box for visual determination of the hydrocarbon liquids level.
Siphon prevention hole	A small hole near the top of a storage tank downcomer to prevent a siphon effect and backflow of liquid from the tank to the separator.
Storage tank	An atmospheric storage tank for condensate equipped with a PRV to maintain the pressure below a design threshold (e.g., 16 oz/in^2).
Thermal mass flowmeter	Thermal mass flowmeters consist of a heated sensor inserted in a flowing gas. The flowing gas transports heat away from the sensor and an electronic circuit increases or decreases the input voltage to maintain a constant sensor temperature or constant temperature difference with a reference sensor. The electrical power required to maintain this sensor temperature or temperature difference correlates to the mass flow rate of the gas. Thermal flow meter measurement accuracy depends on the relative compositions (i.e., heat transfer properties) of the calibration gas and the actual process gas. Different calibration gas and process gas compositions can cause a bias in the actual process gas flowrate measurement.
Vane anemometer	Vane anemometers are mechanical velocity meters. Fluid velocity measurement is based on a vane wheel rotating at a speed proportional to the fluid velocity.
Vapor control system	A vapor control system is the system used to contain, convey, and control vapors from hydrocarbon liquids (including flashing, working, and breathing losses, as well as any natural gas carry-through to storage tanks) at a tank system. A vapor control system includes a tank system, piping to convey vapors from a tank system to emission control device(s) (e.g., a combustion device and/or vapor recovery unit), fittings, connectors, liquid knockout vessels, openings on storage tanks (such as PRVs and thief hatches), and emission control devices.
VOC burner	A combustor for storage tank headspace vapors.
Well cycle	A time period that encompasses the initial fluid flow from a production well to the separator until the end of the final associated separator-to-storage tank dump. A well cycle is typically automatically initiated when the well casing / sales gas pipeline pressure differential exceeds a threshold value. Well cycles can also be manually initiated. The

	sequence of flows to the separator is residual liquids in the flowline from the previous well cycle followed by gas, hydrocarbon liquids, and water from the well tubing. Gas is produced to a sales pipeline and produced liquids are periodically dumped from the separator to the tank.
Working losses	Working losses occur when storage tank headspace gases are displaced from the tank during liquid loading (i.e., the liquid level increases).

Executive Summary

E.1 Project Introduction and Purpose

This report presents the results of a pressurized hydrocarbon liquids sampling and analysis (PHLSA) Study conducted by Southern Petroleum Laboratories (SPL) and sponsored by Noble Energy, Inc. The purpose of the PHLSA Study was to isolate individual variables of the sampling and analytical methods typically used to obtain information regarding the flash potential and makeup of pressurized hydrocarbon liquids and to identify protocols for determining how these samples can be reliably obtained, handled, and analyzed to produce accurate analytical results for practical application in modeling flashing losses. Based on this purpose, the following primary objectives were developed and relied upon to organize the study methodology and Work Plan:

1. Evaluate procedures for the collection and analysis of pressurized hydrocarbon (HC) liquids samples, and develop recommendations for best practices to incrementally improve these procedures;
2. Evaluate the use of Process Simulation Model/Equation of State (PSM/EOS) calculations based on analytical results for pressurized HC liquids samples to estimate the flash gas generated (i.e., gas volume and composition) when pressurized HC liquids are dumped to atmospheric storage tanks; and
3. Estimate the uncertainties of measured and PSM/EOS calculated flash gas-to-oil ratios (FGOR) and other parameters.

E.2 PHLSA Study Methodology

To accomplish the study purpose and primary objectives, the study was structured to follow a logical order to evaluate:

- Analytical methods and laboratory handling procedures for pressurized HC liquids samples;
- Pressurized HC liquids sample collection parameters, which included: 1) sample collection rate; 2) sample collection cylinder type; 3) sample collection initiation time after the end of a well cycle; and 4) sample collection location (i.e., oil box oil level sight glass or sample probe installed downstream of the oil box);
- Operational performance checks (OPC) for pressurized HC liquids sample collection and analysis results;
- Collection and analysis of pressurized HC liquids samples, over a range of separator operating conditions and various storage tank operating conditions, in conjunction with

instrumentation to measure separator and tank process parameters (e.g., pressures, temperatures, flow rates), and associated storage tank HC mass balances and FGORs; and

- Process Simulation Model/Equation of State software programs to calculate FGORs and sample bubble point pressures (P_{BP}) based on analytical results for pressurized HC liquids samples.

Noble Energy, Inc. recommended to SPL a typical oil and gas (O&G) production facility at which to conduct the field portion of the study (Test Facility), and facilitated the collection of pressurized HC liquids samples, produced gas samples, direct flash gas measurements, and related process data. The Test Facility is a vertical O&G production well site located in the Denver-Julesberg (DJ) Basin. Hydrocarbon liquids classified as condensate, with an API gravity of approximately 60 degrees, are produced at the Test Facility. The primary facility equipment is comprised of a well, a three-phase separator, atmospheric storage tanks for condensate and produced water, and a volatile organic compound (VOC) enclosed combustion device (i.e., VOC burner) downstream of the condensate tank. Test Facility equipment and operating modifications were made to allow isolation and control of key operating parameters, and instrumentation was installed to measure process parameters. Laboratory-specific study tasks were conducted at the SPL facility in Houston. Section 2 provides additional detail regarding the Test Facility as well as flash gas generation, sample collection and analysis methods for pressurized HC liquids, OPCs, and PSM/EOS calculations.

The study followed a Project Work Plan (Appendix I) and a Quality Assurance Project Plan (QAPP) (Appendix I.1) developed by SPL with input from agency and industry experts including a Technical Advisory Panel (TAP) consisting of representatives of the United States Environmental Protection Agency (Scott Patefield, Sara Loiacono, and Michael Stovern), the Colorado Department of Public Health and Environment (Alicia Frazier), Air Pollution Testing, Inc. (Mike Pearson), and Noble Energy, Inc. (Alon Mandel, Bill Obermann, and Susan Gomez). Other significant contributors included Movilab (Ricardo Aguiar) and Innovative Environmental Solutions (Thomas McGrath and James McCarthy).

The study produced sub-reports on Uncertainty Analysis (Appendix II), Sampling and Analysis Data (Appendix III), Process Measurements Data and Measured Storage Tank Mass Balance and FGOR Calculations (Appendix IV), and PSM/EOS Calculations (Appendix V).

Table E-1 provides a project overview by summarizing the primary project tasks. These tasks are referenced in the summary of the PHLSA study data and findings in Section E.3.

Table E-1. Project Overview / Summary of Primary PHLSA Study Tasks

Task	Description
1. Initial Sample Collection	Pressurized condensate samples were collected at the Test Facility and analyzed using three different methods for pressurized condensate: GPA 2186M, GPA 2103M, and flash liberation. A composite condensate composition was used for Task 2.
2. Development of Certified Reference Material (CRM)	A NIST-traceable CRM (i.e., a gravimetrically blended condensate standard with low compositional uncertainty) was developed. The CRM was used to evaluate different Analytical Methods (Tasks 3 & 4) and OPCs (Task 7), to conduct the Sample Handling Perturbation Study (Task 6), and as the CRM for calibrations throughout the study.
3. Multi-Lab Analytical Methods Study	CRM samples were analyzed by four different laboratories (labs) using the GPA 2186M, GPA 2103M, and flash liberation analytical methods to compare the methods and variability of results from different labs.
4. SPL Analytical Methods Performance & Uncertainty	This task estimated the accuracy, precision, and overall uncertainty of the GPA 2186M, GPA 2103M, and flash liberation analytical methods. CRM samples were analyzed by SPL using the three methods, and the results compared to the gravimetrically determined CRM composition from Task 2. Two versions of GPA 2103M were evaluated.
5. Process Measurement Uncertainty Analysis	Instruments to measure process parameters (e.g., pressures, temperatures, flowrates) were evaluated to estimate and minimize measurement uncertainty. Uncertainties in process measurements propagate to PSM/EOS FGOR calculations, and atmospheric storage tank HC mass balance and flash gas generation/FGOR calculations.
6. Lab Sample Handling Perturbation Study	CRM samples were used to evaluate the impact of lab sample handling parameters (e.g., temperature, pressure, mixing, and gas chromatograph (GC) sample injection rate) on compositional analyses of pressurized condensate samples to develop recommendations for proper handling of lab samples.
7. Operational Performance Checks	Operational performance checks (e.g., initial pressure test (IPT) P_{BP}, PSM/EOS calculated P_{BP}) to assess the reliability of pressurized HC liquids sampling and analysis results were evaluated to develop recommendations for conducting these checks.
8. Sample Collection Perturbation Study	The impact of sample collection parameters (e.g., cylinder type, location, rate, start time) on pressurized HC liquids sampling and analysis results were evaluated to develop recommendations for sample collection procedures. Perturbation samples were initially collected in January 2016 and also later in conjunction with Task 9.
9. Winter and Summer Three-Separator Pressure Range Study	This task investigated the effects of separator pressure and temperature on pressurized HC liquids sampling and analysis results, and the effects of separator conditions and storage tank temperature on flash gas generation. In the winter and in the summer, the separator was operated at three different nominal pressures (identified as "high" (HP ~ 260 psig), "mid" (MP ~ 225 psig), and "low" (LP ~ 175 psig)) and replicate pressurized condensate samples were collected concurrent with process measurements for storage tank HC mass balance and FGOR calculations.
10. Data Analysis	The uncertainties of storage tank HC mass balance and FGOR measurements were estimated. The sensitivity of PSM/EOS calculations to key parameters and the uncertainties of PSM/EOS FGOR and P_{BP} calculations were estimated.

The methodology for conducting each of these tasks is described in more detail in Section 3.

E.3 Summary of PHLSA Study Data and Findings

Sections E3.1 to E.3.7 introduce specific PHLSA Study objectives and present associated data and findings.

A consideration when reviewing these data is that the ratio of the PSM/EOS calculated bubble point pressure (at the sample collection temperature (T_{SC})) using the measured HC liquids composition to the separator pressure during sample collection (P_{BP}/P_{SC}) is used to evaluate the reliability of pressurized HC liquids sample collection and analysis results (i.e., measured sample compositions). P_{BP}/P_{SC} near 1.0 have historically been considered an indication that the sample and associated analytical results are representative of separator HC liquids in equilibrium with the separator gas during sample collection. For this project, extensive effort was made to collect condensate samples from the separator at or near equilibrium conditions, and large deviations of P_{BP}/P_{SC} from 1.0 indicate possible sample collection and/or analytical bias.

E.3.1 Objective: Identify protocols for collection, handling and analysis of pressurized HC liquids samples to obtain accurate results to assess flashing losses from storage tanks

E.3.1.1 Evaluations of Analytical Methods

Two evaluations of analytical methods were conducted, an SPL laboratory study (Task 4) and a multi-laboratory study with four participating labs (Task 3). National Institute of Standards and Technology (NIST)-traceable CRMs, which are gravimetrically blended condensate standards with low compositional uncertainty (e.g., less than 0.5% for methane (C1) to pentanes (C5) and hexanes and higher HCs (C6+)), were developed for these method evaluations (Task 2). Three analytical methods, which are the most prevalent pressurized HC liquids methods industry-wide, were evaluated: GPA 2103M, GPA 2186M, and flash liberation. “GPA” refers to the Gas Processors Association and “M” attached to the analytical method indicates lab-specific modifications.

Figure E-1 presents results from the SPL laboratory study and compares the sum of the C1–C5 HCs for each of the three analytical methods to the CRM values (ratios closer to 1.0 (i.e., the red line) indicate more accurate analytical results). SPL GPA 2103M had the best performance based on accuracy (i.e., agreement with the CRM values) and precision (i.e., data scatter), and had the lowest uncertainty for the gravimetrically blended components (refer to Table E-3 below). SPL flash liberation had the poorest performance based on these criteria. These ΣC1-C5 results are generally representative of the results for the individual HCs (i.e., methane, ethane, propane, butanes, and pentanes), which are presented in Section 4.2. SPL GPA 2103M also had the best performance for the measurement of the molecular weight (MW) and specific gravity (SG) of the decanes and higher HCs (C10+) fraction. GPA 2013 directly measures these parameters, whereas GPA 2186 and flash liberation calculate these values based on compositional analysis results. It should be noted that the CRMs were specifically blended to mimic the pressurized condensate at the Test Facility, and SPL analytical results for different fluids could yield different results.

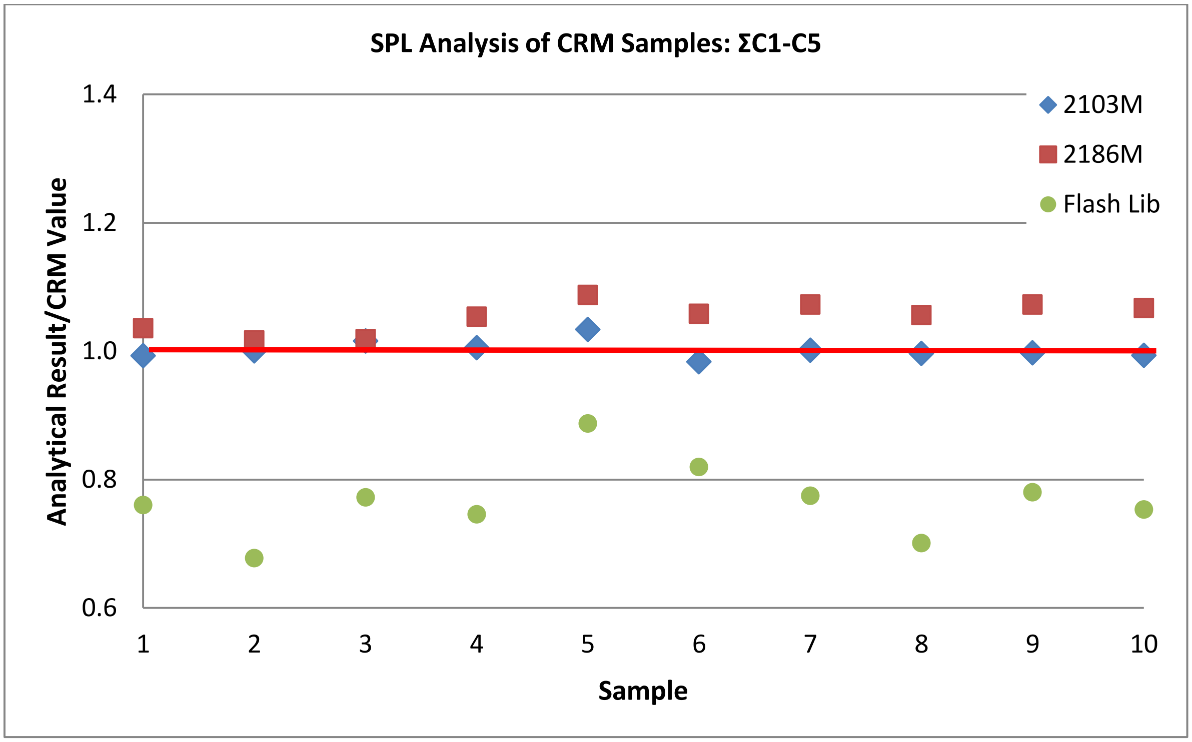

Figure E-1. Results of SPL analytical methods evaluation: ΣC1-C5 vs. CRM value.

Figure E-2 presents results from the multi-laboratory study and compares the sum of the C1–C5 HCs for each of the three analytical methods to the CRM values. Four different analytical laboratories participated and analyzed six CRM samples by each method (only Lab 4 analyzed samples by all three methods). For the GPA 2103M analyses, Lab 2 and Lab 4 results have good accuracy (i.e., are within about 5% of the CRM value) and precision (i.e., little data scatter); however, Lab 1 results differ from the CRM values by about 25%. Although the Lab 1 results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3) and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M results for Lab 3 and Lab 4 are less precise than the GPA 2103M results (i.e., more scatter in the data), and the GPA 2186M analytical results for Lab 3 and Lab 4 differ from the CRM values by up to about 15%. Lab 2 GPA 2186M and GPA 2103M results have similar accuracy and precision. The flash liberation results for Lab

3 have similar accuracy and precision as the GPA 2186M results. Lab 4 results differ from the CRM values by up to about 30% and have similar data scatter as the GPA 2186M results. Lab 1 flash liberation results have considerable scatter and differ from the CRM by up to about 10%. These ΣC1-C5 results are generally representative of the results for the individual HCs (i.e., methane, ethane, propane, butanes, and pentanes), which are presented in Section 4.3.

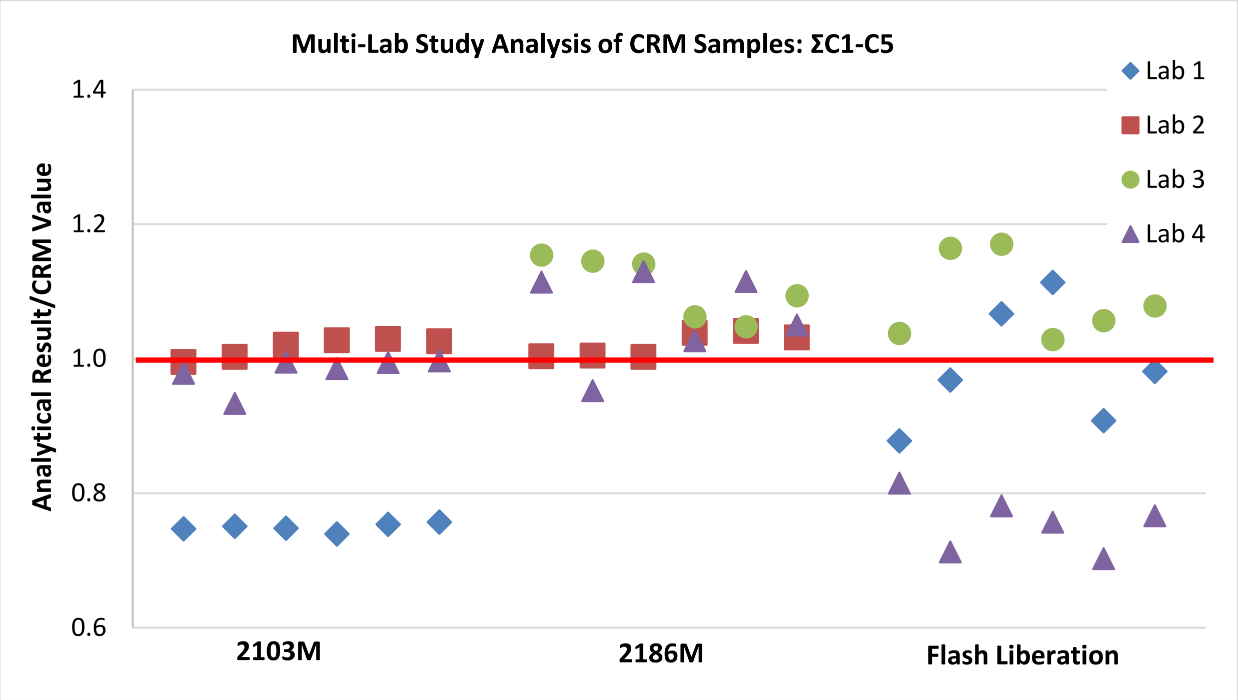

Figure E-2. Results of multi-lab study analytical methods evaluation: ΣC1-C5 vs. CRM value by Analytical Method and Laboratory.

Key considerations and findings for the multi-lab study include:

- The multi-lab study had a limited scope and was not intended to be a comprehensive and robust Inter-laboratory study to estimate the reproducibility[1] of the methods. The multi-lab study results are specific to the participating laboratories and analyzed CRMs, and should not be considered representative of the industry-wide performance for these analytical methods.
- The accuracy and precision of the analytical results varied by method and by laboratory, and this suggests O&G producers would benefit from a means to compare the performance of different laboratories and analytical methods. For example, analytical laboratories could be asked to provide uncertainty estimates for reported parameters based on a standard ISO-

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[1] Reproducibility is precision under reproducibility conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

based or similar uncertainty estimate methodology that is audited and verified by an accredited third party.

Sections 4.2 and 4.3 provide a more comprehensive presentation and discussion of the results of the analytical methods evaluation tasks.

E.3.1.2 Evaluations of Laboratory Sample Handling Parameters

Task 6 evaluated the impact of laboratory sample handling parameters (e.g., temperature, pressure, sample collection cylinder mixing, and purge rate (i.e., GC sample injection rate)) on pressurized HC liquids samples compositional analysis (CO_2, N_2, and C1–C6+). Sample mixing (number of cylinder rocks) and pressure prior to GC injection significantly impacted analytical results (based on a statistical significance criterion of 95%). Sample cylinder type (floating piston constant pressure (CP) or liquid/water displacement constant volume (CV)) was found to influence CO_2 and N_2, and have borderline statistically significant influence on methane. Purge rate and temperature did not significantly impact analytical results.

Section 4.4 provides a more comprehensive presentation and discussion of the results of the lab sample handling parameters evaluation task.

E.3.1.3 Evaluation of Sample Collection Parameters

The impact of key sample collection parameters on pressurized HC liquids sample collection and analysis results were evaluated by Task 8:

- **Sample collection initiation time** after the end of the well cycle (less than 0 (i.e., during the well cycle), less than 30 (typically ~ 15), 90, and 150 minutes after the well cycle).

  Results for sequentially collected samples during two well cycles showed decreases in P_{BP}/P_{SC} and methane concentration when the sample collection initiation time was increased from less than 30 minutes to 90 minutes after the end of the well cycle. Gas flow from the separator to the gathering pipeline between the collection of these samples is a suspected cause, at least in part, of the change in HC liquids composition (i.e., the sales gas flow changed the equilibrium condition in the separator, and the methane content and bubble point pressure of the separator liquid was reduced). Based on these results, a study guideline to collect samples within 30 minutes of the well cycle end was adopted for subsequent sample collection. An additional consideration is that collecting a pressurized HC liquids sample soon after a well cycle increases the probability that the sample composition will be the same as or very similar to the liquids that flowed from the separator to the storage tank.

- **Sample collection rate** (20, 40, 60, 100, and 180 ml/min)

  Sample collection rate had no discernible effect on P_{BP}/P_{SC}. It should be noted that these samples were collected from sample probes installed about two feet below the separator gas/liquid interface, and were pressurized in the lab to 1,100 psi. Such a pressure is expected to dissolve any gas that evolved (i.e., flashed) during sample collection. Sample collection rate may have a larger impact under different conditions, such as samples collected closer to the gas/liquid interface. For example, the gas/liquid interface could only be a few inches above the sample collection location at an oil box oil level sight glass, and a rapid sample rate could entrain gas. For subsequent PHLSA Study sample collection, conservative sample collection rates of 60 ml/min or less were used.

- **Sample cylinder type** (CP cylinder and CV cylinder)

  To evaluate sample cylinder type, CP cylinder/CV cylinder sample pairs were simultaneously collected throughout the study. Analysis of the paired CP/CV results determined a low bias in CV cylinders for CO_2 (~ 10% of the average concentration) and methane (~ 5% of the average concentration), and these biases impacted associated PSM/EOS calculated values of P_{BP} and FGOR. It is suspected that some of the CO_2 and methane in the pressurized condensate samples partitioned to the water in the CV cylinders. The solubilities of CO_2 and methane in water support this theory.

- **Sample collection location** (sample probe and oil box oil level sight glass)

  The separator oil box sight glass is a practical sampling location for many separators. The impact of using the sight glass as a sample collection location was evaluated by simultaneously collecting pressurized condensate samples from two sample probes and the sight glass. Figure E-3 compares P_{BP}/P_{SC} for samples collected from the two sample probes and the sight glass for nine well cycles. For the CP cylinder sampling, there is negligible difference between the P_{BP}/P_{SC} for the paired sight glass and probe samples (refer to the paired blue and pink diamonds). However, for the CV cylinder sampling, P_{BP}/P_{SC} for the paired sight glass and probe samples differ by more than 20% for the MP1 and LP2 well cycles (refer to the paired red and pink squares). It is not understood why the CV sight glass samples differed from the probe samples.

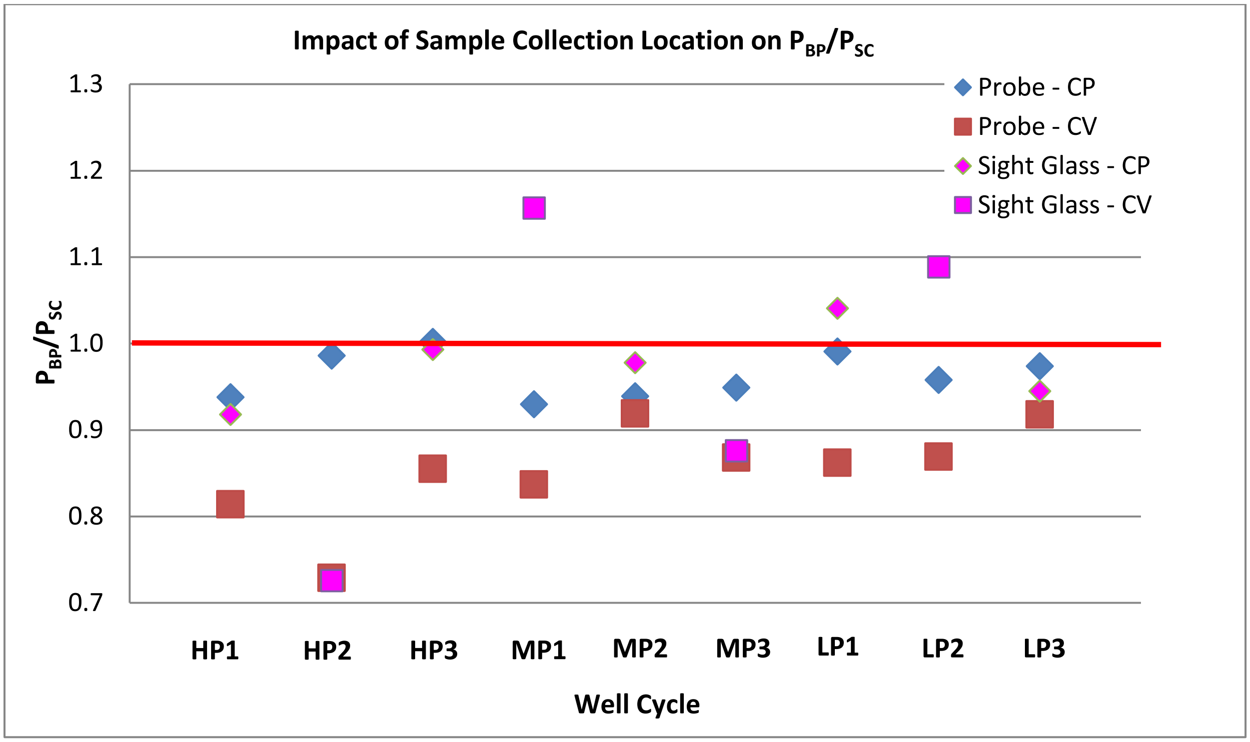

Figure E-3. Impact of sample collection location on P_{BP}/P_{SC}.

Section 4.5 provides a more comprehensive presentation and discussion of the results of the sample collection parameters evaluation task.

E.3.2 Objective: Identify operational performance checks for the hydrocarbon liquids analysis results to verify that the analytical results are of acceptable quality

Task 7 evaluated the reliability of OPCs to develop recommendations for conducting these checks. The collection, transport, and analysis of pressurized HC liquids samples is a complex process. Non-equilibrium process streams, sample collection anomalies, sample leakage and loss of volatile species, analytical biases and errors, and other factors can contribute to anomalous analytical results for HC liquids composition. The intent of an OPC is to evaluate whether the composition of a pressurized HC liquids sample determined from laboratory analysis is a reasonable representation of the process stream composition at gas/liquid equilibrium. For the purposes of this study, an OPC should provide confidence that a PSM/EOS calculated flash gas volume (i.e., FGOR) and composition, based on analytical results for a pressurized HC liquids sample, is a reasonable estimate of the actual flash gas generation.

Ideally, an OPC would: 1) consistently identify representative pressurized HC liquids samples as representative (based on some measurable criteria) and consistently identify non-representative pressurized HC liquids samples as non-representative; and 2) be relatively simple and practical to implement. Four OPCs for pressurized HC liquids samples were evaluated for this study. Three OPCs determined the bubble point pressure and calculated P_{BP}/P_{SC}:

- **Bubble point pressure by PSM/EOS calculation**. The P_{BP} for a pressurized HC liquids sample is calculated using the analytical results for the sample and a PSM/EOS software program.
- **Laboratory densitometer measurement of sample P_{BP}**. The P_{BP} for a pressurized HC liquids sample is directly measured using a densitometer.
- **Initial Pressure Test P_{BP}**. The P_{BP} for a pressurized HC liquids sample is directly measured in a laboratory by initially raising the sample pressure above P_{SC} and then slowly reducing the pressure until it stabilizes at P_{BP} when bubbles of flash gas form. If the lab temperature during the IPT differs from the T_{SC}, the IPT P_{BP} is adjusted to the T_{SC} using PSM/EOS calculations.

A fourth OPC **compares HC liquids density measurements conducted at the production facility by a Coriolis meter and in the lab with a densitometer**, with large differences between the two density measurements suggesting the HC liquids sample may have been compromised.

For all the OPCs, it is imperative that accurate and calibrated instruments are used for the temperature and pressure measurements during sample collection and laboratory procedures.

E.3.2.1 Summary of findings for operational performance checks

The primary results and findings of the OPC evaluations were:

- Due to practical considerations and apparent measurement anomalies, two OPCs were found to be unreliable during the study: 1) densitometer measurement of sample P_{BP}, and 2) comparing HC liquids density measurements conducted at the production facility by a Coriolis meter and in the lab with a densitometer.
- Bubble point pressures of pressurized HC liquids samples are strongly impacted by nitrogen (i.e., air) and methane, and PSM/EOS calculated FGOR estimates are much less dependent on the concentrations of these volatile compounds in pressurized HC liquids samples. Thus, 1) air contamination caused by incomplete purging of sample collection equipment, or 2) a non-equilibrium methane concentration for a sample (e.g., loss during sample collection, transport and handling, and/or from a non-equilibrium separator) may cause an anomalous P_{BP} estimate when an associated FGOR and flash gas composition are reliable for estimating flash gas VOC generation and/or flash gas mass generation for storage tank vapor control system design.

  - PSM/EOS calculations show that a 20% reduction in the methane concentration in a typical condensate sample results in about a 16% change in P_{BP} but only about a 5% change in FGOR.
  - For a sample with about 0.15 wt% N_2 (~ 0.48 mole %), the with-N_2 P_{BP} was about 21% greater than the without-N_2 P_{BP}, whereas the associated FGOR only increased about 3%.
  - If the nitrogen in a sample is determined to be air contamination, PSM/EOS calculations should be based on a without-N_2 sample composition.

- PSM/EOS calculated FGOR and P_{BP}/P_{SC} (and P_{BP}) are <u>not</u> strongly correlated. Figure E-4 compares PSM/EOS calculated FGOR and P_{BP}/P_{SC} for pressurized condensate samples collected in three well cycle pressure ranges: high-, mid-, and low-pressure. These data suggest that P_{BP}/P_{SC} may not be an optimal OPC if the goal of pressurized HC liquids sample collection and analysis is to estimate FGOR. As noted above, P_{BP} is much more sensitive to changes in methane concentration than FGOR, and inaccuracy in a pressurized HC liquids sample methane concentration may cause a large bias in the PSM/EOS calculated P_{BP} but have much less effect on the FGOR calculation.

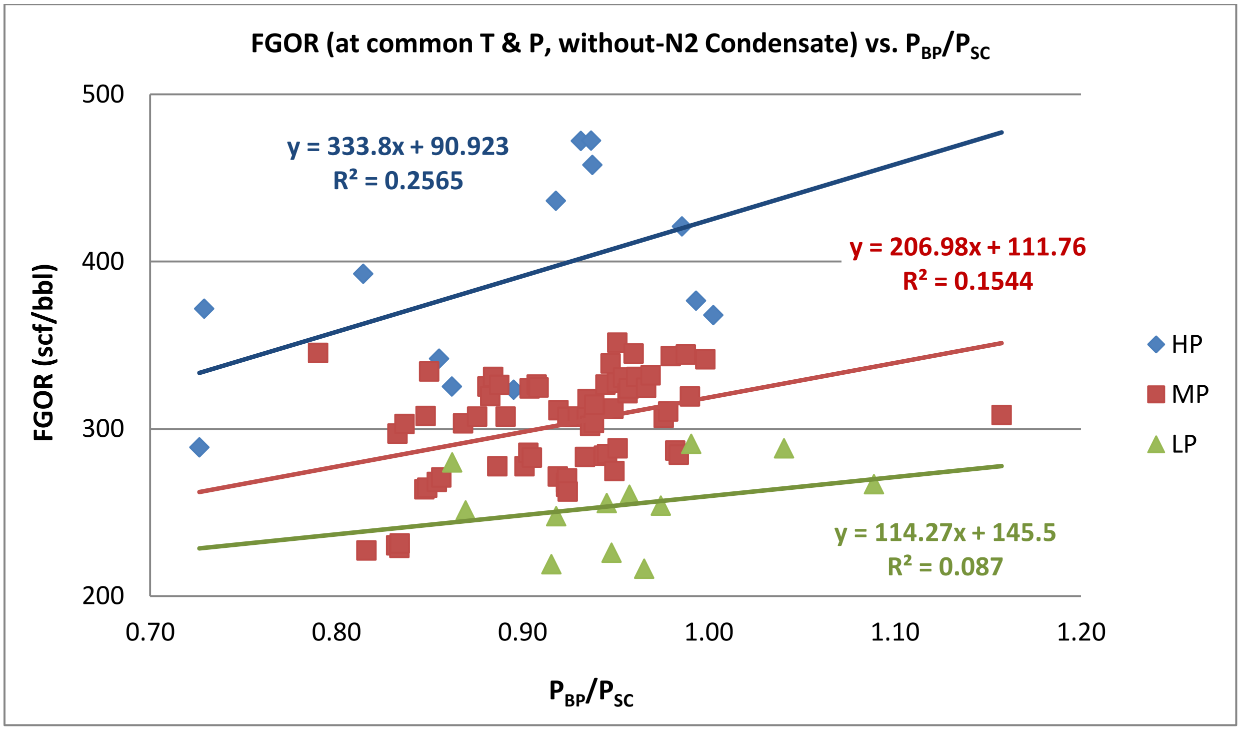

Figure E-4. PSM/EOS calculated FGOR (at common pressure and temperature) vs. P_{BP}/P_{SC} based on without-N_2 pressurized condensate samples.

- The study results indicate that an IPT P_{BP} determination would not be an optimal OPC if the goal of the pressurized HC liquids sample collection and analysis is to estimate FGOR. This is because while an IPT measurement checks the sample P_{BP} after collection and transport, it does not evaluate the analytical results (i.e., an IPT is conducted prior to lab analysis), and FGOR and IPT P_{BP}/P_{SC} are not strongly correlated. In addition, air contamination can bias an IPT P_{BP} measurement, but air in a sample is not necessarily a reason for sample rejection.
- The IPT P_{BP}/P_{SC} and PSM/EOS calculated P_{BP}/P_{SC} could be used as preliminary sample screening criteria, with anomalous results flagged for further scrutiny.
- Acceptance of pressurized HC liquids composition results should depend on the ultimate data use and engineering judgment.
  - The study data suggest that PSM/EOS calculated FGOR and flash gas composition could be an appropriate OPC for samples collected to estimate FGOR and flash gas composition (e.g., data for storage tank vapor control system design and/or flash gas VOC generation estimates). Acceptance criteria could be based on comparing the FGOR and flash gas composition to historical trends for similar production facilities. More conservative/stringent OPC acceptance criteria would be expected to reduce the chance of using a non-representative sample, but increase the chance of rejecting a representative sample.
    - Lacking appropriate historical FGOR and flash gas composition data to determine sample acceptance criteria, PSM/EOS calculated P_{BP}/P_{SC} could be used as a conservative OPC for samples collected to estimate FGOR and flash gas composition. Pressurized condensate samples for this project were collected and analyzed under very controlled conditions, and none were statistical outliers for PSM/EOS calculated FGOR, whereas several of the P_{BP}/P_{SC} were statistical outliers. This suggests that P_{BP}/P_{SC} would be a conservative OPC because some samples that have outlier P_{BP}/P_{SC} (and would be rejected) could have a representative FGOR estimate. For this study, P_{BP}/P_{SC} ranged from about 0.73 to 1.16, and this range could be a minimum for OPC acceptance criteria, although the applicability of these findings to other production facilities with real-world separator operation and sample collection imperfections cannot be determined.
    - Because pressurized HC liquids methane content and P_{BP} are strongly correlated, P_{BP}/P_{SC} could be an effective OPC for samples collected to estimate flash gas methane generation.

Section 4.6 provides a more comprehensive presentation and discussion of the results of the OPCs evaluation task.

E.3.3 Objective: Identify proper procedures for conducting process simulations to quantify peak instantaneous vapor flow rates using pressurized HC liquids analysis results

This study used four commercially available PSM/EOS software programs to calculate flash gas generation estimates from analytical results for pressurized HC liquids for Task 10. The Peng-Robinson EOS is commonly used in the O&G industry and was used to conduct calculations by all four software programs. Good agreement between PSM/EOS calculated FGORs and measured FGORs (i.e., FGORs agree within uncertainties of the calculated and measured values) suggests the Peng-Robinson EOS and the PSM/EOS process configuration used for this study (i.e., the PSM/EOS process flow diagram was customized to mimic the equipment and material stream flows being modeled) calculate reasonable estimates of FGOR values. Recommended proper procedures for PSM/EOS calculations of FGOR and P_{BP} also include:

- Accurate measurement of PSM/EOS calculations input parameters:
    - the separator pressure and liquid temperature;
    - the storage tank bottom temperature for tanks with downcomers;
    - the storage tank gas headspace temperature;
    - the barometric pressure;
    - for tanks with downcomers, the tank liquid height, tank liquid density, and tank downcomer exit height. These parameters, the barometric pressure, and an estimate of the average storage tank headspace gauge pressure are used to calculate an estimate of the total pressure at the downcomer exit; and
    - for tanks with downcomers, an estimate of separator-to-tank fluid flow partitioning through the siphon prevention hole (SPH)[2].
- A pressurized HC liquids compositional analysis that includes, at a minimum, C1–C10+ and an accurate determination of the plus fraction density and molecular weight.

An observation from the testing was that actual maximum gas flowrates during well cycles were significantly less than (e.g., ~ 60 to 70% of) an associated theoretical potential peak instantaneous vapor flow rate (PPIVFR).[3]

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[2] A siphon prevention hole is a small hole near the top of a storage tank downcomer to prevent a siphon effect and backflow of liquid from the tank to the separator.

[3] PPIVFR is defined as the maximum instantaneous amount of vapors routed to a vapor control system during normal operations, including flashing, working, and breathing losses, as determined using a tank emissions model. For the purposes of the PHLSA study, the PPIVFR was calculated by assuming that the entire gas volume generated during a separator well cycle exits the tank at a steady rate for a time period equal to the duration of the separator dumps during the well cycle (e.g., in engineering units of kg/sec).

Section 4.7.4 provides a more comprehensive presentation and discussion of the results of the PSM/EOS calculations.

E.3.4 Objective: Highlight key potential sources of uncertainty in estimating flash gas generation

PSM/EOS calculated estimates of flash gas generation (conducted for Task 10) are sensitive to:

- Separator temperature and pressure. These separator operating parameters impact the composition of pressurized HC liquids that flows from the separator to the tank; and
- Tank liquids and headspace gas temperatures and pressures, and fluids partitioning through the SPH for tanks equipped with downcomers. These tank operating parameters impact the final state of the post-flash fluids.

Therefore, uncertainties in these parameters will be sources of uncertainty in flash gas generation estimates, and these uncertainties were estimated by Task 5. Other sources of uncertainty in flash gas generation estimates include the pressurized HC liquids compositional analysis and the limitations of the EOS used for the equilibrium calculations. The compositional analysis uncertainty will be impacted by uncertainty and any bias in the analytical methodology, any potential changes to the liquids composition during sample collection and transport, and the assumption of separator gas/liquid equilibrium during sample collection. Uncertainties of SPL analytical results for pressurized HCs were estimated from Task 4 measurements.

In sum, uncertainty estimates for PSM/EOS calculations of FGOR show high sensitivity to tank bottom temperature, separator pressure and temperature, assumptions regarding separator dump-to-tank fluids SPH partitioning, and HC liquids components with high analytical uncertainty. These are large potential sources of uncertainty in flash gas generation estimates.

Section 4.7.4 provides a more comprehensive presentation and discussion of the results of the PSM/EOS calculations.

E.3.5 Objective: Identify methods to determine and account for the variability of key input parameters

Table E-2 lists key input parameters for PSM/EOS calculations of FGOR and P_{BP}, and potential methods to determine and account for the uncertainty and variability of these parameters. A parameter uncertainty refers to the uncertainty of a single point in time measurement (e.g., a separator pressure measurement uncertainty of +/- 5 psi) and a parameter variability could refer to the parameter range during a time period (e.g., a separator pressure ranged from 100 to 200 psig during a year) or data documenting the frequency and range of parameter variations during a time period.

Table E-2. Input Parameters for PSM/EOS Calculations and Potential Methods to Estimate Associated Uncertainty and Variability

PSM/EOS Parameter	Potential Methods to	
	Estimate Uncertainty	**Estimate Variability**
Separator pressure	• Instrument manufacturer specs • Instrument calibration records	• Gathering line pressure records • Supervisory Control and Data Acquisition (SCADA) records • Operator records/observations
Separator temperature[A]	• Instrument manufacturer specs • Instrument calibration records	• SCADA records • Operator records/observations
Tank liquids temperature[B]	• Instrument manufacturer specs • Instrument calibration records	• Warm and cold weather measurements; and • Early morning & mid-afternoon measurements
Tank headspace gas temperature[C]	• Instrument manufacturer specs • Instrument calibration records	• Warm and cold weather measurements; and • Early morning (pre-sun rise) & mid-afternoon (sunny day) measurements
Tank headspace gas pressure	• Engineering estimate (dynamic parameter during a well cycle)	• Estimate from VOC burner on/off pressure settings
Barometric pressure	• Instrument manufacturer specs • Instrument calibration records	• National Oceanic and Atmospheric Administration records
Tank liquids height	• SCADA instrument manufacturer specs • Tank gauging SOP	• SCADA records • Tank gauging records • Liquids hauling records
Tank liquids density	• Measurement method specs	• Collect & analyze warm weather and cold weather tank samples
SPH fluid flow partitioning[D]	• Engineering estimate • Controlled/lab study	• Engineering estimate • Controlled/lab study
Pressurized HC liquids composition[E]	• Analytical methods uncertainty	• Collect samples over typical ranges of separator temperature and pressure • Use PSM/EOS calculations to vary the temperature and pressure of a sample and estimate composition change

A. Separator temperature can be highest during cold weather months when the separator heater is operating.

B. Liquids temperature may be estimated from direct resistance temperature detector (RTD) measurements or less accurate tank wall temperature measurements.

C. Gas temperature may be estimated from direct RTD measurements or less accurate tank wall temperature measurements.

D. Direct measurement of the partitioning of separator to tank fluid flow through a SPH is likely not practical. Controlled laboratory studies to quantify this partitioning under various operating conditions may be needed.

E. Additional uncertainty from sample collection and transport anomalies, and the assumption of separator gas/liquid equilibrium during sample collection can be minimized by stabilizing the separator temperature and pressure for one or more well cycles prior to sample collection, and using samples with P_{BP}/P_{SC} close to 1.0.

E.3.6 Objective: Evaluate the variability of summer/winter effects on input parameters used in determining flashing losses

The effects of parameters which differ during winter and summer operation, and impact flash gas generation were evaluated for Task 9. These include separator liquids temperature (which impacts the separator HC liquids composition) and tank liquid and gas temperatures (which impacts the final state of the post-flash liquids and gas). Measured and PSM/EOS calculated FGORs were larger during the summer (July) three-pressure testing than during the winter (March) three-pressure testing. The differences were primarily caused by higher separator temperatures during the winter and higher tank temperatures during the summer. A review of the average temperatures for the separator HC liquids, tank bottom liquids, and tank headspace gas for each well cycle during winter and summer tests shows:

- Generally higher **separator liquid temperatures** during the winter testing than during the summer testing. Winter temperatures ranged from about 58 to 92°F (impacted by the separator heater operation) and summer temperatures ranged from about 62 to 86°F (impacted by ambient temperature).
- Higher **tank liquid temperatures** during the summer testing than during the winter testing. These temperatures were impacted by ambient temperature and solar heating, and ranged from about 44 to 47°F in the winter and from about 75 to 83°F in the summer.
- Generally higher **tank headspace gas temperatures** during the summer testing than during the winter. These temperatures were impacted by ambient temperature and solar heating, and ranged from about 49 to 85°F in the winter and from about 71 to 100°F in the summer.

Section 4.7.1 provides a more comprehensive presentation and discussion of the variability of summer/winter effects on input parameters used in determining flashing losses.

E.3.6.1 Winter/Summer Three-Pressure Testing Finding: Daily storage tank temperature increases impacted storage tank HC mass balances and measured FGORs

The summer and winter three-pressure testing measurements showed trends of improved storage tank HC mass balances (i.e., measured mass of flash gas generated / [pre-flash HC liquids mass – post-flash HC liquids mass]) and higher FGOR as the testing progressed from morning to afternoon. Figure E-5 presents the summer testing tank mass balance results with mass balance on the y-axis and well cycle start time and tank bottom liquids temperature on the x-axis. Data from three days of testing - at high-pressure, mid-pressure, and low-pressure - are presented. The vertical lines represent the 95% confidence interval for the data. The high-pressure well cycles results (blue diamonds) are illustrative, with tank mass balance improving from 20% during early morning testing (77°F tank bottom temperature) to about 100% during late afternoon testing (83°F tank bottom temperature). The measured FGOR for these well cycles increased from about 80 to about 330 scf/bbl. These results indicate a “quenching” of flash gas generation when the tank liquids are relatively cold; that is, less flash gas was measured when tank liquids were colder in the morning than in the afternoon. Separator dump fluids are a mix of liquid and gas, and adiabatic flash calculations and estimates of the underground separator-to-tank pipeline temperature suggest these dump fluids are colder than the tank bottom liquids temperature. The measured flash gas generation is thought to be primarily the sum of the dump fluids gas and “secondary” flash gas that evolves as the dump liquids temperature increases as the dump liquids mix with warmer tank liquids. Relatively cooler tank liquids in the morning would be expected to reduce such secondary flash gas generation. A second consideration is that colder morning tank liquids may be under-saturated after cooling overnight (without any condensate production) and absorb some dump fluids flash gas.

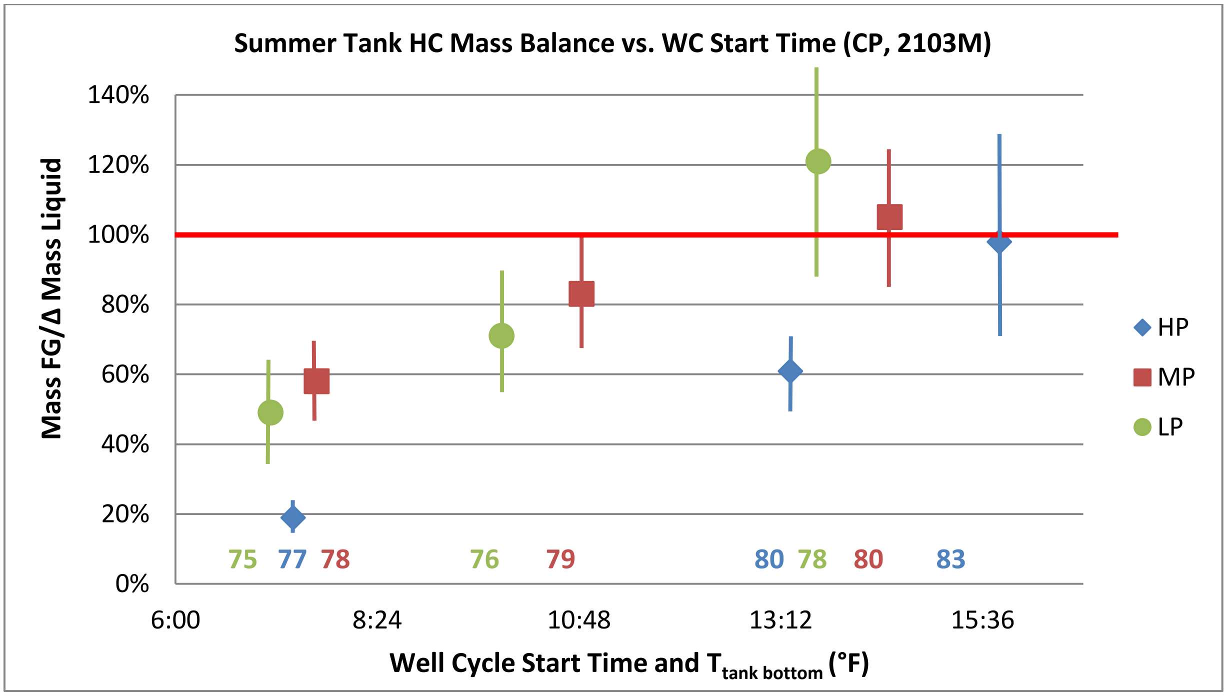

Figure E-5. Storage tank HC mass balance vs. well cycle start time and tank liquids temperature.

Other primary observations from these measurements and associated PSM/EOS calculations include:

- When tank mass balances were close to 100% (suggesting reliable measurements and minimal quenching of flash gas generation in the tank), measured FGORs generally agreed with associated PSM/EOS calculated FGORs within a 95% confidence interval.

- Measured FGORs generally increased with separator pressure, decreased with separator temperature, and increased with tank temperature. For similar separator operating conditions, summer FGORs were about twice the winter FGORs.

Sections 4.7.2 and 4.7.3 provide a more comprehensive presentation and discussion of the summer and winter three-pressure testing results.

E.3.6.2 Winter/Summer Three-Pressure Testing Finding: Recent separator operating history may impact HC liquids sample composition and gas/liquid equilibrium temperature and pressure

HC liquids samples are a mix of new (i.e., produced during the pre-sample collection well cycle) and residual separator liquids in unknown proportions. If fluids from the pre-sample collection well cycle have a different composition (i.e., gas/liquid equilibrium temperature and pressure) than the residual separator liquids, the assumption that the true HC liquids sample equilibrium pressure and temperature are those measured during sample collection may have a large error. Such conditions would complicate the understanding and interpretation of pressurized HC liquids sampling and analysis results. The implication for sample collection is to attempt to maintain a steady separator temperature and pressure for one or more well cycles prior to sample collection, and then maintain these conditions during the well cycle and sample collection. However, this may not be practical if the sales gas pipeline pressure is changing and/or if separator gas is used to fuel the separator heater during cold weather operation.

E.3.6.3 Winter/Summer Three-Pressure Testing Finding: Storage tank breathing losses were minimal or non-existent during many nights, particularly in winter

This suggests that, if a directly measured breathing rate is used to estimate annual breathing losses, the time factor (e.g., hours per year) should be consistent with the data used to estimate the breathing loss rate. For example, if a breathing rate was measured during the afternoon of a hot sunny day, this breathing rate should not be applied to 8,760 hours per year.

E.3.7 Objective: Evaluate the accuracy of the pressurized HC liquids sample results

The accuracy, precision, and overall uncertainty of SPL analytical results for pressurized HC liquids were estimated from analyses of gravimetrically blended CRM samples. Table E-3 lists the estimated analytical uncertainties for GPA 2103M, GPA 2186M, and flash liberation analysis of pressurized HC liquids components by SPL. These uncertainty analysis results show:

- SPL GPA 2103M analytical results generally had lower uncertainties than SPL GPA 2186M and SPL flash liberation for the gravimetrically blended light end compounds (i.e., C1–C5) that are primary flash gas components, and for C6+, which is also a gravimetrically blended component.

- Analytical results for N_2 in CRM samples have high uncertainties, partially caused by N_2 concentrations close to the method detection limit.
- SPL flash liberation had the highest uncertainties for the C1–C5 HCs and for C6+.

Table E-3. Summary of SPL Analytical Methods Uncertainty Estimates

Compound	Uncertainty of Wt% Analytical Results (95% Confidence Interval)		
	Analytical Method		
	SPL GPA 2103M	SPL GPA 2186M	SPL Flash Liberation
CO_2*	1.7%	21.0%	8.6%
N_2	5.7%	41.0%	17.0%
Methane*	2.0%	2.7%	16.0%
Ethane*	1.3%	3.4%	9.2%
Propane*	1.0%	1.9%	6.7%
iso-Butane*	0.6%	1.0%	14.0%
n-Butane*	1.1%	1.5%	13.0%
iso-Pentane*	1.9%	2.2%	22.0%
n-Pentane*	0.9%	1.8%	4.7%
iso-Hexane	3.0%	1.7%	4.6%
n-Hexane	7.6%	5.9%	31.0%
Heptanes	2.7%	1.9%	1.1%
Octanes	3.5%	4.1%	1.5%
Nonanes	4.4%	3.2%	2.8%
C10+	3.8%	3.4%	1.4%
Benzene	7.9%	4.5%	-
Toluene	2.6%	0.9%	-
Ethylbenzene	18.0%	17.0%	-
Xylenes	3.1%	1.5%	2.7%
C6+*	0.2%	0.4%	0.7%
C7+	1.0%	0.8%	1.9%
C8+	1.8%	2.1%	2.1%

*Gravimetrically blended component.

Table E-4 lists the estimated analytical uncertainties for GPA 2103M, GPA 2186M, and flash liberation analysis of condensate components based on the results of the multi-lab study (e.g., the data presented in Figure E-2). For GPA 2103M, uncertainties estimated with the Lab 1 statistical outliers included and removed are presented. Primary considerations and findings for these uncertainty analysis results include:

- Uncertainty estimates for the GPA 2103M results are generally a factor of 2 or more greater with the Lab 1 outliers included than with the Lab 1 outliers removed.
- GPA 2103M analytical results (Lab 1 outliers removed) generally had slightly lower uncertainties than GPA 2186M for gravimetrically blended light end HCs (i.e., C1–C5) that are the primary flash gas components and C6+ that was also a gravimetrically blended component. GPA 2186M analytical results generally had lower uncertainties than GPA 2103M analytical results (Lab 1 outliers removed) for individual HC species C6 and heavier.
- GPA 2103M analytical results (Lab 1 outliers included) had higher uncertainties than GPA 2186M for most of the HC species.
- Flash liberation analytical results had higher uncertainties than GPA 2103M (Lab 1 outliers removed) and GPA 2186M for most of the HC species. Flash liberation analytical results had some higher uncertainties and some lower uncertainties than GPA 2103M (Lab 1 outliers included).
- Analytical results for nitrogen in CRM samples have high uncertainty, and this could be due, at least in part, to nitrogen concentrations near the analytical detection limit.
- The multi-lab study had a limited scope and was not intended to be a comprehensive and robust Inter-laboratory study to estimate the reproducibility of the methods. The analytical uncertainties listed in Table E-4 are specific to the participating laboratories and analyzed CRMs, and should not be considered estimates of the industry-wide uncertainties for these analytical methods.

Table E-4. Summary of Uncertainty Estimates for Analytical Methods Based on Multi-Lab Study Results

Compound	Uncertainty of Wt% Analytical Results (%U, 95% CI)			
	Analytical Method			
	GPA 2103M (Lab 1 outliers included)	GPA 2103M (Lab 1 outliers removed)	GPA 2186M	Flash Liberation
CO2*	9.1%	4.5%	21.0%	6.4%
Nitrogen*	27.0%	41.0%	54.0%	48.0%
Methane*	11.0%	2.0%	2.7%	10.0%
Ethane*	13.0%	2.6%	3.4%	6.5%
Propane*	4.7%	1.0%	1.9%	7.9%
iso-Butane*	7.8%	0.7%	1.0%	13.0%
n-Butane*	4.5%	0.7%	1.5%	12.0%
iso-Pentane*	8.5%	2.5%	2.2%	40.0%
n-Pentane*	4.9%	0.7%	1.8%	8.6%
iso-Hexane	13.0%	5.4%	1.5%	4.6%
n-Hexane	12.0%	4.5%	5.9%	28.0%
Heptanes	15.0%	4.9%	1.9%	2.5%
Octanes	13.0%	7.8%	4.1%	2.5%
Nonanes	9.3%	4.9%	3.2%	9.3%
C10+	12.0%	2.7%	3.4%	4.2%
Benzene	27.0%	7.4%	4.5%	-
Toluene	8.2%	2.6%	0.9%	-
Ethylbenzene	15.0%	19.0%	17.0%	-
Xylenes	5.6%	2.8%	3.0%	5.9%
C6+*	2.2%	0.3%	0.4%	1.4%
C7+	6.4%	1.2%	0.8%	3.6%
C8+	6.1%	1.7%	2.1%	4.5%

*Gravimetrically blended component.

Sections 4.2 and 4.3 provide a more comprehensive presentation and discussion of the results of the analytical methods evaluation tasks.

E.4 Recommended Best Practices for Protocols

Based on the PHLSA Study results, some generally applicable best practice guidelines for protocols for pressurized HC liquids sample collection, laboratory sample handling and analysis, PSM/EOS calculations, and OPCs can be recommended. These include:

1. Determine whether high concentrations of N_2 measured in pressurized HC liquids samples (e.g., higher than PSM/EOS calculated equilibrium estimates) are native or air from a sampling artifact, and mathematically remove artifact N_2 prior to PSM/EOS calculations.
2. Analytical lab reports should include analytical uncertainty estimates for reported parameters based on an audited ISO-based or similar uncertainty estimate methodology.
3. Data users should review analytical lab reports for errors and anomalies.
4. Lab sample handing procedures should include a pre-injection sample pressure at least 300 psi greater than the sample collection pressure, and 18 or more mixing rocks for sample homogeneity.
5. Calibrated and highly accurate pressure gauges and temperature sensors should be used during all sample collection and laboratory procedures.
6. Collect pressurized HC liquids samples as soon as possible after a well cycle. Document, as able, that the separator temperature and pressure have been fairly stable since the well cycle *prior to* the sample collection well cycle.
7. Other recommended HC liquids sample collection procedures include: collect the sample from a location with routine liquid circulation; use a sample collection rate of 60 ml/min or less; record the sample collection pressure and temperature at the start, middle, and conclusion of sample collection; and be aware of potential biases for samples collected in CV cylinders.
8. To estimate flash gas generation for atmospheric storage tank vapor control system design, collect a pressurized HC liquids sample during high pressure/low temperature separator operation that is expected to produce liquids with close to a maximum potential FGOR. Associated PSM/EOS calculations of FGOR should use maximum anticipated tank temperatures, minimum anticipated tank pressure, and conservative assumptions regarding separator dump-to-tank fluids SPH partitioning. Assume a conservative flash gas heating value.

   Rather than using a theoretical PPIVFR to determine atmospheric storage tank vapor control system capacity requirements, a dynamic model approach is recommended.

9. To estimate an annual flash gas generation volume and composition (e.g., to develop an emission factor for emission inventory purposes), collect a pressurized HC liquids sample during average pressure/average temperature separator operation that is expected to produce liquids with close to an annual average FGOR. Associated PSM/EOS flash gas generation calculations should use annual average tank temperatures and pressures, and average assumptions regarding separator dump-to-tank fluids SPH partitioning.
10. Avoid, if possible, collecting samples during very cold weather when separator heater operation may be changing the separator pressure and liquids composition, mixing of cold well cycle fluids and hot residual separator fluids may be incomplete, and/or sample collection could be compromised (e.g., due to paraffin deposition on cold sample cylinder walls).
11. Suggested guidelines for OPCs for pressurized HC liquids samples include:
    a. Measure sample pressure and temperature during sample collection and during lab analysis with highly accurate, calibrated instruments.
    b. Determine an IPT P_{BP}/P_{SC} and/or a PSM/EOS calculated P_{BP}/P_{SC} to identify potential anomalies with the sample, and flag anomalous results for further scrutiny.
    c. As appropriate, adjust N_2 levels in HC liquids compositions prior to PSM/EOS calculations (e.g., if sample N_2 is determined to be sample collection artifact air, set N_2 level to zero).
    d. Acceptance of pressurized HC liquids composition results should depend on the ultimate data use and engineering judgment (e.g., compare results to historical trends for similar production facilities).

Section 5.2 provides a more comprehensive discussion of these recommended best practices.

E.5 Applicability and Limitations of PHLSA Study Findings

The results and findings of the PHLSA Study for pressurized HC liquids sample collection and analysis, and subsequent PSM/EOS calculations apply to the Test Facility production equipment, operating conditions, and process streams. The applicability of these findings and conclusions to other O&G production locations has not been determined. That is, while study findings have broader applicability, and some general recommendations are provided in Section E.4, the applicability of these results and findings to other O&G production liquids (e.g., different API gravity), different equipment (e.g., separator design), equipment operating conditions (e.g., separator operating pressure and temperature, tank temperatures), sample collection and analysis methods, and PSM/EOS calculation approaches has not been determined.

1.0 Introduction

Oil and gas production processes include the separation of HC liquids, water, and gas. Hydrocarbon liquids dumped from pressurized separators to atmospheric storage tanks will release or “flash” volatile components (i.e., gas) during the pressure drop. Accurate estimates of flash gas generation (i.e., gas volume and composition) are important for designing efficient storage tank vapor controls (flash gas can be vented to atmosphere if tank emission controls are insufficient, and conservative over-design is not cost-effective) and for developing reliable emission inventories. However, collecting, handling, and analyzing HC liquids under pressure while maintaining sample integrity has been found to be a challenge in the O&G industry. Additional uncertainty stems from complex calculations used to estimate flash gas generation from analytical results for pressurized HC liquids (i.e., the liquids composition). Historical pressurized HC liquids composition data can have high variability where sample collection and analysis imperfections, as well as process measurement and calculation anomalies, are likely contributors to this variability and associated high uncertainty in flash gas generation estimates. A better understanding of the parameters that impact pressurized HC liquids sample collection, handling, and analysis is needed such that compositions measured by analytical labs represent the pressurized liquids that flow from separators to atmospheric storage tanks. A better understanding is also needed of the parameters that impact subsequent calculations of flash gas generation. This project was an important step to address these methodological needs.

This report presents the results of a PHLSA Study conducted by SPL and sponsored by Noble Energy, Inc.

The purpose of the PHLSA Study was to isolate individual variables of the sampling and analytical methods typically used to obtain information regarding the flash potential and makeup of pressurized hydrocarbon liquids and to identify protocols for determining how these samples can be reliably obtained, handled, and analyzed to produce accurate analytical results for practical application in modeling flashing losses. Based on this purpose, the following primary objectives were developed and relied upon to organize the study methodology and Work Plan:

- Evaluate procedures for the collection and analysis of pressurized HC liquids samples, and develop recommendations for best practices to incrementally improve these procedures;
- Evaluate the use of PSM/EOS calculations based on analytical results for pressurized HC liquids samples to estimate the flash gas generated when pressurized HC liquids are dumped to atmospheric storage tanks; and

- Estimate the uncertainties of measured and PSM/EOS calculated FGORs and other parameters.

To accomplish the study purpose and primary objectives, pressurized HC liquids samples were collected at a Test Facility using a variety of sampling procedures over a range of process conditions (e.g., separator temperatures and pressures), and the samples were analyzed using industry standard test methods. During select samples, comprehensive measurements of the temperature, pressure, flowrate, and composition of all separator and storage tank inlet and outlet process flows were conducted for mass balance calculations and to provide data for PSM/EOS calculations. Testing was conducted during the summer (warm storage tank liquid temperatures) and during the winter (cold storage tank liquid temperatures).

This section introduces the PHLSA Study and the study purpose. Section 2 provides background information about O&G production, gas emissions from HC liquids storage tanks, pressurized liquids sampling and analysis procedures, and PSM/EOS calculations. Section 3 presents the study methodology and tasks, and Section 4 presents the study results. Conclusions and recommendations, including recommendations for pressurized HC liquids sample collection and analysis and associated PSM/EOS calculations, are discussed in Section 5. References (e.g., test method citations) are provided throughout the report in the text and in footnotes, and Section 6 includes a summary list of these references. The appendices include supporting information and documents and, for some tasks, more detailed results than presented in this report.

2.0 Background

This section provides information and discussion to support the PHLSA Study methodology, results, and conclusions and recommendations in the following sections. This background discussion includes:

- oil and gas production equipment, operations, process streams, and oil storage tank flash gas control systems at traditional vertical well production facilities, including specific information for the PHLSA Study Test Facility;
- oil storage tank flash gas generation, breathing losses, and working losses, and parameters that impact flash gas generation and emissions;
- pressurized HC liquids sample collection and analysis procedures, and associated operational performance checks; and
- the use of analytical results for pressurized HC liquids samples in PSM/EOS calculations to estimate FGORs.

2.1 Oil and Gas Production Equipment and Operations Overview

The field portion of the study (i.e., pressurized HC liquids samples collection and process measurements) was conducted at a Noble Energy well location located in the DJ Basin. Figure 2-1 is a schematic of the Test Facility, which is typical of a traditional vertical well production facility and primarily consists of a well, three-phase separator, atmospheric storage tanks for condensate and produced water, and a VOC burner to combust condensate tank gas emissions. The well is classified as an oil well by the Colorado Oil and Gas Conservation Commission (COGCC) with a gas-to-oil ratio (GOR) of about 8,000 scf/bbl and produces HC liquids with an API gravity of about 60 degrees, which is a condensate. Test Facility process flows and equipment operation include:

- **Well-to-separator fluids flow**. Produced fluids (gas, condensate, and water) flow from the well through an underground flowline to the three-phase separator during each well cycle. Typically, a well cycle is automatically initiated when the well casing/sales gas pipeline pressure differential exceeds a threshold value. Well cycles can also be manually initiated. The sequence of flows to the separator is residual liquids in the flowline from the previous well cycle followed by gas, condensate, and water from the well tubing. Well fluids flows can cause the separator temperature to change during a well cycle as discussed below. For this testing, a well cycle was determined to be completed after the last separator-to-tank HC liquids dump (discussed below).

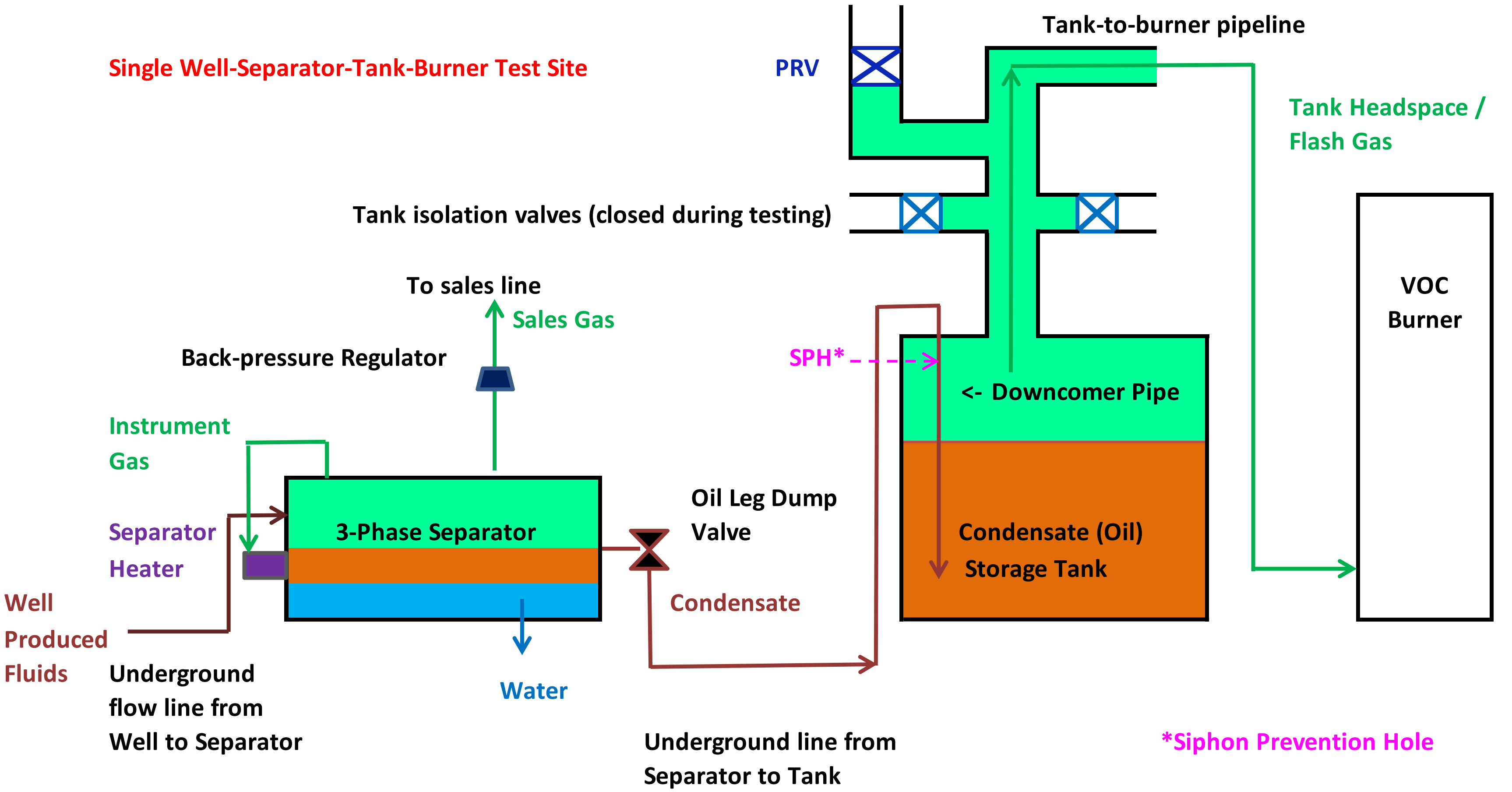

Figure 2-1. Test Facility schematic.

- **Separator fluids flow**. The separator outputs are gas to the sales pipeline, condensate to the condensate storage tank through the oil leg dump valve, and produced water to a water storage vessel through the water leg dump valve. Water production from this well was a small fraction (i.e., ~ 10%) of the condensate production, the flash gas-to-water ratio (FGWR) for the pressurized water was extremely low (i.e., FGWR was less than 3 scf/bbl), and the water storage vessel was not connected to the condensate storage tank vapor control system (i.e., the tank-to-burner pipeline and VOC burner); thus, the produced water was a minor focus of the testing (i.e., select samples were collected and analyzed to document the FGWR).
- **Separator operating pressure**. During normal operation, the separator operating pressure equilibrates with the sales gas pipeline pressure. A back-pressure regulator was installed on the sales gas line for this testing to allow control of the separator pressure. If the sales gas line pressure was less than the target testing pressure, the back-pressure regulator maintained the separator at the target testing pressure. If the sales line pressure was greater than the target testing pressure, gas from the separator was bypassed to a compressor (not shown in Figure 2-1) to boost the gas to the sales line pressure and maintain the separator at the target testing pressure.
- **Separator heater operation**. Pressurized gas from the separator headspace supplies the instrument gas system, and is used to fuel the separator heater during cold weather to prevent freezing of separator liquids. The separator heater operation is not a static process and separator temperatures can change during a well cycle when well fluids at a temperature different than the separator temperature enter the separator and the heater cycles on and off accordingly. Normally, the separator heater operation causes the separator pressure to drop between well cycles; however, during the testing the separator heater was fueled with instrument gas supplied by other separators at the production facility in an effort to maintain a constant separator pressure. The impact of the separator heater operation on pressurized HC liquids sample collection considerations and separator operation during the testing are further discussed throughout this report.
- **Separator-to-tank dump fluids flow**. As liquids flow from the well, the HC liquids level in the separator rises and spills over a weir to an oil box. When the oil box level reaches a prescribed level, the oil leg dump valve float initiates the dump valve opening and HC liquids flow from the oil box to the underground pipeline to the storage tank. The rapid pressure drop across the dump valve causes volatile components to flash, and flow to the storage tank is a mix of residual HC liquids in the underground pipeline (from the previous well cycle), new "post-flash" HC liquids from the oil box, and the flash gas. At the Test Facility, these fluids flow into the tank through a "downcomer" pipe and the majority of the fluids

enter the tank about one foot above the tank bottom and mix with the tank liquids. There is a small (i.e., ~ 3/8 inch) SPH at the top of the downcomer and a fraction of the produced fluids flows directly into the tank headspace. Between separator dumps, the underground pipeline pressure equilibrates with the tank headspace gas pressure through the SPH. Additional considerations for the separator-to-tank dump fluids flow include:

- **Separator HC liquids history and composition**. The HC liquids that spill over the weir and are dumped to the separator are a mixture of new HC liquids (i.e., produced during the well cycle) and residual HC liquids (i.e., HC liquids that remained in the separator from previous well cycles). The proportion of the two HC liquids in the separator dump HC liquids is not known, and this proportion could impact the equilibrium pressure and temperature, and composition of the HC liquids from the separator dump. For example, the new HC liquids could be produced into a separator operating at 250 psig to push gas down the sales gas pipeline, whereas the residual HC liquids could have been at 150 psig because the previous well cycle was at this pressure and/or fueling the separator heater could have reduced the separator pressure. Under such circumstances, the true dump HC liquids equilibrium pressure is likely an unknown value between 150 and 250 psig. As discussed throughout this report, the true dump HC liquids equilibrium pressure impacts evaluations of the validity of pressurized HC liquids samples and PSM/EOS calculations of flash gas emissions based on HC liquids sample composition.
- **Tank liquid and gas temperatures**. Depending on the time of the year and the day, the tank bottom liquids can be colder or hotter than the separator dump fluids and the ambient and tank headspace gas. The ambient and tank headspace gas temperatures both tend to increase during the daylight hours, and the tank headspace temperature is strongly affected by direct sunlight (i.e., no clouds) and radiative heating of the tank surface. Conversely, the tank liquids have a much greater mass, and the liquids seasonal and diurnal temperature changes are typically much slower than the gas temperature changes.
- **Flash gas generation**. The flash gas generation (i.e., FGOR and flash gas composition) primarily depends on the HC liquids composition, separator pressure and temperature, and final post-flash HC liquids temperature and pressure (refer to Section 2.2 for additional detail). If the final post-flash HC liquids temperature (i.e., tank bottom temperature in the vicinity of the downcomer outlet) is greater than the temperature of the fluids flowing from the separator, then there could be a secondary flash in the tank bottom as the flowing liquids heat up and release volatile compounds. Conversely, if the final post-flash liquids temperature is less than the temperature of the fluids flowing from the separator, then some flash gas could condense in the tank bottom when the flowing fluids cool. Adiabatic flash calculations and the estimated temperature of the

  underground separator-to-tank pipeline suggest that fluids entering the tank will be relatively cold (e.g., 40 – 50°F).

  - **Tank side-fill option**. Storage tanks can also operate using a side-fill where the HC liquids and gas from the separator dumps enter the tank near the top into the tank headspace gas. This would change the post-flash temperature and the flash gas generation rate. This configuration was not used at the Test Facility.

- **Storage tank pressure and vacuum control**. A PRV is installed on the storage tank roof and set to release gas at a pressure below the maximum design operating pressure of the tank. The PRV release pressure setting was 14 oz/in^2 during the testing. The tank vacuum level was controlled by the thief hatch installed on the roof, and the thief hatch allowed air inflow when the tank pressure was sub-atmospheric (e.g., at night when the tank headspace gas cooled).

- **Tank-to-burner pipeline gas flow**. Gas entering the tank bottom (i.e., flash gas) rises through the tank liquids to the tank headspace to mix with the existing tank headspace gas, and the increase in tank headspace gas pressure causes headspace gas to flow through the tank-to-burner pipeline to the VOC burner to be combusted. The headspace gas is a mixture of the flash gas from the recent well cycle, flash gas from previous well cycles, HCs volatilized as breathing losses (including some HCs heavier than typical flash gas), and often a small amount of air drawn in through the vacuum relief device when the temperature drops (e.g., at night). At the Test Facility, the test tank for the well was isolated by valves from other tanks associated with other wells.

2.2 Atmospheric Storage Tank Gas Generation: Flash Gas, Breathing Losses, and Working Losses

Vapors are released from HC liquids storage tanks due to flash gas generation, and breathing and working losses.

Flash gas generation, which is represented by the FGOR value, depends on the well fluids composition (i.e., HC liquids with higher concentrations of C4 and lighter compounds tend to produce more flash gas), and the operating pressures and temperatures of the separator and storage tank. Figure 2-2 shows the following general impacts of separator and tank pressures and temperatures on flash gas generation:

- FGOR increases with separator pressure (P_{sep}) because larger fractions of volatile compounds partition to the liquid phase in the separator at higher pressures, and subsequently flash in the tank;

- FGOR decreases with separator temperature (T_{sep}) because larger fractions of volatile compounds partition to the gas phase in the separator at higher separator temperatures;
- FGOR decreases with tank pressure (P_{tank}) because smaller fractions of volatile compounds partition to the gas phase in the tank at higher pressures. The range of possible pressures at the bottom of the tank (where separator fluids enter the tank through the downcomer) is relatively smaller than the typical ranges for P_{sep}, T_{sep}, and T_{tank}; thus, P_{tank} has a smaller impact on the FGOR than these other parameters; and
- FGOR increases with tank temperature (T_{tank}) because larger fractions of volatile compounds partition to the gas phase in the tank at higher temperatures.

The impact of these operating parameters on FGOR is further discussed in Section 4.7.

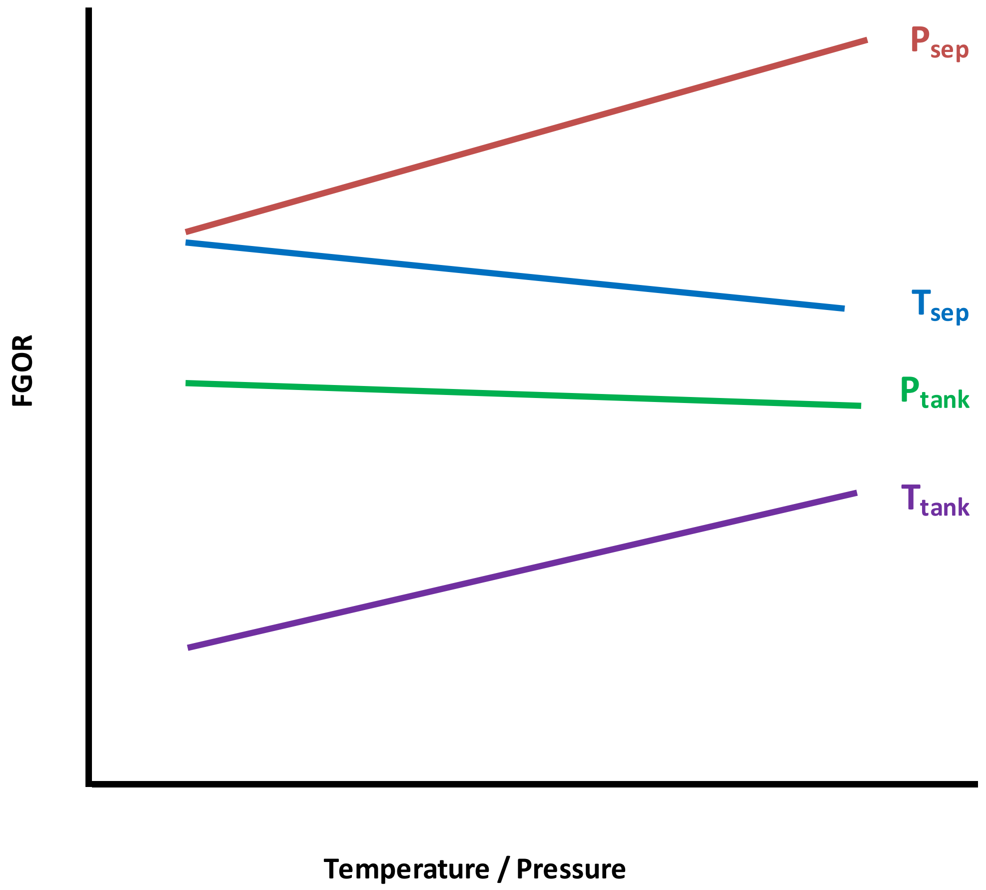

Figure 2-2. Impact of separator and tank pressures and temperatures on flash gas generation.

2.3 Pressurized Hydrocarbon Liquids Sample Collection and Analysis Methods

2.3.1 Sample Collection Methods

Pressurized HC liquids samples were collected using two methods from GPA Midstream Standard 2174-14, "Obtaining Liquid Hydrocarbons Samples for Analysis by Gas Chromatography."

- Floating Piston/Constant Pressure Cylinder Method; and
- Water Displacement/Constant Volume Cylinder Method.

These sample collection methods were selected for the study because they are the predominant methods used in the O&G industry. A primary difference between the two methods is that the sample liquid contacts another liquid (typically water) during CV cylinder sampling, whereas in a CP cylinder the sample liquid only contacts the stainless-steel walls of the cylinder and a greased piston seal. Questions about the two sampling methods include whether sample liquid components partition to the CV cylinder liquid by a significant amount, and whether the CP cylinder seal grease interacts with and absorbs heavy HCs by a significant amount. CV cylinders, in general, cost about an order of magnitude less than CP cylinders and are smaller and lighter, and thus are easier to handle and transport.

Figure 2-3 is a schematic of a floating piston/constant pressure cylinder sampling system. The CP cylinder has a movable piston with the sample on the product side and an inert pressurizing gas, helium (He) for this project, on the pre-charge side. Argon and nitrogen are alternative pressurizing gases for this sample collection method. These alternatives were not used for this study because they could be detected in the sample if the piston seal leaks. The piston is sealed by o-rings, Teflon rings, or other means to prevent leakage between the piston and the cylinder wall. All wetted components must be non-reactive with the sample material, the inert gas, and any cleaning solvents. Prior to sample collection, the sample probe and sample line are purged with pressurized HC liquids to remove air and any other residual material. The pressurized HC liquids sample is collected through a sample line connected to a sample probe by releasing the inert gas on the pre-charge side at a controlled rate until approximately 80% fill is indicated.

The friction of the piston seals presents a challenge when attempting to control sample collection rate. Several means of sample collection rate control were used during the study. One utilized a back-pressure regulator as a controller for the release of inert gas. The other used an automatic sampler pump to push the sample into the cylinder at a consistent rate. Both methods provide more precise control than manually throttling the cylinder relief valve.

Figure 2-4 is a schematic of a water displacement/constant volume cylinder sampling system. The primary components of this system are a double valve sample cylinder pre-filled with water and a vessel to measure the volume of displaced liquid (e.g., a graduated cylinder). Prior to sample collection, the sample probe and sample line are purged with pressurized HC liquids to remove air and any other residual material. The pressurized HC liquids sample is collected through a sample line connected to a sample probe. The sample cylinder is vertically orientated and sample collection is conducted by releasing the water, which is displaced by pressurized HC liquid, from the cylinder bottom at a controlled rate. The sample collection rate is measured by timing the change in the volume in the displaced water vessel until approximately 80% fill is indicated. The source valve is closed and about 50% of the residual water is removed to allow safe and legal transportation. To assist the timing of sample collection rate, the graduated cylinder used to collect displacement fluid was pre-marked at 20% fill levels with a marker.

Ethylene glycol is an alternative pre-charge liquid for this sample collection method. This alternative was not used for this study.

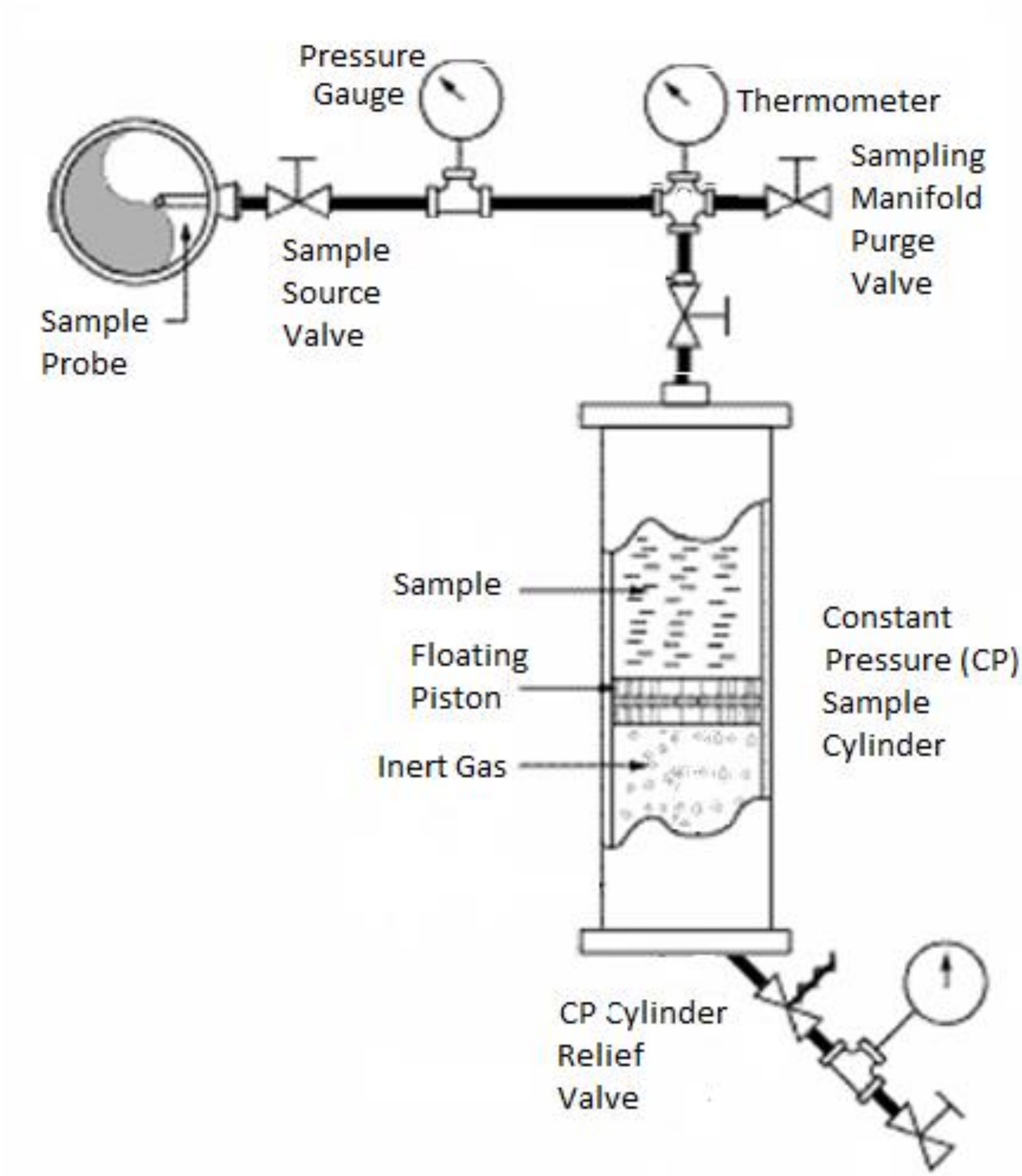

Figure 2-3. Floating piston/constant pressure cylinder sampling system with sampling manifold.

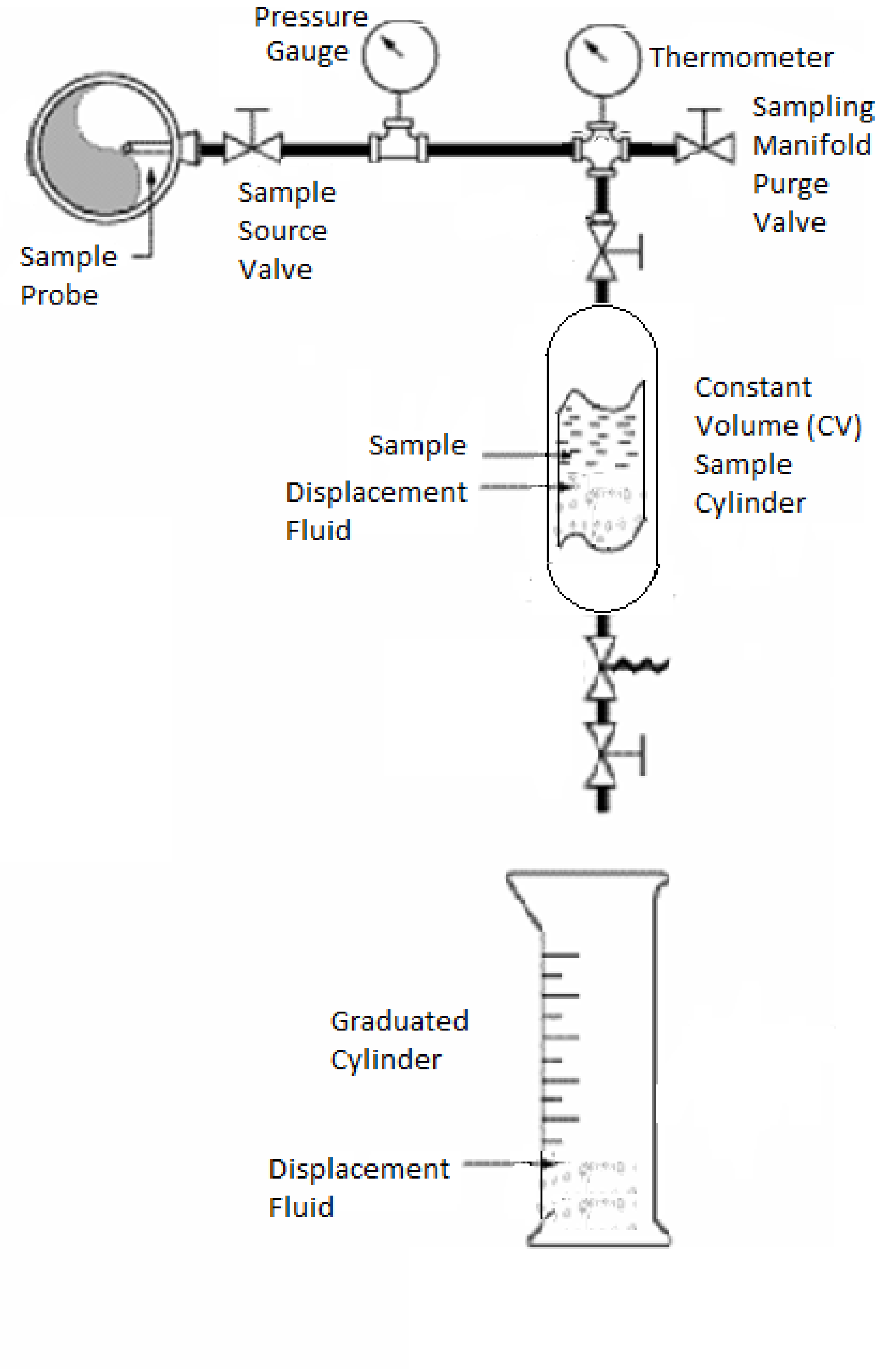

Figure 2-4. Constant volume cylinder using water displacement with sampling system manifold.

2.3.2 Sample Analysis Methods

The majority of the pressurized HC liquids samples collected during this study were analyzed using two GPA Midstream methods.

- GPA Standard 2186-14 “Method for the Extended Analysis of HC Liquids Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography,” and
- GPA Standard 2103-03 “Tentative Method for the Analysis of Natural Gas Condensate Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography.”

These sample analysis methods were selected for the study because they are commonly used in the O&G industry, and the compositional analysis results are inputs to PSM/EOS FGOR and P_{BP} calculations. Flash liberation analysis is another common analytical method for pressurized HC samples, and was used to analyze select samples. For a flash liberation analysis, a pressurized oil sample is flashed in the lab under controlled conditions and the resulting liquid and gas volumes are measured and analyzed. The following provides overviews of these analytical methods and notes specific procedures and modifications used by SPL.

GPA 2186 (Extended Liquid Analysis)

This method covers the compositional analysis of natural gas liquid streams where precise physical property data of the C6+ fraction are acquired by combining the analysis described in GPA Standard 2177-13 “Analysis of Natural Gas Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography“, with an extended analysis of the C6+ components using capillary gas chromatography according to GPA 2186. This method is applicable for de-methanized mixes through light gasoline fractions that may contain components such as nitrogen, carbon dioxide and/or HC complexes (C1–C14) that fall within the ranges shown in GPA 2186. Table 2.1 is identical to the tables in the scopes of GPA 2177 and GPA 2186, and lists the components and compositional ranges for those methods. At this time, GPA 2186 does not contain specific details for components heavier than heptanes.

Table 2-1. Components and Concentration Ranges for GPA 2186

Component	Concentration Range (Mole %)
Nitrogen	0.005 – 5.0
Carbon Dioxide	0.005 – 5.0
Methane	0.001 – 5.0
Ethane	0.001 – 95.0
Propane	0.001 – 100.0
iso-Butane	0.001 – 100.0
n-Butane (may include 2,2-Dimethylpropane)	0.001 – 100.0
iso-Pentane	0.001 – 15.0
n-Pentane	0.001 – 15.0
Hexanes	0.001 – 15.0
Heptanes+	0.001 – 5.0

Components in the HC liquids mixture are physically separated by gas chromatography and compared to calibration data previously obtained under identical operating conditions on a mixture of known composition. Two separate fixed volumes of sample in the liquid phase are isolated by the sample inlet valves. Each volume is injected into its corresponding chromatographic system, effectively splitting the analysis into two sections. The first is a packed column with a Thermal Conductivity Detector (TCD) and the second is a capillary column with a Flame Ionization Detector (FID). These two chromatographic systems are in the form of two different instruments.

The first sample volume is injected onto the packed column/TCD instrument, and analyzes nitrogen through n-pentane, with the C6+ components grouped as a single composite peak at the beginning of the chromatogram. This is accomplished by using a short precut column in front of a longer analytical column, and back-flushing the short column when n-pentane has entered the longer analytical column.

The second sample volume is injected onto the capillary column extended/FID instrument. Major components of interest (normal-paraffins and aromatics) are calibrated in a similar manner to the TCD instrument. The FID detector is a mass sensitive device, and therefore non-calibrated minor peak areas are used to calculate mass fractions. The non-calibrated peaks area percents are calculated as weight fractions. The calibrated peaks weight fractions and the non-calibrated peak weight fractions are summed and then normalized to 1.000000.

Because the molecular weight of the C6+ fraction is an unknown in the TCD analysis, the molecular weight and density are calculated for the C6+ from the FID portion of the analysis and then used in the calculation of weight percents for the TCD compounds. All other compounds from the TCD analysis use the molecular weights and densities from GPA Standard 2145-16 "Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas Industry." The weight percentage of the TCD compounds are calculated, and the C6+ weight fractions from the FID portion are multiplied by the weight percent of the C6+ in the TCD portion.

SPL GPA 2186M (Extended Liquid Analysis - modified)

This method is analytically the same as the GPA 2186 method described above; however, the results are not normalized. Rather, any difference in the compositional total from 100% is added to the C10+ component. Normalization is the mathematical adjustment made so that the analysis compositional totals equal 100%. This is accomplished by dividing each unnormalized component value by the unnormalized total, and multiplying by 100. The illustrative example in Table 2-2 shows the effect of adding the difference to the "plus" fraction (C10+ by Difference) rather than using normalization. As illustrated here, all values except the "plus" value are unchanged and the "plus" value receives all of the difference (i.e., 100% - unnormalized total).

Table 2-2. GPA 2186 Normalization / GPA 2186M Unnormalization Comparison

Component	Unnormalized Values	Normalized Values (GPA 2186)	C10+ by Difference (GPA 2186M)
Carbon Dioxide	0.138	0.211	0.138
Nitrogen	0	0.000	0
Methane	2.062	3.158	2.062
Ethane	3.026	4.635	3.026
Propane	3.314	5.076	3.314
iso-Butane	1.447	2.216	1.447
n-Butane	4.569	6.999	4.569
iso-Pentane	4.744	7.267	4.744
n-Pentane	6.716	10.287	6.716
Hexanes	9.122	13.973	9.122
Heptanes	10.254	15.707	10.254
Octanes	7.229	11.073	7.229
Nonanes	4.592	7.034	4.592
Decanes +	8.072	12.364	42.787
Total	**65.285**	**100.000**	**100.000**

GPA 2103

GPA 2103 TCD Analysis

This analysis is intended for mixtures containing greater than 20% C6+ (or greater than 5% C7+) fractions. Table 2-3 lists the components and compositional ranges for this method. The 2103 TCD analysis is similar to the 2177 chromatographic analysis, except that the C6+ is back-flushed out to vent instead of onto the column; therefore, this fraction is ignored in the chromatographic analysis. The physical properties of the C6+ fraction are determined by direct measurements.

SPL GPA 2103M-C10 (Extended Condensate Analysis)

GPA 2103M requires several ancillary analytical methods to directly measure the physical properties to perform the calculations needed to complete the overall analysis. SPL uses the following additional analyses required to calculate the C10+ fraction:

- Physical Shrinkage determination (Field method is documented in API Manual of Petroleum Measurement Standards (MPMS) Chapter 20);
- ASTM D-2001-07 (2012) “Standard Test Method for Depentanization of Gasoline and Naphthas“;
- ASTM D86M-16a “Standard Test Method for Distillation of Petroleum Products and Liquid Fuels at Atmospheric Pressure”;
- ASTM D5002-16 “Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer”;
- Molecular Weight by Cryette, methodology based on manufacturer user’s manual;
- ASTM D2887M (High Temperature Simulated Distillation) “Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography”; and
- GPA 2186-14 “Tentative Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography”.

Table 2-3. Components and Concentration Ranges for GPA 2103

Component	Concentration Range (wt%)
Nitrogen	0.005 – 5.000
Carbon Dioxide	0.005 – 5.000
Methane	0.001 – 40.000
Ethane	0.001 – 15.000
Propane	0.001 – 15.000
iso-Butane	0.001 – 15.000
n-Butane (may include 2,2-Dimethylpropane)	0.001 – 15.000
iso-Pentane	0.001 – 15.000
n-Pentane	0.001 – 15.000
Hexanes	0.001 – 50.000
Heptanes+	5.000 – 80.000

Physical Shrinkage Determination

This method covers the determination of the physical volume shrinkage of pressurized crudes and condensates from meter conditions to stock tank conditions at atmospheric pressure and ambient temperature. An aliquot of the sample is physically flashed to atmospheric pressure. Approximately 200 cubic centimeters of liquid sample is displaced by water into a known volume piston cylinder from the pressurized sample cylinder at ambient temperature and a pressure slightly above sampling conditions. The sample is slowly flashed from the top of the piston cylinder and the remaining liquid portion is collected and measured in a graduated burette. The amount of gas flashed is measured and a physical shrink factor (i.e., post-flash HC liquids volume/pre-flash HC liquids volume) is calculated for the sample material.

ASTM D-2001 Depentanization

This test method covers the removal of pentanes and lighter HCs from gasolines, naphthas, and similar petroleum distillates to prepare samples suitable for further analysis. This test method determines the volume percent of bottoms remaining after depentanization. An aliquot of sample is distilled into an overhead (C5 and lighter) fraction and a bottoms (C6+) fraction or "cut." The volume of bottoms is measured and the C6+ volume percent, based on the charge, is calculated as described in the ASTM D2001 methodology.

ASTM D86M Modified Atmospheric Distillation

This distillation process is performed in the D86 manual distillation apparatus, and the procedure is modified to distill only the C6+ bottom cut from the ASTM D2001 depentanization process described above. Rather than measuring the entire boiling point range of the sample material, a C10 cut off temperature is used to produce a bottom cut of predominately C10+ components.

ASTM D5002 Density by Densitometer

This test method covers the determination of the density, API gravity, and specific gravity of petroleum distillates and viscous oils that can be handled as liquids with vapor pressures below 14.5 psi and viscosities below approximately 15,000 centistokes at the temperature of the test. A small volume of sample liquid is introduced into an oscillating sample tube and the change in oscillating frequency cause by the change in the mass of the tube is used in conjunction with calibration data to determine the sample density. This procedure is performed on the post-flash liquid volume from the shrinkage determination, the C6+ cut from the depentanization, and the C10+ cut from the additional D86 modified distillation.

Molecular Weight by Cryette

This test method covers the calibration and operation of a cryette for the determining the molecular weight of an unknown non-aqueous sample by freeze point depression. Prior to the determination, the instrument is calibrated with a solvent blank and a known calibration standard. Samples (or a batch of samples) are then analyzed. A solvent blank and a calibration standard are then re-analyzed to verify that the calibration has not shifted.

GPA 2103M-C100+ (Modified Extended Condensate Analysis)

The GPA 2103 C10+ analysis listed above may implement an additional modification to extend values out to hectanes and higher HCs (C100+) values. The ASTM D2887M procedure listed below would be performed in addition to those listed above.

ASTM D2887M High Temperature Simulated Distillation

This chromatographic method utilizes an inlet column and a capillary column, both of which are subject to a temperature program. An FID is used with a data acquisition system operating in the slice mode. A calibration mixture is used to develop a retention time versus boiling point curve. A solution of the reference HC liquids is used to determine the response factor. Solvent injections are made and the resulting signal is subtracted from both the response factor standard and the sample chromatogram. Finally, the sample solution is injected and, with the use of the response factor, the amount of sample recovered is calculated. After converting the retention times of the sample slices to temperature, the boiling point distribution can be calculated up to the recovered amount.

Because the FID is essentially a mass sensitive device, the D2887 analysis chromatogram area percent is equivalent to the weight percent of each carbon grouping (sample sliced by carbon number). The procedure is modified to allocate the weight percent for each carbon number grouping to the total C10+ determined from the GPA 2186 extended liquid analysis.

SPL Flash Liberation Method

A Sprague pump connected to the bottom of a CV sample cylinder (or helium is used to move the piston for a CP cylinder) is used to transfer a portion of the sample from the top of the sample cylinder into a smaller (75 ml) water-filled cylinder. This cylinder is attached to a manifold in a heated bath and allowed to equilibrate. An evacuated cylinder is attached to the manifold downstream of a gas flow meter (Alicat) outside of the bath. The Alicat laminar flow meter measures the flashed gas, and the liquid residue is collected and measured to calculate shrinkage factor. The shrinkage and flash gas are used to calculate the FGOR. The flash gas sample is analyzed by GPA 2286-14 “Method for the Extended Analysis for Natural Gas and Similar Gaseous Mixtures by Temperature Program Gas Chromatography”. The liquid residue is analyzed by GPA 2186M. The liquid and gas analyses are recombined using the determined FGOR to yield the pressurized condensate analysis.

2.3.3 Operational Performance Checks for Pressurized Hydrocarbon Liquids Sample Collection and Analysis

The collection, transport, and analysis of pressurized HC liquids samples is a complex process. Non-equilibrium process streams, sample collection anomalies, sample leakage and loss of volatile species, analytical biases and errors, and other factors can contribute to anomalous analytical results for HC liquids composition. The intent of an OPC is to evaluate whether the composition of a pressurized HC liquids sample determined from laboratory analysis is a reasonable representation of the process stream composition at gas/liquid equilibrium. For the purposes of this study, an OPC should provide confidence that a PSM/EOS calculated flash gas volume (i.e., FGOR) and composition, based on analytical results for a pressurized HC liquids sample, is a reasonable estimate of the actual flash gas generation. FGOR is directly measured by a flash liberation analysis, and an appropriate OPC would need to correlate with FGOR results. Producing representative HC liquids composition results generally requires collecting a sample from a process stream at or near gas/liquid equilibrium; minimizing sample distortion during collection, transportation, and lab procedures (i.e., lab handling of sample); accurate sample analysis, and QA-checked calculations and final results.

Ideally, an OPC would: 1) consistently identify representative pressurized HC liquids samples as representative (based on some measurable criteria) and consistently identify non-representative pressurized HC liquids samples as non-representative; and 2) be relatively simple and practical to implement. Operational performance checks that were evaluated during this study included the following that are currently used by industry in varying degrees:

- **Bubble point pressure check by PSM/EOS calculation**. The intent of this OPC is to provide an indication of the viability of the pressurized HC liquids sample collection, transport, lab handling, and analysis processes. It is conducted by calculating a pressurized HC liquids P_{BP}, at the sample collection temperature, using the analytical results for a sample and a PSM/EOS software program. This pressure is compared to the P_{SC}, with P_{BP}/P_{SC} close to 1.0 historically considered an indication that the pressurized HC liquids sample is representative of the separator liquid (at gas/liquid equilibrium) at the time the sample was collected and that the analytical results are acceptable.
- **Lab densitometer measurement of sample bubble point pressure**. The intent of this OPC is to provide an indication of the viability of the pressurized HC liquids sample collection, transport, and lab handling processes. The densitometer is calibrated at the sample collection temperature over a density range extending above and below the density of the fluid under test. The pressurized HC liquids sample is pressurized at least 200 psi above the P_{SC} and an aliquot is transferred to the densitometer. The pressure is slowly decreased, and the density slowly drops until the sample reaches its P_{BP} and the density drops drastically and the pressure bounces (begins to climb and then stabilizes). P_{BP}/P_{SC} is calculated and values near 1.0 are considered an indication that the pressurized HC liquids sample is representative of the separator liquid (at gas/liquid equilibrium) at the time the sample was collected. Figure 2-5 is an example densitometer output with density on the left of the screen and pressure on the right of the screen.

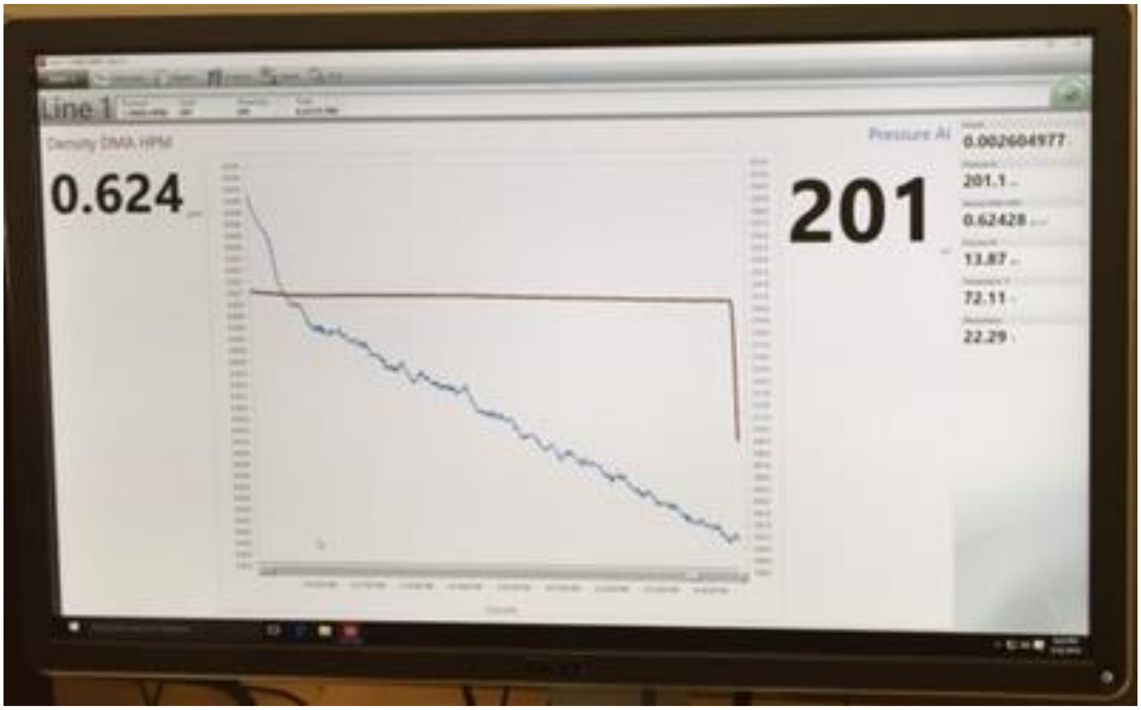

Figure 2-5. Pressurized densitometer bubble point determination.

- **Initial Pressure Test measurement of sample bubble point pressure**. The intent of this OPC is to provide an indication of the viability of the pressurized HC liquids sample collection, transport, and lab handling processes. An IPT is typically conducted prior to analysis. The pressure of a sample, maintained at the sample collection temperature, is raised above the P_{SC} (e.g., by using high pressure He for CP cylinders and pressurized water for CV cylinders). The pressure is then slowly reduced until the pressure stabilizes (i.e., stops decreasing and begins to increase slightly). The stable pressure indicates that bubbles of flash gas are forming, and this pressure is a measure of the sample P_{BP} (i.e., IPT P_{BP}). IPT P_{BP}/P_{SC} is calculated and values near 1.0 are considered an indication that the pressurized HC liquids sample is representative of the separator liquid (at gas/liquid equilibrium) at the time the sample was collected. If the lab temperature (T_{Lab}) during the IPT differs from the T_{SC}, the IPT P_{BP} is adjusted to the T_{SC} using PSM/EOS calculations: IPT P_{BP} at T_{SC} = IPT P_{BP} at T_{Lab} * (PSM/EOS P_{BP} at T_{SC}/PSM/EOS P_{BP} at T_{Lab})
- **Comparing HC liquids density measurements conducted at the production facility by a Coriolis meter and in the lab with a densitometer** with large differences between the two density measurements suggesting the HC liquids sample may have been compromised during collection, transport, lab handling and/or the density measurements.

For all the OPCs, it is imperative that the temperature and pressure measurements during sample collection and during lab procedures utilize accurate and calibrated instruments.

There are numerous reasons why a sample P_{BP} determined from a PSM/EOS calculation, IPT, or densitometer measurement can differ from the P_{SC}. These reasons can include bias/errors during the sample collection, transport, and analysis process, and/or other factors including:

- Bias/error in the sample collection pressure measurement;
- Bias/error in the sample collection temperature measurement;
- Bias/error in the pressure and/or temperature measurements during lab procedures (e.g., an IPT);
- Separator pressure and temperature history prior to well cycle. If the separator pressure and/or temperature prior to the well cycle are different than during the well cycle and the sample collection, then the sample could be a mix of new and residual HC liquids with a different P_{BP} than the P_{SC}. For example, the separator HC liquids equilibrium pressure could be lower than the separator pressure during the well cycle and sample collection because the separator was at a lower pressure during a prior well cycle (e.g., the gathering line pressure increased in the interim) and/or due to separator heater operation; that is, in sum, the separator liquid and gas were not in equilibrium at the separator operating pressure and temperature when the pressurized HC liquids sample was collected;
- Separator pressure and/or temperature variation during sample collection (i.e., pressurized HC liquids composition changing during sample collection);
- Sampling or analytical processes that introduce atmospheric air (nitrogen measured in subsequent analysis);
- Bias/error in the analytical process; and
- PSM/EOS calculation assumptions that shift the phase envelop from the true equilibrium curve (e.g., PSM/EOS calculations are impacted by C10+ properties, selected EOS, and other parameters).

The impacts of these external factors emphasize the need for **accurate separator temperature and pressure measurements, control of process conditions, and understanding of PSM/EOS calculations.** These issues are further discussed throughout the report.

2.4 Process Simulation Model/Equation of State Calculations of FGOR and Flash Gas Composition

Process Simulation Model/Equation of State software programs are used extensively in the O&G industry. For air permitting, they are used to estimate flash gas generation in atmospheric storage tanks. Four commonly used commercially available PSM/EOS programs were used in this study to calculate flash gas generation estimates. Peng-Robinson is a commonly used EOS, and is the only option for one of the programs used in the study; thus, the Peng-Robinson EOS was used for the calculations by all four PSM/EOS programs for this study. Steady state equilibrium models were used in this study, and this approach is consistent with standard industry practice for air permitting models. Because flash gas generation in atmospheric storage tanks and gas flow from the tank to a burner are not steady state processes, a dynamic model (i.e., a tank-to-burner gas flow rate hydraulics model that considers the flash gas generation rate and composition, tank headspace volume, tank-to-burner pipeline gas flow capacity, and VOC burner capacity), in conjunction with a PSM/EOS equilibrium model, would improve estimates of storage tank flash gas flow rates (and more accurately determine storage tank vapor control system capacity requirements). Such a dynamic model was beyond the scope of this project.

EOS models are thermodynamic equations that relate changes in process stream variables such as pressure, volume, and temperature to changes in the process stream physical state and composition. For this study, the pressure, volume, temperature, and composition of a pressurized HC liquids sample (collected and analyzed as described in Section 2.3) are input into the PSM/EOS. The pressure and temperature of the atmospheric storage tank are also PSM/EOS inputs. The model calculates an estimated change in pre-flash to post-flash liquids volume (shrinkage), the flash gas volume relative to post-flash liquids volume (i.e., the FGOR), and the flash gas composition. The composition of the post-flash liquid is also calculated.

EOS Phase Envelope Diagrams

Figure 2-6 is a Phase Envelope for one of the study samples, and is a graphic representation of the EOS thermodynamic model output. The Y-axis shows pressure (psia) and the X-axis shows temperature (°F). The red line is the Bubble Point curve and the blue line is the Dew Point curve. To the left of and above the red line is the Liquid Region, and a HC mixture in this area is 100% liquid. For a HC mixture in the Liquid Region, as the pressure is decreased and/or the temperature is increased, vapor will first form at the red Bubble Point line; thus, a liquid on the Bubble Point line is in equilibrium with the process gas at those conditions. To the right of and below the red line is the 2-Phase Region, and a HC mixture in this region has both liquid- and gas-phase components. If the temperature and pressure during the collection of a pressurized

HC liquids sample are not within an acceptable tolerance of this red line, then it is likely that the sampling and analysis results are not representative of an equilibrium fluid at those conditions. For example, the green star shows the sample conditions (i.e., sample collection temperature and pressure) and proximity to the red line. In this case, the sample conditions are almost centered on the line, indicating that the measured pressurized HC liquids sample composition is likely representative of a liquid in equilibrium with the process gas at those conditions.

Also shown is the Vapor Region to the right of and below the blue Dew Point curve. For gas sample compositions, the same general data review process applies. Sample collection temperature and pressure should be within an acceptable tolerance of this line. The red diamond in Figure 2-6 is the Cricondenbar Point, and represents the highest pressure at which a 2-phase mixture can exist. The blue square is the Cricondentherm Point and represents the highest temperature at which a 2-phase mixture can exist. The yellow dot is the Critical Point and mixtures above this temperature and pressure are supercritical fluids.

Separator gas and liquid are assumed to be at equilibrium in the separator during sample collection (i.e., the sample liquid is saturated with gas). Therefore, it is imperative to minimize pressure and temperature changes during the sample collection process. Changes in pressure or temperature can cause phase change. If the pressure drops or the temperature increases during sample collection, then the sampling conditions enter the 2-Phase region. That is, the sample drops below its Bubble Point pressure, gas bubbles form in the liquid, and the subsequent analysis of this fluid have excess lighter (i.e., higher vapor pressure) components and the resulting plot would show the green star in the 2-Phase Region.

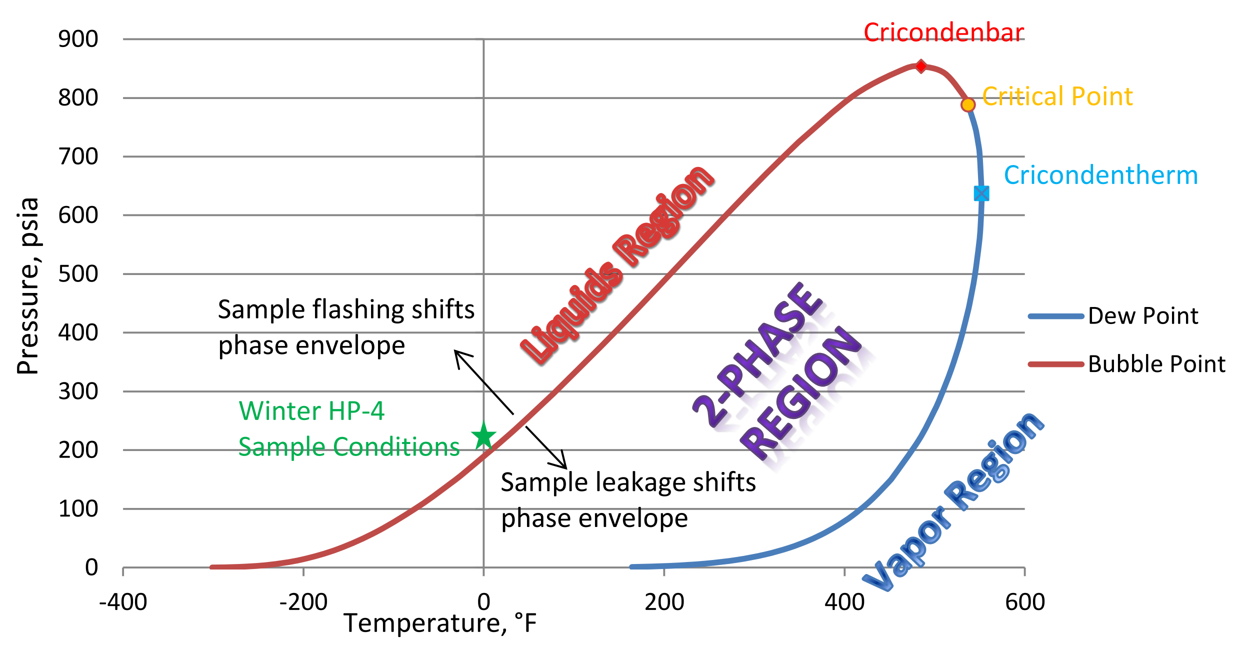

Figure 2-6. Phase envelope for a PHLSA Study condensate sample.

In contrast, if the sample cylinder leaks, lighter HCs gasify more rapidly than heavier HCs and therefore have more losses than the heavier compounds. The subsequent analysis of this fluid will cause the red line to be lower, and the green star would be further into the Liquid Region.

3.0 PHLSA Study Methodology

To address the project objectives, the PHLSA Study methodology included:

- Development of a NIST-traceable CRM (i.e., a gravimetrically blended condensate standard with low compositional uncertainty) that was used as a calibration standard and as the basis for evaluations of laboratory methods;
- Evaluation of laboratory sample handling procedures and analytical methods (e.g., GPA 2103M, GPA 2186M, flash liberation);
- Evaluation of sample collection parameters (e.g., sample cylinder type and sample collection rate, location, and initiation time);
- Evaluation of OPCs for pressurized condensate sample collection and analysis results;
- Collection and analysis of pressurized condensate samples over a range of separator operating conditions;
- Comprehensive monitoring of separator and tank pressures, temperatures, and flowrates during the well cycles associated with the collection of the pressurized condensate samples;
- Calculations of atmospheric storage tank mass balances and “measured” FGORs from the monitoring data;
- PSM/EOS calculations of FGORs based on the pressurized condensate compositions; and
- Statistical and uncertainty analyses of primary results.

This section covers this methodology and includes:

- A discussion of modifications to the Test Facility to facilitate the PHLSA Study (Section 3.1);
- A project overview and a discussion of the primary project tasks (Section 3.2). This section includes:
  - An overview of the instrumentation used to measure key process parameters at the Test Facility. These measurements were used to calculate atmospheric storage tank mass balances and measured FGORs; and
  - A summary of the data analysis including uncertainty analyses.
- A description of the methodology used to evaluate the process simulation models including sensitivity analyses to determine which PSM/EOS inputs have the largest impact on calculated FGORs (Section 3.3).

3.1 Test Facility Modifications

Modifications were made to the Test Facility to facilitate the PHLSA Study. These equipment and operating modifications were primarily to allow isolation and control of key operating parameters, and included:

- Instrument gas from other separators at the production facility was piped to the separator heater (refer to Figure 2-1). This allowed independent control of both the separator temperature and pressure during cold weather testing; that is, the separator heater could be operated without using the separator headspace gas as heater fuel and reducing the separator pressure. Without this modification, the separator pressure would steadily drop between well cycles, and this would be normal operation for most separators during cold weather operation.
- A back-pressure regulator was installed on the sales gas line for this testing to allow control of the separator pressure independent of the sale gas line pressure (refer to Figure 2-1). If the sales gas line pressure was less than the target testing pressure, the back-pressure regulator maintained the separator at the target testing pressure. If the sales line pressure was greater than the target testing pressure, gas from the separator was bypassed to a compressor to boost the gas to the sales line pressure and maintain the separator at the target testing pressure. Without this modification, the separator would operate at a pressure slightly above the current sales line pressure during the well cycle.
- A “vortex breaker” was installed in the separator oil box outlet with the intent to prevent a vortex from forming in the oil box and pulling separator gas into the oil leg and to the atmospheric storage tank. Such entrained gas would bias directly measured FGORs (discussed in Section 3.2.9) and could bias the pressurized condensate samples. However, gas carry through from a vortex has not been observed at other production facilities and, in hindsight, the vortex breaker was an unnecessary precaution.
- As discussed in Section 2.1, pressurized HC liquids samples are a mix of new HC liquids (i.e., HC liquids produced during the well cycle) and residual HC liquids (i.e., HC liquids in the separator from previous well cycles). The proportion of these two HC liquids in the separator dump HC liquids is not known, and this proportion could impact the equilibrium pressure and temperature of the separator dump/sample HC liquids if the two HC liquids have different compositions. Reasonable estimates of the separator dump/sample HC liquids true equilibrium pressure and temperature are needed to evaluate the samples’ validity (i.e., conduct OPCs) and for PSM/EOS calculations of flash gas generation. The equilibrium pressure and temperature are typically assumed to be the separator operating pressure and temperature during the well cycle and subsequent pressurized HC liquids sample collection. This assumption could have a large error if the residual HC liquids

equilibrium pressure and temperature differ from the separator operating conditions. To minimize this potential error for this testing, the separator was maintained at the target pressure and temperature between well cycles. The pressure control was tighter than the temperature control. In addition, when the separator pressure and temperature needed to be changed for a new test condition, the well was cycled at least one time at the new condition without sample collection to flush some residual HC liquids and allow the separator HC liquids and gas to equilibrate at the new target operating condition. Without this modification, the true HC liquids equilibrium pressure and temperature could be quite different than the separator operating conditions during the recent well cycle and during sample collection. The implications of this "separator history" issue for collection of representative "real-world" pressurized HC liquids samples are discussed in Section 5.

- As shown schematically in Figure 3-1, the pipe between the separator oil box and the Coriolis meter to measure the HC liquids flow (upstream of the separator dump valve) was extended and three sample probes were installed at six-inch intervals. These probes were installed according to the guidelines of API MPMS Chapter 8.7.8 for representative sample collection. Multiple probes allowed the collection of simultaneous samples and sample collection perturbation studies such as CP vs. CV cylinders. Without this modification, and what is likely typical for many pressurized HC liquids samples, single pressurized HC liquids samples would be collected from the base of the sight glass for the oil box. The sight glass location is much closer to the separator gas/liquid interface than the sample probes (i.e., about six inches vs. two feet).
- The tank-to-burner pipeline was insulated and heat-traced from the tank outlet to downstream of the pipeline gas flow meters. The pipeline gas temperature was maintained at least 30°F above the ambient to preclude condensation that could interfere with the gas flow measurements.
- Instruments to measure process pressures, temperatures, and flows from the separator to the VOC burners were installed as discussed in Section 3.2.9 and Appendix IV.

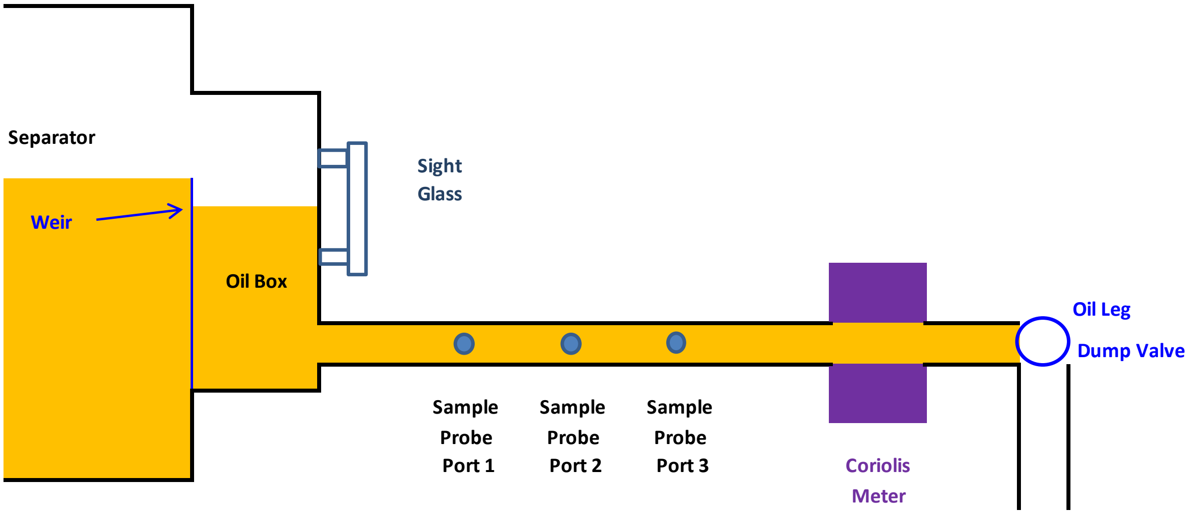

Figure 3-1. Sample probes and sight glass sample collection location schematic.

3.2 Project Overview and Primary Tasks

The project was structured to follow a logical order to evaluate:

- Analytical methods and laboratory sample handling procedures for pressurized HC liquids samples;
- Pressurized HC liquids sample collection parameters, which included 1) sample collection rate; 2) sample cylinder type; 3) sample collection initiation time after the end of a well cycle; and 4) sample collection location (i.e., oil box oil level sight glass or sample probe installed downstream of the oil box);
- Operational performance checks for pressurized HC liquids sample collection and analysis results;
- Collection and analysis of pressurized condensate samples, over a range of separator operating conditions and various storage tank operating conditions, in conjunction with instrumentation to measure separator and tank process parameters (e.g., pressures, temperatures, flow rates), and associated storage tank HC mass balances and FGORs; and
- PSM/EOS calculations of P_{BP} and FGOR based on analytical results for pressurized HC liquids samples.

Table 3-1 provides a project overview by introducing the primary project tasks, and additional detail and discussion of these tasks is provided in the sub-sections that follow. Appendix I is the Project Work Plan with a complete description and discussion of the tasks. In some cases, results from earlier tasks were used to provide insight into preferred methods and procedures to use for ongoing study tasks.

Table 3-1. Project Overview / Summary of Primary PHLSA Study Tasks

Task	Description
1. Initial Sample Collection	Pressurized condensate samples were collected at the Test Facility and analyzed using three different methods for pressurized condensate: GPA 2186M, GPA 2103M, and flash liberation. A composite condensate composition was used for Task 2.
2. Development of Certified Reference Material	A NIST-traceable CRM (i.e., a gravimetrically blended condensate standard with low compositional uncertainty) was developed. The CRM was used to evaluate different Analytical Methods (Tasks 3 & 4) and OPCs (Task 7), to conduct the Sample Handling Perturbation Study (Task 6), and as the CRM for calibrations throughout the study.
3. Multi-Lab Analytical Methods Study	CRM samples were analyzed by four different laboratories (labs) using the GPA 2186M, GPA 2103M, and flash liberation analytical methods to compare the methods and variability of results from different labs.
4. SPL Analytical Methods Performance & Uncertainty	This task estimated the accuracy, precision, and overall uncertainty of the GPA 2186M, GPA 2103M, and flash liberation analytical methods. CRM samples were analyzed by SPL using the three methods, and the results compared to the gravimetrically determined CRM composition from Task 2. Two versions of GPA 2103M were evaluated.
5. Process Measurement Uncertainty Analysis	Instruments to measure process parameters (e.g., pressures, temperatures, flowrates) were evaluated to estimate and minimize measurement uncertainty. Uncertainties in process measurements propagate to PSM/EOS FGOR calculations, and atmospheric storage tank HC mass balance and flash gas generation/FGOR calculations.
6. Lab Sample Handling Perturbation Study	CRM samples were used to evaluate the impact of lab sample handling parameters (e.g., temperature, pressure, mixing, and gas chromatograph sample injection rate) on compositional analyses of pressurized condensate samples to develop recommendations for proper handling of lab samples.
7. Operational Performance Checks	Operational performance checks (e.g., initial pressure test P_{BP}, PSM/EOS calculated P_{BP}) to assess the reliability of pressurized HC liquids sampling and analysis results were evaluated to develop recommendations for conducting these checks.
8. Sample Collection Perturbation Study	The impact of sample collection parameters (e.g., cylinder type, location, rate, start time) on pressurized HC liquids sampling and analysis results were evaluated to develop recommendations for sample collection procedures. Perturbation samples were initially collected in January 2016 and also later in conjunction with Task 9.
9. Winter and Summer Three-Separator Pressure Range Study	This task investigated the effects of separator pressure and temperature on pressurized HC liquids sampling and analysis results, and the effects of separator conditions and storage tank temperature on flash gas generation. In the winter and in the summer, the separator was operated at three different nominal pressures (identified as "high" (HP ~ 260 psig), "mid" (MP ~ 225 psig), and "low" (LP ~ 175 psig)) and replicate pressurized condensate samples were collected concurrent with process measurements for storage tank HC mass balance and FGOR calculations.
10. Data Analysis	The uncertainties of storage tank HC mass balance and FGOR measurements were estimated. The sensitivity of PSM/EOS calculations to key parameters and the uncertainties of PSM/EOS FGOR and P_{BP} calculations were estimated.

3.2.1 Task 1. Initial Sample Collection

This task collected simultaneous (i.e., multiple sample locations/probes) and sequential (i.e., from a single sample location/probe) pressurized condensate samples at the Test Facility to characterize the condensate composition. Table 3-2 shows the sample collection matrix which included collection of simultaneous CP cylinder samples from three sample probes with six-inch spacing as shown in Figure 3-1. The samples were analyzed by SPL using four different methods (GPA 2186M, GPA 2103M (C10+), GPA 2103M (C100+), and flash liberation), and a composite of the measured condensate compositions was the target composition for the CRM developed in Task 2. A well cycle in the midst of the sample collection precluded drawing conclusions regarding the impact of sample collection start time from these data, and a sample collection initiation time matrix was repeated for Task 8.

Table 3-2. Initial Sample Collection Test Matrix

Operating Conditions	**Pressurized Condensate**				**Process Measure-ments**
	Sampling Parameters	**Sequential Samples**	**Simultaneous Samples**	**Lab Analyses and PSM/EOS Calculations**	
P_{sep} ~ 220 psig	GPA 2174; 500 ml CP sample cylinder; Sample rate: 60 ml/min.				
	Sample location: sample probe 1				
T_{sep} ~ 80°F	**S11.** Sample start: < 30 min. after well cycle	X	I	All samples	P_{sep}, P_{SC}
	S12. Sample start: after sample **S11**	X	II	GPA 2103M (TCD portion only: C1-5)	T_{sep}, T_{SC}
Separator Heater Off	**S13.** Sample start: after sample **S12**	X	III		ρ_{oil}
	S14. Sample start: after sample **S13**	X	IV		
	S15. Sample start: after sample **S14**	X	V	Density and P_{BP} by Densitometer	$T_{sep\ gas}$
	S16. Sample start: after sample **S15**	X	VI		
	Sample location: sample probe 2				
	S21. Sample start: < 30 min. after well cycle	Y	I	P_{BP} at T_{SC} by PSM/EOS	
	S22. Sample start: after sample **S21**	Y	II		
	S23. Sample start: after sample **S22**	Y	III		
	S24. Sample start: after sample **S23**	Y	IV		
	S25. Sample start: after sample **S24**	Y	V		
	S26. Sample start: after sample **S25**	Y	VI	Select Samples	
	Sample location: sample probe 3			GPA 2186 C1-10+	
	S31. Sample start: < 30 min. after WC	Z	I	GPA 2103M C1-10+	
	S32. Sample start: after sample **S31**	Z	II	GPA 2103M C1-100+	
	S33. Sample start: after sample **S32**	Z	III		
	S34. Sample start: after sample **S33**	Z	IV	Flash Lib	
	S35. Sample start: after sample **S34**	Z	V		
	S36. Sample start: after sample **S35**	Z	VI		

3.2.2 Task 2. Certified Reference Material Development

A NIST-traceable CRM was developed specifically for this study as a baseline reference material. The CRM was a gravimetrically blended pressurized condensate standard with low compositional uncertainty, and the target composition was based on a composite of the pressurized condensate samples collected and analyzed for Task 1. Analytical accuracy is impacted by the calibration standard uncertainty, the similarity of the calibration standard to the samples under analysis, and the analytical method precision. Because the CRM was custom-made to simulate the Test Facility condensate and was gravimetrically blended for low compositional uncertainty, its use as a GC calibration standard throughout the PHLSA Study was expected to improve analytical accuracy. The CRM was also used to evaluate different Analytical Methods (Task 3 and Task 4) and different OPCs (Task 7), and to conduct the Sample Handling Perturbation Study (Task 6). Task 2 of the Work Plan (Appendix I) details the CRM preparation.

3.2.3 Task 3. Multi-Laboratory Analytical Methods Study

CRM samples were analyzed by four different labs using three different analytical methods to compare the methods and the variability of results from different labs. Table 3-2 summarizes the multi-lab study matrix and lists the analytical methods used by each lab and the CRM samples analyzed. As noted in the table, “M” attached to an analytical method refers to a modified method. Each participating lab was requested to use the listed analytical methods with lab-specific modifications to provide best performance. The multi-lab study had a limited scope and was not intended to be a comprehensive and robust Inter-laboratory study to estimate the reproducibility of the methods (refer to Appendix II, Section 3.2 for additional discussion).

CRM1 was the PHLSA Study CRM, and a second gravimetrically blended reference material, CRM2, was prepared. CRM2 was blended with a slightly different composition than CRM1 to change the composition measured by each analytical subset of GPA-2103M.

- The first analytical subset is GC-TCD determination of C1-C5 compounds concentrations, and a greater amount of iso-butane was added to CRM2 than to CRM1.
- The second detection subset is a naphtha distillation cut followed by GC-FID analysis to determine C6–C10+ HCs including key isomers such as BTEX (i.e., benzene, toluene, ethyl benzene, and xylenes), and a greater amount of toluene was added to CRM2 than to CRM1.
- The third subset measures the physical properties of the “heavy” C10+ fraction. A distillation cut produces a C10+ fraction, and C10+ fraction SG is measured by a density

meter and MW is determined by other means such as cryette. A greater amount of undecane (C11) was added to CRM2 than to CRM1.

The addition of these three compounds to CRM2 had the effect of diluting other compounds relative to CRM1; thus, the concentrations of all analytes differed in CRM 1 and CRM2.

Table 3-3. Summary of Multi-Lab Study CRM Analyses

Analytical Lab	Analytical Method (M = modified)	Number of CRM1 Analyses	Number of CRM2 Analyses
1	GPA 2103M	3	3
	Flash Liberation	3	3
2	GPA 2103M	3	3
	GPA 2186M	3	3
3	GPA 2186M	3	3
	Flash Liberation	3	3
4	GPA 2103M	3	3
	GPA 2186M	3	3
	Flash Liberation	3	3

3.2.4 Task 4. SPL Analytical Methods Performance and Uncertainty Evaluation

This task estimated the accuracy, precision, and overall uncertainty of four different methods used by SPL for pressurized condensate analysis, with an objective to identify preferred methods to use for the rest of the study. CRM samples were analyzed and Table 3-4 summarizes the test matrix. Three of the analytical methods measure C1-C10+, and the fourth measures C1-C100+. The C1-C100+ analytical method was included to assess how increased analytical detail impacts PSM/EOS calculations. Using the compositional analysis results, PSM/EOS was used to calculate FGOR, P_{BP} and density. The two methods with the best precision and accuracy (e.g., based on certified CRM composition vs. measured composition), lowest uncertainty, and best operational performance (evaluated by density and P_{BP}) were used for pressurized HC liquids samples analyses for the remainder of the study.

Table 3-4. Summary of the Analytical Method Performance and Uncertainty Evaluation

No. of Samples	Lab Analyses for Each Sample	PSM/EOS Calculations for Each Analysis
10 CRM samples	GPA 2186 (C1 – C10+)[A] GPA 2103M (C1 – C10+)[A] GPA 2103M (C1 – C100+)[B] Flash Liberation (C1 – C10+)[A]	Bubble point pressure @ T_{sep} Density @ P_{sep}, T_{sep}

A. C1–C9 compounds individually quantified, and C10+ compounds reported as a total.

B. C1–C99 compounds individually quantified, and C100+ compounds reported as a total.

3.2.5 Task 5. Process Measurement Uncertainty Analysis

This task evaluated instruments to measure process temperatures, pressures, and flow rates to estimate and minimize the uncertainty of these process parameter measurements. This task was conducted in conjunction with Task 9 and Task 10.

3.2.6 Task 6. Laboratory Sample Handling Perturbation Study

This task evaluated the impact of laboratory sample handling parameters on analytical results for pressurized condensate samples composition, and was designed to identify proper protocols for handling pressurized condensate samples. The sample handling parameters that were evaluated included:

- **Temperature** – this is the sample cylinder temperature prior to sample aliquot extraction and GC injection. This temperature must be below the sample bubble point temperature to preclude a two-phase sample and to prevent sample flashing during the analysis.
- **Pressure** – this is the sample cylinder pressure prior to sample aliquot extraction and GC injection. This pressure must be above the sample bubble point pressure to preclude a two-phase sample and to prevent sample flashing during the analysis.
- **Mixing** – this is the number of times a sample is "rocked" prior to sample aliquot extraction and GC injection. The sample must be well-mixed and homogeneous prior to sample aliquot extraction for a representative analysis.
- **GC sample purge/injection rate** – this is the flow rate of sample aliquot through the GC sample inlet. A concern with higher injection rates is the potential for premature flashing.

Table 3-5 lists the sample handling perturbation matrix. The baseline condition represents the sample handling condition (perturbation) least likely to incur losses of volatile components, and each perturbation was conducted while holding the other parameters at the baseline condition. Each perturbation listed in Table 3-5 was conducted for both CP cylinder CRM samples and CV cylinder CRM samples, and a sample aliquot associated with each perturbation was analyzed for C1–C5 compounds and C6+. A total of 16 perturbations were conducted, with the baseline conditions run at the beginning, middle and end of the study. Lighter, more volatile HCs (i.e., C1–C5) are most likely to be impacted by sample handling conditions and were the focus of the analyses. The analytical procedure used in these tests was GPA 2177M, where the modification was to not normalize the raw GPA 2177 analytical totals that were less 100%; rather, the difference is included in the C6+ fraction. This GPA 2177M analysis is effectively the portion of GPA 2186M and GPA 2103M used to determine the pentanes and lighter composition.

Table 3-5. Laboratory Sample Handling Perturbations for CP and CV Cylinders

Parameter	Pert 1	Pert 2	Pert 3	Pert 4	Baseline^{A}	Pert 1	Pert 2	Pert 3	Pert 4
Mixing (number of cylinder rocks)	0	6	12	18	**24**				
Purging (ml/sec)					**1**	2	4	8	12
Pressure (psia)^{B}	365	415	465	515	**1,115**				
Temperature (°F)					**55**	65	70	73^{C}	75

A. Figures in Bold indicate the most conservative sample handling conditions.
B. Liquid standard Bubble Point = 218 psia.
C. Lab temperature.

3.2.7 Task 7. Operational Performance Checks Evaluation

This task evaluated the OPCs for pressurized condensate samples and analytical results that were introduced in Section 2.3.3. Sample collection and analytical results from Tasks 4, 8, and 9 were used for the evaluation.

3.2.8 Task 8. Sample Collection Perturbation Study

Several pressurized HC liquids sample collection protocols were evaluated and these included GPA Standard 2174, a California Air Resources Board (CARB) draft test protocol, API E&P Tanks 3.0 Program User's Manual, Annex C[4], and Texas Commission on Environmental Quality (TCEQ) APDG 5942[5]. The CARB and the TCEQ methods (and more recently Colorado Department of

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[4] API Publication 4697. Production Tank Emissions Model, E&P TANK Version 3.0 User's Manual: Sampling Protocol

[5] TCEQ APDG 5942 "Calculating Volatile Organic Compounds (VOC) Flash Emissions from Crude Oil and Condensate Tanks at Oil and Gas Production Sites", Revised May 2012

Public Health and Environment (CDPHE) PS Memo 17-01[6]) are derivatives of GPA 2174 (i.e., they reference GPA 2174). The E&P Tanks sampling protocol includes three sample collection methods: evacuated cylinder, gas displacement, and liquids displacement. The liquids displacement method mirrors GPA 2174, and the evacuated cylinder and gas displacement methods cause the sample liquids to extensively flash in the sample cylinder and were considered to be less controlled and practical than the GPA 2174 sample collection methods. Thus, this study evaluated the most prevalently used GPA 2174 sample collection methods for the O&G industry:

- Floating Piston/CP Cylinder Method; and
- Water Displacement/CV Cylinder Method.

As noted previously, a primary difference between the two methods is that the sample liquid contacts another liquid (typically water) during CV cylinder sampling, whereas in a CP cylinder the sample liquid only contacts the stainless-steel walls of the cylinder and a greased piston seal.

This task collected data to evaluate the impact of key sample collection parameters on pressurized HC liquids sample collection and analysis results to develop recommendations for sample collection procedures and related operational parameters and seasonal implications. Parameters evaluated were:

- Sample collection rate (20, 40, 60, 100, and 180 ml/min)
- Sample collection initiation time after the end of the well cycle (less than 0 (i.e., during the well cycle), less than 30 (typically ~ 15), 90, and 150 minutes after the well cycle)
- Sample collection location (sample probe and oil box oil level sight glass)
- Sample cylinder type (CP cylinder and CV cylinder)

Sample collection perturbation tests were conducted during three test series at the Test Facility:

- January 2016 sample collection perturbation study tests that are summarized in Table 3-6;
- March 2016 winter three-pressure range tests that are summarized in Table 3-7; and
- July 2016 summer three-pressure range tests that are summarized in Table 3-8.

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[6] CDPHE PS Memo 17-01 “Flash Gas Liberation Analysis Method for Pressurized Liquid Hydrocarbon Samples”

Data to evaluate the impact of sample cylinder type were collected during all of these test series. Paired CV and CP cylinder samples were simultaneously collected during every sampling event using probe 1 and probe 3. The CV and CP cylinders were randomly switched between probe 1 and probe 3 to address possible sample probe bias. The samples were analyzed using GPA 2103M and GPA 2186M as noted in Tables 3-6, 3-7, and 3-8.

Table 3-6. Sample Collection Perturbation Study Test Matrix (January 2016)

Operating Conditions	**Pressurized Condensate**				**Process Measure-ments**
	Sampling Parameters^{A}	**Sequential Samples**	**Simultaneous Samples**	**Lab Analyses, PSM/EOS Calculations & OPC**	
P_{sep}: ~ 225 psig T_{sep}: ~ 80°F Separator Heater On	GPA 2174; 500 ml **CV Sample Cylinder**; Sample location: sample probe 1 or 3			GPA 2103M C1-10+, and BTEX	P_{sep}, P_{SC} T_{sep}, T_{SC} ρ_{oil} $T_{sep\ gas}$
	Sample start time: after well cycle (WC) starts Sample rate (SR): *60 ml/min*.	**X**	**I**		
	BASELINE: Sample start time: < 30 min. after WC end SR: *60 ml/min*.	**X**	**II**	GPA 2186M C1-10+, and BTEX	
	Sample start time: 90 min. after WC end SR: *60 ml/min*.	**X**	**III**	Bubble Point Pressure at T_{SC} by PSM/EOS	
	Sample start time: 150 min. after WC end SR: *60 ml/min*.	**X**	**IV**	Density at T_{SC} by PSM/EOS	
	Sample start time: < 30 min. after WC end SR: *20 ml/min*.		**V**	Density and Bubble Point Pressure by Densitometer	
	Sample start time: < 30 min. after WC end SR: *100 ml/min*.		**VI**		
	GPA 2174; 500 ml **CP Sample Cylinder**; Sample location: sample probe 3 or 1			Bubble Point Pressure by IPT	
	Sample start time: after well cycle (WC) starts Sample rate (SR): *60 ml/min*.	**Y**	**I**		
	BASELINE: Sample start time: < 30 min. after WC end SR: *60 ml/min*.	**Y**	**II**		
	Sample start time: 90 min. after WC end SR: *60 ml/min*.	**Y**	**III**		
	Sample start time: 150 min. after WC end SR: *60 ml/min*.	**Y**	**IV**		
	Sample start time: < 30 min. after WC end SR: *20 ml/min*.		**V**		
	Sample start time: < 30 min. after WC end SR: *100 ml/min*.		**VI**		

3.2.9 Task 9. Winter and Summer Three-Separator Pressure Range PHLSA Study

This task investigated the effect of separator pressure and hot versus cold weather on pressurized HC liquids sample collection and analysis results, and flash gas generation (directly measured and PSM/EOS calculated FGOR). In the winter and in the summer, the separator was operated at three different pressures intended to cover the typical range of operating pressures for separators in the DJ Basin. Target separator operating pressures were LP ~ 175 psig, MP ~ 225 psig, and HP ~ 260 psig. Replicate (a minimum of three) tests were conducted at each pressure. A test comprised all measurements conducted during a well cycle which included pressurized condensate samples and tank-to-burner pipeline gas samples collected concurrent with process measurements for well cycle storage tank mass balance and FGOR calculations. Essentially the same test matrix was conducted in the winter and in the summer, and key differences are noted below.

Winter Testing

Table 3-7 summarizes the winter three-pressure range test matrix and lists the target separator operating conditions, pressurized condensate sample collection parameters, and associated lab analyses and PSM/EOS calculations for each sample. This testing was conducted in March 2016. Table 3-8 summarizes the process samples (e.g., tank headspace gas) that were collected and analyzed in conjunction with pressurized condensate samples during each winter testing well cycle. Figure 3-2 shows the primary process temperature, pressure, and flow rate measurements conducted during each well cycle, and Table 3-9 introduces the related instruments. Two considerations of note for these measurements include:

- The tank-to-burner pipeline gas flow rate rapidly increases at the start of each separator liquids dump (and flash gas release) and decreases after the end of the dump, and such rapidly changing flow rates are difficult to measure. The gas flow measurement was further complicated because the gas composition and temperature (which impact instrument response and accuracy) differed for each well cycle, and differed from the calibration gas composition and temperature. Two thermal mass gas flow meters (Fox Flow 1 and Fox Flow 2 in Figure 3-2) were installed in series in the tank-to-burner pipeline. A third flow meter, a vane anemometer (also shown in Figure 3-2), which has a different measurement principle, was installed for the summer testing as discussed below.

  Thermal mass flowmeters measure gas mass flow using a heated element that loses heat to flowing gas, and the gas mass flowrate is correlated to the electrical power required to maintain a constant heated element temperature. The response of these instruments is impacted by the pipeline gas composition and associated heat transfer properties (e.g., density, viscosity, thermal conductivity). When the process gas composition deviates from the calibration gas composition, there is a bias and measurement accuracy is reduced.

Corrections were applied to account for process gas differences from calibration conditions. Vane anemometers measure volumetric flow rate and are less impacted by gas composition. Appendix IV presents the methodologies used to adjust the measured flowrates for all three flowmeters based on process conditions versus calibration conditions. Multiple flow meters were employed with the idea that agreement or differences between the redundant meters would provide insight into the viability and accuracy of these measurements.

- FGOR for a well cycle is calculated using the volume of post-flash condensate produced during the well cycle, and storage tank mass balance calculations for a well cycle require the composition of the post-flash condensate. A Coriolis meter (CM Flow in Figure 3-2) was used to measure the pre-flash condensate production upstream of the separator dump valve; however, the post-flash condensate production was not directly measured. Weathered condensate samples were collected from the storage tank and analyzed, but this liquid had been weathering for months and very likely had a different composition than post-flash condensate that was produced during a recent well cycle. To address these two issues, a pressurized condensate sample was collected for each well cycle immediately after collection of the primary samples. These samples were flashed in the lab at the tank liquid temperature during the well cycle, and the post-flash HC liquids were analyzed for HC components by GPA 2103M. The measured shrinkage factor (post-flash HC liquids volume/pre-flash HC liquids volume) and the post-flash HC liquids composition were used for direct measurement FGOR and tank mass balance calculations as discussed in Appendix IV.

Appendix IV introduces all the process measurements conducted during each well cycle, provides more detailed descriptions of the associated instrumentation, and tabulates the average, maximum, minimum, and standard deviation of each measurement during each well cycle.

Table 3-7. PHLSA Study Winter Testing High-, Mid-, and Low-Pressure Range Test Matrix

Target WC Operating Conditions	Pressurized Condensate					Notes
	Sampling Parameters	**No. of Samples: Collect/ Analyze /Archive**	**Sequential Samples**	**Simultaneous Samples**	**Lab Analyses, PSM/EOS Calculations & OPC**	
	GPA 2174 Sample rate: 20 ml/min. Sample cylinder volume: 500 cc / 400 ml Sample location: sample probe Sample start time: < 30 min. after well cycle (WC) end				GPA 2103M C1-10+, and BTEX GPA 2186M C1-10+, and BTEX Bubble Point Pressure at T_{SC} by PSM/EOS[D] Bubble Point Pressure at 72°F by PSM/EOS[D] IPT Bubble Point Pressure at 72°F[D] IPT Bubble Point Pressure at T_{sc}[D] Density and Bubble Point Pressure by Densitometer	Each Pressurized Condensate sample along with corresponding Process Samples and Process Measurements were used to calculate a unique measured FGOR and Tank Mass Balance, and in a FGOR Model using 4 different PSM/EOS software programs
High-P WCs $P_{sep} > 250$ psig T_{sep} ~ 85°F	CV cylinder	4/3/1[A]	X	I		
	CP cylinder	4/3/1[A]		I		
	CP cylinder	3/2/1[B]	X			
Mid-P WCs P_{sep} ~ 225 psig T_{sep} ~ 85°F	CV cylinder	3/2/0[C]	Y	II		
	CP cylinder	3/3/0		II		
	CP cylinder	3/3/0[B]	Y			
Low-P P_{sep} ~ 175 psig T_{sep} ~ 85°F	CV cylinder	3/2/0[C]	Z	III		
	CP cylinder	3/3/0		III		
	CP cylinder	3/3/0[B]	Z			

A. High-pressure well cycle 2 (W-HP2) samples archived because separator pressure was very unstable during the well cycle

B. "Tank Sim" samples were collected immediately after the primary samples, flashed in the lab at the tank liquid temperature during the well cycle/sample collection, and the post-flash liquids was analyzed for HC components by GPA 2103 M (C1 - C10+, and BTEX). The measured shrinkage factor (post-flash liquids volume/pre-flash liquids volume) and the post-flash liquids composition were used for direct measurement FGOR and storage tank mass balance calculations as discussed in Appendix IV.

C. Rupture disc failure on CV cylinder for mid-pressure well cycle 2 (W-MP2) and low-pressure well cycle 2 (W-LP2)

D. IPTs were conducted at lab temperature (72°F). IPT P_{BP} at T_{sc} estimated to be equal to IPT P_{BP} at 72°F *(P_{BP} at T_{SC} by PSM/EOS / P_{BP} at 72°F by PSM/EOS).

Table 3-8. PHLSA Study Winter 3-Pressure Testing: Process Samples Collection and Analysis

Parameter	Minimum Number of Samples per WC[A]	Lab Analyses for Each Sample[A]
Storage Tank Vent Gas	9[B]	Portable GC
	1	Tedlar bag sample, Portable GC
	1	Evacuated sample bomb, GPA 2286
Separator/ Sales Gas	1	GPA 2286
Storage Tank Weathered Condensate	6[C]	GPA 2103M (C1 - C10+, and BTEX)
Pressurized Separator Water	1[D]	Water Flash Test and GPA 2286M

A. Refer to the PHLSA Study QAPP (Appendix I.1) for measurement/test method details.

B. Plan was to perform at least 3 pre-well cycle, 3 during-well cycle (well cycle duration permitting) and 3 post-well cycle portable GC analyses for each well cycle.

C. Three storage tank samples were collected at the start of the testing and three samples were collected at the end of the testing.

D. One pressurized separator water sample was collected for each of the three operating pressure ranges.

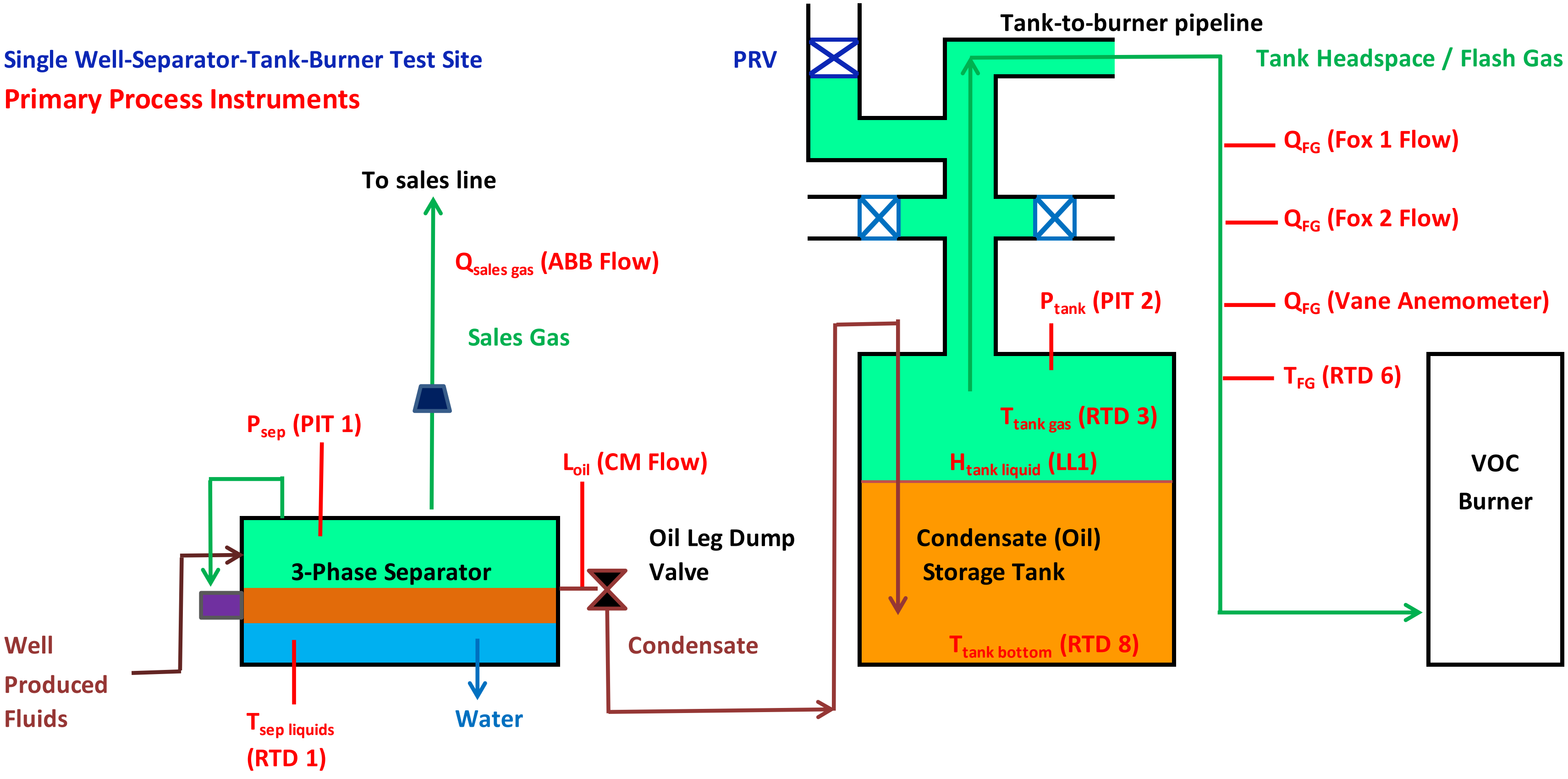

Figure 3-2. Primary process measurements during three-pressure testing.

Table 3-9. Instrumentation for Primary Process Measurements

Parameter	Instrument Type	Instrument ID	Engineering Units
P_{sep} – separator pressure	Pressure transducer	PIT 1	psig
T_{sep} – separator liquids temperature	Resistance Temperature Detector	RTD 1	°F
$Q_{sales\ gas}$ – sales gas flowrate	Orifice plate differential pressure meter	ABB Flow	MCFD[A]
L_{oil} – pre-flash oil production	Coriolis meter	CM Flow	bbl/day[A]
P_{tank} – tank headspace gas pressure	Pressure transducer	PIT 2	oz/in^2
$T_{tank\ gas}$ – tank headspace gas temperature	Resistance Temperature Detector	RTD 3	°F
$H_{tank\ liquid}$ – tank liquid level	Tank liquid level sensor	LL1	inches
$T_{tank\ bottom}$ – tank liquids temperature 1 foot above tank bottom	Resistance Temperature Detector	RTD 8	°F
Q_{FG} – tank-to-burner pipeline gas flow	Thermal mass gas flow meter	Fox 1 flow	MCFD[A]
Q_{FG} – tank-to-burner pipeline gas flow	Thermal mass gas flow meter	Fox 2 flow	MCFD[A]
Q_{FG} – tank-to-burner pipeline gas flow	Vane anemometer	Vane anemometer	m^3/hr[A]
T_{FG} – tank-to-burner pipeline gas temperature	Resistance Temperature Detector	RTD 6	°F

A. Instrument measures instantaneous flow rate and has a totalizer function.

Summer Testing

Table 3-10 summarizes the summer three-pressure range test matrix and lists the target separator operating conditions, pressurized condensate sample collection parameters, and associated lab analyses and PSM/EOS calculations for each sample. As shown in Table 3-10, the testing included additional well cycles and samples for the sample collection perturbation study task. These included samples collected from the oil box sight glass simultaneously with samples collected from the sample probes, and samples collected using a range of sample collection rates. This testing was conducted in July 2016. Table 3-11 summarizes the process samples that were collected and analyzed in conjunction with pressurized condensate samples during each well cycle during the summer testing. Figure 3-2 and Table 3-9 summarize the primary process temperature, pressure, and flow rate measurements collected during each well cycle. Notable process changes from the winter testing included:

- The separator heater was not operating because freezing was not a concern.
- In addition to the two thermal mass gas flow meters (Fox Flow 1 and Fox Flow 2 in Figure 3-2), a third flowmeter was installed in series to measure the gas flow in the tank-to-burner pipeline. The third flow meter was a vane anemometer (also shown in Figure 3-2) and is a different measurement technology than the thermal mass gas flow meters. Because the vane anemometer measures volumetric flow, it was anticipated that changing gas composition would have minimal impacted on the gas flow measurement. Three flow meters were employed with the idea that agreement or differences between the redundant meters, with different measurement principles, would provide insight into the viability and accuracy of these measurements.
- The storage tank liquid level was at about 90% (as opposed to about 70% in the winter) to reduce the headspace volume and dilution of the flash gas by gases produced to the tank headspace by breathing. This was done in an attempt to collect tank-to-burner pipeline gas samples that better represented the flash gas composition. To compensate for the reduced flash gas control capacity resulting from the smaller tank headspace, and preclude tank over-pressure events:
    - the separator dump valve trim size (i.e., orifice size) was reduced from 1/2” to 3/8” to reduce the oil flow rate to the tank and the flash gas generation rate; and
    - an additional VOC burner was installed.
- A practice of emptying the separator oil box before and at the end of each well cycle was implemented such that the entire volume of oil produced during the well cycle passed through the Coriolis meter.
- A solar radiation meter was installed and the measurements used to interpret the breathing cycle data. That is, process data (i.e., tank headspace pressure and temperature) used to calculate breathing losses was selected based on similar solar radiation levels as during the well cycle.

Appendix IV introduces all the process measurements conducted during each well cycle, provides more detailed descriptions of the associated instrumentation, and tabulates the average, maximum, minimum, and standard deviation of each measurement during the well cycles.

Table 3-10. PHLSA Study Summer Testing High-, Mid-, and Low-Pressure Range Test Matrix

Target WC Operating Conditions	Pressurized Condensate					Notes
	Sampling Parameters	**No. of Samples**	**Sequential Samples**	**Simultaneous Samples**	**Lab Analyses, PSM/EOS Calculations & OPC**	
	GPA 2174 Sample rate: 20 ml/min. Sample cylinder volume: 500 cc / 400 ml Sample location: sample probe Sample start time: < 30 min. after well cycle (WC) end				GPA 2103M C1-10+, and BTEX GPA 2186M C1-10+, and BTEX Bubble Point Pressure at T_{SC} by PSM/EOS[G] Bubble Point Pressure at 72°F by PSM/EOS[G] IPT Bubble Point Pressure at 72°F[G] IPT Bubble Point Pressure at T_{sc}[G] Density and Bubble Point Pressure by Densitometer	Each Pressurized Condensate sample along with corresponding Process Samples and Process Measurements were used to calculate a unique measured FGOR and Tank Mass Balance, and in a FGOR Model using 4 different PSM/EOS software programs
High-P WCs P_{sep} > 250 psig T_{sep} ~ ambient[E]	CV sampling	3	X	I		
	CP sampling	3		I		
	CP sampling from sight glass[A], or CV sampling from sight glass[A]	2 1		I		
	CP sampling[B]	3[B]	X	I-1		
	CP sampling[C]	3[C]		I-1		
Mid-P WCs P_{sep} ~ 225 psig T_{sep} ~ ambient[E]	CV sampling[D]	5	Y	II		
	CP sampling[D]	5		II		
	CV sampling from sight glass[A], or CP sampling from sight glass[A]	2 1		II		
	CP sampling[B]	3[B]	Y	II-1		
	CP sampling[C]	3[C]		II-1		
Mid-P WCs P_{sep} ~ 225 psig T_{sep} ~ ambient[E]	CV sampling, Rate = 40 ml/min	2		IV[F]		
	CP sampling, Rate = 40 ml/min	2		IV[F]		
	CV sampling, Rate = 60 ml/min	2		V[F]		
	CP sampling, Rate = 60 ml/min	2		V[F]		
	CV sampling, Rate = 100 ml/min	2		VI[F]		
	CP sampling, Rate = 100 ml/min	2		VI[F]		

Target WC Operating Conditions	Pressurized Condensate					Notes
	Sampling Parameters	No. of Samples	Sequential Samples	Simultaneous Samples	Lab Analyses, PSM/EOS Calculations & OPC	
	CV sampling, Rate = 180 ml/min	2		**VII^{F}**		
	CP sampling, Rate = 180 ml/min	2		**VII^{F}**		
Low-P P_{sep} ~ 175 psig T_{sep} ~ ambient^{E}	CV sampling	3	**Z**	**III**		
	CP sampling	3		**III**		
	CP sampling from sight glass^{A}, or CV sampling from sight glass^{A}	2 1		**III**		
	CP sampling^{B}	3^{B}	**Z**	**III-1**		
	CP sampling^{C}	3^{C}		**III-1**		

A. Sample collection perturbation study samples. Sight glass samples collected using best practices including flushing the sight glass prior to well cycle.

B. "Tank Sim" samples were collected immediately after the primary samples, flashed in the lab at the tank liquid temperature and absolute pressure at tank downcomer exit (about 1 foot from tank bottom) during the well cycle/sample collection, and the post-flash HC liquids was analyzed for HC components by GPA 2103 M (C1 - C10+, and BTEX). The measured shrinkage factor (post-flash liquids volume/pre-flash HC liquids volume) and the post-flash HC liquids composition were used for direct measurement FGOR and storage tank mass balance calculations as discussed in Appendix IV.

C. "Densitometer" samples collected after the primary samples for densitometer measurements (e.g., to measure bubble point pressure, density).

D. Three sets of samples collected at 20 ml/min, two sets of samples collected at sample collection rates indicated for well cycles 1 and 2 in Table 10A of the Work Plan (Appendix I).

E. The separator heater was not operating during the testing.

F. Refer to Table 10A of the Work Plan for sample collection schedule.

G. IPTs were conducted at lab temperature (72°F). IPT P_{BP} at T_{sc} estimated to be equal to IPT P_{BP} at 72°F *(P_{BP} at T_{SC} by PSM/EOS / P_{BP} at 72°F by PSM/EOS).

Table 3-11. PHLSA Study Summer 3-Pressure Testing: Process Samples Collection and Analysis

Parameter	Minimum Number of Samples per WC[A]	Lab Analyses for Each Sample[A]
Storage Tank Vent Gas	9[B]	Portable GC
	1	Tedlar bag sample, Portable GC
	1	Evacuated sample bomb, GPA 2286
Separator/ Sales Gas	1	GPA 2286
Storage Tank Weathered Condensate	2[C]	GPA 2103M (C1-C10+, and BTEX)
Pressurized Separator Water	1[D]	Water Flash Test and GPA 2286M

A. Refer to QAPP (Appendix I.1) for measurement/test method details.
B. Plan was to perform at least 3 pre-well cycle, 3 during-well cycle (well cycle duration permitting) and 3 post-well cycle portable GC analyses for each well cycle.
C. One composite storage tank sample was collected at the start of the testing and one composite sample was collected at the end of the testing.
D. One pressurized separator water sample was collected.

3.2.10 Task 10. Data Analysis

Table 3-12 provides an overview of the data analysis task. Example calculations and additional discussion of the data analysis are provided with the results in Section 4.

Table 3-12. Summary of PHLSA Study Data Analysis

Task	Description of Data Analyses
1. Initial Sample Collection	A composite condensate composition was determined from the pressurized condensate samples analytical results. This composite condensate composition was used for Task 2.
2. Development of Certified Reference Material	The analytical and gravimetric data used to develop the CRM were used to estimate the CRM uncertainty.
3. Multi-lab Study	Analytical results for the CRM samples were analyzed to evaluate the three different analytical methods and variability by lab.
4. Analytical Method Performance and Uncertainty	SPL calibration and analysis data were analyzed to estimate the uncertainty and bias of each of the analytical methods evaluated for this task.
5. Process Measurement Uncertainty Analysis	The uncertainty of each process measurement was estimated based on instrument manufacturer specifications, calibration data, replicate measurements, and for some instruments, engineering judgment.
6. Sample Handling Perturbation Study	The impacts of lab sample handling parameters – temperature, pressure, mixing, GC sample injection rate, and sample cylinder type – on pressurized condensate samples compositional analyses were evaluated.
7. Operational Performance Checks	OPCs (e.g., IPT P_{BP}, PSM EOS P_{BP}) were evaluated and recommendations for conducting OPCs and acceptance criteria for OPCs were discussed.
8. Sample Collection Perturbation Study	The impact of sample collection parameters (e.g., cylinder type, location, rate, start time) on pressurized HC liquids sampling and analysis results were evaluated.
9. Winter and Summer Three-Separator Pressure Range PHLSA Study	The impact of separator pressure and winter vs. summer conditions on directly measured and PSM/EOS calculations of FGOR and storage tank mass balance were investigated. The uncertainty of these measurements and calculations were estimated, and the sensitivity of PSM/EOS calculations to various input parameters was investigated.

3.3 Process Simulation Model/Equation of State FGOR Calculations

The calculation of FGOR estimates using PSM/EOS software programs was introduced in Section 2.4. PSM/EOS estimates of FGOR, flash gas composition, and post-flash oil volume and composition using pressurized condensate composition were calculated using four different commercially available process simulation software programs identified as Sim1, Sim2, Sim3, and Sim4. The Sim1 process flow simulations were developed first, and the Sim2 and Sim3 process flow simulations were designed to match Sim1. Sim1, Sim2, and Sim3 allow the user to customize the Process Flow Diagram (PFD) to mimic the equipment and material stream flows being modeled. Sim4 has a fixed PFD with only a separator, flash valve, and storage tank. In addition to the FGOR calculations, the P_{BP} at separator temperature based on pressurized condensate composition was estimated using Sim1, Sim2, and Sim3.

The four software packages were used to conduct four separator/storage tank system simulations (i.e., PFDs) based on different equipment and process flows:

1. **Separator mass balance**. For each well cycle from the winter and summer three-pressure testing (refer to Section 3.2.9), measured volumes and compositions of sales gas, oil production, and water production were recombined into a single well output/separator input process stream that was input to each PSM/EOS software program. Separator sales gas, oil, and water outputs were calculated and compared to the measured volumes to check the performance of the software programs.
2. **“Simple” FGOR**. FGORs and flash gas compositions were calculated for each well cycle from the winter and summer three-pressure testing based on the pressurized condensate composition, separator pressure, separator liquids temperature, the pressure at the tank bottom at the downcomer exit, and the temperature of the storage tank liquids at the downcomer exit. This model assumed that all the separator dump fluids flowed to the storage tank bottom through the downcomer.
3. **“Complex” FGOR**. This model considers the SPH in the downcomer (about one foot from the top of the tank) that was introduced in Section 2.1. It was assumed that the majority of the separator dump fluids flowed to the storage tank bottom through the downcomer, and a small fraction of the fluids flowed through the SPH directly into the tank headspace. Because temperature and pressure differ at the top and bottom of the tank, the “Simple” FGOR model was altered to attempt to account for this effect by modeling a fraction of the fluid flow at the tank headspace temperature and pressure, and the remaining fluid at the tank bottom temperature and pressure. Thus, FGORs and flash gas compositions were calculated for each well cycle from the winter and summer three-pressure testing based on the pressurized oil composition, separator temperature and pressure, tank bottom temperature and pressure, estimated separator dump-to-tank fluids SPH partitioning, and

the tank headspace temperature and pressure. Appendix V provides additional detail regarding the SPH and this model.

4. **Dead oil**. As discussed in Section 4.7, directly measured storage tank mass balances improved (i.e., were closer to 100%) as each testing day progressed and tank liquid temperatures increased. Less flash gas was measured when tank liquids were colder in the morning than in the afternoon, and it was hypothesized that a “quenching” of flash gas generation occurs when the tank liquids are relatively cold. Separator dump fluids are a mix of liquid and gas, and adiabatic flash calculations and estimates of the underground separator-to-tank pipeline temperature suggest these dump fluids are colder than the tank bottom liquids temperature. The measured flash gas generation is thought to be primarily the sum of the dump fluids gas and “secondary” flash gas that evolves as the dump liquids temperature increases as the dump liquids mix with warmer tank liquids. Relatively cooler tank liquids in the morning would be expected to reduce such secondary flash gas generation. A second consideration is that colder morning tank liquids may be under-saturated after cooling overnight (without any condensate production) and absorb some dump fluids flash gas. To evaluate this theory, the FGOR model was modified to add a sufficient volume of “dead oil” to the pressurized condensate flash calculations such that the PSM/EOS calculated FGOR equaled the directly measured FGOR.

Appendix V includes the process simulation modeling guidelines with the PFDs for the PSM/EOS calculations, data input and output specifications, and detailed results of the PSM/EOS calculations for the PHLSA Study.

3.4 Uncertainty Analyses Calculations

Chapters 13.1 and 13.3 of API MPMS were the primary guidelines for calculating uncertainty estimates for the PLHSA study. The latter is based upon JCGM 100:2008, the 2008 edition of the International Organization of Standards (ISO) Guide to the Expression of Uncertainty in Measurement (GUM), which was developed as guide for writers of technical standards.

For some critical measurement components, such as GC analytical methods or CRM preparation, selected ASTM and ISO standards were determined to be more appropriate for uncertainty estimate calculations than the API general standards.

In some cases, critical thinking, working group consensus, and professional judgement were used to discuss and agree upon appropriate uncertainty estimate approaches. Appendix II documents the approach and results for primary uncertainty estimates.

4.0 PHLSA Study Results

This section presents the results of the PHLSA Study, and includes:

- A discussion of air in pressurized condensate samples caused by a sampling artifact, and associated adjustment of analytical results;
- The results of the SPL pressurized condensate analytical methods performance evaluation (Task 4);
- The results of the multi-laboratory study of pressurized condensate analytical methods (Task 3);
- The results of the laboratory sample handling perturbation study (Task 6);
- The results of the sample collection perturbation study (Task 8);
- The results of the operational performance checks evaluation (Task 7);
- The results of the winter and summer three-separator pressure range testing (Task 9);
- The results of the PSM/EOS FGOR calculations and associated uncertainty estimates; and
- The results of the analysis of pressurized produced water samples.

The results presented in this section include tables, figures, and discussion summarizing measurement data, and, where applicable, data and discussion from associated uncertainty analyses and/or PSM/EOS calculations. The appendices provide more detailed measurement data and calculations.

The majority of the pressurized condensate results presented in this section are for GPA 2103M analysis of a CP cylinder sample. For each of these results, there are corresponding GPA 2103M analysis of a CV cylinder sample, GPA 2186M analysis of a CP cylinder sample, and GPA 2186M analysis of a CV cylinder sample. All of these corresponding results have similar general trends as the GPA 2103M/CP cylinder results, and these results are provided in the appendices.

4.1 Air in Pressurized Condensate Samples

Supporting data for the information in this section 4.1 is in Appendix VI (PHLSA Study Task 8 Sample Collection Data.xlsm).

During pressurized condensate analyses, nitrogen and oxygen essentially co-elute from the GC column and are detected as a single peak. This $N_2 + O_2$ peak is reported as nitrogen. The majority of the pressurized condensate samples had very low concentrations of nitrogen;

however, higher concentrations were observed for some samples and the entire data set was subsequently reviewed to assess possible impact. Figure 4-1 shows the weight percent nitrogen measured by GPA 2103M analysis in pressurized condensate CP cylinder samples (blue shaded data) and CV cylinder samples (orange shaded data). The samples are from the January 2016 sample collection perturbation tests and the winter and summer 3-pressure testing. For each of the six data sets (i.e., Summer CP, Summer CV, etc.), the weight percent N_2 values are ordered from lowest to highest. Nitrogen concentrations were generally very low. About 10% of the samples had less than 0.0005 weight percent N_2 (i.e., N_2 reported as < 0.001 wt%) and N_2 in about 40% of the samples was reported to be 0.001 wt% or less. These low levels indicate negligible native levels of nitrogen and/or oxygen in the produced liquids, and that higher concentrations were very likely a result of air from incomplete purging of sample collection equipment. PSM/EOS calculations estimate a N_2 concentration of about 0.003 wt% for Test Facility condensate at 260 psig and 60°F (i.e., high pressure/low temperature operation), and this estimate supports the contention that there were negligible native levels of nitrogen and/or oxygen in the produced liquids. The data show that high N_2 concentrations were more prevalent in CV cylinder samples, and discussion with sampling personnel determined that it is more difficult to purge a CV cylinder sampling system prior to sample collection than to purge a CP cylinder system.

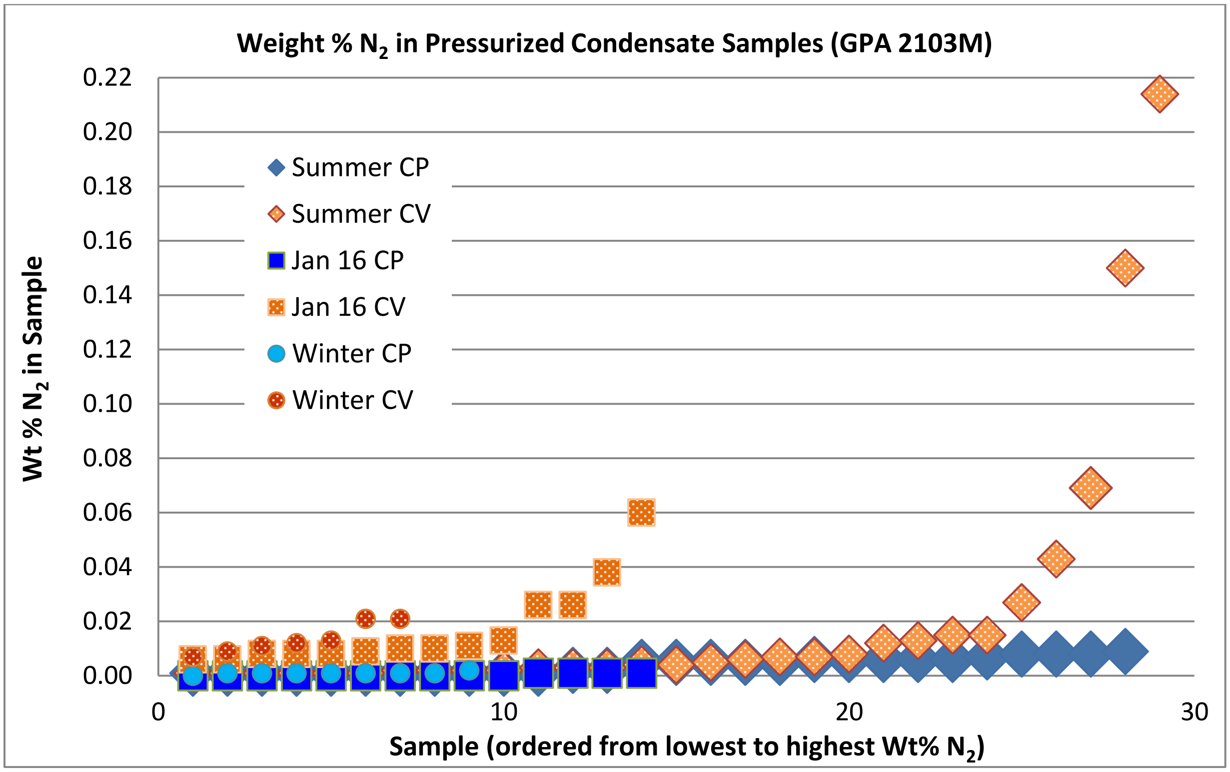

Figure 4-1. Weight percent nitrogen in pressurized condensate samples, GPA 2103M analysis.

Nitrogen/air will readily volatize out of sample; thus, N_2/O_2 content has a strong impact on PSM/EOS calculations of P_{BP}, and, to a lesser extent, FGOR. For example, for the sample with about 0.15 wt% N_2 (~ 0.48 mole%), the PSM/EOS calculated P_{BP} using the with-N_2 condensate composition was 281 psia versus a P_{BP} of 231 psia (~ 21% increase) for a without-N_2 composition (i.e., the N_2 was mathematically removed from the sample analysis and the composition was re-normalized). The PSM/EOS calculated FGOR was 315 scf/bbl with-N_2 versus 306 scf/bbl without-N_2 (~ 3% increase). Figure 4-2 shows corresponding weight percent nitrogen results from the GPA 2186M analysis, and the data and trends are consistent with the GPA 2103M analytical results.

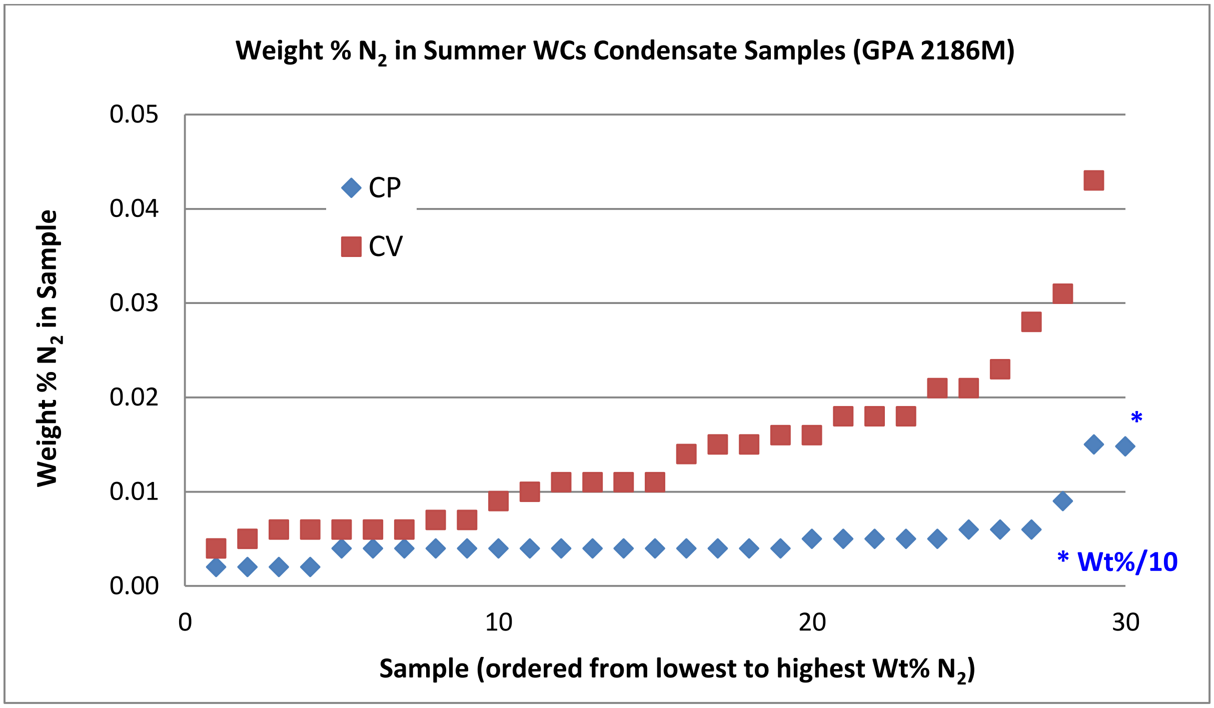

Figure 4-2. Weight percent nitrogen in pressurized condensate samples, GPA 2186M analysis.

Because the air in the samples was most likely a sampling artifact and was not in the liquids that flowed from the separator to the tank, and because the air strongly impacts PSM/EOS calculations, condensate compositions with nitrogen mathematically removed (i.e., “without-N_2” compositions) were generally used for PSM/EOS calculations and for measured FGOR and storage tank mass balance calculations to preclude biased results. For select data analyses, when the pressurized condensate nitrogen concentration was 0.02 mol% (~ 0.005 wt%) or less, the as-measured (i.e., “with-N_2”) condensate composition was used. Without-N_2 condensate compositions were used for samples with higher nitrogen levels. PSM/EOS calculations determined that nitrogen levels of ~ 0.005 wt% had negligible impact on P_{BP} and FGOR estimates.

4.2 SPL Analytical Methods Performance and Uncertainty Evaluation

Supporting data for the information in Section 4.2 is in Section 4 of Appendix II and Appendix VI (PHLSA Study Task 4 SPL Methods Evaluation.xlsm).

This task (Task 4, refer to Section 3.2.4) compared the results of four different analytical methods used by SPL for pressurized condensate analysis to evaluate the performance of the methods and to identify preferred method(s) for continued use as the PHLSA Study proceeded. The methods chosen are commonly used for analyses used in the estimation of flashing emissions, and include GPA 2186M, GPA 2103M (C10+), GPA 2103M (C100+) and flash liberation. CRM's were analyzed by SPL using the four methods, and the results compared to the gravimetrically determined CRM composition using the ratio of analytical results to the gravimetrically certified CRM values. Ten CRM's were analyzed by all four methods for a total of ten analyses per method. Table 4-1 provides an example CRM composition and the estimated uncertainty for each of the components, and these results are representative of the uncertainties for all the CRMs. The CRM uncertainty estimates were calculated considering the uncertainties of parameters that impact the gravimetric blending process including feedstocks purity; balance linearity, minimum division, repeatability, and bias; buoyancy; and published values of the molecular weights and densities of the blend components. Refer to Section 2 of Appendix II for additional detail regarding the CRM uncertainty calculations.

Table 4-1. CRM 101259 Composition and Uncertainty Estimates[A]

Component	Concentration (mole percent)	Relative Uncertainty (%)[B]
Carbon Dioxide	0.383	0.35%
Nitrogen	0.014	1.82%
Methane	5.858	0.475%
Ethane	5.389	0.397%
Propane	5.630	0.372%
iso-Butane	2.222	0.428%
n-Butane	6.428	0.362%
iso-Pentane	5.805	0.358%
n-Pentane	8.351	0.354%
C6+	59.266	0.273%

A. Data from Appendix II "Annex 1. Certified Reference Materia_Rev0_050717.pdf"

B. Relative uncertainty at 95% level of confidence

Table 4-2 shows the primary steps required to conduct each of the analytical methods, and identifies some of the primary commonalities and differences. The only difference between a

GPA 2103M (C10+) analysis and a GPA 2103M (C100+) analysis is the addition of a simulated distillation (ASTM D7169) to separate the C11–C100+ compounds. GPA 2103M and GPA 2186M both use a GC/TCD analysis to quantify the C1 through C5 compounds in pressurized condensate, and flash liberation uses GC/TCD to measure C1 – C5 in the flash gas and dead oil produced by the lab flash.

Flash liberation directly measures the FGOR and the flash gas composition, whereas GPA 2103M and GPA 2186M require PSM/EOS calculations to estimate FGOR and flash gas composition. It should be noted that there is not a standard or consensus method (e.g., a GPA or ASTM method) for flash liberation analyses, but that it is understood that all labs follow the general methodology described in Table 4-2. GPA 2103M includes a physical shrinkage measurement and physical determinations of C6+ and C10+ molecular weights and densities, whereas GPA 2186M and flash liberation calculate these parameters using assumptions that can contribute to inaccuracies as discussed below. GPA 2186M is the simplest method because all steps are GC analyses.

Table 4-2. Summary and Comparison of SPL Analytical Methods for Pressurized Condensate

Lab Activity	GPA 2103M C10+ / C100+	GPA 2186M	SPL Flash Liberation
Summary:	Pressurized condensate C1-C5 (with N2 & CO2), C6-C9, & C10+ / C100+ fractions are separated and analyzed by GC methods, and then mathematically recombined to estimate the condensate composition	Pressurized condensate analyzed by two GC methods to determine C1-C5 and C6+ fractions, and then the two fractions are mathematically recombined to estimate the condensate composition	Pressurized condensate is flashed in the lab, the flash gas and dead oil fractions are measured to determine FGOR & analyzed by GC methods. The two fractions are mathematically recombined to estimate pre-flash oil composition
Physical separation of pressurized condensate sample in lab:	1. Physical shrinkage to determine shrinkage factor and obtain C6+ fraction (pressurized liquid) 2. Distillation of C6+ to separate C6-C9 and C10+ / C100+ fractions (pressurized liquids)	NA	Pressurized condensate flashed in the lab into flash gas and dead oil fractions
Measurement of N2, CO2, C1 - C5:	Pressurized condensate compositional analysis by GC/TCD, similar to GPA 2177	Pressurized condensate compositional analysis by GC/TCD, similar to GPA 2177	Flash gas compositional analysis by GPA 2286 Dead oil compositional analysis by GPA 2186M Dead oil compositional analysis by GC/TCD, similar to GPA 2177
Measurement of C6+:	C6+ fraction (pressurized liquid) analysis by GC/FID	Pressurized condensate analysis by GC/FID	Dead oil compositional analysis by GPA 2186M Dead oil compositional analysis by GC/FID
C6+ MW	Physically measure by Cryette method	Calculate based on analytical results per GPA 2186 and GPA 2145	Calculate based on analytical results per GPA 2186 and GPA 2145
C6+ density/SG	Density determinations by density meter for C6+	Calculate based on analytical results per GPA 2186 and GPA 2145	Calculate based on analytical results per GPA 2186 and GPA 2145
C6-C9 & C10+ MW	Physically measure by Cryette method	Calculate based on analytical results per GPA 2186 and GPA 2145	Calculate based on analytical results per GPA 2186 and GPA 2145
C6-C9 & C10+ density/SG	Physically measure by densitometer	Calculate based on analytical results per GPA 2186 and GPA 2145	Calculate based on analytical results per GPA 2186 and GPA 2145
Recombination for pressurized condensate composition	Combine TCD & FID analyses (using physically determined volumes, density and molecular weights)	Combine TCD with FID analyses by bridging or allocation GPA 2186**M** does not normalize raw GPA 2177 analytical totals < 100%; rather the difference is included in the C6+ fraction	Mathematical recombination of oil and gas fractions by GOR to determine pressurized liquid composition
FGOR determination:	PSM/EOS calculations using pressurized condensate composition	PSM/EOS calculations using pressurized condensate composition	Determined from measured flash gas and dead oil volumes

Figures 4-3 to 4-8 compare SPL lab results to CRM values for the gravimetrically blended components: methane, ethane, propane, butanes, pentanes, and the C6+ fraction. C1-C5 HCs are of interest because they are primary components of storage tank flash gas. Figures 4-9 to 4-10 compare lab results to CRM values for the C10+ SG and MW. These parameters are of interest because they are inputs to PSM/EOS calculations. Considerations when reviewing these data include:

- The y-axis shows the ratio of the lab results and the CRM value, and ratios close to 1.0 (i.e., the red line) indicate accurate analytical results.
- The x-axis indicates the 10 CRM samples that were analyzed.
- The HC components in the gravimetrically blended CRM samples have very low uncertainties (i.e., 0.5% or less as shown in Table 4.1). The uncertainties of the CRM C10+ SG and MW are estimated to be about 2%.

Figure 4-3 presents analytical results for methane in CRM samples measured by the four SPL methods. The SPL GPA 2103M analyses generally have the best accuracy (i.e., agreement with the CRM values) with all analytical results within 5% of the CRM value and good precision (i.e., little data scatter). The SPL GPA 2186M analytical results ranged from about 5% to 15% greater than the CRM value, with more data scatter than the SPL 2103M results. The SPL flash liberation results ranged from about 5% to 50% greater than the CRM values and the data have considerably more scatter than the results for the other SPL analytical methods.

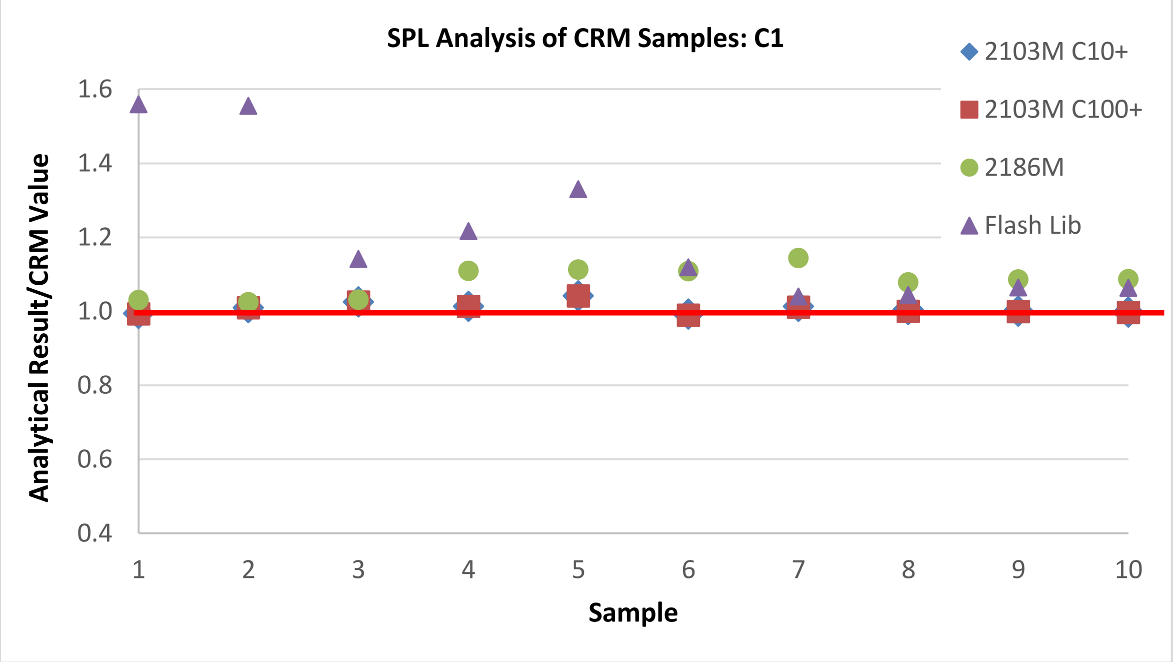

Figure 4-3. Results of SPL analytical methods evaluation: Methane vs. CRM value.

Figure 4-4 presents analytical results for ethane in CRM samples measured by the four SPL methods. The SPL GPA 2103M analyses generally have the best accuracy with all analytical results within 5% of the CRM value and good precision. The SPL GPA 2186M analytical results ranged from about zero to 15% greater than the CRM value, with more data scatter than the SPL 2103M results. The SPL flash liberation results ranged from about 10% less than to about 50% greater than the CRM values and the data have considerably more scatter than the other SPL analytical methods.

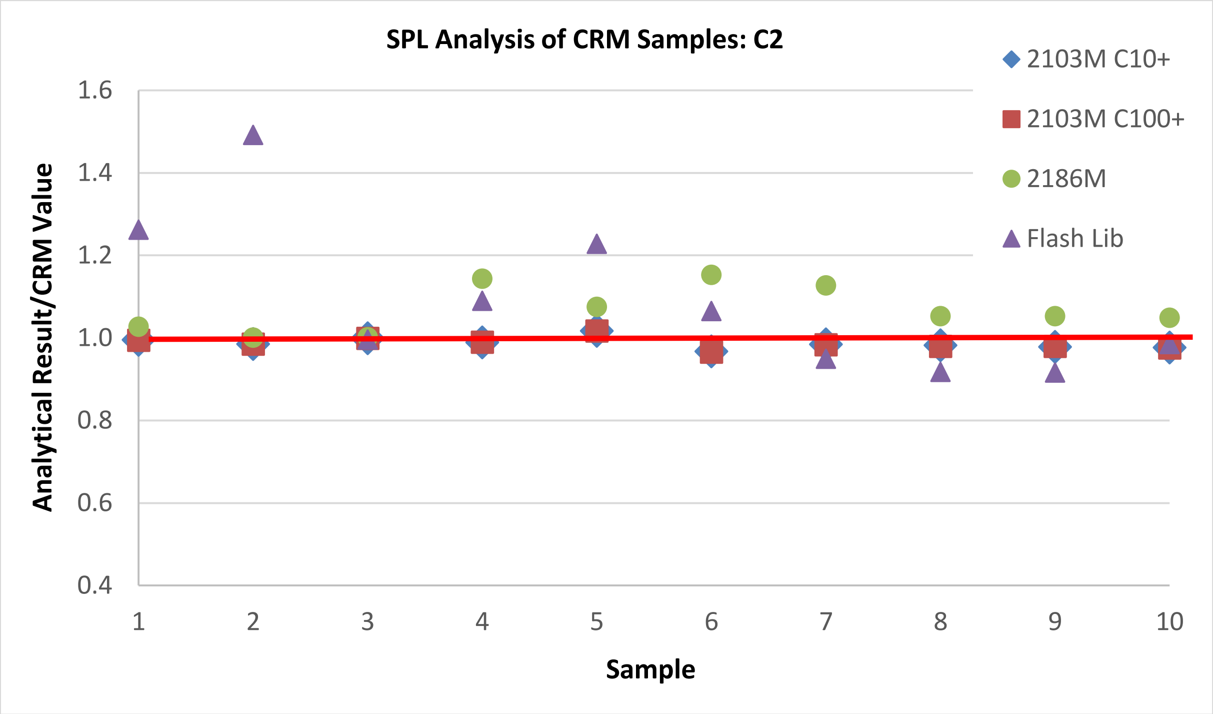

Figure 4-4. Results of SPL analytical methods evaluation: Ethane vs. CRM value.

Figure 4-5 presents analytical results for propane in CRM samples measured by the four SPL methods. The SPL GPA 2103M analyses generally have the best accuracy with all analytical results within 5% of the CRM value and good precision. The SPL GPA 2186M analytical results ranged from about 2% to 10% greater than the CRM value, with more data scatter than the SPL 2103M results. The SPL flash liberation results ranged from about 15% less than to about 15% greater than the CRM values and the data have considerably more scatter than the results for the other SPL analytical methods.

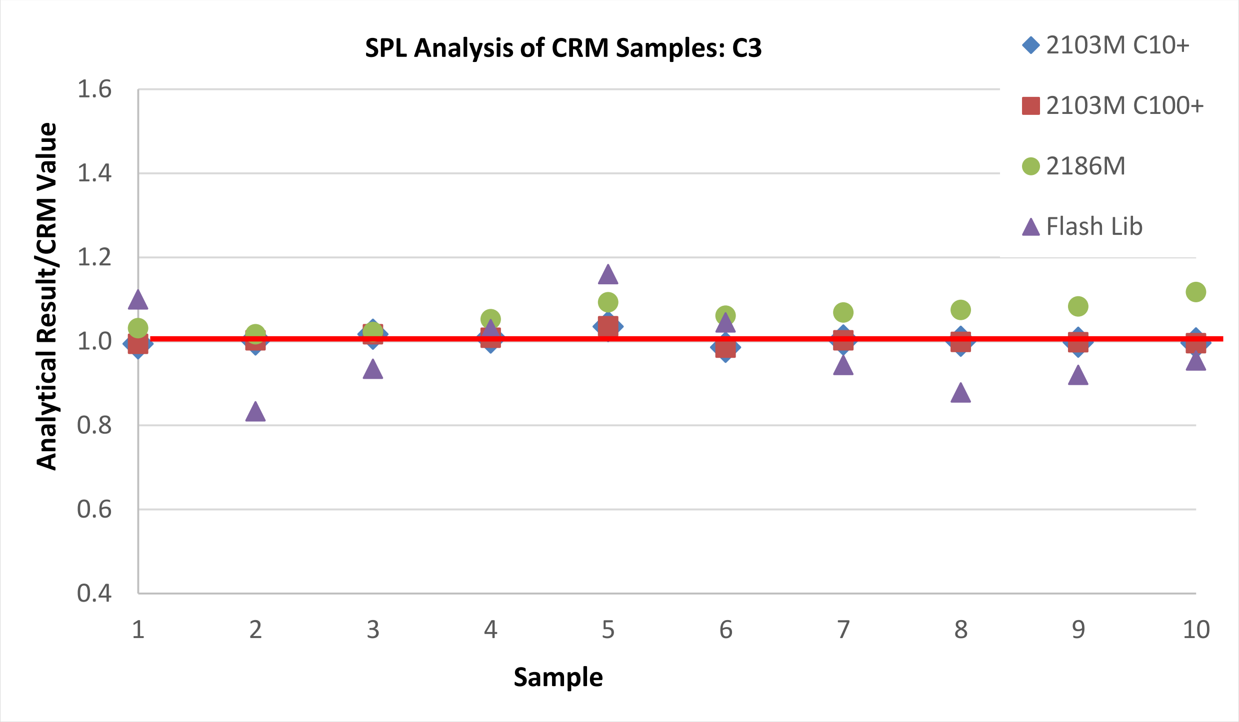

Figure 4-5. Results of SPL analytical methods evaluation: Propane vs. CRM value.

Figure 4-6 presents analytical results for butanes in CRM samples measured by the four SPL methods. The SPL GPA 2103M analyses generally have the best accuracy with all analytical results within 5% of the CRM value and good precision. The SPL GPA 2186M analytical results ranged from about 2% to 10% greater than the CRM value, with slightly more data scatter than the SPL 2103M results. The SPL flash liberation results ranged from about 10% to 60% less than the CRM values and the data have considerably more scatter than the results for the other SPL analytical methods.

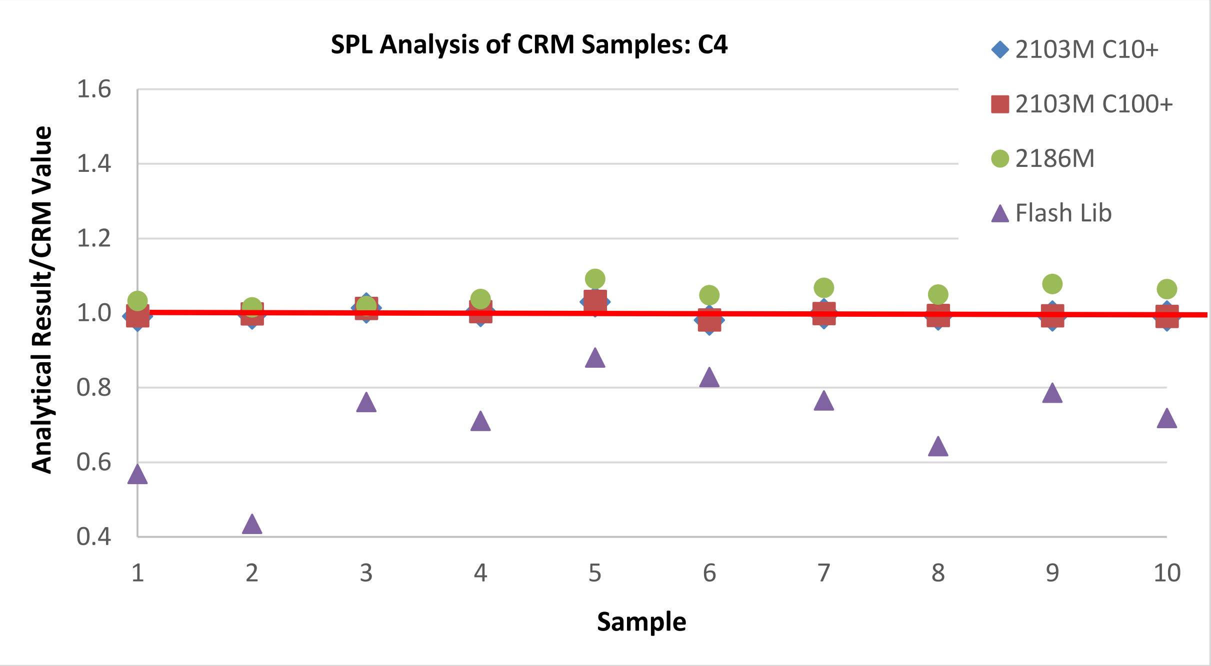

Figure 4-6. Results of SPL analytical methods evaluation: Butanes vs. CRM value.

Figure 4-7 presents analytical results for pentanes in CRM samples measured by the four SPL methods. The SPL GPA 2103M analyses generally have the best accuracy with all analytical results within 5% of the CRM value and good precision. The SPL GPA 2186M analytical results ranged from about 2% to 10% greater than the CRM value, with slightly more data scatter than the SPL 2103M results. The SPL flash liberation results ranged from about 25% to 45% less than the CRM values and the data have more scatter than the results for the other SPL analytical methods.

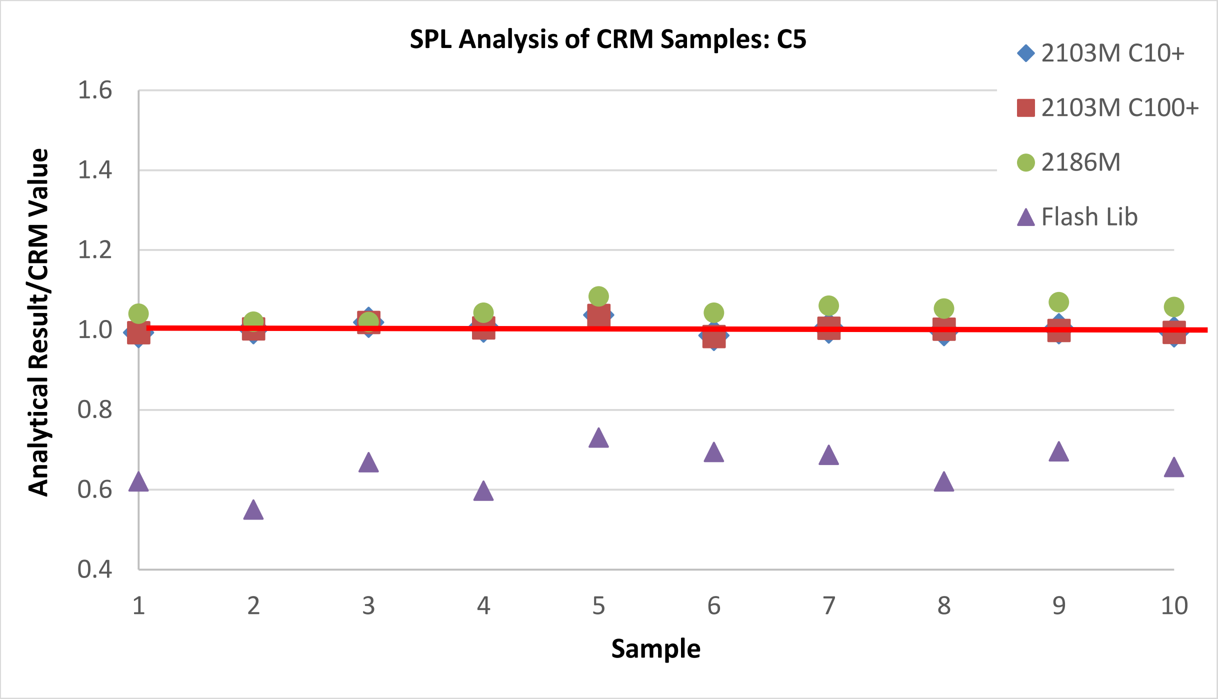

Figure 4-7. Results of SPL analytical methods evaluation: Pentanes vs. CRM value.

Figure 4-8 presents analytical results for C6+ HCs in CRM samples measured by the four SPL methods. Note that the y-axis scale differs from Figures 4-3 to 4-7. The SPL GPA 2103M analyses generally have the best accuracy with all analytical results within 1% of the CRM value and good precision. The SPL GPA 2186M analytical results were within about 2% of the CRM value, with slightly more data scatter than the SPL 2103M results. The SPL flash liberation results ranged from about 3% to 8% greater than the CRM values and the data have more scatter than the results for the other SPL analytical methods.

The slightly superior performance (i.e., better accuracy and precision) of SPL GPA 2103M relative to SPL GPA 2186M for the C1 to C6+ HCs may be because, at least in part, GPA 2103 was developed for the analysis of condensate and GPA 2186 was designed for the analysis of natural gas liquids.

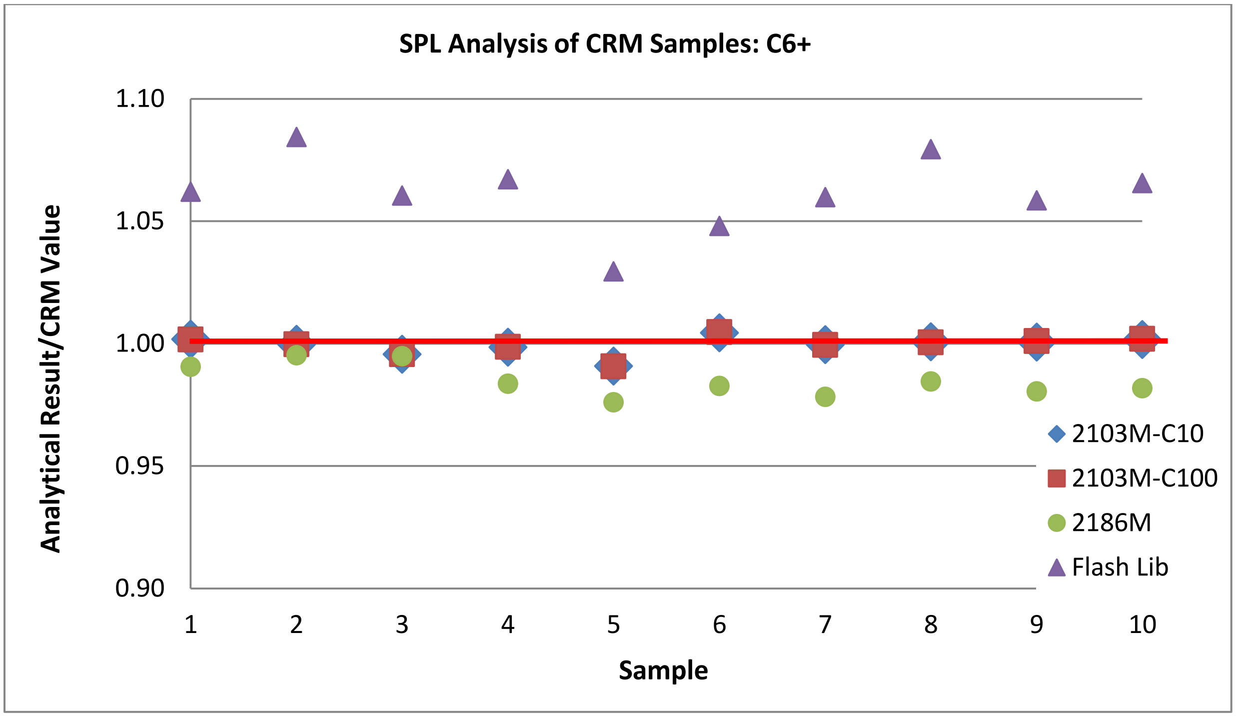

Figure 4-8. Results of SPL analytical methods evaluation: C6+ vs. CRM value.

Figure 4-9 presents analytical results for CRM samples C10+ MW measured by the four SPL methods. The <u>SPL GPA 2103M</u> analyses generally have the best accuracy with analytical results ranging from about 0% to 7% of the CRM value. The <u>SPL flash liberation</u> results ranged from about 7% to 8% less than the CRM values with very little data scatter. The <u>SPL GPA 2186M</u> analytical results were consistently about 35% less than the CRM value with very little data scatter.

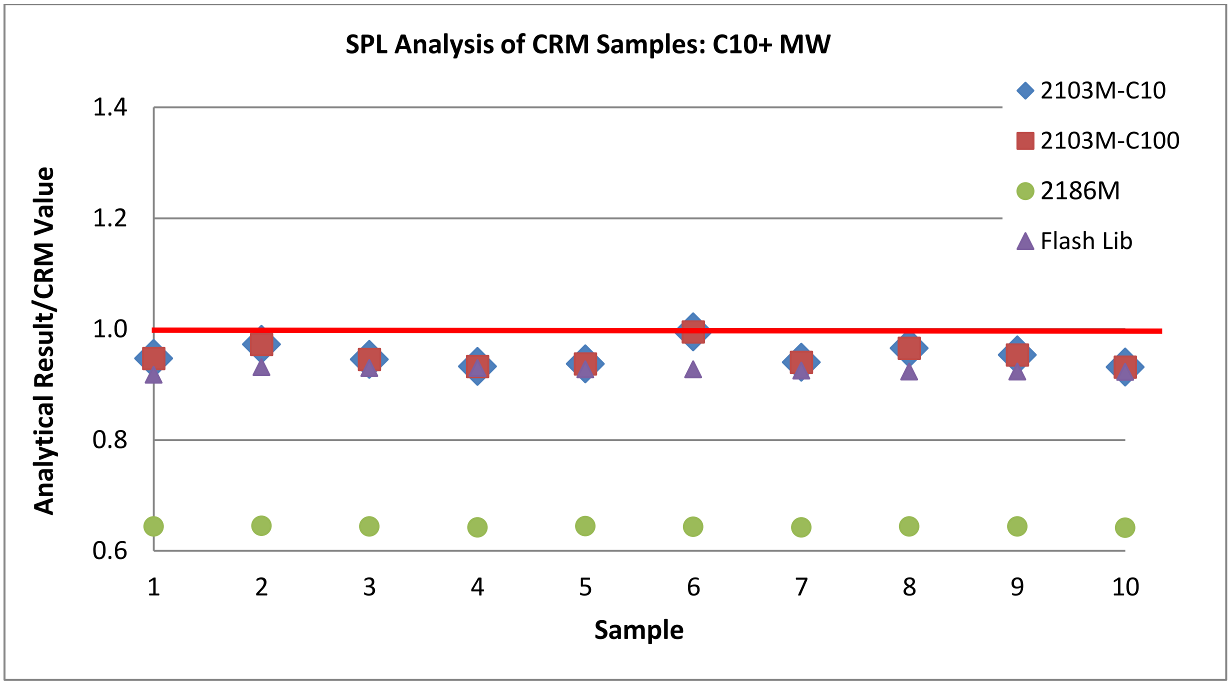

Figure 4-9. Results of SPL analytical methods evaluation: C10+ MW vs. CRM value.

Figure 4-10 presents analytical results for CRM samples C10+ SG measured by the four SPL methods. The SPL GPA 2103M analyses generally have the best accuracy with analytical results consistently about 1% less than the CRM value. The SPL flash liberation results were consistently about 7% less than the CRM values with very little data scatter. The SPL GPA 2186M analytical results were consistently about 9% less than the CRM value with very little data scatter.

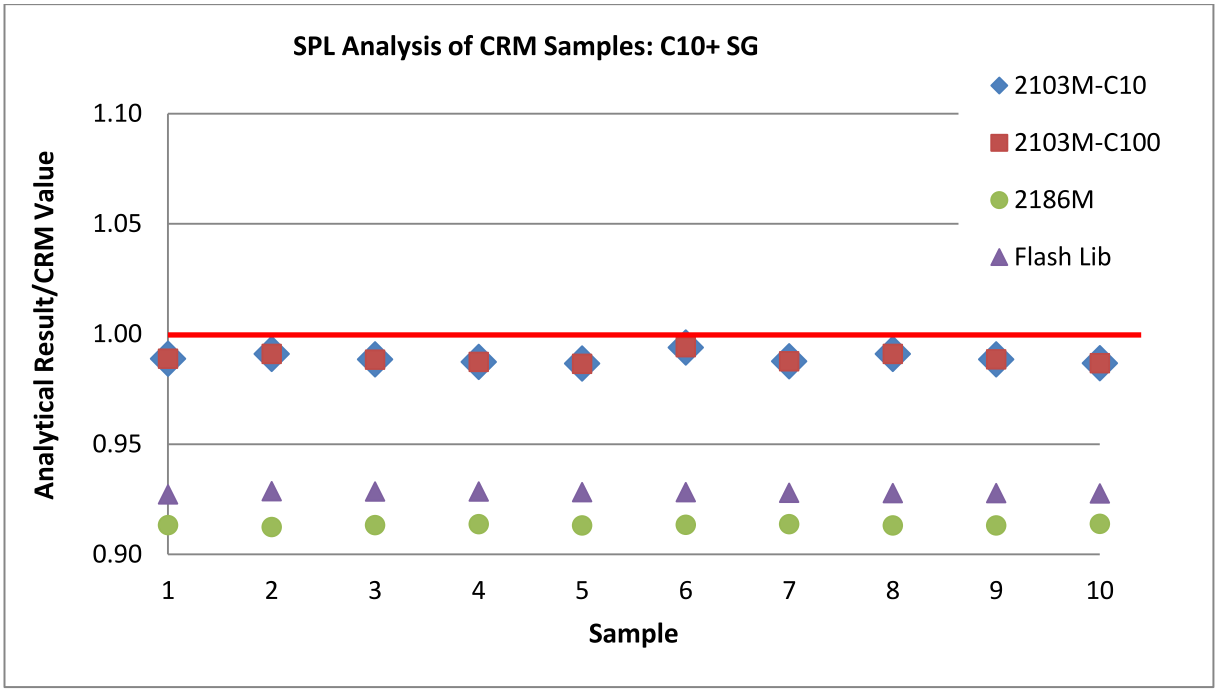

Figure 4-10. Results of SPL analytical methods evaluation: C10+ SG vs. CRM value.

The data in Figures 4-9 and 4-10 indicate better accuracy for direct measurement of C10+ MW and SG (i.e., by SPL GPA 2103M) than for the calculated values (i.e., by SPL GPA 2186M and SPL flash liberation).

This analytical method comparison and evaluation was conducted prior to the winter and summer three-pressure testing, and GPA 2103M (C10+) and GPA 2186M were selected as the analytical methods for these tests. This selection was based on the accuracy and variability observed in the results of this task, and on other considerations that included:

- The purpose of the PHLSA Study includes evaluating pressurized condensate sampling and analytical methods to produce accurate analytical results for practical application in modeling flashing losses. GPA 2103 and GPA 2186 are more typically used to determine pressurized oil composition for PSM/EOS flash gas calculations than flash liberation results (i.e., the flash liberation method directly measures flash gas volume and composition); thus, the use of GPA 2103 and GPA 2186 better addresses this project goal; and

- GPA 2103M (C10+) and GPA 2103M (C100+) produced similar analytical results and PSM/EOS calculations based on these results were also quite similar (e.g., PSM/EOS calculated FGORs using the C10+ and C100+ analytical results agreed within less than 1%). GPA 2103 (C10+) was selected for future testing because GPA 2103 (C100+) is considerably more expensive due to the additional analytical steps. Section 4.7.4 discusses PSM/EOS calculations based on GPA 2103M (C10+) and GPA 2103M (C100+) analyses of the same pressurized condensate samples.

It should be noted that the test material was a CRM specifically blended to mimic the pressurized condensate at the Test Facility and that analytical results for different fluids could yield different results.

Table 4-3 lists the estimated analytical uncertainties for GPA 2103M, GPA 2186M, and flash liberation analysis of condensate components by SPL. Note that these are relative uncertainties at a 95% confidence interval (CI). These estimates are based on analyses of CRM samples over the course of the PHLSA Study. These uncertainty analysis results show:

- SPL GPA 2103M analytical results generally had lower uncertainties than SPL GPA 2186M and SPL flash liberation for the gravimetrically blended light end compounds (i.e., C1–C5) that are primary flash gas components, and for C6+.
- Analytical results for nitrogen in CRM samples have high uncertainty and this could be due, at least in part, to nitrogen concentrations near the analytical detection limit.
- SPL flash liberation had the highest uncertainties for the gravimetrically blended C1-C5 HCs and for C6+.

Table 4-3. Summary of Uncertainty Estimates for SPL Analytical Methods

Compound	Uncertainty of Wt% Analytical Results (%U, 95% CI)		
	Analytical Method		
	SPL GPA 2103M	SPL GPA 2186M	SPL Flash Liberation
Carbon Dioxide*	1.7%	21.0%	8.6%
Nitrogen*	5.7%	41.0%	17.0%
Methane*	2.0%	2.7%	16.0%
Ethane*	1.3%	3.4%	9.2%
Propane*	1.0%	1.9%	6.7%
iso-Butane*	0.6%	1.0%	14.0%
n-Butane*	1.1%	1.5%	13.0%
iso-Pentane*	1.9%	2.2%	22.0%
n-Pentane*	0.9%	1.8%	4.7%
iso-Hexane	3.0%	1.7%	4.6%
n-Hexane	7.6%	5.9%	31.0%
Heptanes	2.7%	1.9%	1.1%
Octanes	3.5%	4.1%	1.5%
Nonanes	4.4%	3.2%	2.8%
C10+	3.8%	3.4%	1.4%
Benzene	7.9%	4.5%	—
Toluene	2.6%	0.9%	—
Ethylbenzene	18.0%	17.0%	—
Xylenes	3.1%	1.5%	2.7%
C6+*	0.2%	0.4%	0.7%
C7+	1.0%	0.8%	1.9%
C8+	1.8%	2.1%	2.1%

*Gravimetrically blended component.

Table 4-4 presents a summary of estimated analytical biases by component and method for the SPL analytical results. Analytical method bias is an estimate of a systematic measurement error, and the data in Table 4-4 was determined from a linear regression between analytical results and certified values. Note that these biases are absolute values in units of weight percent. Current GPA methods practice does not address bias, and the data analysis for this study follows that practice. For example, reported analytical results are not adjusted for bias, and the uncertainty estimates presented in Table 4-3 and used for subsequent uncertainty calculations, such as for the uncertainties of directly measured FGOR and storage tank mass balance, do not consider bias. These data are presented for informational and discussion purposes; for example, a bias assessment could be considered for a comprehensive method evaluation (e.g., to select an optimal analytical method for an application).

Table 4-4. Summary of Bias Estimates for SPL Analytical Methods

Compound	Weight % Bias		
	Analytical Method		
	SPL GPA 2103M	SPL GPA 2186M	SPL Flash Liberation
Carbon Dioxide*	7.6%	-17.0%	11.0%
Nitrogen*	13.0%	-44.0%	88.0%
Methane*	0.8%	-3.1%	12.0%
Ethane*	1.8%	-9.9%	7.1%
Propane*	0.4%	-7.7%	7.9%
iso-Butane*	1.1%	-11.0%	15.0%
n-Butane*	0.7%	-8.8%	17.0%
iso-Pentane*	1.8%	-1.5%	88.0%
n-Pentane*	0.4%	-3.9%	21.0%
iso-Hexane	0.6%	5.8%	15.0%
n-Hexane	1.0%	-3.0%	5.1%
Heptanes	1.0%	-12.0%	1.3%
Octanes	1.6%	-15.0%	7.0%
Nonanes	5.2%	-20.0%	31.0%
C10+	4.3%	19.0%	1.8%
Benzene	0.9%	-4.1%	—
Toluene	1.5%	8.3%	—
Ethylbenzene	7.0%	23.0%	—
Xylenes	5.8%	27.0%	2.2%
C6+*	0.05%	1.7%	3.0%
C7+	0.7%	3.2%	1.1%
C8+	2.5%	5.9%	3.4%

*Gravimetrically blended component.

4.3 Multi-Laboratory Analytical Methods Study

Supporting data for the information in Section 4.3 is in Section 3 of Appendix II and Appendix VI (PHLSA Study Task 3_Multi lab Data.xlsm).

For this task (Task 3, refer to Section 3.2.3), Certified Reference Materials with two different compositions (identified as CRM1 and CRM2) were analyzed by four different labs using three different analytical methods (GPA 2186M, GPA 2103M, and flash liberation) to compare the methods and the variability of results from different labs. Each participating lab was requested to use lab-specific modifications to provide best performance. The "M" attached to the analytical methods refers to associated modifications used for best practices. Not every lab performed all three analytical methods. For each analytical method, each lab analyzed three CRM1 samples and three CRM2 samples.

Figures 4-11 to 4-16 compare lab results to CRM values for the gravimetrically blended components: methane, ethane, propane, butanes, pentanes, and the C6+ fraction. C1-C5 HCs are of interest because they are primary components of storage tank flash gas. Figures 4-17 and 4-18 compare lab results to CRM values for the total C10+ SG and MW. These parameters are of interest because they are inputs to PSM/EOS calculations. Considerations when reviewing these data include:

- The y-axis shows the ratio of the reported lab results and the CRM value, and ratios close to 1.0 (i.e., the red line) indicate accurate analytical results.
- The x-axis indicates the analytical method for the CRM samples.
- The HC components in the gravimetrically blended CRM samples have very low uncertainties (i.e., 0.5% or less as shown in Table 4.1). The uncertainties of the CRM C10+ SG and MW are estimated to be about 2%.

Figure 4-11 presents the multi-lab study analytical results for methane. For the GPA 2103M analyses, Lab 2 and Lab 4 results have good accuracy (i.e., are within about 5% of the CRM value) and precision (i.e., little data scatter); however, Lab 1 results differ from the CRM values by about 25%. Although the Lab 1 methane results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3), and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M results for Lab 3 and Lab 4 are generally less precise than the GPA 2103M results (i.e., more scatter in the data). Lab 2 GPA 2186M and GPA 2103M results have similar accuracy and precision, and the GPA 2186M analytical results for Lab 3 and Lab 4 differ from the CRM values by up to about 15%. The flash liberation methane results for Lab 3 and Lab 4 are generally less accurate than GPA 2103M and GPA 2186M results (i.e., differ from the CRM values by up to about 25 to 30%) and the data scatter is similar to the GPA 2186M results. Lab 1 flash liberation results have considerable scatter and differ from the CRM values by about 15 to 25%.

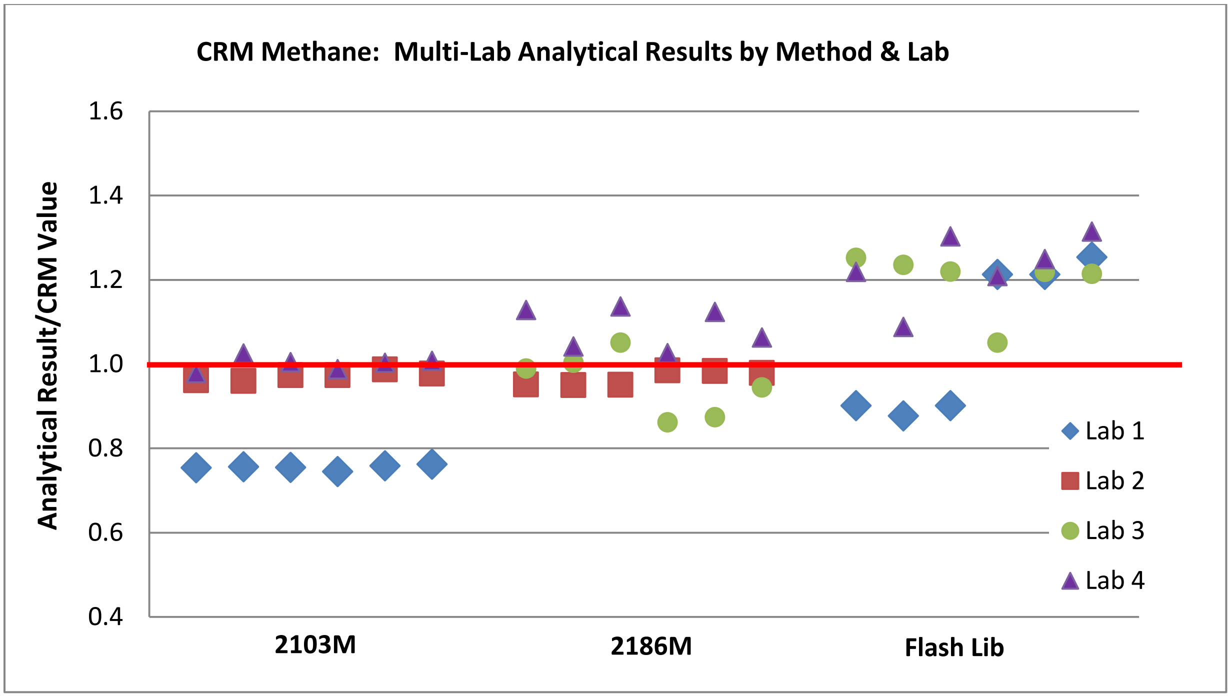

Figure 4-11. Results of multi-lab study analytical methods evaluation: Methane vs. CRM value.

Figure 4-12 presents the multi-lab study analytical results for ethane. For the GPA 2103M analyses, Lab 4 results have the best accuracy and Lab 2 results are within about 10% of the CRM value, and both labs show good precision; however, Lab 1 results differ from the CRM values by about 25%. Although the Lab 1 ethane results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3) and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M and GPA 2103M results generally have similar precision. Lab 2 accuracies for GPA 2186M and GPA 2103M are similar, and the GPA 2186M analytical results differ from the CRM values by up to about 10% for Lab 4 and up to about 20% for Lab 3. The flash liberation ethane results for Lab 3 are generally more accurate than the GPA 2186M results and the opposite trend is observed for Lab 4. Data scatter for Lab 3 and Lab 4 is similar to the GPA 2186M results. Lab 1 flash liberation results have considerable scatter and differ from the CRM by up to about 20%.

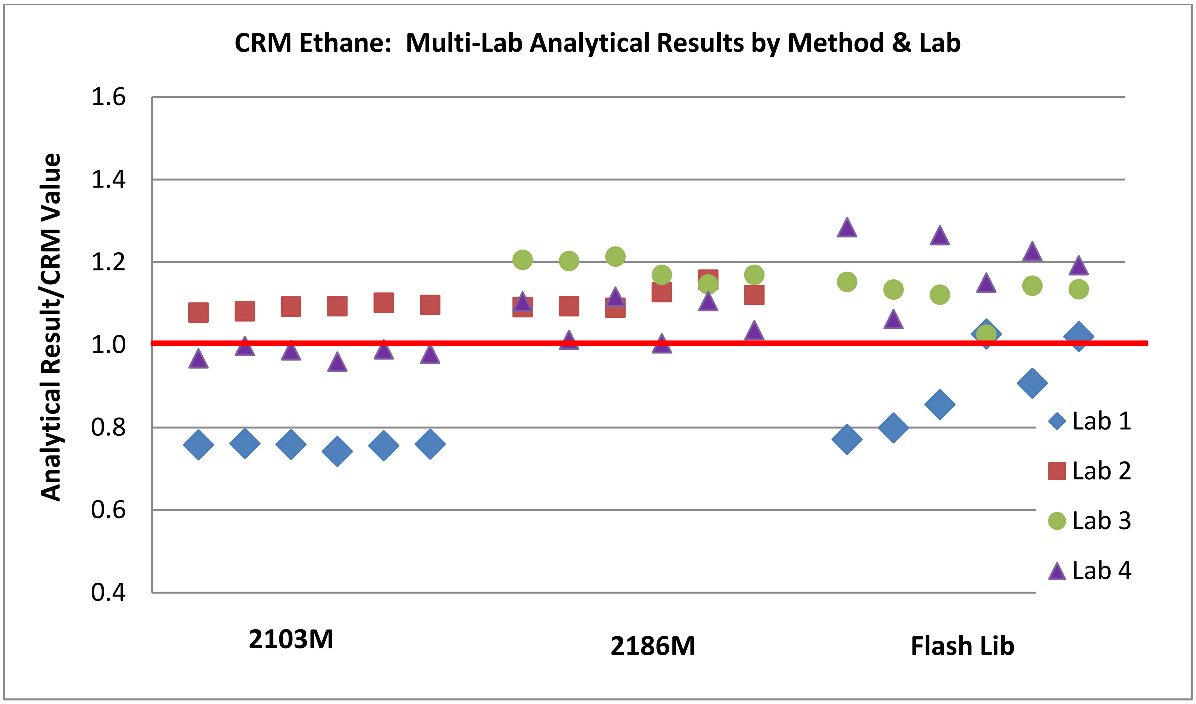

Figure 4-12. Results of multi-lab study analytical methods evaluation: Ethane vs. CRM value.

Figure 4-13 presents the multi-lab study analytical results for propane. For the GPA 2103M analyses, Lab 2 and Lab 4 results have good accuracy (i.e., are within about 5% of the CRM value) and precision; however, Lab 1 results differ from the CRM values by about 25%. Although the Lab 1 propane results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3) and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M results for Lab 4 are less precise than the GPA 2103M results, and Lab 3 GPA 2186M data have similar precision as the GPA 2103M results. Lab 2 GPA 2186M and GPA 2103M results have similar accuracy and precision. The GPA 2186M analytical results for Lab 3 and Lab 4 differ from the CRM values by up to about 15%. The flash liberation propane results for Lab 3 and Lab 4 are generally the least accurate and demonstrate the largest data scatter. Lab 1 flash liberation results have considerable scatter and differ from the CRM by up to about 25%.

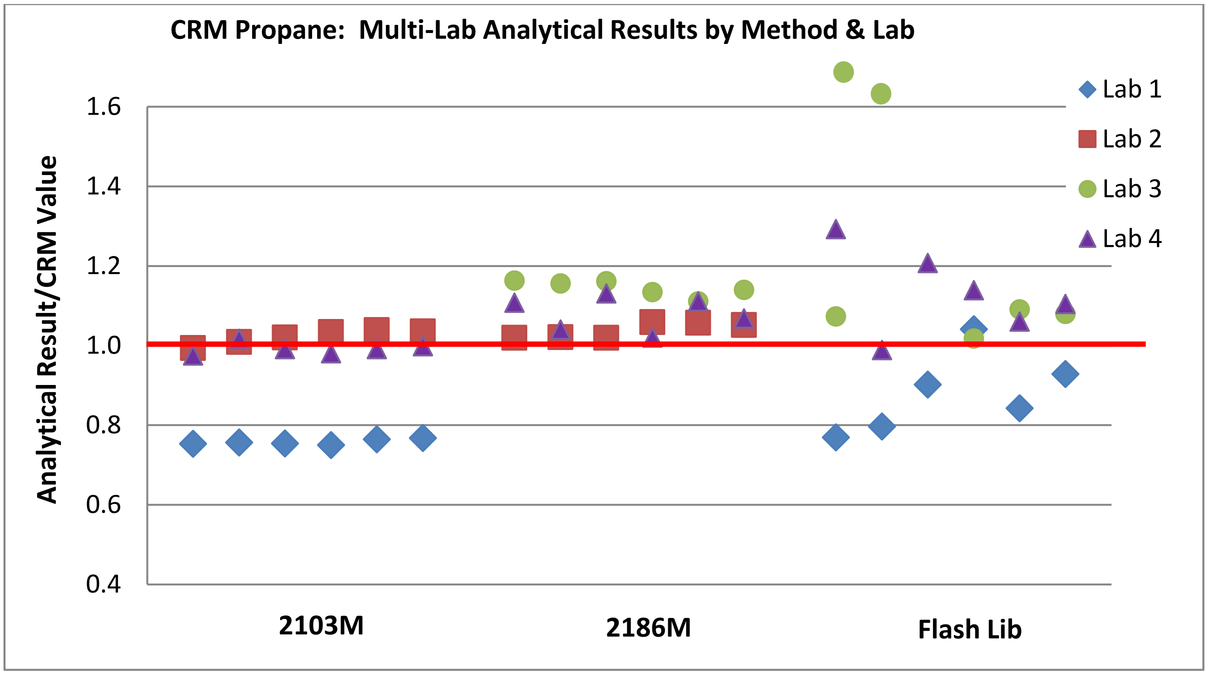

Figure 4-13. Results of multi-lab study analytical methods evaluation: Propane vs. CRM value.

Figure 4-14 presents the multi-lab study analytical results for butanes. For the GPA 2103M analyses, Lab 2 and Lab 4 results have good accuracy (i.e., are within about 5% of the CRM value) and precision; however, Lab 1 results differ from the CRM values by about 25%. Although the Lab 1 butanes results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3) and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M results for Lab 3 and Lab 4 are less precise than the GPA 2103M results. Lab 2 GPA 2186M and GPA 2103M results have similar accuracy and precision, and the GPA 2186M analytical results for Lab 3 and Lab 4 differ from the CRM values by up to about 45% and 15%, respectively. The flash liberation butanes results for Lab 3 are generally more accurate and precise than the GPA 2186M results. Lab 4 results differ from the CRM values by up to about 50% and have more data scatter than the GPA 2103M and GPA 2186M results. Lab 1 flash liberation results have considerable scatter and differ from the CRM by up to about 15%.

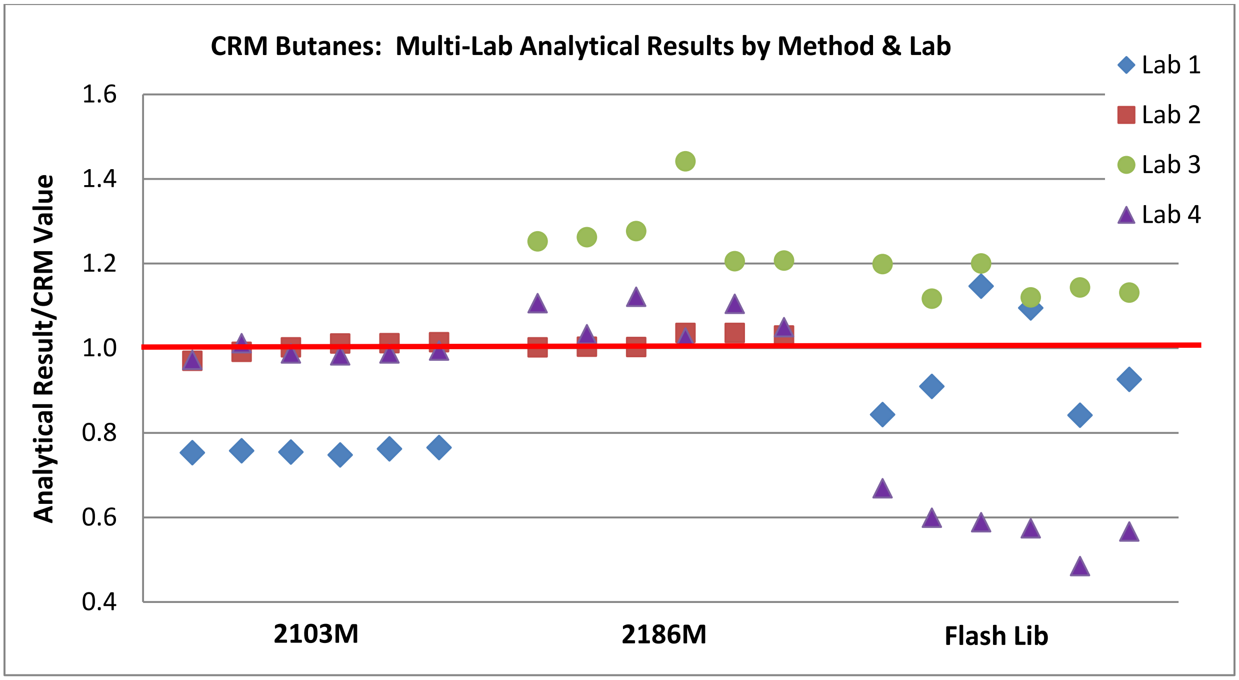

Figure 4-14. Results of multi-lab study analytical methods evaluation: Butanes vs. CRM value.

Figure 4-15 presents the multi-lab study analytical results for pentanes. For the GPA 2103M analyses, Lab 2 and Lab 4 results have the best accuracy (i.e., are within about 5% of the CRM value for all but one sample) and generally show good precision; however, Lab 1 results differ from the CRM values by about 25%. Although the Lab 1 pentanes results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3) and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M results for Lab 3 and Lab 4 are less precise than the GPA 2103M results. Lab 2 GPA 2186M and GPA 2103M results have similar accuracy and precision, and the GPA 2186M analytical results differ from the CRM values by up to about 15% for Lab 3 and Lab 4. The flash liberation pentanes results for Lab 3 have similar accuracy and precision as the GPA 2186M results. Lab 4 results differ from the CRM by 30 to 40% although with less data scatter than the GPA 2186M results. Lab 1 flash liberation results have considerable scatter and differ from the CRM by up to about 15%.

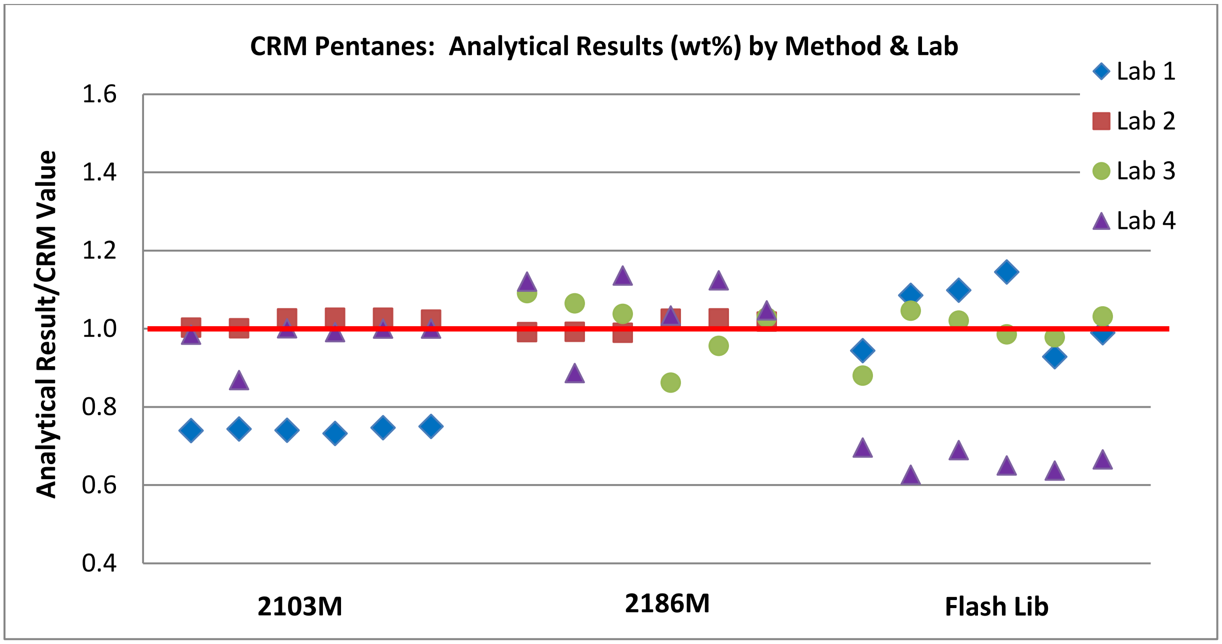

Figure 4-15. Results of multi-lab study analytical methods evaluation: Pentanes vs. CRM value.

Figure 4-16 presents the multi-lab study analytical results for total C6+ HCs. Note that the y-axis scale differs from Figures 4-11 to 4-15. The analytical accuracy and precision trends for the C6+ HCs are generally consistent with the trends observed for the lighter compounds; however, the data are inverted around the red Analytical Result/CRM Value = 1.0 line. For example, the low bias observed for the Lab 1 GPA 2103M analysis of C1–C5 compounds is balanced by a high bias for the C6+ HCs.

For the GPA 2103M analyses, Lab 2 and Lab 4 results have good accuracy (i.e., compare within about 1 to 2% of the CRM value) and generally show good precision; however, Lab 1 results differ from the CRM values by about 6%. Although the Lab 1 C6+ results have poor accuracy, the results are very precise suggesting a systematic bias rather than random analytical errors. The Lab 1 results were determined to be statistical outliers (refer to Appendix II, Section 3.3) and outlier investigation discussion with Lab 1 indicated possible analyst error for these samples. The GPA 2186M results for Lab 3 and Lab 4 are less precise than the GPA 2103M results (i.e., more scatter in the data). Lab 2 GPA 2186M and GPA 2103M results have similar accuracy and precision, and the GPA 2186M analytical results differ from the CRM values by up to about 4% for Lab 3 and Lab 4. The flash liberation C6+ results for Lab 3 have similar accuracy and precision as the GPA 2186M results. Lab 4 results differ from CRM values by about 5 to 8%, and have similar precision as the GPA 2186M results. Lab 1 flash liberation results have considerable scatter and differ from the CRM by up to about 3%.

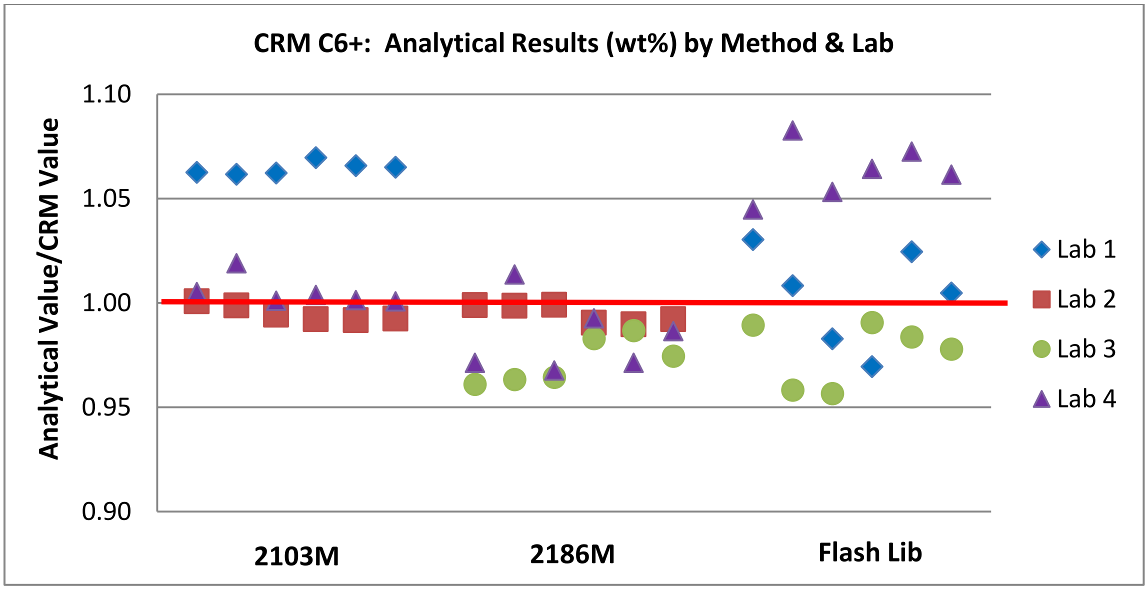

Figure 4-16. Results of multi-lab study analytical methods evaluation: C6+ vs. CRM value.

Figures 4-17and 4-18 present the multi-lab study analytical results for C10+ SG and MW, respectively. GPA 2103M directly measures these parameters, whereas GPA 2186M and flash liberation calculate these values based on analytical results. For this testing, the direct measurement method generally produced more accurate results.

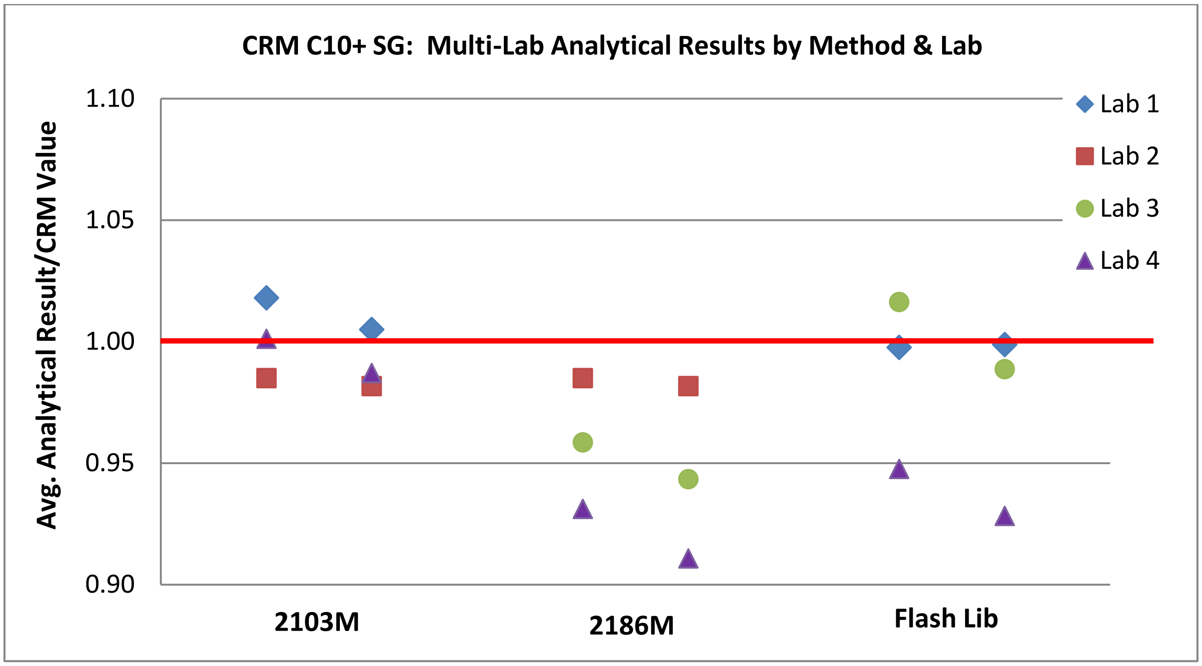

Figure 4-17. Results of multi-lab study analytical methods evaluation: C10+ SG vs. CRM value.

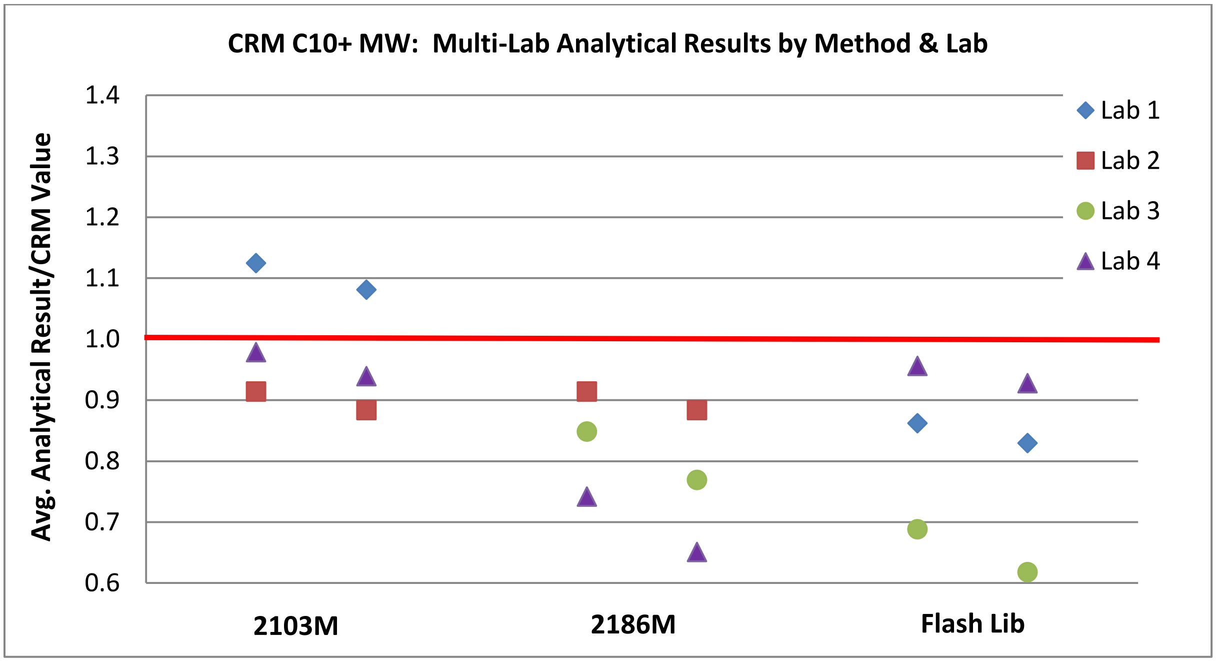

Figure 4-18. Results of multi-lab study analytical methods evaluation: C10+ MW vs. CRM value.

Table 4-5 lists the estimated analytical uncertainties for GPA 2103M, GPA 2186M, and flash liberation analysis of condensate components based on the results of the multi-lab study. Note that these are relative uncertainties at a 95% confidence interval. For GPA 2103M, uncertainties estimated with the Lab 1 statistical outliers included and removed are presented. Primary observations for these uncertainty analysis results include:

- Uncertainty estimates for the GPA 2103M results are generally a factor of 2 or more greater with the Lab 1 outliers included than with the Lab 1 outliers removed.
- GPA 2103M analytical results (Lab 1 outliers removed) generally had slightly lower uncertainties than GPA 2186M for gravimetrically blended light end compounds (i.e., C1–C5) that are the primary flash gas components and C6+ that was also a gravimetrically blended component. GPA 2186M analytical results generally had lower uncertainties than GPA 2103M analytical results (Lab 1 outliers removed) for individual HC species C6 and heavier.
- GPA 2103M analytical results (Lab 1 outliers included) had higher uncertainties than GPA 2186M for most of the HC species.
- Flash liberation analytical results had higher uncertainties than GPA 2103M (Lab 1 outliers removed) and GPA 2186M for most of the HC species. Flash liberation analytical results had some higher uncertainties and some lower uncertainties than GPA 2103M (Lab 1 outliers included).
- Analytical results for nitrogen in CRM samples have high uncertainty, and this could be due, at least in part, to nitrogen concentrations near the analytical detection limit.

Table 4-5. Summary of Uncertainty Estimates for Analytical Methods Based on Multi-Lab Study Results

Compound	Uncertainty of Wt% Analytical Results (%U, 95% CI)			
	Analytical Method			
	GPA 2103M (Lab 1 outliers included)	GPA 2103M (Lab 1 outliers removed)	GPA 2186M	Flash Liberation
CO2*	9.1%	4.5%	21.0%	6.4%
Nitrogen*	27.0%	41.0%	54.0%	48.0%
Methane*	11.0%	2.0%	2.7%	10.0%
Ethane*	13.0%	2.6%	3.4%	6.5%
Propane*	4.7%	1.0%	1.9%	7.9%
iso-Butane*	7.8%	0.7%	1.0%	13.0%
n-Butane*	4.5%	0.7%	1.5%	12.0%
iso-Pentane*	8.5%	2.5%	2.2%	40.0%
n-Pentane*	4.9%	0.7%	1.8%	8.6%
iso-Hexane	13.0%	5.4%	1.5%	4.6%
n-Hexane	12.0%	4.5%	5.9%	28.0%
Heptanes	15.0%	4.9%	1.9%	2.5%
Octanes	13.0%	7.8%	4.1%	2.5%
Nonanes	9.3%	4.9%	3.2%	9.3%
C10+	12.0%	2.7%	3.4%	4.2%
Benzene	27.0%	7.4%	4.5%	-
Toluene	8.2%	2.6%	0.9%	-
Ethylbenzene	15.0%	19.0%	17.0%	-
Xylenes	5.6%	2.8%	3.0%	5.9%
C6+*	2.2%	0.3%	0.4%	1.4%
C7+	6.4%	1.2%	0.8%	3.6%
C8+	6.1%	1.7%	2.1%	4.5%

*Gravimetrically blended component.

4.3.1 Summary of Findings for the Multi-Laboratory Analytical Methods Study

Key considerations and findings from the multi-laboratory analytical methods evaluation task for pressurized HC liquids include:

- As discussed in Section 3.2.3, the multi-lab study had a limited scope and was not intended to be a comprehensive and robust Inter-laboratory study to estimate the reproducibility of the methods. The analytical uncertainties listed in Table 4-5 are specific to the participating laboratories and analyzed CRMs, should not be considered estimates of the industry-wide uncertainties for these analytical methods.

Lab 1 2103M results have an apparent systematic bias of sufficient magnitude that these results are statistical outliers. Lab 1 did not analyze the CRM samples using GPA 2186M; thus, it is not known if this systematic bias would also impact GPA 2186M results. GPA 2103 has more analytical steps than GPA 2186 and flash liberation (refer to Section 2.3.2) and this greater complexity could have contributed to the biased results, or the bias could simply have been caused by errors by a single analyst. In sum, because the multi-lab study has a small data set, any anomalous data have a large impact on statistical analyses; thus, strong conclusions regarding these analytical methods based on the multi-lab study are not recommended.

- The accuracy and precision of the analytical results varied by method and by laboratory, and this suggests oil and gas producers would benefit from a means to compare the performance of different laboratories and analytical methods. Analytical laboratories could be asked to provide uncertainty estimates for reported parameters based on a standard ISO-based or similar uncertainty estimate methodology that is audited and verified by an accredited third party. For example, ISO Standard 17025 “General requirements for the competence of testing and calibration laboratories“ specifies general requirements for the reporting of uncertainties for analytical results. Accreditation bodies for calibration laboratories can require labs to participate in Proficiency Tests to validate their claimed uncertainty, and some laboratories regularly participate in Proficiency Tests to assess performance and confirm reported uncertainty.

4.4 Laboratory Sample Handling Perturbation Study

Supporting data for the information in this Section 4.4 is in Section 5 of Appendix II and in Appendix VI (PHLSA Study Task 6 Sample Handling Data.xlsm).

This task (Task 6, refer to Section 3.2.6) evaluated the impact of laboratory pressurized HC liquids sample handling parameters – temperature, pressure, sample cylinder mixing, and purging (i.e., GC sample injection rate) – on pressurized HC liquids samples compositional analyses. The industry analytical standards provide some guidance, as do manufacturers of sample cylinders, but comprehensive laboratory sample handling procedures are not available. CRM samples were used for these tests as described in Section 3.2.6. The task results were used to develop recommendations for proper handling of laboratory samples.

Figure 4-19 shows the impact of the number of cylinder rocks prior to GC injection on PSM/EOS calculations of FGOR. The effect of mixing rocks is more pronounced for CP cylinders than for CV cylinders, but both show some effect of improper (i.e., incomplete) mixing. For CP cylinders, with less mixing it appears that there are more light ends in the GC injection aliquot causing higher FGOR. Figure 4-20 shows the impact of sample pressure prior to GC injection on PSM/EOS calculations of FGOR. The effects of sample pressure are evident for CV cylinders although CP cylinders show no effect. Figure 4-21 shows the impact of sample pressure prior to GC injection on PSM/EOS calculations of bubble point pressure, and the data show that the bubble point pressure is impacted by sample pressure for both cylinder types.

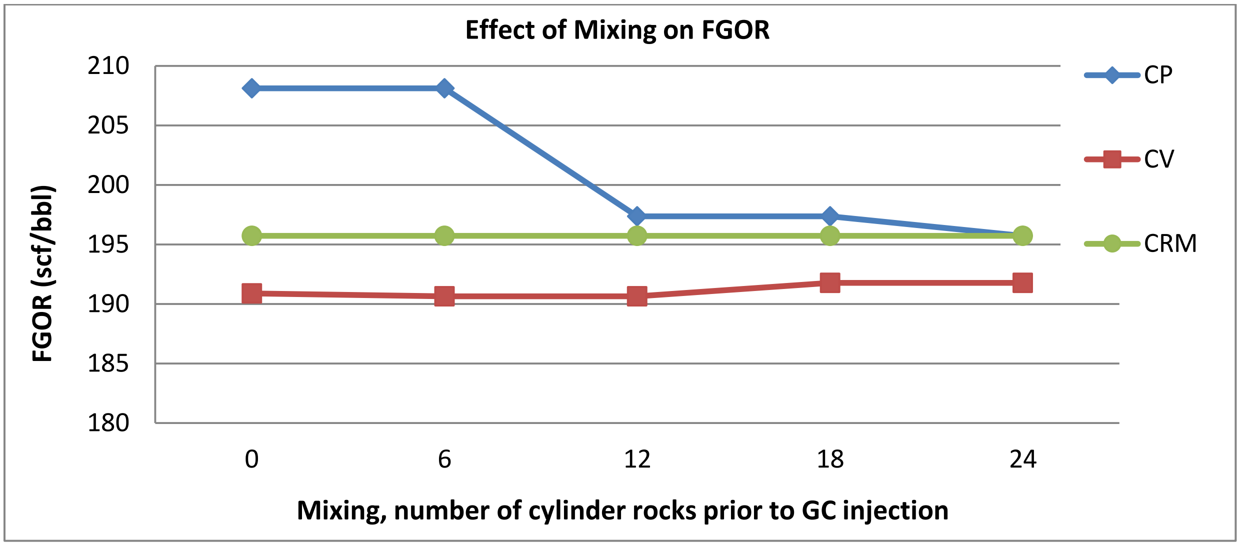

Figure 4-19. Effect of mixing (number of cylinder rocks) on PSM/EOS calculated FGOR.

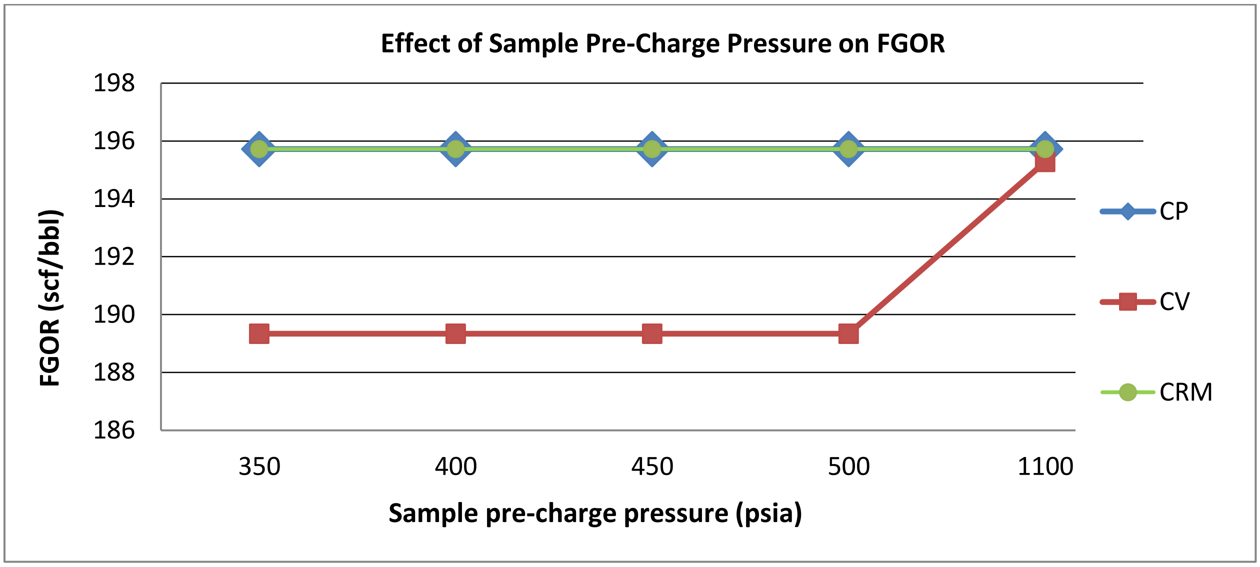

Figure 4-20. Effect of sample pressure on PSM/EOS calculated FGOR.

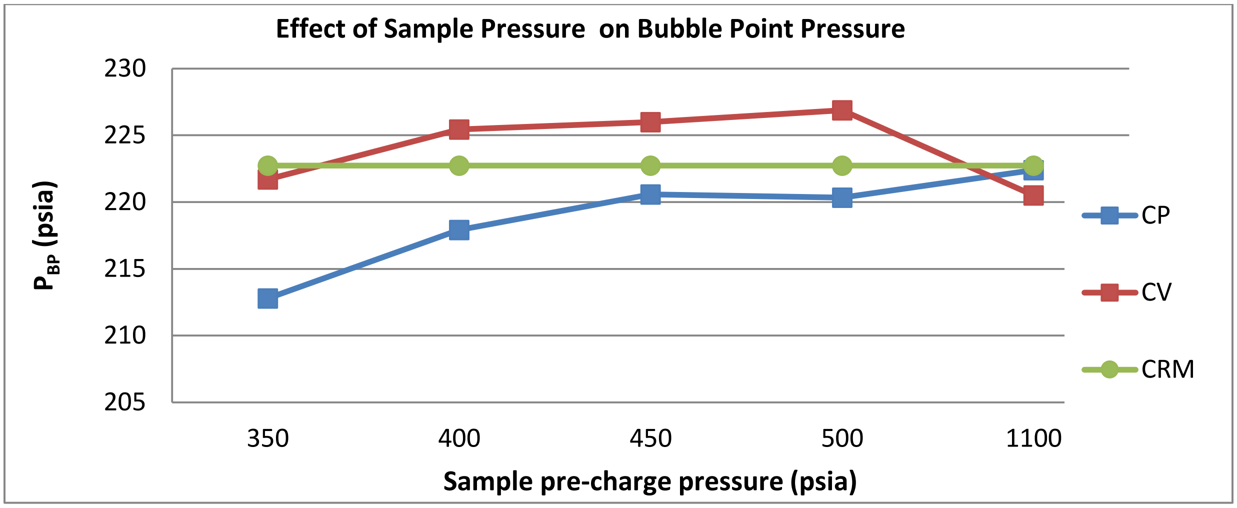

Figure 4-21. Effect of sample pressure on PSM/EOS calculated bubble point pressure.

The study results indicate that sample pressure and number of mixing rocks impact the sample analysis results. Sample purge rate and temperature did not impact the analytical results. For the remainder of the study, the least rigorous sample handling parameters combination that did not produce sample distortion was used, and included 24 sample rocks, lab temperature, 1,115 psia sample pressure and 8 ml per second purge rate.

ASTM E1169 “Standard Practice for Conducting Ruggedness Tests” assesses the statistical significance (i.e., at a 95% level of confidence) of a method parameter (e.g., sample temperature, sample mixing) over method outcomes, and was used to determine the impact of the sample handling perturbations on analytical results. Table 4-6 summarizes the results of this statistical analysis.

Table 4-6. Summary of Ruggedness Tests for Lab Sample Handling Perturbations.

Sample Handling Parameter*	CRM Component									
	CO_2	N_2	CH_4	C2H6	C3H8	i-C4	n-C4	i-C5	n-C5	C6+
CP/CV	X	X								
Mixing				X		X	X	X	X	
Purge Rate										
Pressure			X		X	X				X
Temperature										

* Parameters that have a statistically significant impact (i.e., $\alpha \leq 0.05$) on the indicated CRM component are marked with an X.

The primary findings of the sample handling perturbations ruggedness analysis for the PHLSA Study include:

- The statistical analysis indicates that the cylinder pre-charge pressure and mixing (i.e., number of cylinder rocks) impact the analytical results for volatile compounds in the pressurized condensate samples (refer to Table 4-6). There is insufficient statistical evidence to conclude that sample purge rate and sample temperature have influence over the analytical results of tested samples.
- Sample collection cylinder type (CP cylinder or two valve CV cylinder) influences carbon dioxide and nitrogen. The impact of cylinder type on methane was borderline statistically significant (i.e., $\alpha = 0.051$).
- To minimize bias in the analysis of volatile components, the results of this study indicate that the pre- charge pressure should be 500 psig or more for samples with bubble point pressures of 225 psig or lower. GPA guidelines recommend that the pre-charge sample pressure be a minimum 300 psi greater than the sample collection pressure, and this guidance is consistent with the findings of this study and would apply for samples collected from separators with higher pressures. The number of mixing rocks for sample homogenization should be 18 or more.

4.5 Sample Collection Perturbation Study

Supporting data for the information in Section 4.5 is in Section 6 of Appendix II and Appendix VI (NE PHLSA Study Task 8 Sample Collection Data.xlsm; NE PHLSA Study Task 8_Sample Collection Initiation Data.xlsm).

This task (Task 8, refer to Section 3.2.8) collected data to evaluate the impact of key sample collection parameters on pressurized HC liquids sampling and analysis results. Parameters evaluated were:

- Sample collection initiation time after the end of the well cycle (less than 0 (i.e., during the well cycle), less than 30 (typically ~ 15), 90, and 150 minutes after well cycle);
- Sample collection rate (20, 40, 60, 100, and 180 ml/min);
- Sample cylinder type (CP cylinder and CV cylinder); and
- Sample collection location (sample probe and oil box oil level sight glass).

P_{BP}/P_{SC} as a Data Quality Indicator

Throughout this section and sections that follow, the quality of pressurized condensate sample collection and analysis results (i.e., measured composition) is evaluated using the ratio of the PSM/EOS calculated bubble point pressure (at sample collection temperature) using the measured condensate composition and the separator pressure during sample collection (i.e., P_{BP}/P_{SC}). P_{BP}/P_{SC} is used as a data quality indicator or OPC, with ratios near 1.0 historically considered an indication that a HC liquids sample and associated analytical results are representative of separator HC liquids in equilibrium with the separator gas during sample collection. Deviations of P_{BP}/P_{SC} from 1.0 indicate possible sample collection and/or analysis bias, and/or that the collected sample may not have been in equilibrium with the gas in the separator at the sample collection temperature and pressure. That is, if a pressurized HC liquids sample was not at gas/liquid equilibrium when collected, then P_{BP}/P_{SC} could deviate from unity even if the sample collection, transport, laboratory handling, and analysis were sound and the measured sample composition accurately represented the separator liquid. Therefore, use of P_{BP}/P_{SC} as a data quality indicator is based on the assumption of separator gas/liquid equilibrium during sample collection as well as accurate measurements of separator temperature and pressure and reliable PSM/EOS bubble point pressure calculations. As discussed in Section 3.1, the separator was operated, as best able, at the target test pressure and temperature between well cycles to promote gas/liquid equilibrium and isolate P_{BP}/P_{SC} as a data quality indicator for pressurized condensate sampling and analysis results. OPC data analysis and discussion that follow show that P_{BP} is very sensitive to methane and nitrogen (i.e., air) in the condensate samples, and that samples that have a non-equilibrium methane concentration (e.g., loss during sample collection, transport and handling, and/or sample collection from a non-equilibrium separator) or have some air contamination may have anomalous P_{BP}/P_{SC}, but still provide reasonable estimates of FGOR and flash gas composition. Thus, P_{BP}/P_{SC} is likely a very conservative OPC for sample collection and analysis results. In this report, P_{BP}/P_{SC} is based on a PSM/EOS calculated bubble point pressure unless otherwise indicated.

4.5.1 Sample Collection Initiation Time Study

This study evaluated the impact of sample collection initiation time on measured pressurized condensate composition. Samples were collected near the beginning of the PHLSA Study (January 2016 sample collection for Task 8) to determine sample collection guidelines for subsequent tasks. Two series of samples were collected with sample collection initiated at various intervals after the end of a well cycle: < 0 (i.e., during the well cycle), < 30 (~ 15), 90, and 150 minutes after well cycle. At each interval, a CP cylinder sample and a CV cylinder sample were simultaneously collected. Figure 4-22 shows the impact of sample collection initiation time on P_{BP}/P_{SC} for two sets of sequentially collected samples for two well cycles. The separator temperature changed during the 150-minute sample collection period, therefore all P_{BP} for each well cycle were calculated at a common temperature equal to the average of the separator temperatures for the < 0- and < 30-minute samples. The data show a decrease in P_{BP}/P_{SC} from the < 30 minute to the 90-minute samples. Figure 4-23 shows the impact of sample collection initiation time on methane for the two well cycles. The data show a decrease in methane from the < 30 minute to the 90-minute samples, similar to the P_{BP}/P_{SC}. It should be noted that the separator heater was not firing separator headspace gas during these tests and that the separator pressure and temperature were fairly stable from the end of the well cycle until the last sample was collected 150 minutes after the end of the well cycle. For well cycle 2, sales gas flow from the separator to the gathering pipeline between the collection of the < 30 minute and the 90-minute samples is a suspected cause, at least in part, of the change in HC liquids composition. Other potential contributing factors to the changes in the P_{BP}/P_{SC} and methane concentration with time could have been some combination of loss of volatiles by the pressurized condensate, liquid stratification at the sample location, and/or some other factors.

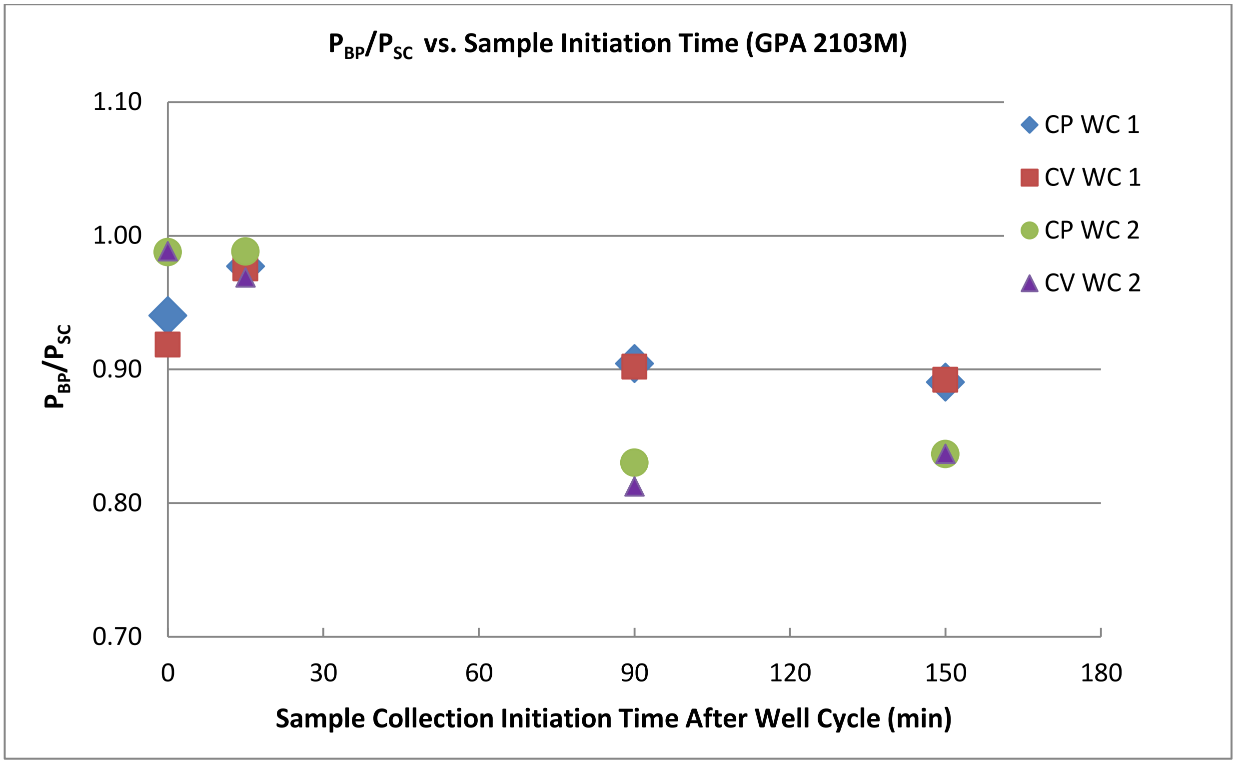

Figure 4-22. Impact of sample collection initiation time on P_{BP}/P_{SC}.

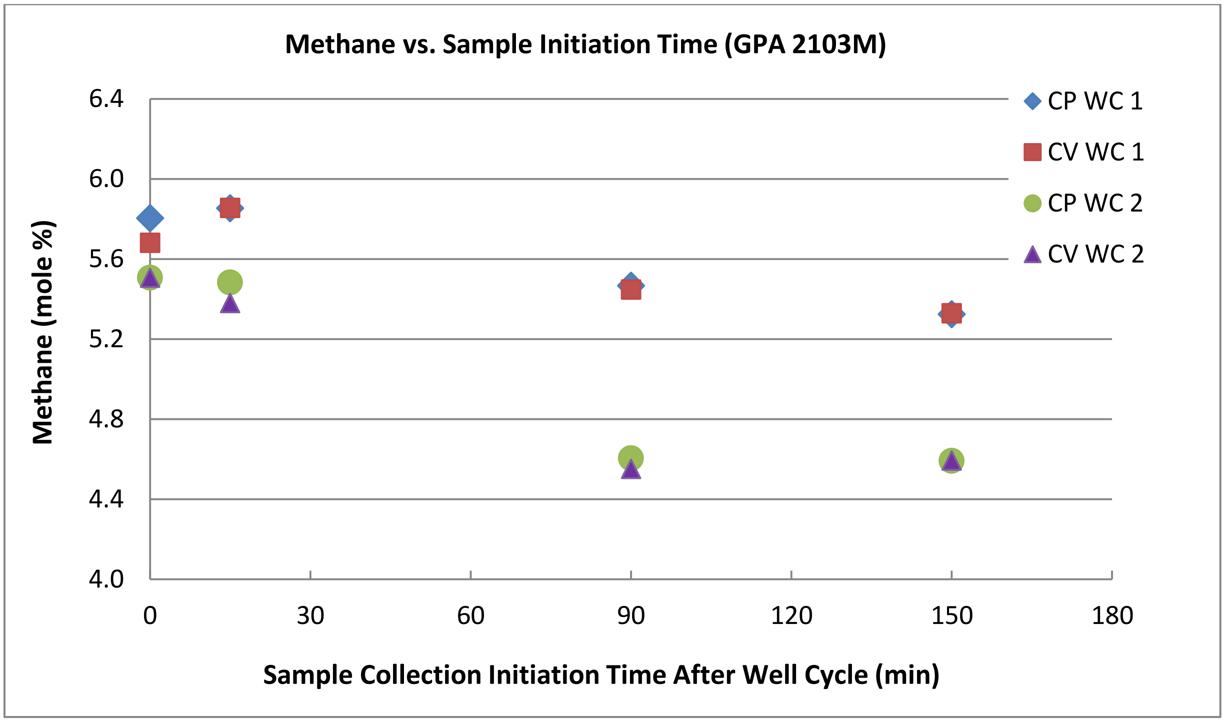

Figure 4-23. Impact of sample collection initiation time on condensate methane concentration.

The results indicated that, for this testing, samples should be collected soon after the end of a well cycle. Based on these results, a project guideline to collect samples within 30 minutes of well cycle completion was adopted. These samples were collected under controlled separator conditions (i.e., efforts were made to maintain a stable separator pressure and temperature), and the impact of sample initiation time on the pressurized condensate sample composition would likely be exacerbated if the separator pressure and/or temperature were changing; for example, due to changes in sales line pressure and/or use of separator headspace gas as heater fuel. Thus, collecting a pressurized HC liquids sample soon after a well cycle increases the probability that the sample composition will be the same as or very similar to the liquids that flowed from the separator to the storage tank.

4.5.2 Sample Cylinder Type Study

The impact of sample cylinder type, CP cylinder or CV cylinder, on pressurized condensate sampling and analysis results was evaluated by simultaneously collecting CP cylinder and CV cylinder samples over the course of the PHLSA Study (Task 8). A total of 42 paired CP/CV samples were collected using alternate sample probes (probe locations 1 and 3 in Figure 3-1) over the tested ranges of separator operating condition, sample collection rate, and sample collection initiation time after well cycle completion. The samples were analyzed using GPA 2103M and GPA 2186M.

Paired CP cylinder/CV cylinder pressurized condensate sample results (i.e., composition and PSM/EOS calculated parameters P_{BP} (at separator temperature) and FGOR) were evaluated using the following steps to identify potential differences between the sample collection methods during the PHLSA Study.

- **Statistical outliers check**. Check data for statistical outliers using the Grubbs test and the Dixon's Q-test. Consider datum a statistical outlier if identified as an outlier by both tests. The following analyses were then conducted on the full data set and the data set with the statistical outliers removed.
- **Tabulate basic comparative statistics**.
  - Calculate the percent of paired CP/CV samples for which the CP value is greater than the CV value; and
  - Calculate the ratio of d_{avg} (i.e., average of [CP parameter – CV parameter]) and the parameter average (i.e., [CP parameter average + CV parameter average]/2); that is, calculate d_{avg} as a percentage of the average measured value.

- **Normal probability distribution check**. Evaluate whether the data set of paired differences can be assumed to have a normal probability distribution. Histograms were developed and goodness-of-fit tests based on use of the chi-square distribution were conducted.
- **Wilconxan Sign-Rank Test**. The Wilconxan Sign-Rank Test (WSRT) was used to determine whether CP vs. CV results were significantly different. The WRST can be applied when the population cannot be assumed to have a normal distribution, and was used to test the null hypothesis that two populations are identical (i.e., mean of the paired differences population = 0). If the null hypothesis was rejected, then conclude that the CP cylinder results (e.g., condensate species, P_{BP}, FGOR) differ from the CV cylinder results.
- **Paired data comparisons t-statistic test**. A paired data comparisons test was used to determine whether CP vs. CV results were significantly different. Two null hypothesis tests were conducted:
  - The mean of the paired differences population = 0. If the null hypothesis is rejected, then conclude that CP cylinder results differ from CV cylinder results.
  - The mean of the paired differences population is $\leq$ analytical uncertainty. If the null hypothesis is rejected, then conclude that CP cylinder results differ from CV cylinder results by an amount that is greater than the analytical uncertainty.

  The paired data comparisons t-statistic test assumes that the data are approximately normally distributed, and this assumption may not be valid for all the data sets evaluated. However, the t-statistic test is robust, and when considered with other data analyses, provides useful information.

Statistical data summary

Table 4-7 summarizes the statistics for the entire set of paired CP/CV cylinders pressurized condensate samples differences data, and Table 4-8 summarizes the statistics for the set of paired CP/CV cylinders samples differences data with statistical outliers removed. The tables include data for the compounds and parameters identified as having a statistically significant difference between CP and CV samples using the paired data comparisons t-statistic test. Key observations include:

- For carbon dioxide and methane:
  - For all or a large fraction of the paired CP/CV cylinder samples, the CP sample had a higher concentration than the CV sample:

    - For 100% of the paired CP/CV cylinder samples, the CP sample had a higher concentration of CO_2, and the average difference was about 10.7% (9.4% in Table 4-8) of the average CO_2 concentration; and
    - For 81% (80% in Table 4-8) of the paired CP/CV cylinder samples, the CP sample had a higher concentration of methane, and the average difference was about 5.6% (4.8% in Table 4-8) of the average methane concentration.
  - The WSRT rejects the null hypothesis that the CP samples and CV samples populations are identical; and
  - The paired data comparisons t-statistic test rejects the null hypothesis that the mean of the paired differences population is less than the analytical uncertainty at a 99% level of confidence. This rejection leads to the conclusion that the CP cylinder sample results differ from the CV cylinder samples results by an amount that is greater than the analytical uncertainty.

  The results indicate there is a difference between the CO_2 and methane measured in CP cylinder and CV cylinder samples of pressurized condensate, and that samples collected using CV cylinders had lower CO_2 and methane concentrations than samples collected using CP cylinders. It is theorized that some of the CO_2 and methane in the pressurized condensate samples partitioned to the water in the CV cylinders. The water from the CV cylinders was not analyzed for this project; however, the solubility of CO_2 and methane in water support this theory. The data analysis presented below under "*Impact of Separator/Sample Temperature on Condensate Methane and CO_2 Concentrations*," which evaluates the impact of separator sample temperature on methane and CO_2 concentrations, also supports this idea.

  These volatile compound differences would be expected to result in higher PSM/EOS calculated values of P_{BP} and FGOR for pressurized condensate samples collected with CP cylinders. This expectation is supported by the data. As shown in Tables 4-7 and 4-8, for 85+% of the paired samples, PSM/EOS calculated values of P_{BP} and FGOR for pressurized condensate samples collected with CP cylinders are greater than the values for the paired CV cylinder. The average difference is about 5% for both parameters.

- For the other compounds in Tables 4-7 and 4-8, the null hypothesis for the paired data comparisons t-statistic test is that the mean of the paired differences population is less than the analytical uncertainty. The t-statistic test results show that this null hypothesis cannot be rejected at a 95% level of confidence. This leads to the conclusion that the CP cylinder sample results for the other compounds in Table 4-7 and Table 4-8 do not differ from the CV cylinder sample results by an amount that is greater than the analytical uncertainty.

Table 4-7. Summary Statistics for CP/CV Cylinders Paired Samples Differences Data

Compound / Parameter	Number of Paired Samples	di > 0 (d=CP-CV)	d_{avg} / ((CP+CV)/2)	Normal Data Distribution?	Wilconxan Sign-Rank Test [A] (H_0: d = 0)	Paired Sample t-stat (H_0: d = 0)	t-critical (95% CI, 2-tailed)	Paired Sample t-stat $[H_0: (\|d\| - U^{B}) < 0]$	t-critical (99% CI, 1-tail)	t-critical (95% CI, 1-tail)
Carbon Dioxide	42	100%	10.7%	No	Reject H_0	7.07	2.021	5.95	2.423	1.684
Methane	42	81%	5.6%	No	Reject H_0	4.37	2.021	2.82	2.423	1.684
Ethane	42	74%	1.5%	No	Reject H_0	4.09	2.021	0.65	2.423	1.684
Propane	42	62%	0.7%	Yes	Reject H_0	2.44	2.021	-0.78	2.423	1.684
Heptanes	42	50%	-1.9%	No	Accept H_0	2.47	2.021	-1.01	2.423	1.684
Octanes	42	43%	-2.3%	No	Reject H_0	2.58	2.021	-1.35	2.423	1.684
PSM/EOS $P_{\text{Bubble Point}}$ @ T_{SC}	42	88%	4.9%	No	Reject H_0	4.58	2.021	NA		
PSM/EOS FGOR @ P_{tank}, T_{tank}	42	86%	5.0%	No	Reject H_0	4.33	2.021	NA		

A. Test the null hypothesis that two populations are identical, applies to non-normal probability distributions

B. Analytical method uncertatinty for the lab.

Table 4-8. Summary Statistics for CP/CV Cylinders Paired Samples Differences Data, with Statistical Outliers Removed

Compound / Parameter	Number of Paired Samples	di > 0 (d=CP-CV)	d_{avg} / ((CP+CV)/2)	Normal Data Distribution?	Wilconxan Sign-Rank Test [A] (H_0: d = 0)	Paired Sample t-stat (H_0: d = 0)	t-critical (95% CI, 2-tailed)	Paired Sample t-stat $[H_0: (\|d\| - U^{B}) < 0]$	t-critical (99% CI, 1-tail)	t-critical (95% CI, 1-tail)
Carbon Dioxide	41	100%	9.4%	No[C]	Reject H_0	13.60	2.021	11.13	2.423	1.684
Methane	41	80%	4.8%	No	Reject H_0	4.63	2.021	2.72	2.423	1.684
Ethane	42	74%	1.5%	NA	Reject H_0	4.09	2.021	0.65	2.423	1.684
Propane	42	62%	0.7%	NA	Reject H_0	2.44	2.021	-0.78	2.423	1.684
Heptanes	42	50%	-1.9%	NA	Accept H_0	2.47	2.021	-1.01	2.423	1.684
Octanes	42	43%	-2.3%	NA	Reject H_0	2.58	2.021	-1.35	2.423	1.684
PSM/EOS $P_{\text{Bubble Point}}$ @ T_{SC}	41	88%	4.3%	No	Reject H_0	4.95	2.021	NA		
PSM/EOS FGOR @ P_{tank}, T_{tank}	41	85%	4.4%	No	Reject H_0	4.37	2.021	NA		

A. Test the null hypotheis that two populations are identical, applies to non-normal probability distributions

B. Analytical method uncertatinty for the lab.

C. Borderline normal distribution.

Impact of Separator/Sample Temperature on Condensate Methane and CO_2 Concentrations

To further consider CO_2 and methane behavior in CP and CV cylinders, the impact of sample collection temperature on condensate methane and CO_2 concentrations in CP and CV cylinders was examined. The results for the mid-pressure (i.e., ~ 225 psig) well cycles were used for this evaluation to isolate the impact of separator temperature from separator pressure effects. The majority of the condensate samples were collected with the separator operating at mid-pressure, and the mid-pressure data provides a robust data set (i.e., 25 CP samples and 25 CV samples) for data analyses attempting to isolate parameters (e.g., pressurized condensate composition) that could be affected by separator pressure.

Figure 4-24 compares PSM/EOS calculated P_{BP}/P_{SC} to T_{sc} for CP and CV cylinders samples. P_{BP}/P_{SC} increased with T_{sc} for CV cylinder samples but decreased with T_{sc} for CP cylinder samples. Figure 4-25 graphs PSM/EOS calculated P_{BP} for CP cylinder and CV cylinder samples against T_{sc}, and shows the same trends (i.e., P_{BP} increased with T_{sc} for CV cylinder samples but decreased with T_{sc} for CP cylinder samples). If all other parameters are held constant, an increase in T_{sc} would be expected to drive a larger fraction of the volatile compounds to the gas phase in the separator and reduce the P_{BP}. This expected trend is observed for the CP cylinders but the opposite trend is seen for the CV cylinders.

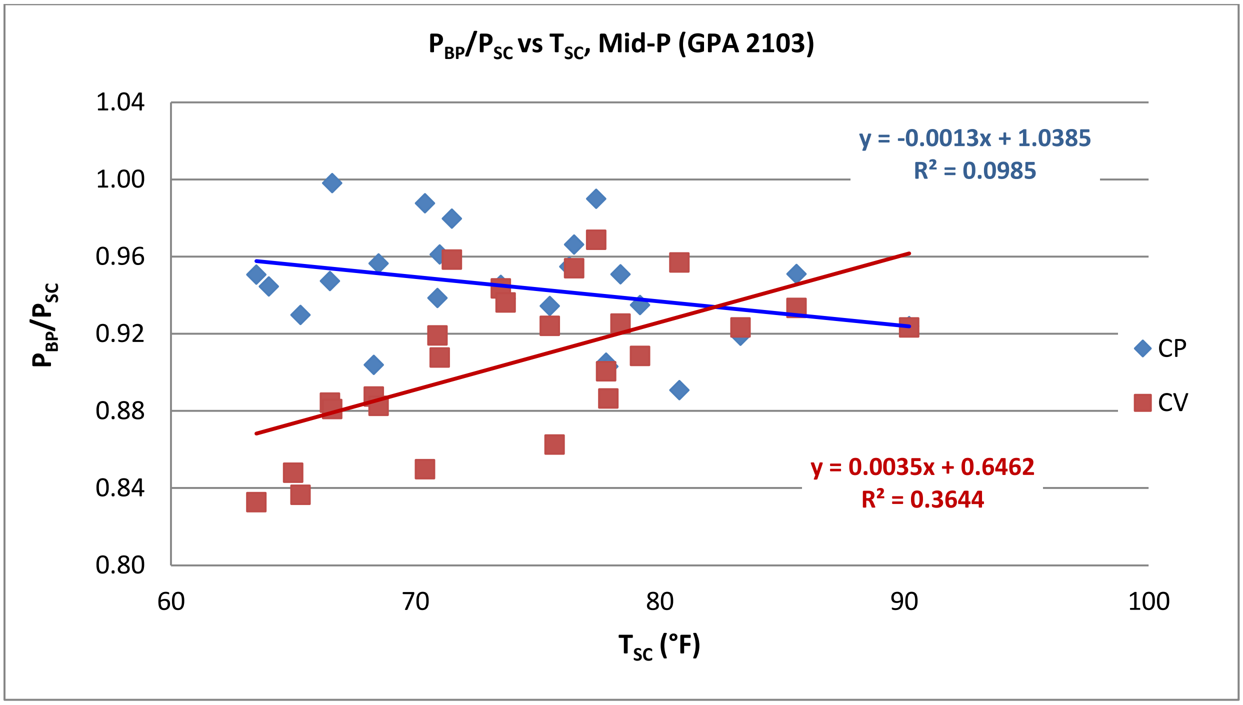

Figure 4-24. Impact of sample collection temperature on P_{BP}/P_{SC}.

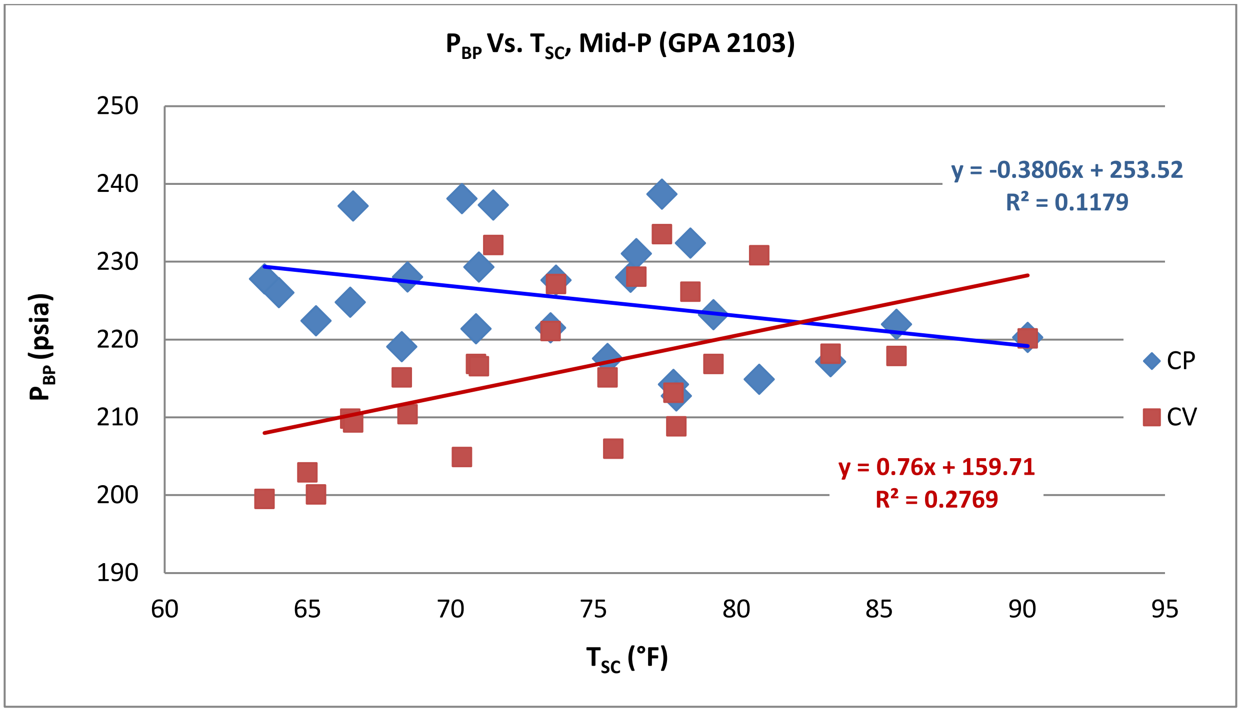

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Figure 4-25. Impact of sample collection temperature on P_{BP}.

Figure 4-26 compares CO_2 and methane concentrations for CP and CV cylinders and T_{sc}. The general trend observed for methane in CP cylinders is higher T_{sc} resulting in lower concentrations in the pressurized condensate sample. However, T_{sc} has no discernable impact on methane in CV cylinders (i.e., the slope and the R^2 for the linear regression equation are essentially zero). CO_2 concentrations in CV cylinder samples decrease slightly as T_{sc} increases, but both the slope and the R^2 for the CV CO_2 linear regression equation are less than the slope and the R^2 for the CP CO_2 linear regression equation. This indicates temperature had less impact on CO_2 concentration in CV cylinder condensate samples than in CP cylinder samples.

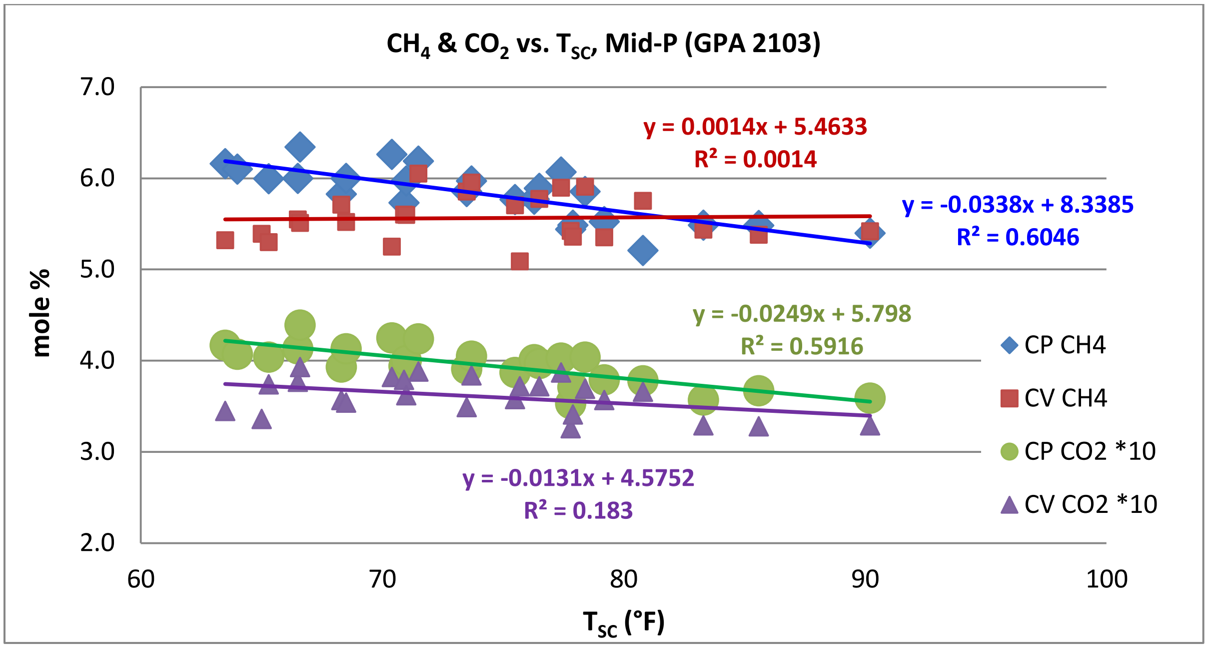

Figure 4-26. Impact of sample collection temperature on CO_2 and methane.

At lower T_{sc}, higher concentrations of methane are observed in CP cylinder samples but not in CV cylinder samples; that is, methane concentrations trend lower than anticipated at lower T_{SC} for CV samples. A similar trend is observed for CO_2. Low methane and CO_2 concentrations in CV cylinder samples at lower T_{sc} are theorized to be due to the increased solubility of methane and CO_2 in water at lower temperatures, and methane and CO_2 partitioning to the water fraction in the CV cylinder samples. These phenomena are consistent with the results of the CP/CV cylinder comparison presented in the previous section, and would help to explain the P_{BP} vs. T_{SC} trends observed in Figures 4-24 and 4-25 because methane and CO_2 concentrations in pressurized condensate samples have a large impact on PSM/EOS calculations of P_{BP}. These results, and CP vs. CV cylinder data presented above, suggest that there is a potential CO_2 and methane bias in CV cylinder samples, particularly at colder separator temperatures, and that the ultimate use of condensate analytical results should be considered when selecting a sample cylinder type.

4.5.3 Sample Collection Rate Study

The impact of sample collection rate on measured pressurized condensate composition was evaluated by collecting samples over the course of the study at various rates: 20, 40, 60, 100, and 180 ml/min.

Figure 4-27 includes all the pressurized condensate samples collected from the sample probes and shows that, for this project, the sample collection rate had no measurable impact on P_{BP}/P_{SC} for CP cylinders or for CV cylinders (i.e., the coefficient of determination "R^2" for each of the linear regression equations is nearly zero). Figure 4-28 includes the samples collected from the sample probes during only the mid-pressure well cycles, and the data show the same trend. It should be noted that these samples were collected from sample probes installed about two feet below the separator gas/liquid interface, and were pressurized in the lab to 1,100 psi prior to GC injection. Such a pressure is expected to dissolve any gas that evolved (i.e., flashed) during sample collection. Sample collection rate may have a larger impact under different conditions, such as samples collected closer to the gas/liquid interface. For example, the gas/liquid interface could only be a few inches above the sample connection at an oil box sight glass, and a rapid sample rate could entrain gas. For the remainder of the PHLSA Study, conservative sample collection rates of 60 ml/min or less were used.

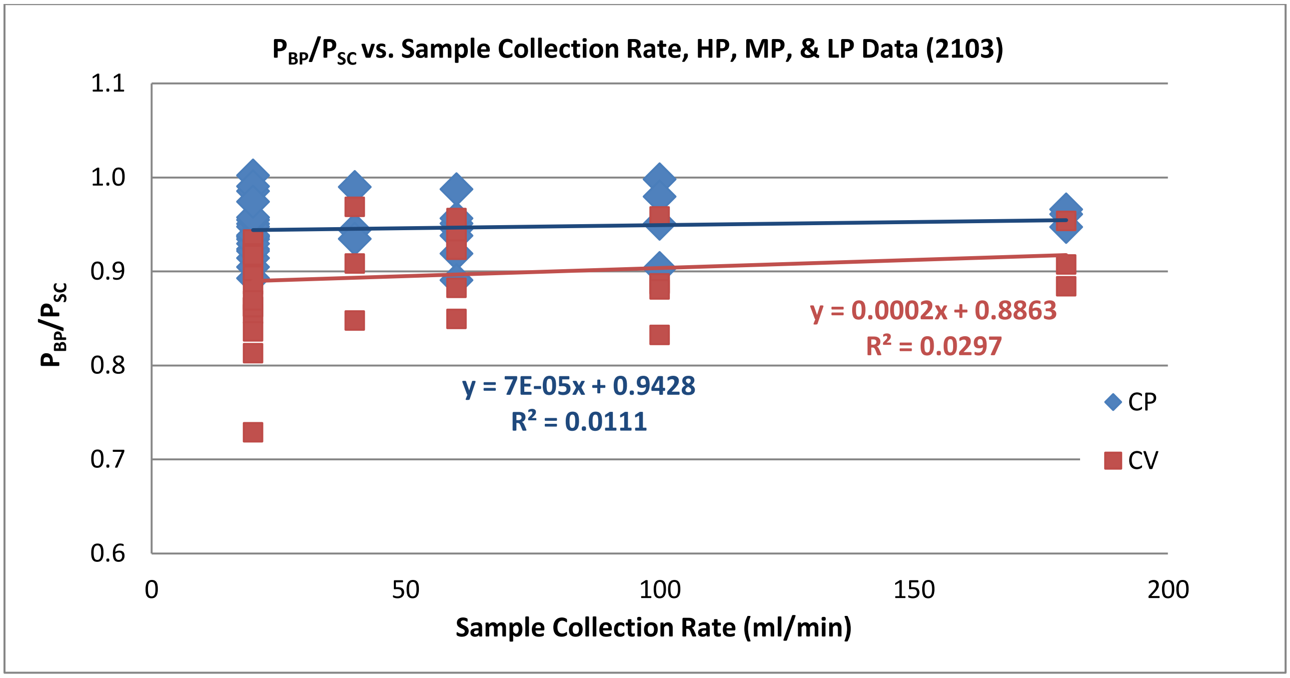

Figure 4-27. Impact of sample collection rate on P_{BP}/P_{SC}, low-, mid-, & high-pressure well cycles.

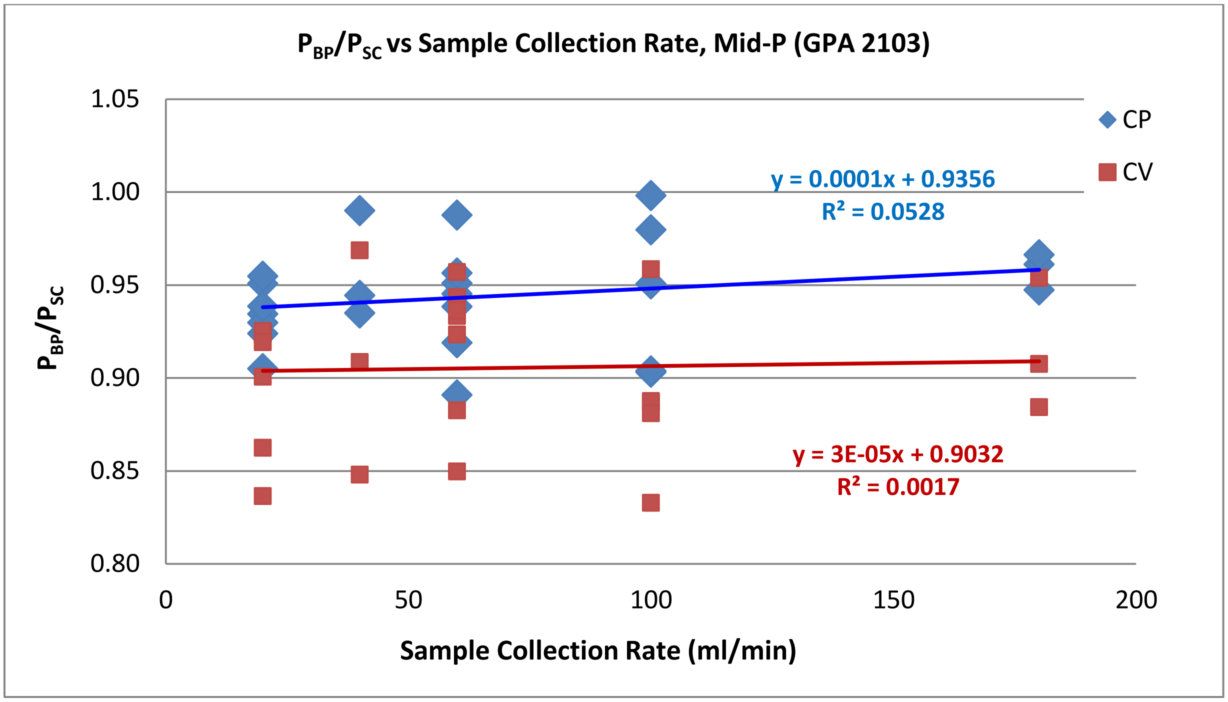

Figure 4-28. Impact of sample collection rate on P_{BP}/P_{SC}, mid-pressure well cycles.

The mid-pressure (i.e., ~ 225 psig) data set was used for subsequent sample collection rate data analyses involving pressurized condensate properties that would be expected to be affected by separator pressure. These results include the following:

- Figure 4-29 shows that sample collection rate had minimal, if any, impact on condensate sample concentrations of CO_2 and CH_4 (i.e., the coefficients of determination "R^2" for the linear regression equations are less than 0.10). The CO_2 concentrations are multiplied by ten on this graph to scale with the methane data.
- Figure 4-30 shows that CP cylinder condensate sample concentrations of C10+ decreased with sample collection at the highest sample rate. This could be due, at least in part, to mass discrimination at the higher sample collection rates. The impact of sample collection rate is less distinguishable for CV cylinder samples due to greater data scatter.
- Figure 4-31 shows that CP cylinder condensate C10+ SG increased with higher sample collection rates. The impact is most pronounced at the highest sample rate, and the same trend was observed for the C10+ MW. It is not known why the C10+ SG increased with higher sample collection rates, whereas the condensate concentrations of C10+ decreased with higher sample collection rates. If mass discrimination contributed to the lower C10+ concentrations at higher sampling rates, then a less dense/lower SG C10+ fraction would be anticipated. The impact of sample collection rate is less distinguishable for CV cylinder samples due to greater data scatter.

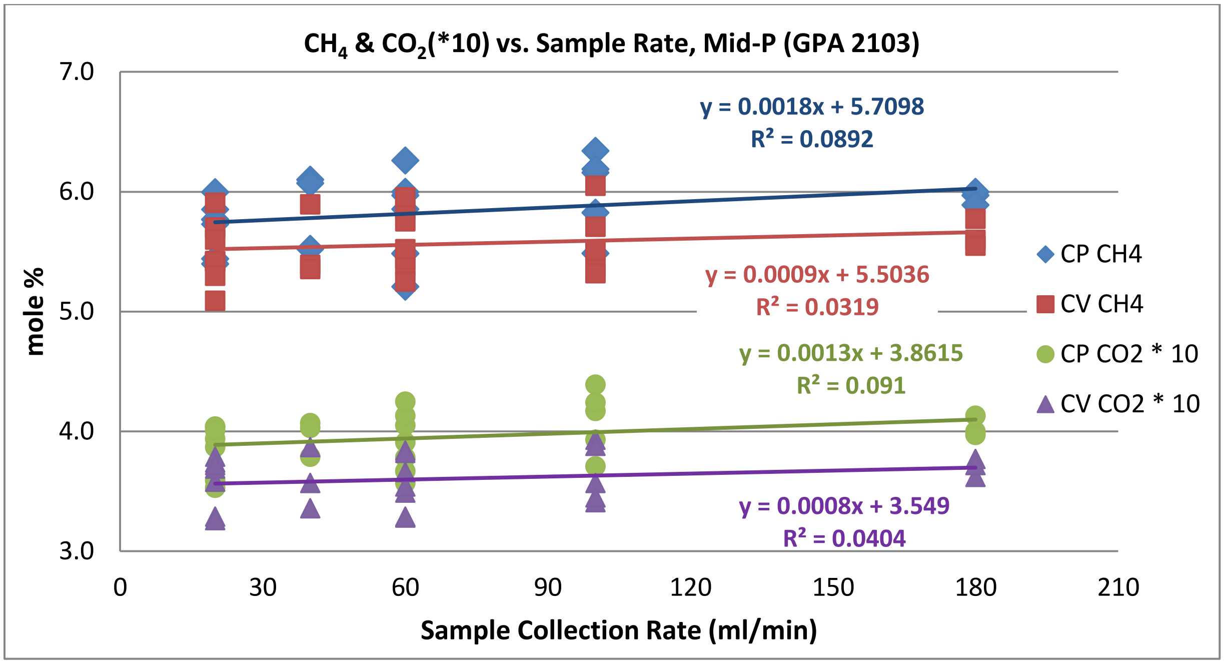

Figure 4-29. Impact of sample collection rate on pressurized condensate samples concentrations of CH_4 and CO_2.

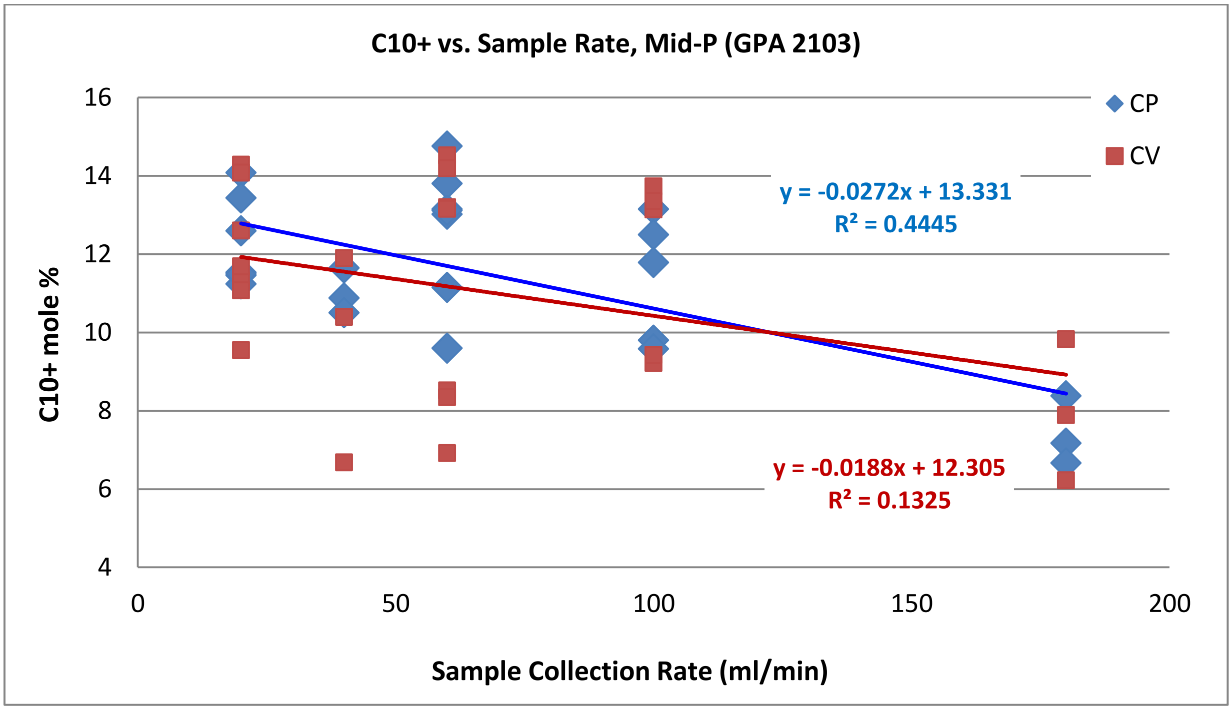

Figure 4-30. Impact of sample collection rate on pressurized condensate samples C10+ concentrations.

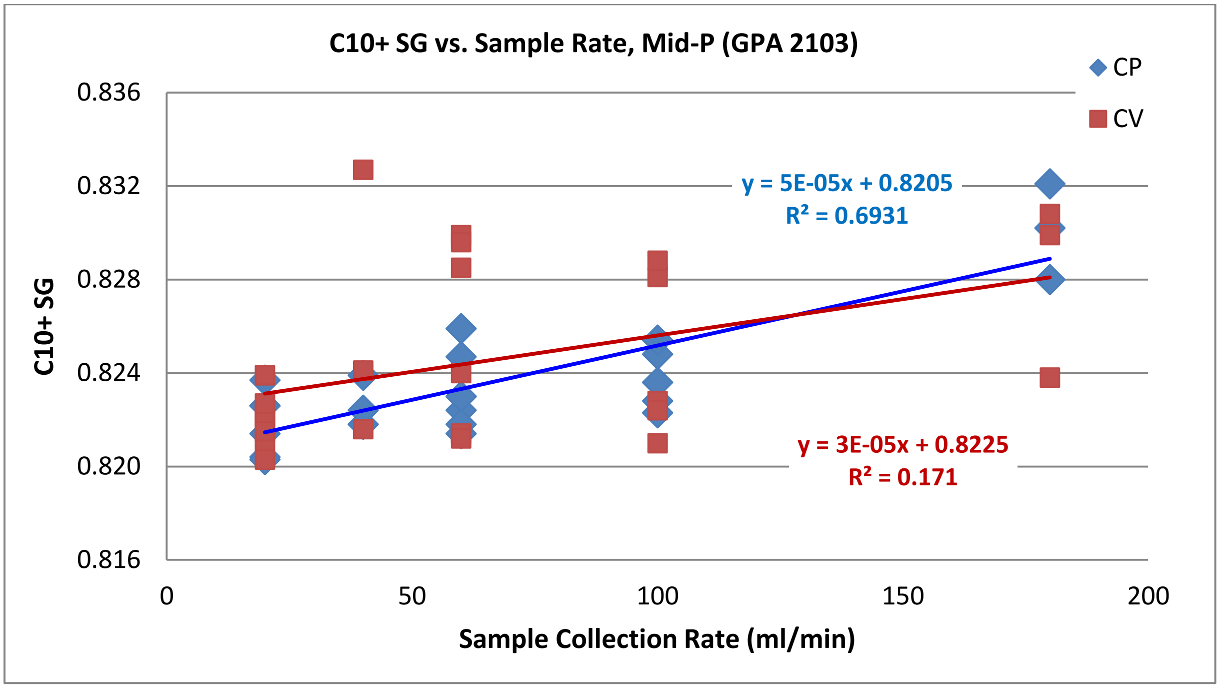

Figure 4-31. Impact of sample collection rate on condensate C10+ specific gravity.

4.5.4 Oil Level Sight Glass Sample Collection Study

The separator oil box oil level sight glass is a practical sampling location for many separators. The impact of the sight glass as a sample collection location was evaluated by simultaneously collecting pressurized condensate samples from two sample probes and the sight glass.

Figure 4-32 compares P_{BP}/P_{SC} for samples collected from the two sample probes and the sight glass for nine well cycles. Bubble point pressures (at the sample collection temperature) were calculated by PSM/EOS, with P_{BP}/P_{SC} greatly deviating from 1.0 indicative of possible sample collection bias. During each of the well cycles, a CP cylinder sample and a CV cylinder sample were collected from the sample probes, and either a CP or CV cylinder sample was collected from the sight glass location. The data in Figure 4-32 show that for CP cylinder sampling, there is no discernible difference between the P_{BP}/P_{SC} for the paired sight glass and probe samples (i.e., refer to the paired blue and pink diamonds, differences range from 1 to 5% and neither the sample probe or sight glass sample P_{BP}/P_{SC} was consistently greater). However, for CV cylinder sample collection for the MP1 and LP2 well cycles, P_{BP}/P_{SC} for the sight glass sample was more than 20% greater than P_{BP}/P_{SC} for the paired probe sample (refer to the paired red and pink squares). It is not understood why the CV sight glass samples differed from the probe samples.

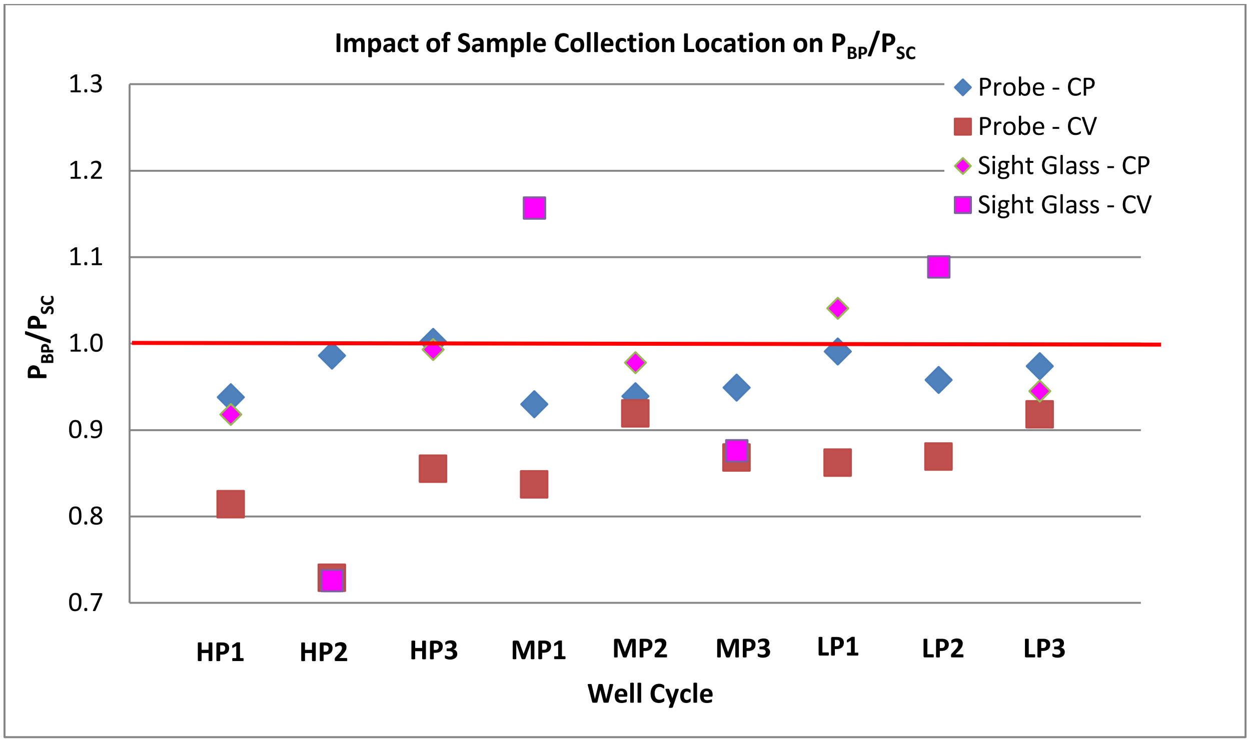

Figure 4-32. Impact of sample collection location on P_{BP}/P_{SC}.

Table 4-9 provides summary statistics for the paired samples that show:

- The sight glass (SiG) CV cylinder samples had higher P_{BP}/P_{SC} and higher concentrations of CO_2 and methane than the sample probe (Pr) CV cylinder samples (column 6, yellow highlighted data).
- Paired data comparisons t-statistic test calculations, as described in Section 4.5.2, were conducted for the entire sight glass/sample probe samples data set (i.e., CP and CV samples), and for the CP samples and CV samples only. For all of the measured condensate compounds and C10+ properties, none of the t-statistics are greater than $t_{critical}$ for a 95% CI (Columns 7-9).
  - This observation applies for the combined CP & CV data, and the CP only and CV only data.
  - Although CV samples show some large differences between the sample probe and sight glass results (e.g., for CO_2 and methane), the small data set and large standard deviation result in a large standard error and small t-statistic. A larger data set may reveal statistically significant differences for the CV sample collection, although CV sampling complications discussed above may have contributed to the data scatter.

Table 4-9. Sight Glass/Sample Probe Paired Samples Comparison Summary Statistics (GPA 2103M)

Compound/Parameter	Eng. Units	d_{Avg} (Pr - SiG)	d_{avg} (Pr - SiG)/ Avg (Pr & SiG)			t-statistic = ABS(d_{avg}/Std Error)		
		CP & CV	CP & CV	CP	CV	CP & CV	CP	CV
Carbon Dioxide	mole %	-0.0349	-9.35%	0.92%	-23.7%	1.66	0.76	2.37
Methane	mole %	-0.4439	-7.93%	-0.69%	-17.8%	1.56	0.36	1.70
Ethane	mole %	0.0014	0.02%	0.82%	-0.99%	0.01	1.74	0.20
Propane	mole %	0.1808	2.33%	0.94%	4.12%	1.28	2.04	0.96
iso-Butane	mole %	0.0784	2.99%	1.08%	5.48%	1.60	2.12	1.29
n-Butane	mole %	0.2580	3.22%	1.01%	6.12%	1.77	1.90	1.55
iso-Pentane	mole %	0.1783	3.48%	1.30%	6.32%	1.92	2.28	1.61
n-Pentane	mole %	0.2633	3.67%	1.40%	6.65%	1.92	2.34	1.59
n-Hexane	mole %	0.0301	0.49%	2.52%	-1.94%	0.21	0.82	0.51
Heptanes	mole %	-0.3487	-2.60%	-3.72%	-1.28%	1.50	1.27	0.70
Octanes	mole %	-0.2656	-2.58%	-6.04%	1.62%	0.85	1.31	0.53
Nonanes	mole %	-0.1142	-2.53%	-5.99%	1.75%	0.73	1.01	0.91
Decanes Plus	mole %	0.2449	2.31%	6.93%	-3.47%	0.48	1.07	0.50
PSM/EOS P_{BP} @ T_{SC}	psia	-13.6967	-6.34%	-0.43%	-14.3%			
PSM/EOS FGOR @ P_{tank}, T_{tank}	scf/bbl	-1.1686	-0.38%	1.29%	-2.68%			

Table 4-10 lists the CO_2, methane, and ethane (volatile components) and P_{BP}/P_{SC} data for the well cycles that included sample collection from the sight glass. The data highlighted with green and a light pattern are for well cycle HP-2. The two CV samples that had low P_{BP}/P_{SC} near 0.73 also had very low CO_2, methane, and ethane concentrations relative to the other high-pressure well cycle tests. The probe CV cylinder sample had very high nitrogen levels (reported results are for a without-N_2 sample), but no anomalies were identified for the CV sight glass sample. The data highlighted with red and a medium pattern are for well cycles MP-1 and LP-2. The two CV sight glass samples had high P_{BP}/P_{SC}, 1.09 and 1.16, driven by high CO_2, methane, and ethane concentrations. P_{BP}/P_{SC} values for these two CV sight glass samples were the highest measured for the entire project and it is not understood why the CV sight glass samples differed from the two probe samples.

In sum, for this project, collecting pressurized condensate samples from the sight glass with a CP cylinder does not appear to have any discernable impact on the sample composition; however, collecting pressurized condensate samples from the sight glass with a CV cylinder did not produce consistent and reliable results.

Table 4-10. Sight Glass/Sample Probe Samples Summary Data (GPA 2103M)

Well Cycle:	**HP-1**			**HP-2**			**HP-3**		
	Mole %			Mole %			Mole %		
Cylinder Type	CV	CP	CP - Sight Glass	CP	CV	CV - Sight Glass	CV	CP	CP - Sight Glass
CO_2	0.37	0.47	0.45	0.45	0.21	0.38	0.42	0.44	0.44
Methane	5.96	7.03	6.83	6.99	4.89	4.96	5.67	6.89	6.83
Ethane	6.57	7.10	6.94	6.80	6.52	5.76	6.53	6.49	6.45
P_{BP}/P_{SC}	0.81	0.94	0.92	0.99	0.73	0.73	0.86	1.00	0.99
Well Cycle:	**MP-1**			**MP-2**			**MP-3**		
	Mole %			Mole %			Mole %		
Cylinder Type	CP	CV	CV - Sight Glass	CV	CP	CP - Sight Glass	CP	CV	CV - Sight Glass
CO_2	0.40	0.37	0.46	0.38	0.39	0.40	0.40	0.37	0.38
Methane	6.00	5.30	7.70	5.60	5.73	6.06	5.77	5.09	5.16
Ethane	6.09	6.01	6.60	6.16	6.16	6.14	6.13	6.04	6.09
P_{BP}/P_{SC}	0.93	0.84	1.16	0.92	0.94	0.98	0.95	0.87	0.88
Well Cycle:	**LP-1**			**LP-2**			**LP-3**		
	Mole %			Mole %			Mole %		
Cylinder Type	CV	CP	CP - Sight Glass	CP	CV	CV - Sight Glass	CV	CP	CP - Sight Glass
CO_2	0.31	0.34	0.35	0.32	0.29	0.35	0.29	0.32	0.31
Methane	4.07	4.80	5.09	4.53	4.08	5.34	4.27	4.57	4.41
Ethane	5.18	5.40	5.40	5.18	5.08	5.45	4.99	5.07	5.04
P_{BP}/P_{SC}	0.86	0.99	1.04	0.96	0.87	1.09	0.92	0.97	0.95

4.6 Operational Performance Checks

Supporting data and information for Section 4.6 are in Appendix VI (PLHSA Study_Task 7_OPC.xlsx).

This task (Task 7, refer to Section 3.2.7) evaluated the OPCs for pressurized condensate samples and analytical results. The analysis of OPC data initially focused on PSM/EOS calculated P_{BP}/P_{SC}. Other OPCs introduced in Section 2.3.3 were also evaluated. The OPC data analysis and evaluation approach included:

1. PSM/EOS calculated P_{BP}/P_{SC} data review and analysis to identify statistical outliers that could indicate anomalous (i.e., non-representative) condensate composition results.
2. Comparison of condensate nitrogen, methane, CO_2, and ethane concentrations with PSM/EOS calculated P_{BP}/P_{SC} to determine if: A) anomalous P_{BP}/P_{SC} correspond to anomalous concentrations of these volatile compounds, and/or B) if non-anomalous P_{BP}/P_{SC} correspond to non-anomalous concentrations of these volatile compounds. That is, PSM/EOS calculated P_{BP}/P_{SC} correlations with condensate nitrogen, methane, CO_2, and ethane concentrations were evaluated.
3. Comparison of PSM/EOS calculated P_{BP}/P_{SC} and PSM/EOS calculated FGOR values to determine if P_{BP}/P_{SC} and FGOR are correlated. This data analysis is based on the understanding that, for the purposes of this study, identifying reliable FGOR estimates is the ultimate goal of an OPC. In sum, this analysis is to determine whether anomalous P_{BP}/P_{SC} correspond to anomalous FGOR estimates, and/or if non-anomalous P_{BP}/P_{SC} correspond to non-anomalous FGOR estimates. The first check attempts to evaluate whether the P_{BP}/P_{SC} identifies non-representative FGORs (and associated pressurized condensate sample and analysis results) as non-representative, and the second check attempts to evaluate whether the P_{BP}/P_{SC} identifies representative FGORs (and associated pressurized condensate sample and analysis results) as representative.
4. Comparison of IPT P_{BP}/P_{SC} and PSM/EOS calculated FGOR values to determine if IPT P_{BP}/P_{SC} and FGOR are correlated. This data analysis is based on the understanding that identifying reliable FGOR estimates is the ultimate goal of an OPC. In sum, this analysis is to determine whether anomalous IPT P_{BP}/P_{SC} correspond to anomalous FGOR estimates, and/or if non-anomalous IPT P_{BP}/P_{SC} correspond to non-anomalous FGOR estimates.
5. Calculation of P_{BP}/P_{SC} based on densitometer measurements of P_{BP}, and associated data review and analysis to identify P_{BP}/P_{SC} statistical outliers that could indicate anomalous/non-anomalous condensate samples and whether they correspond to anomalous/non-anomalous FGOR estimates.

6. Comparison of separator condensate density measured at the production site by the Coriolis meter and condensate sample density measured at the lab by densitometer, and associated data review and analysis to identify statistical outliers that could indicate anomalous/non-anomalous condensate samples and whether they correspond to anomalous/non-anomalous FGOR estimates.
7. Development of suggested general guidelines for OPCs.

4.6.1 P_{BP}/P_{SC} Statistical Outliers and Impact of Nitrogen in Samples

Figure 4-33 presents the P_{BP}/P_{SC} data for all the pressurized condensate samples collected during the project. The P_{BP}/P_{SC} data are ordered from lowest to highest. These P_{BP} were calculated using PSM/EOS software and condensate compositions with the nitrogen mathematically removed (i.e., "without N_2" P_{BP}). Figure 4-34 presents P_{BP}/P_{SC} data with the P_{BP} calculated using the as measured condensate compositions that include the measured nitrogen concentrations (i.e., "with N_2" P_{BP}). Figure 4-35 shows the impact of nitrogen in pressurized condensate samples on P_{BP}/P_{SC} by plotting P_{BP}/P_{SC} (with-N_2) / P_{BP}/P_{SC} (without-N_2) against nitrogen concentration. There is a positive linear relationship, with higher nitrogen concentrations increasing the with-N_2 P_{BP} above the "true" without-N_2 P_{BP}. At a nitrogen concentration of 0.2 mole %, P_{BP}/P_{SC} is increased about 10% above the without-N_2 level and at a nitrogen concentration of 0.1 mole %, P_{BP}/P_{SC} is increased about 5%. Nitrogen has less impact on FGOR than on P_{BP}. As noted in Section 4.1, PSM/EOS calculations show that for a sample with about 0.15 wt% N_2 (~ 0.48 mole %), the with-N_2 P_{BP} was about 21% greater than the without-N_2 P_{BP}, whereas the associated FGOR only increased about 3%.

The reported "N_2" for these analyses is actually N_2 + O_2 that co-elute from the GC and are quantified as one peak and reported as N_2, and, as discussed in Section 4.1, the source of the nitrogen in the samples is air from incomplete purging of sample collection equipment. Thus, the without-N_2 data are more representative of the condensate that flowed from the separator to the tank, and the results based on the without-N_2 condensate compositions are the primary focus of the data analysis. The results based on the with-N_2 condensate are included to supplement the data analysis and to illustrate the importance of estimating the true nitrogen concentration in HC liquids samples. The **black** letters in Figures 4-33 to 4-35 indicate samples that, based on initial inspection, could be outliers, and the **red** letters indicate samples that have relatively high nitrogen concentrations and may warrant further review.

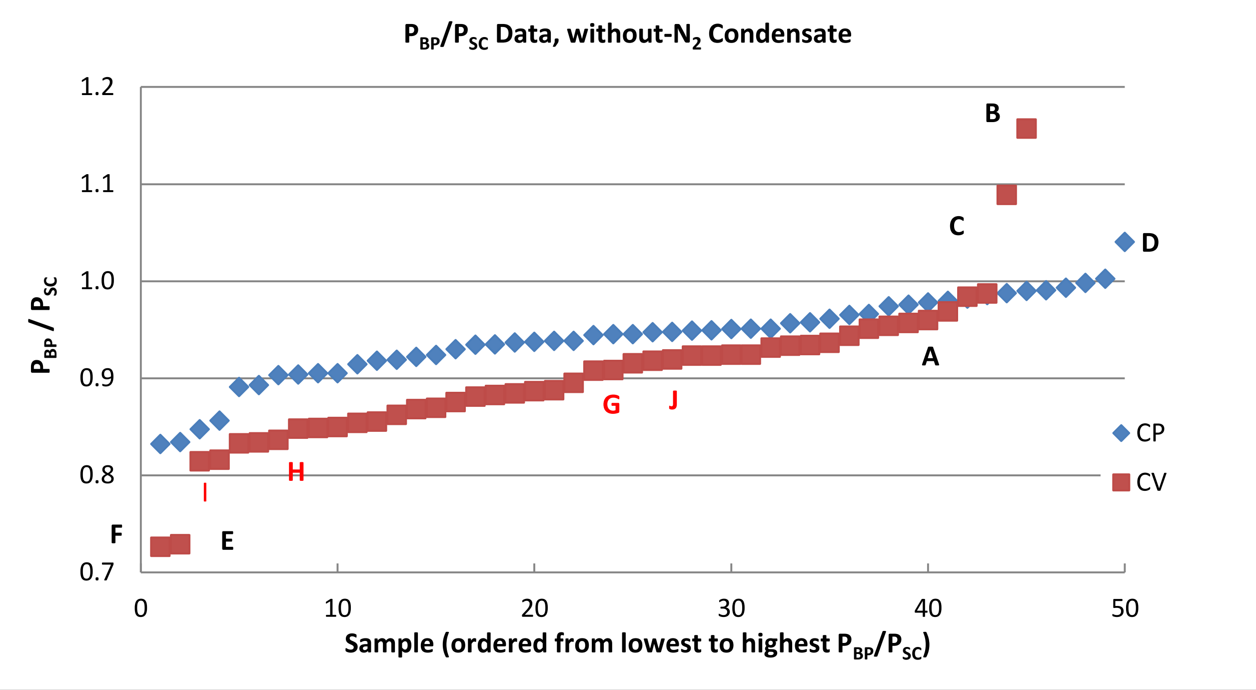

Figure 4-33. P_{BP}/P_{SC} data for pressurized condensate samples without nitrogen.

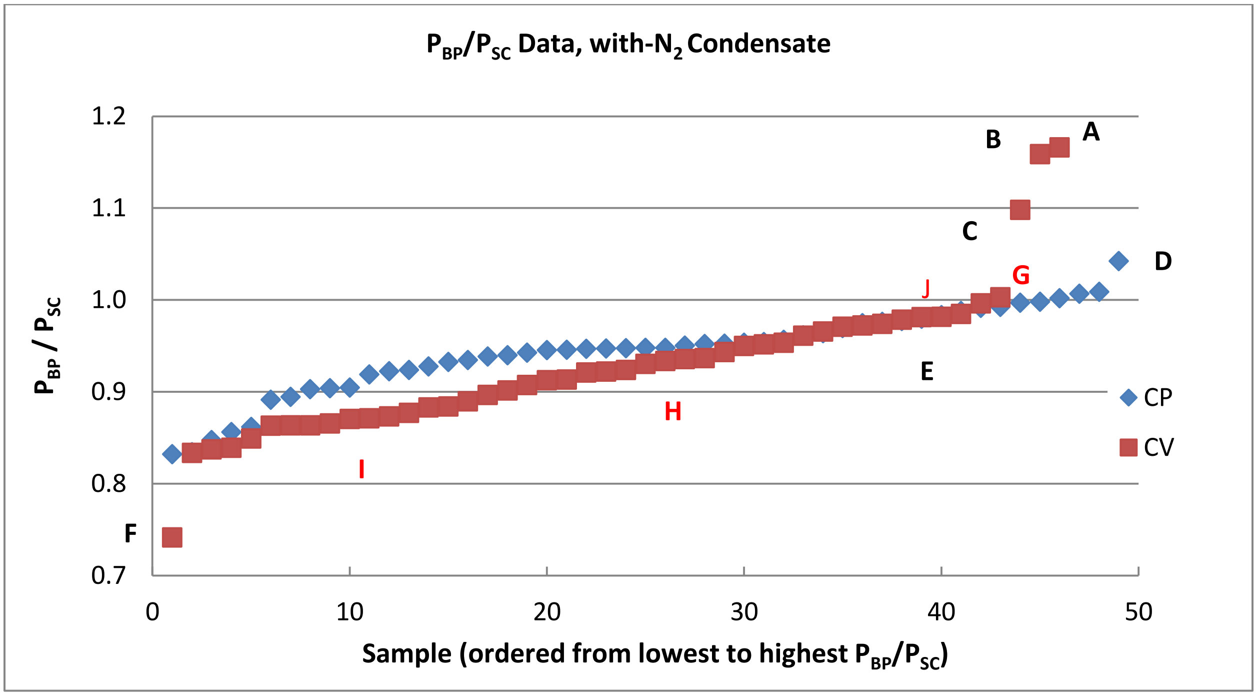

Figure 4-34. P_{BP}/P_{SC} data for pressurized condensate samples with nitrogen.

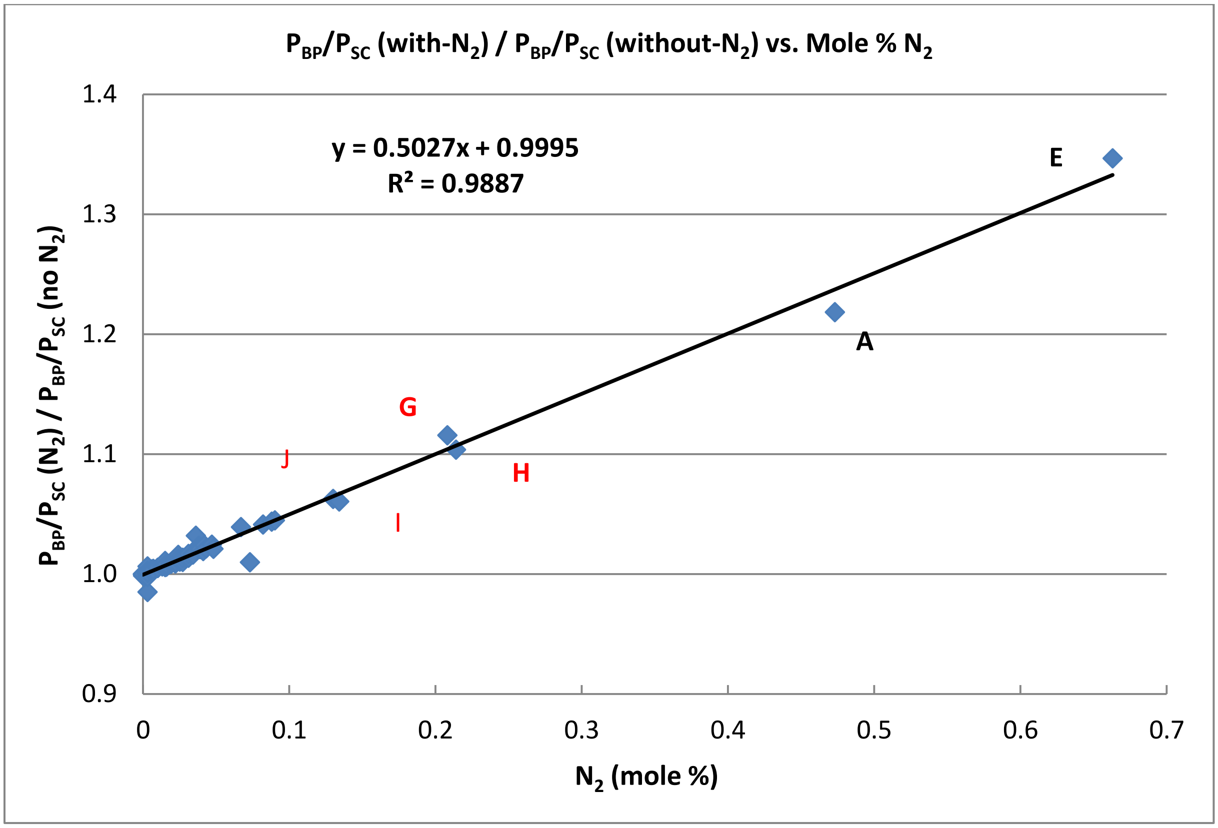

Figure 4-35. P_{BP}/P_{SC} (with-N_2 condensate) / P_{BP}/P_{SC} (without-N_2 condensate) vs. nitrogen concentration in pressurized condensate samples.

Initial observations for these data include:

- About 95% of the samples in Figures 4-33 and 4-34 have P_{BP}/P_{SC} between 0.80 and 1.05. Over 90% of the samples have P_{BP}/P_{SC} less 1.0. The average P_{BP}/P_{SC} for the without-N_2 samples is about 0.92 and the average P_{BP}/P_{SC} for the with-N_2 samples is about 0.94. These trends suggest non-equilibrium liquid samples (e.g., from changes in the separator pressure and/or temperature between the end of the well cycle and sample collection, a slight drop in separator temperature was typical for most well cycles and this would reduce the PSM/EOS calculated P_{BP}), a slight loss of volatile species being typical during sample collection and handling, a possible low bias in the P_{BP} calculation, or some combination of these and/or other factors.
- Sample A has a with-N_2 P_{BP}/P_{SC} of about 1.17 and a without-N_2 P_{BP}/P_{SC} of about 0.96 (a change of about 22% as shown in Figure 4-35). The high nitrogen level in Sample A, about 0.47 mole %, artificially increased the calculated P_{BP}. This is an example where nitrogen contamination would cause a likely reliable sample (i.e., the without-N_2 P_{BP}/P_{SC} is about 0.96) to be considered questionable (i.e., the with-N_2 P_{BP}/P_{SC} ratio is about 1.17) unless high nitrogen concentrations were investigated as possible air contamination.

- Sample E has a with-N_2 P_{BP}/P_{SC} of about 0.98 and a without-N_2 P_{BP}/P_{SC} of about 0.73 (a change of about 35% as shown in Figure 4-35). The high nitrogen level in Sample E, about 0.66 mole %, artificially increased the calculated P_{BP}. This is an example where nitrogen contamination would cause a possibly questionable sample (i.e., the without-N_2 P_{BP}/P_{SC} is about 0.73) to likely be considered reliable (i.e., the with-N_2 P_{BP}/P_{SC} is about 0.98) unless the high nitrogen concentrations were investigated as possible air contamination.

Statistical tests determined that the P_{BP}/P_{SC} data can be assumed to have a normal probability distribution, and a Generalized Extreme Studentized Deviate (GESD) test[7] (i.e., Grubbs Outlier Test with Rosen Procedure) and Dixon's Q test were conducted to identify outliers for these data sets based on a 95% confidence level (or $\alpha = 0.05$ significance level). Table 4-11 summarizes these results, which identify without-N_2 P_{BP}/P_{SC} less than about 0.75 and greater than about 1.09 as statistical outliers for this study. This would suggest a P_{BP}/P_{SC} acceptance criterion of about 0.92 +/- 0.17. Data point "C", which has a without-N_2 P_{BP}/P_{SC} of about 1.09 and a with-N_2 P_{BP}/P_{SC} of about 1.10, is identified as an outlier by the Dixons Q test but is not identified as an outlier by the GESD test and is thus considered a borderline outlier.

Table 4-11. Results of P_{BP}/P_{SC} Outlier Analysis ($\alpha = 0.05$)

Data Point	**Condensate Samples without-N_2**			**Condensate Samples with-N_2**		
	P_{BP}/P_{SC}	**GESD Test Outlier?**	**Dixon's Q Outlier?**	**P_{BP}/P_{SC}**	**GESD Test Outlier?**	**Dixon's Q Outlier?**
A	0.96	No	No	1.17	Yes	Yes
B	1.16	Yes	Yes	1.16	Yes	Yes
C	1.09	No	Yes	1.10	No	Yes
D	1.04	No	No	1.04	No	No
E	0.73	Yes	Yes	0.98	No	No
F	0.73	Yes	Yes	0.74	Yes	Yes

4.6.2 P_{BP}/P_{SC} vs. Methane, CO_2, and Ethane in Samples

The concentrations of the volatile compounds methane, CO_2, and ethane in pressurized HC liquids samples are impacted by the separator pressure and temperature, with higher pressures and lower temperatures generally increasing concentrations. The following methane, CO_2, and ethane concentration data are from well cycles with different separator pressures and temperatures. To somewhat normalize the concentration data for separator pressure and temperature, and better isolate the impact of these volatile compounds on P_{BP}, the

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[7] ASTM D7915-4: Standard Practice for Application of Generalized Extreme Studentized Deviate (GESD) Technique to Simultaneously Identify Multiple Outliers in a Data Set.

concentration data are segregated into the three target pressure ranges (i.e., high-pressure, mid-pressure, and low-pressure) and adjusted to a common separator temperature of 72°F.

P_{BP}/P_{SC} vs. Methane

Figure 4-36 shows without-N_2 methane concentrations as a function of P_{BP}/P_{SC} for well cycles in the HP, MP, and LP pressure ranges. CP cylinder and CV cylinder results are shown separately. These data show a strong correlation between methane concentration and P_{BP}/P_{SC} (e.g., R^2 for the CV-MP linear regression equation is about 0.97), and that the P_{BP}/P_{SC} outliers (i.e., B, C, E, and F) and data point D with high P_{BP}/P_{SC} are associated with the highest or lowest methane concentrations in the respective target pressure range.

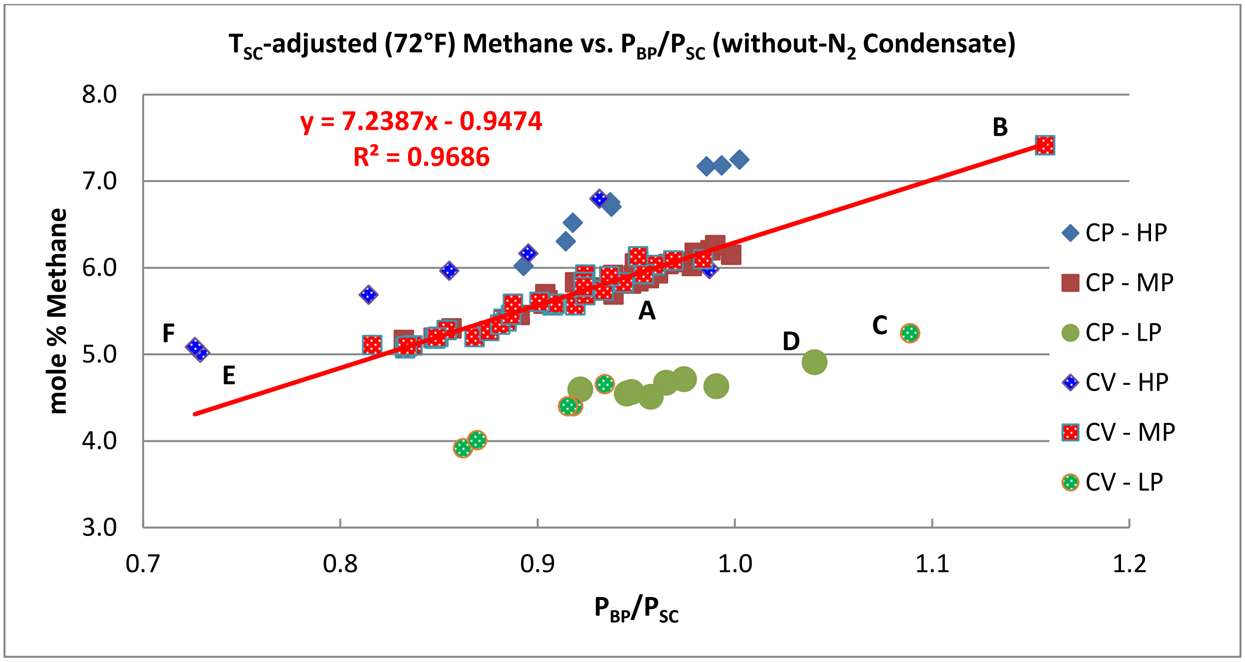


Figure 4-36. P_{BP}/P_{SC} vs. temperature-adjusted methane concentration in pressurized condensate samples (without-N_2).

P_{BP}/P_{SC} vs. CO_2

Figure 4-37 shows CO_2 concentrations as a function of P_{BP}/P_{SC} for well cycles in the HP, MP, and LP pressure ranges. CP cylinder and CV cylinder results are shown separately. These data show a general correlation between CO_2 concentration and P_{BP}/P_{SC}, although not as strong a correlation as between methane and P_{BP}/P_{SC} (e.g., R^2 for the CV-MP linear regression equation is 0.57 vs. 0.97 for methane). The P_{BP}/P_{SC} outliers B, C, and E and data point D with high P_{BP}/P_{SC} are associated with the highest or lowest CO_2 concentrations in the respective target pressure range. However, data point F, which is a statistical outlier for P_{BP}/P_{SC}, does not have an extreme value for CO_2. These data indicate that CO_2 has less impact on P_{BP} than methane. CO_2 concentrations in the pressurized condensate samples were typically about a factor of 20 lower than the methane concentrations.

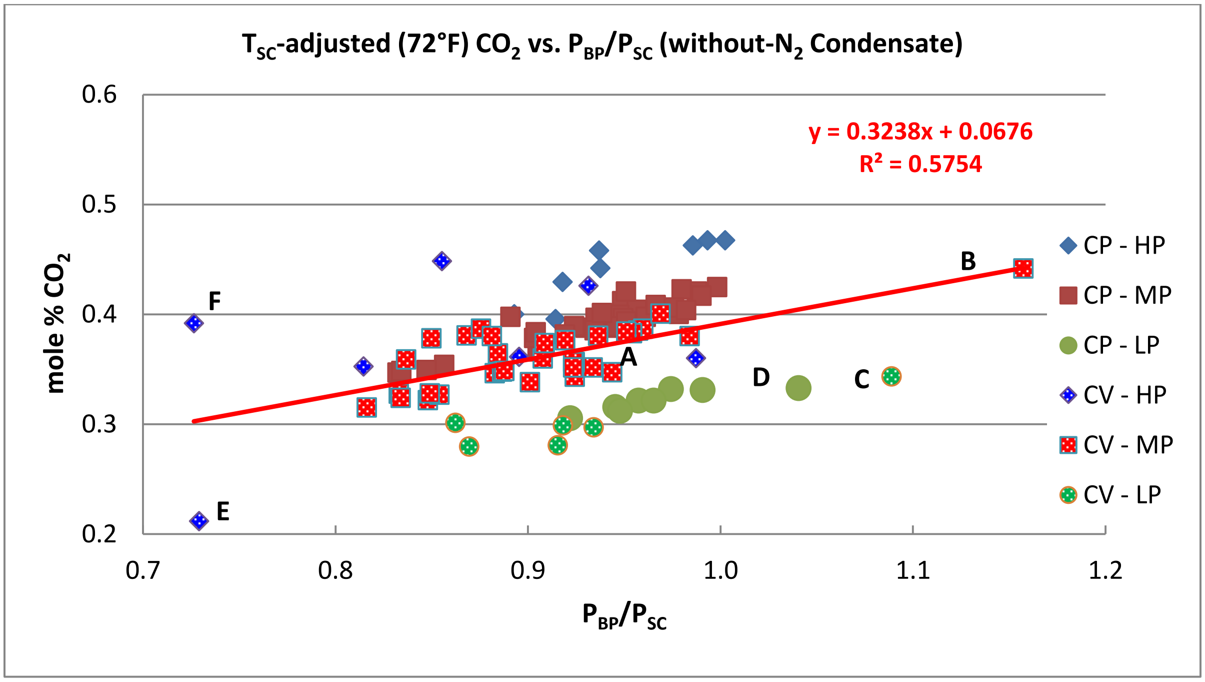


Figure 4-37. P_{BP}/P_{SC} (without-N_2 condensate) vs. temperature-adjusted CO_2 concentrations in pressurized condensate samples.

P_{BP}/P_{SC} vs. Ethane

Figure 4-38 shows ethane concentrations as a function of P_{BP}/P_{SC} for well cycles in the HP, MP, and LP pressure ranges. CP cylinder and CV cylinder results are shown separately. These data show a weak correlation between ethane concentration and P_{BP}/P_{SC} (e.g., R^2 for the CV-MP linear regression equation is about 0.21). Generally, P_{BP}/P_{SC} outliers are not associated with the highest or lowest ethane concentrations. Data point C has the highest ethane concentration of six CV-LP samples but data points B, D, E, and F are not extreme values for ethane and data point A is not a P_{BP}/P_{SC} ratio outlier. These data indicate that ethane has much less impact on P_{BP} than methane.

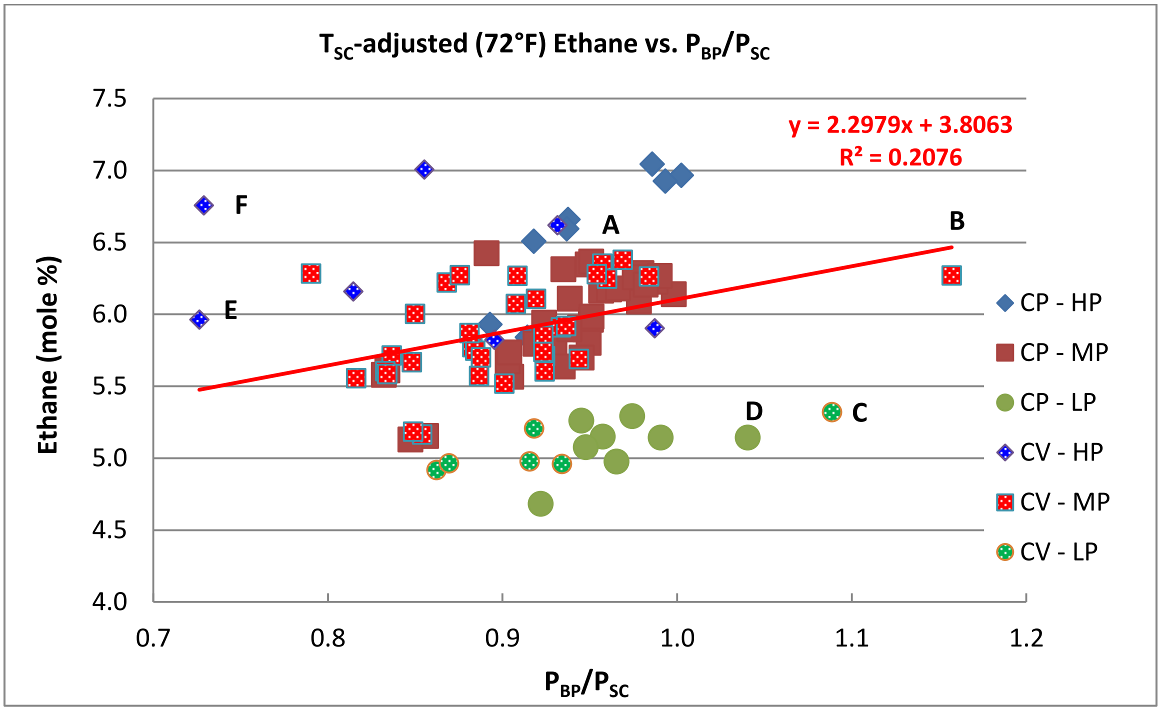


Figure 4-38. P_{BP}/P_{SC} (without-N_2) vs. temperature-adjusted ethane concentration in pressurized condensate samples.

Table 4-12 summarizes the R^2 values for the linear regression equations for methane, CO_2, and ethane for the six cylinder type-pressure range groups. The data generally show the highest correlation (i.e., R^2) for P_{BP}/P_{SC} with methane, then CO_2, and least with ethane. That is, of the three volatile compounds, the data indicate that methane concentration has the largest impact on P_{BP}/P_{SC}.

Table 4-12. R^2 Values from Linear Regression Equations for Methane, CO_2, and Ethane

Cylinder Type – Pressure Range	**R^2 Values from P_{BP}/P_{SC} vs. Mole % Linear Regression Equation**		
	Methane	**CO_2**	**Ethane**
CP-HP	0.89	0.89	0.92
CP-MP	0.94	0.84	0.52
CP-LP	0.71	0.74	0.19
CV-HP	0.71	0.20	0.04
CV-MP	0.97	0.58	0.21
CV-LP	0.93	0.77	0.68

4.6.3 P_{BP}/P_{SC} vs. FGOR

As discussed in Section 2.3.3, an OPC should "consistently identify representative pressurized HC liquids samples as representative (based on some measurable acceptance criteria) and consistently identify non-representative pressurized HC liquids samples as non-representative." The following data analysis uses PSM/EOS calculated FGOR values, in terms of flash gas volume per barrel of post-flash oil (scf/bbl) and flash gas mass/weight per barrel of post-flash oil (lb/bbl), to evaluate the representativeness of the compositions of pressurized HC liquids samples. That is, a pressurized HC liquids sample is assumed to be reasonably representative of the liquid that flowed to the storage tank if the PSM/EOS calculated FGOR, based on the sample composition, is similar to the PSM/EOS calculated FGORs for the population of samples collected under similar conditions. As discussed in Section 2.3.3, for the purposes of this study, an OPC should provide confidence that a PSM/EOS calculated FGOR (both in terms of gas volume and composition), based on analytical results for a pressurized HC liquids sample, is a reasonable estimate of the actual flash gas generation.

For the pressurized condensate samples without-N_2, Figure 4-39 compares PSM/EOS calculated FGOR and PSM/EOS calculated P_{BP}, and Figure 4-40 compares PSM/EOS calculated FGOR and PSM/EOS calculated P_{BP}/P_{SC}. P_{BP}/P_{SC} outliers and other extreme values are identified using the letters introduced above. In addition to the condensate composition, the FGOR calculation is impacted by separator and tank temperatures and pressures that vary by well cycle. To isolate the effect of the condensate composition on the FGOR calculations, a second separator was added to the process flow diagram for the PSM/EOS FGOR calculations, and all measured condensate compositions were brought to a common temperature and pressure in the second separator and then "dumped" to a common tank temperature and pressure. Samples collected during HP well cycles were brought to a common second separator condition, samples collected during MP well cycles were brought to a common second separator condition, and samples collected during LP well cycles were brought to a common second separator condition. The same tank temperature and pressure were used for HP, MP, and LP well cycles. These calculations produced comparable FGORs for each well cycle pressure group in that differences between the FGORs would be primarily a result of differences in the compositions of the condensate samples. Bubble point pressures were calculated using the separator temperature measured during the sample collection. As shown in Figures 4-39 and 4-40, FGOR generally increases with P_{BP} and P_{BP}/P_{SC}; however, there is considerable scatter in the data and the correlations are not strong (e.g., the R^2 values range from about 0.05 to 0.3).

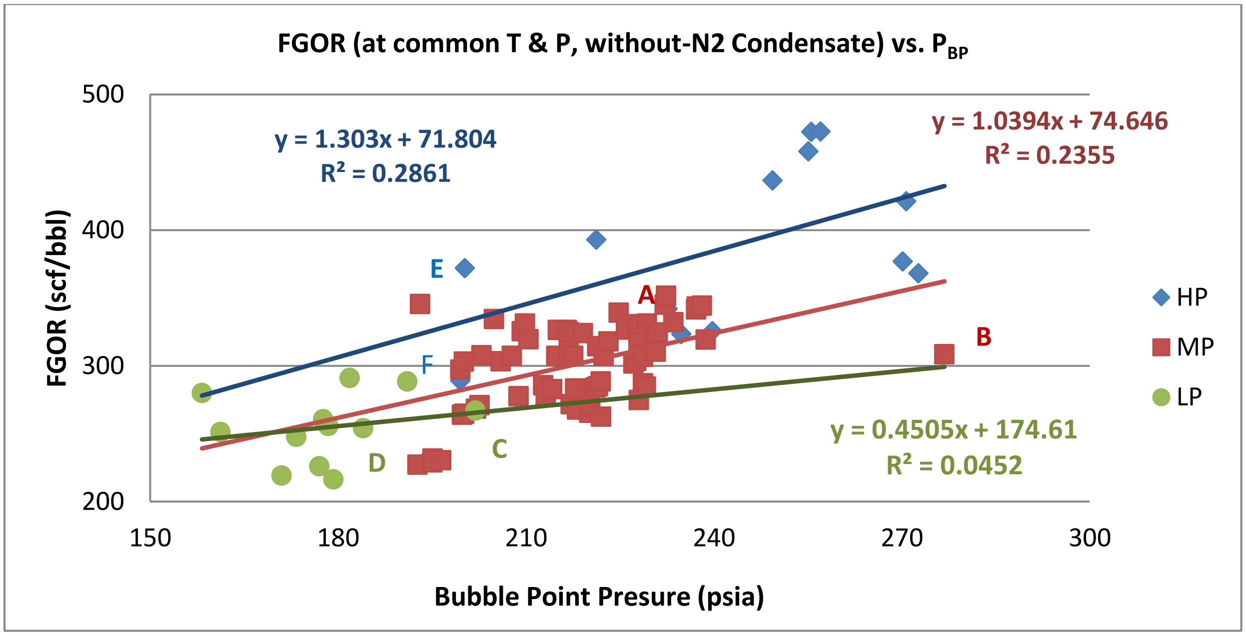


Figure 4-39. PSM/EOS calculated FGOR (at common pressure and temperature) vs. PSM/EOS calculated P_{BP} based on without-N_2 pressurized condensate samples.

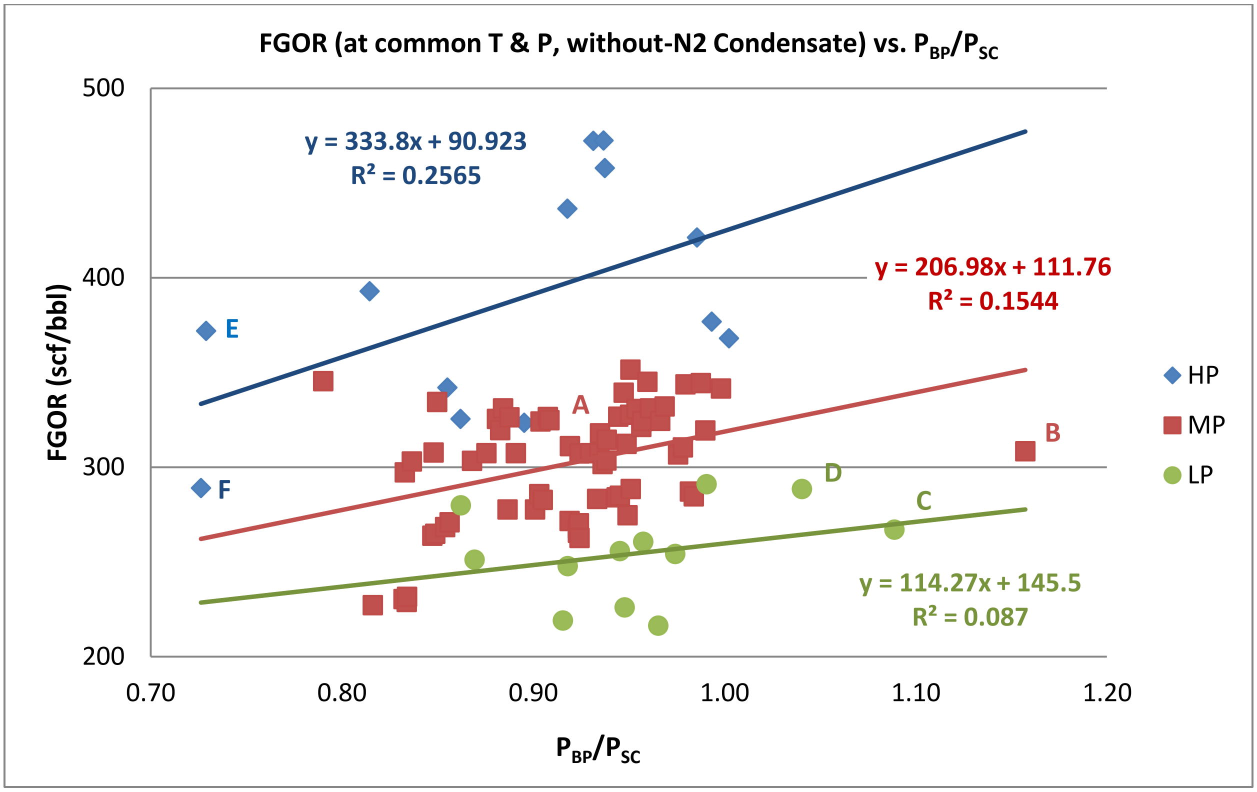


Figure 4-40. PSM/EOS calculated FGOR (at common pressure and temperature) vs. PSM/EOS calculated P_{BP}/P_{SC} based on without-N_2 pressurized condensate samples.

Figure 4-41 graphs the PSM/EOS calculated FGORs (scf/bbl), calculated at common pressure and temperature, for the pressurized condensate samples without-N_2. Figure 4-42 presents this FGOR data in units of lb/bbl. FGOR calculated as scf/bbl and FGOR calculated as lb/bbl are highly correlated, and the data trends in Figure 4-42 mirror those in Figure 4-41. Both figures identify P_{BP}/P_{SC} outliers and other samples with extreme P_{BP}/P_{SC} values using the letters introduced above. With the exception of sample F, the other extreme P_{BP}/P_{SC} value samples are not associated with extreme FGORs. Samples B, C, and E, identified as P_{BP}/P_{SC} outliers in Table 4-11, have FGORs near the median for their well cycle pressure groups.

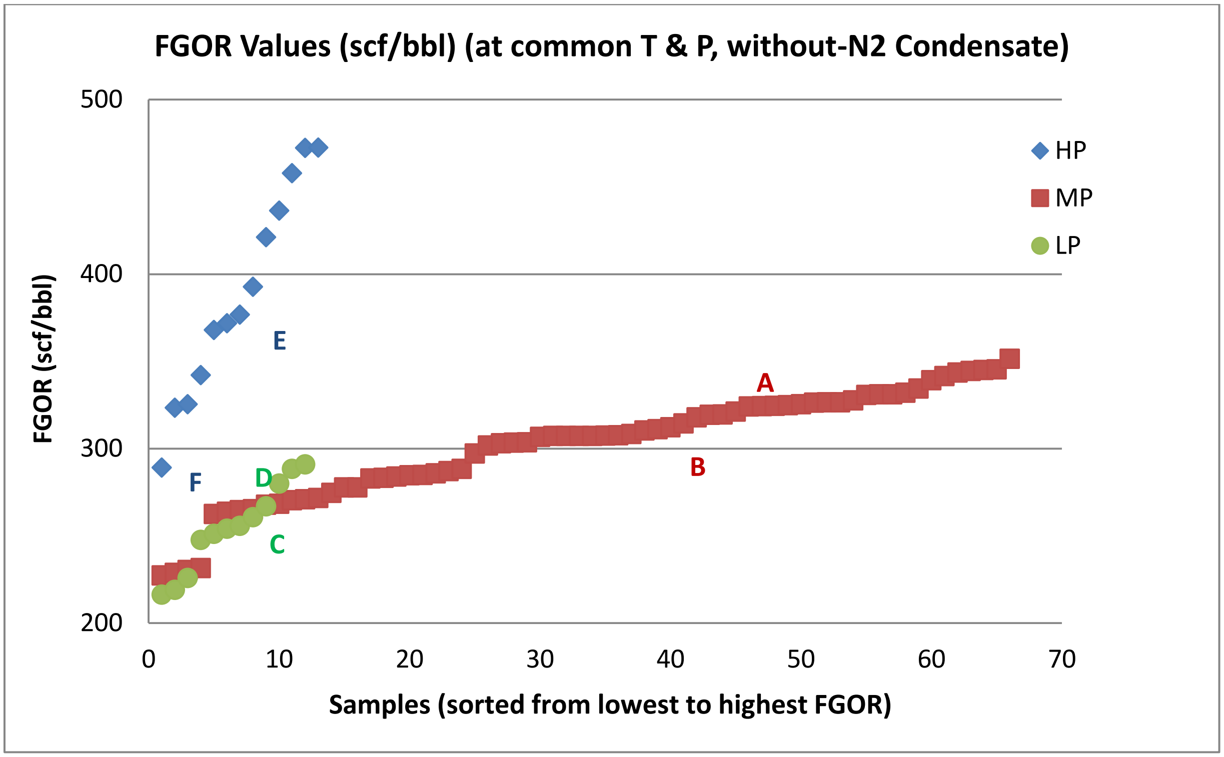


Figure 4-41. PSM/EOS calculated FGOR (scf/bbl), calculated at common pressure and temperature, based on pressurized condensate samples (without-N_2).

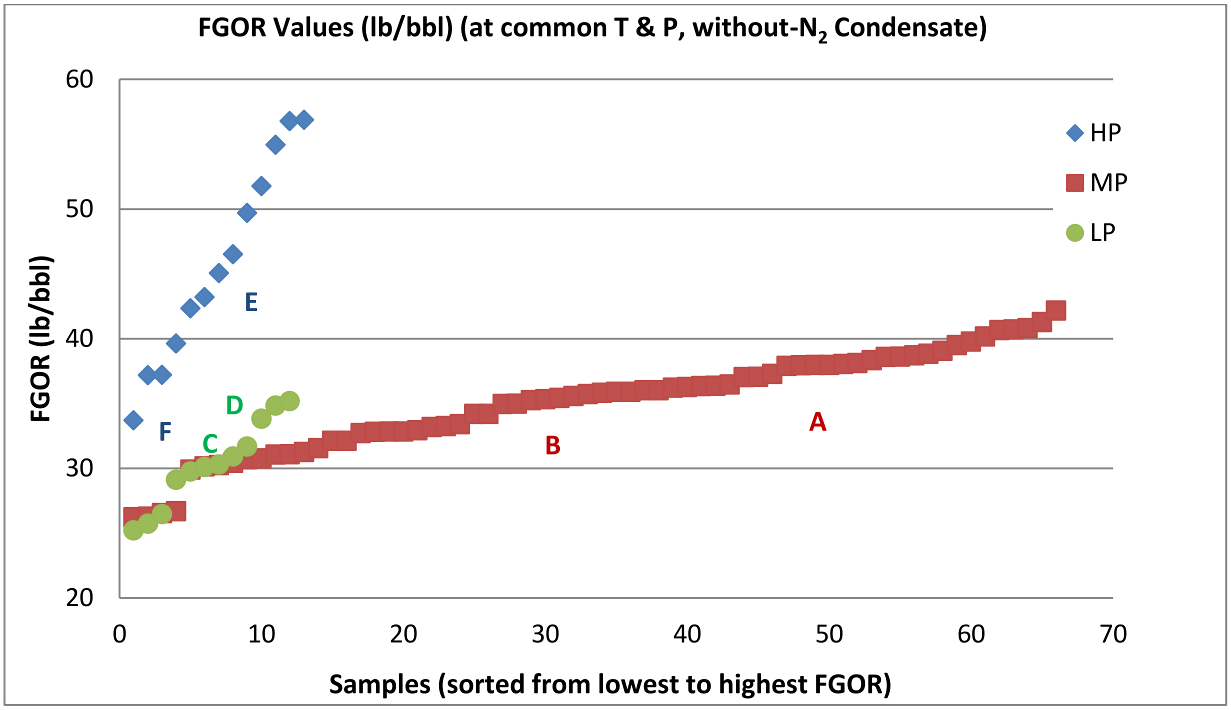


Figure 4-42. PSM/EOS calculated FGOR (lb/bbl), calculated at common pressure and temperature, based on pressurized condensate samples (without-N_2).

Outlier analysis for the PSM/EOS calculated (at common pressure and temperature) FGORs

Similar to the statistical analysis conducted in Section 4.6.1, a GESD test and Dixon's Q test were conducted to identify outliers for these FGOR data sets, and no samples were identified as statistical outliers for FGOR. During this project the pressurized condensate samples were collected from a single source by experienced personnel using dedicated equipment under controlled conditions (e.g., the separator pressure and temperature history were controlled and monitored), and all the samples were analyzed by the same lab by experienced analysts. These optimized sample collection and analysis procedures, and controlled separator operation likely contributed to, at least in part, this finding of zero FGOR statistical outliers.

Summary of Findings Regarding P_{BP}/P_{SC} as an OPC for Samples Collected to Estimate FGOR

The data in Figures 4-39 to 4-42 show that FGOR and P_{BP} are not strongly correlated, and that anomalous/outlier P_{BP}/P_{SC} do not correspond with anomalous/outlier FGORs. Thus, the results of this study suggest that P_{BP}/P_{SC} may not be an optimal OPC for pressurized condensate sample collection and analysis if the ultimate use of the condensate composition results is to estimate FGOR. A possible explanation, at least in part, for the observed FGOR vs. P_{BP}/P_{SC} data scatter is that P_{BP} is strongly impacted by condensate methane concentration, whereas methane is only a fraction of the flash gas generated from a condensate sample. For example, a sample could lose a fraction of the volatile methane, but otherwise be representative of the separator fluids. Such a sample could result in an anomalous P_{BP} calculation (i.e., $P_{BP}/P_{SC} <<1.0$), but a representative FGOR calculation including a representative level of VOCs (i.e., data for flash gas VOC generation estimates) and a representative flash gas MW (i.e., data for storage tank vapor control system design). Methane is not a VOC and is the lightest flash gas component. Select PSM/EOS calculations show that a 20% reduction in the methane concentration in a typical condensate sample results in about a 16% change in P_{BP} but only about a 5% change in FGOR.

Lacking an alternative OPC, PSM/EOS calculated P_{BP}/P_{SC} could be used as a conservative OPC for samples collected to estimate FGOR and flash gas composition. As discussed above, condensate samples for this project were collected and analyzed under very controlled conditions, and none were statistical outliers for PSM/EOS calculated FGOR, whereas several of the PSM/EOS calculated P_{BP} were statistical outliers. This suggests that P_{BP}/P_{SC} would be a conservative OPC because some samples that have outlier P_{BP}/P_{SC} (and would be discarded) would have a representative FGOR estimate. For this study, PSM/EOS calculated P_{BP}/P_{SC} ranged from about 0.73 to 1.16, and this range could be a minimum for OPC acceptance criteria, although the applicability of these findings to other production facilities with real-world separator operation and sample collection imperfections cannot be determined.

Regardless of its applicability as an OPC, P_{BP}/P_{SC} could be used as a screening tool in conjunction with FGOR and/or other measurements in an OPC strategy. For example, anomalous P_{BP}/P_{SC} could be a flag to carefully scrutinize a sample.

P_{BP}/P_{SC} as an OPC for Samples Collected to Estimate Methane

The P_{BP}/methane correlation suggests that P_{BP}/P_{SC} could be an effective OPC for pressurized condensate samples if the ultimate use of the analytical composition results is to estimate flash gas methane. The following data analysis examines the effect of different P_{BP}/P_{SC} acceptance criteria for such an OPC.

A GESD test and Dixon's Q test were conducted to identify outliers for the T_{SC}-adjusted methane data sets (i.e., data in Figure 4-36), and only sample B was determined to be a statistical outlier for methane concentration. Sample B was also identified as a PSM/EOS calculated P_{BP}/P_{SC} statistical outlier. Table 4-13 evaluates, for without-N_2 samples, the impact of various P_{BP}/P_{SC}–based acceptance criteria for pressurized condensate samples.

Table 4-13. P_{BP}/P_{SC} OPC Acceptance Criteria vs. Samples Meeting Criteria and Condensate T_{SC}-adjusted Methane Concentration Outliers (Samples without-N_2)

P_{BP}/P_{SC} Acceptance Criteria	Samples Meeting Acceptance Criteria			Samples <u>Not</u> Meeting Acceptance Criteria		
	Total	T_{SC}-adjusted CH_4 (mole %)		Total	T_{SC}-adjusted CH_4 (mole %)	
		Not Outlier	Outlier		Not Outlier	Outlier
$0.82 \leq P_{BP}/P_{SC} \leq 1.02$	88	88	0	7	6	1
$0.75 \leq P_{BP}/P_{SC} \leq 1.09$	92	92	0	3	2	1
$0.68 \leq P_{BP}/P_{SC} \leq 1.16$	95	94	1	0	0	0

The first column in Table 4-13 lists different P_{BP}/P_{SC} acceptance criteria, with less stringent criterion with each row. The yellow-shaded/light pattern columns summarize the samples that meet these criteria (i.e., the number of samples that met these criteria is listed under "Total"), and the number of these samples that have a condensate T_{SC}-adjusted methane concentration identified as a statistical "Outlier" or "Not Outlier." For example, 88 samples met the P_{BP}/P_{SC} acceptance criteria of $0.82 \leq P_{BP}/P_{SC} \leq 1.02$, and zero of these samples were identified as outliers for T_{SC}-adjusted methane concentration. The blue-shaded/medium pattern columns summarize the samples that do not meet these criteria (i.e., the number of samples that did not meet these criteria is listed under "Total"), and the number of these samples that have a T_{SC}-adjusted methane concentration identified as statistical "Outlier" or "Not Outlier." For example, 7 samples did not meet the P_{BP}/P_{SC} acceptance criteria of $0.82 \leq P_{BP}/P_{SC} \leq 1.02$, and one of these samples was identified as an outlier for T_{SC}-adjusted methane concentration and six of these samples were not identified as outliers for T_{SC}-adjusted methane concentration. Thus, if the P_{BP}/P_{SC} acceptance criteria of $0.82 \leq P_{BP}/P_{SC} \leq 1.02$ is applied, 100% of the samples meeting these criteria would be associated with T_{SC}-adjusted methane concentration estimates that are not outliers. However, 6 of the samples not meeting these criteria would be associated with T_{SC}-adjusted methane concentration estimates that are not statistical outliers, and there is about a 6.3% (i.e., 6/95) chance of not accepting a sample with a T_{SC}-adjusted methane concentration that is not an outlier. For the P_{BP}/P_{SC} acceptance criteria range determined for the without-N_2 data (i.e., $0.75 \leq P_{BP}/P_{SC} \leq 1.09$, refer to Table 4-11), 100% of the samples meeting these criteria are associated with T_{SC}-adjusted methane concentrations that are not outliers, and 2 of the 3 samples not meeting these criteria would be associated with T_{SC}-adjusted methane concentration that are not statistical outliers. Thus, there would be about a 2.1% (i.e., 2/95) chance of not accepting a sample with a T_{SC}-adjusted methane concentration that is not an outlier.

In sum, as would likely be expected, more stringent (i.e., smaller range) P_{BP}/P_{SC} acceptance criteria reduce the chance of accepting a sample with an anomalous T_{SC}-adjusted methane concentration, but increase the probability of not accepting a sample with representative T_{SC}-adjusted methane concentration, whereas less stringent (i.e., larger range) P_{BP}/P_{SC} acceptance criteria increase the chance of accepting a sample with an anomalous T_{SC}-adjusted methane concentration but decrease the probability of not accepting a sample with a representative T_{SC}-adjusted methane concentration.

4.6.4 Initial Pressure Test

The IPT is described in Section 2.3.3. Figure 4-43 compares the IPT P_{BP} for the pressurized condensate samples to the corresponding PSM/EOS calculated common temperature and pressure FGOR (i.e., these FGOR were calculated as described in Section 4.6.3). IPT P_{BP} were estimated as discussed in Section 7.4 of Appendix II. The data in Figure 4-43 show that FGOR generally increases with IPT P_{BP}; however, there is considerable scatter in the data and the correlations are not strong (e.g., the R^2 values range from about 0.1 to 0.4). The PSM/EOS calculated P_{BP}/P_{SC} outliers and other extreme value samples from Table 4-11 are identified. Figure 4-44 plots IPT P_{BP}/P_{SC} data from smallest to largest. Outlier evaluations (i.e., Grubbs and Dixon's Q-test) identify samples E and B as IPT P_{BP} outliers. Sample E (highest N_2 of all samples) and Sample B (highest methane of all samples) are PSM/EOS calculated P_{BP}/P_{SC} outliers for samples without-N_2 (refer to Table 4-11). However, sample C (which is a borderline PSM/EOS calculated P_{BP}/P_{SC} outlier) and sample F (which is a PSM/EOS calculated P_{BP}/P_{SC} outlier) are not identified as outliers/anomalous results by the IPT.

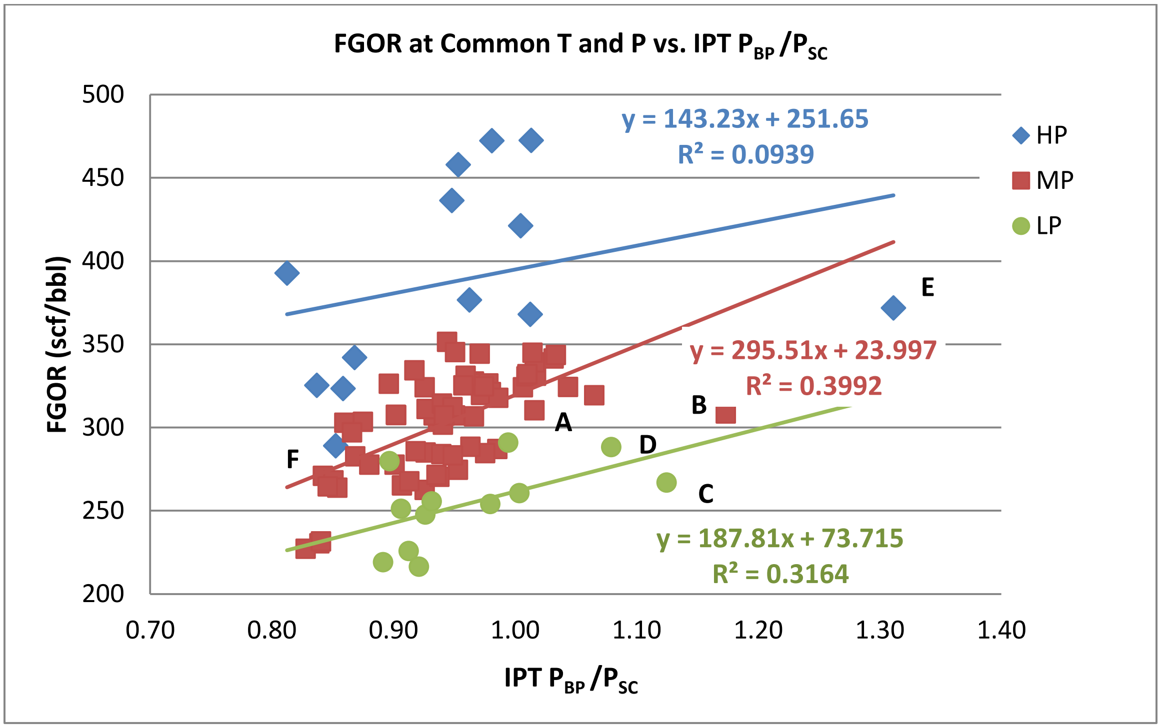


Figure 4-43. Initial Pressure Test P_{BP}/P_{SC} vs. PSM/EOS calculated FGOR (calculated at common pressure and temperature, based on pressurized condensate samples (without-N_2)).

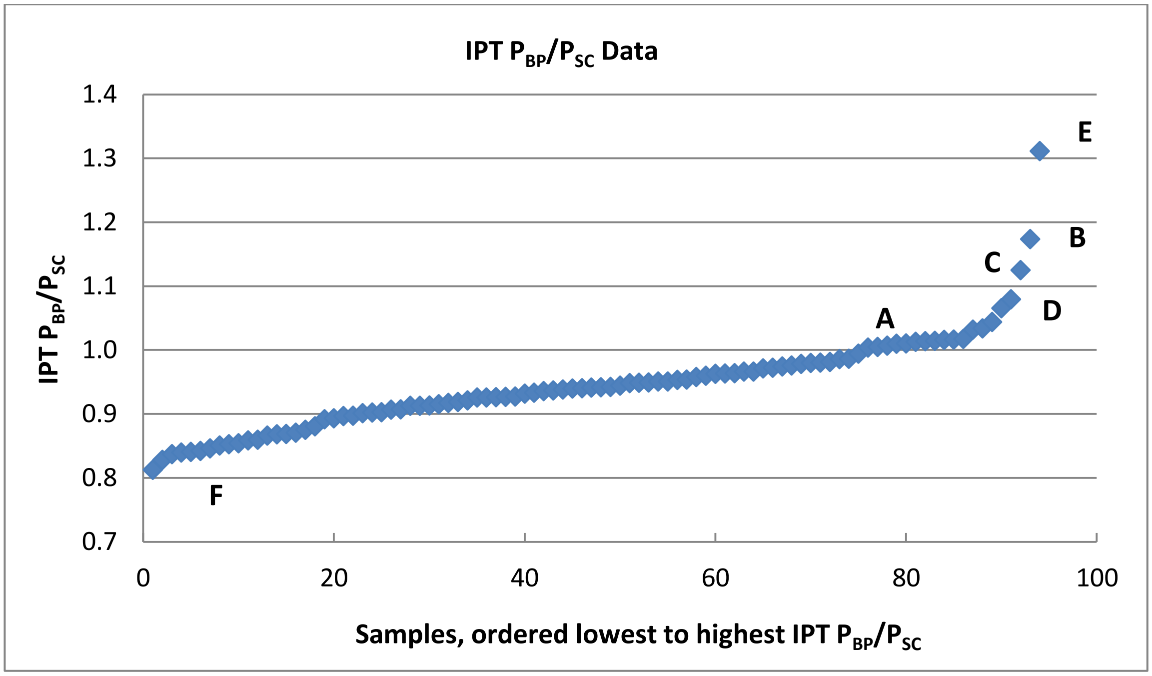


Figure 4-44. Initial Pressure Test data.

Summary of Findings Regarding IPT P_{BP}/P_{SC} as an OPC for Samples Collected to Estimate FGOR

The data in Figure 4-43 show that FGOR and IPT P_{BP}/P_{SC} are not strongly correlated and that anomalous/outlier IPT P_{BP}/P_{SC} do not correspond with anomalous/outlier FGORs. In addition, the IPT is impacted by air in HC liquids samples and anomalous IPT P_{BP}/P_{SC} could be due to air contamination, and the IPT would not be an appropriate “stand-alone” OPC because it does not evaluate the analytical results of a pressurized HC liquids sample. These results indicate that IPT would not be an optimal OPC for pressurized HC liquids samples if the ultimate use of the HC liquids composition results is to estimate FGOR. However, IPT could be used as a screening tool in conjunction with FGOR and/or other measurements in an OPC strategy. For example, anomalous IPT P_{BP}/P_{SC} could be a flag to carefully scrutinize a sample.

4.6.5 Coriolis Meter / Lab Densitometer Condensate Density Measurements Comparison

The comparison of condensate density measurements conducted at the production facility by the Coriolis meter (i.e., flowing density) and in the lab with a digital densitometer by ASTM D4052 was evaluated as a methodology to identify compromised samples. For example, large differences between the two density measurements could trigger further investigation of sample viability.

The density differences for 33 data pairs (i.e., [(flowing density – lab density)/((flowing density + lab density)/2)]) were evaluated and two of the pairs had large differences in the two density measurements and were identified as outliers by Grubb´s test. However, these two sample pairs did not correspond to samples identified as PSM/EOS calculated FGOR (at common temperature and pressure) outliers, or extreme values or outliers by PSM/EOS calculated P_{BP}/P_{SC} or IPT P_{BP}/P_{SC}. The calculated densities based on the analytical results agreed with the Coriolis meter densities within about 2%, and this suggests difficulty with the lab density measurements. In addition, similar to the IPT, this OPC would not be an appropriate “stand-alone” OPC because it does not evaluate the analytical results of a pressurized HC liquids sample. Based on these study results and practical considerations (e.g., many production facilities are not equipped with Coriolis meters and Coriolis meter density instrument calibration would need to be documented), this OPC was found to be unreliable during the PHLSA Study and not considered for further investigation.

4.6.6 Lab Densitometer Measurement of Bubble Point Pressure

Bubble point pressures were determined by digital densitometer as described in Section 2.3.3. The study experience was that using a lab densitometer to measure the P_{BP} is a very time-consuming procedure and has poor accuracy. On average, the measured P_{BP} was 18% lower than the associated P_{SC}. Further development of the equipment and/or P_{BP} measurement procedure would likely be required before this practice could be a viable OPC. Similar to the IPT, this OPC would not be an appropriate "stand-alone" OPC because it does not evaluate the analytical results of a pressurized HC liquids sample. Based on these results, this OPC was found to be unreliable during the PHLSA Study and not considered for further investigation.

4.6.7 Suggested Operational Performance Checks Strategy

Based on these results, recommendations for OPCs include:

- Measure sample pressure and temperature during sample collection (i.e., at the start, middle, and end of sample collection) and during lab analysis with highly accurate, calibrated instruments.
- Conduct an IPT P_{BP} measurement in the lab to identify potential anomalies with the sample collection. An anomalous IPT result (i.e., IPT P_{BP}/P_{SC} significantly differs from 1.0) is not necessarily a reason to discard a sample but it is recommended that such samples be flagged for scrutiny. The IPT, and other physical measurements of P_{BP}, could be biased by non-native nitrogen (i.e., air) in samples.
- As appropriate, adjust nitrogen levels in HC liquids composition results prior to PSM/EOS calculations. For example, compare high nitrogen concentrations to PSM/EOS calculated equilibrium estimates (e.g., PSM/EOS calculations estimate a N_2 concentration of about 0.003 wt% for Test Facility condensate at 260 psig and 60°F (i.e., high pressure/low temperature operation)) or if sales gas records show non-detectable levels of nitrogen in the gas, then it follows that the associated HC liquids would have non-detectable levels of this volatile gas. Use a reliable PSM/EOS software package (e.g., a software that is designed for HC streams similar to the subject sample) to calculate P_{BP} and FGOR. Bubble point pressure should be calculated at the sample collection temperature, and FGOR should be calculated at tank temperatures and pressures that are the same as for historical comparable FGOR estimates. Determine the P_{BP}/P_{SC}, and for samples with P_{BP}/P_{SC} significantly different than 1.0, it is recommended that the results be scrutinized for potential anomalies with the sample collection and analysis.

  Acceptance of HC liquids composition results should depend on the ultimate data use and engineering judgment. For example, for pressurized HC liquids samples collected and analyzed to estimate methane generation, PSM/EOS calculated P_{BP}/P_{SC} may be an appropriate OPC. An appropriate OPC for samples collected to estimate FGOR and flash gas composition (e.g., data for storage tank vapor control system design) and/or VOC generation (e.g., data for flash VOC generation estimates) could be based on comparing the measured FGOR and flash gas composition to historical trends for similar production facilities (i.e., PSM/EOS calculated FGOR could be an optimal OPC).

4.7 Winter and Summer Three-Separator Pressure Range Testing

Supporting data for the information in this sub-section is in Appendix IV and in Appendix VI (NE PHLSA Study Task 9_Three Pressure Testing MB and FGOR.xlsx).

This task (Task 9, refer to Section 3.2.9) investigated the effect of separator pressure and hot versus cold weather on pressurized HC liquids sampling and analysis results, and flash gas generation (directly measured and PSM/EOS calculated FGOR). In the winter and summer, the separator was operated at three different pressures intended to cover typical operating pressures ranges for separators in the DJ Basin (LP ~ 175, MP ~ 225, and HP ~ 260 psig). A minimum of three tests were conducted at each pressure, and well cycle storage tank mass balance and FGOR calculations were conducted. As described in Section 3.2.9, each test comprised comprehensive measurements during a well cycle that included pressurized condensate samples collected in conjunction with process measurements.

Section 4.7.1 evaluates the variability of summer/winter effects on input parameters used in determining flashing losses. Section 4.7.2 presents the results of the summer three-pressure testing including storage tank mass balance measurements, FGOR measurements, and summary PSM/EOS calculations of FGOR based on the analytical results for the pressurized condensate samples. Section 4.7.3 presents corresponding data for the winter testing. The summer testing results are generally considered to be more reliable than the winter testing results. The winter testing was conducted first and lessons learned during these tests were incorporated into improved procedures for the summer testing (refer to Section 3.2.9). In addition, flash gas flowrates were generally a factor of about two greater during the summer testing. Thus, a larger fraction of the gas flow was measured in the flowmeters' optimum range, and a smaller fraction of the gas flow was during severe flowrate transients that impact measurement accuracy. Section 4.7.4 presents additional detail regarding the PSM/EOS calculations including a summary of the sensitivity and uncertainty analyses, and Section 4.7.5 summarizes the analytical results for pressurized produced water samples.

4.7.1 Evaluation of the Variability of Summer/Winter Effects on Input Parameters used in Determining Flashing Losses

Parameters that differ during winter and summer operation, and are used to estimate flash gas generation include separator liquids temperature (which impacts the separator liquid composition), and tank liquid and gas temperatures (which impacts the final state of the post-flash HC liquids and gas). Measured and PSM/EOS calculated FGORs were larger during the summer (i.e., July) than during the winter (i.e., March). The difference was primarily caused by higher separator temperatures during the winter and higher tank temperatures during the summer. Figure 4-45 presents the average temperatures for the separator liquids, tank bottom liquids, and tank headspace gas for each well cycle during the winter and summer tests. These data show:

- Generally higher **separator liquid temperatures** (data indicated by blue diamonds) during the winter testing than during the summer testing.
  - During the winter testing the separator liquid temperature ranged from about 58 to 92°F, and this temperature was impacted by the separator heater operation.
  - During the summer testing the separator liquid temperature ranged from about 62 to 86°F, and this temperature was impacted by ambient temperatures. For example, temperatures trended higher during each test day.
- Higher **tank liquid temperatures** (data indicated by red squares) during the summer testing than during the winter testing. These tank liquid temperatures were measured near the bottom of the tank in the vicinity of the downcomer outlet. These temperatures were impacted by ambient temperature and solar heating, and generally trended higher during each test day.
  - During the winter, the tank liquid temperature ranged from about 44 to 47°F.
  - During the summer, the tank liquid temperature ranged from about 75 to 83°F.
- Generally higher **tank headspace gas temperatures** (data indicated by green circles) during the summer testing than during the winter testing. These temperatures were impacted by ambient temperature and solar heating, and generally trended higher during each test day.
  - During the winter, the tank headspace gas temperature ranged from about 49 to 85°F.
  - During the summer, the tank headspace gas temperature ranged from about 71 to 100°F.

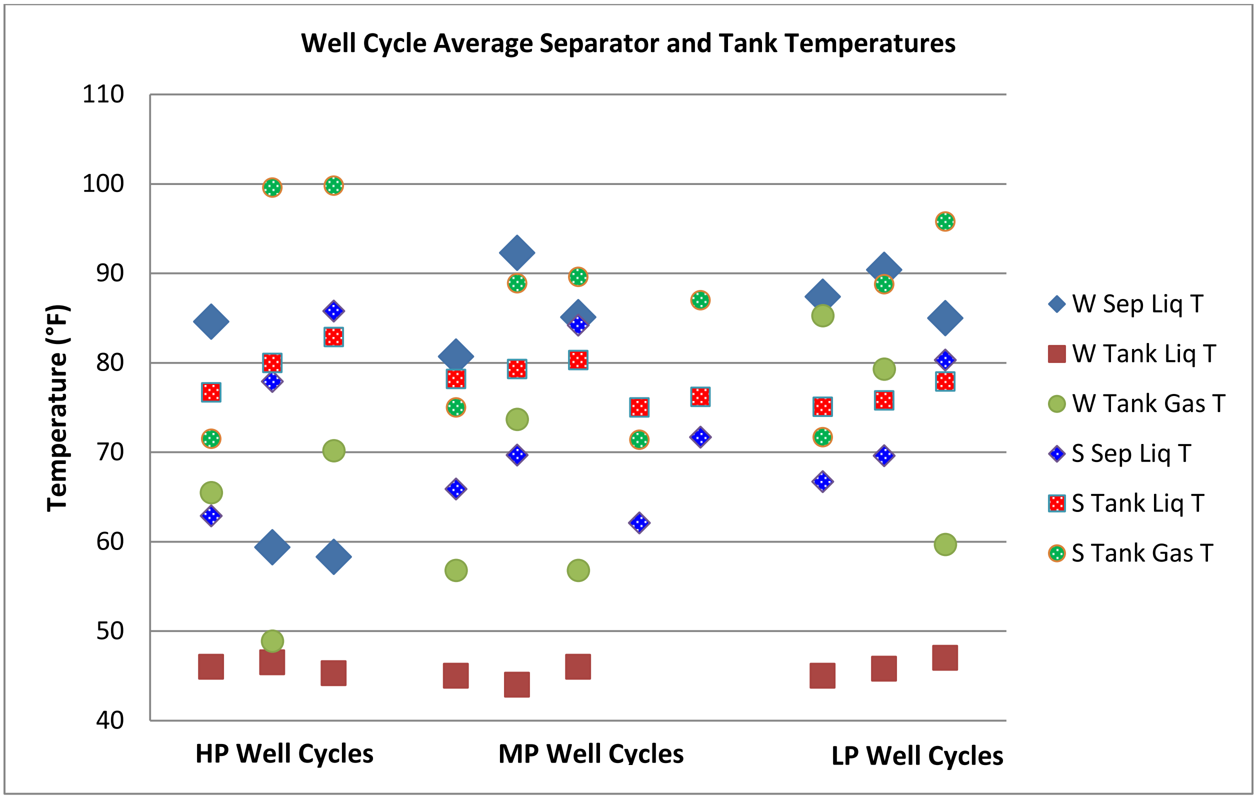


Figure 4-45. Average separator and tank temperatures during winter and summer well cycles.

4.7.2 Summer Three-Pressure Testing Results

Table 4-14 lists the summer testing well cycles and a summary of primary operating parameters. Three tests were conducted during well cycles at the HP separator operating condition, five tests were conducted during well cycles at the MP separator operating condition, and three tests were conducted during well cycles at the LP separator operating condition. The operating parameters listed in the table include the sample collection pressure and temperature, separator pressure and temperature during the well cycle, and storage tank headspace gas temperature and bottom liquid temperature during the well cycle. The tank bottom liquid temperature is the tank oil temperature in the vicinity of the downcomer outlet, about one foot from the bottom of the tank. The sample collection pressure and temperature were recorded during sample collection, which was initiated within 30 minutes of the well cycle end. Most sample collection pressures were 2 to 5 psig less than the average separator pressure during the well cycle (S-MP3 and S-LP1 had differences of 6 and 7 psi, respectively). This is typical because the separator losses some pressure during each liquid dump. Most sample collection temperatures were within 1 to 3°F of the average separator temperature during the well cycle (S-HP3 and S-MP3 had differences of 5 and 8°F, respectively). These measurements suggest that the sampled condensate had a composition similar to the condensate that flowed to the tank during the well cycle.

Table 4-14. Summer Three-Pressure Testing Summary

Well Cycle	Date	Well Cycle Start Time	Separator, Tank, and Sample Collection Temperatures & Pressures, Average for Well Cycle			
			P_{sep} / P_{SC} (psig)	T_{sep} / T_{SC} (°F)	$T_{tank\ gas}$ (°F)	$T_{tank\ bottom}$ (°F)
S-HP1	7/25/2016	7:24	265 / 260	63 / 64	72	77
S-HP2	7/25/2016	13:19	264 / 262	78 / 76	100	80
S-HP3	7/25/2016	15:48	265 / 260	86 / 81	100	83
S-MP1	7/26/2016	7:41	229 / 227	66 / 65	75	78
S-MP2	7/26/2016	10:50	228 / 224	70 / 71	89	79
S-MP3	7/26/2016	14:30	234 / 228	84 / 76	90	80
S-MP4	7/27/2016	7:27	229 / 227	62 / 64	71	75
S-MP5	7/27/2016	10:15	231 / 226	72 / 69	87	76
S-LP1	7/29/2016	7:08	178 / 171	67 / 66	72	75
S-LP2	7/29/2016	9:53	175 / 173	70 / 71	89	76
S-LP3	7/29/2016	13:39	178 / 177	80 / 77	96	78

Mass Balance Measurements

Equation 4-1 is used to calculate the storage tank HC mass balance for a well cycle.

$$ST_{MB} = \frac{Mass_{FG}}{\Delta Mass_{oil}} = \frac{Mass_{FG}}{Mass_{pre\text{-}flash\,oil} - Mass_{post\text{-}flash\,oil}} \qquad \text{Eqn. 4-1}$$

Where:

ST_{MB} = storage tank HC mass balance for a well cycle

$Mass_{FG}$ = measured mass of flash gas generated during a well cycle (kg)

$Mass_{post\text{-}flash\ oil}$ = measured mass of post-flash HC liquids produced during a well cycle (kg)

$Mass_{pre\text{-}flash\ oil}$ = measured mass of pre-flash HC liquids produced during a well cycle (kg)

$\Delta Mass_{oil} = Mass_{pre\text{-}flash\ oil} - Mass_{post\text{-}flash\ oil}$

Mass balances near 1.0 (i.e., 100%) provide confidence in the measured gas and oil (i.e. condensate) volumes, and analytical results for associated process samples. Mass balances that significantly deviate from 100% suggest measurement anomalies, and/or that process streams are not in equilibrium. Appendix IV provides more detailed mass balance equations and a discussion of the many factors and assumptions impacting storage tank mass balances and deviations from 100% (e.g., measurement inaccuracy, single point in time measurements, sample collection vs. operations timing).

Figure 4-46 shows the storage tank HC mass balances for the summer testing well cycles based on GPA 2103M analysis of pressurized condensate samples collected with CP cylinders. The y-axis shows the measured mass balance during the well cycle (i.e., Equation 4-1). The x-axis shows the well cycle start time and results are shown for HP, MP, and LP well cycles. The vertical bars indicate the 95% level of confidence for the calculated mass balances based on the uncertainties of the volume and composition measurements for the condensate and tank headspace gas process streams. It is evident that the mass balances improved (i.e., were closer to 100%) as the day progressed, and the trend was consistent during all four days of testing.

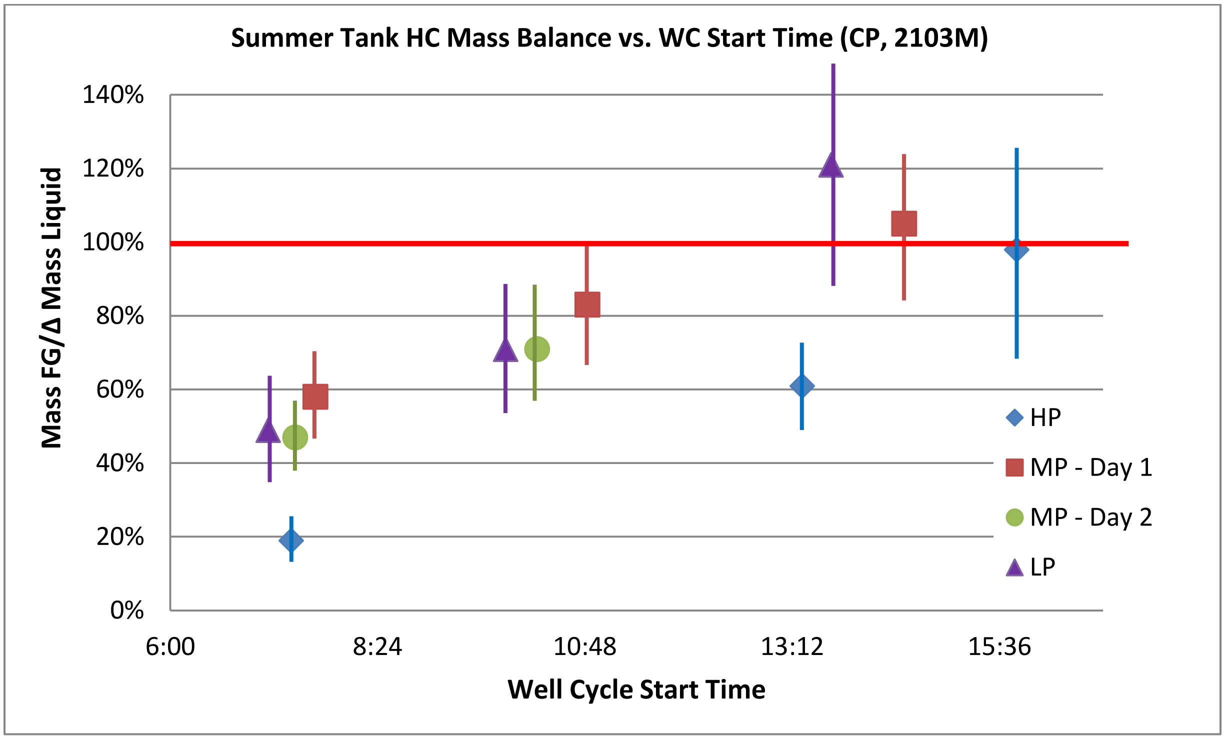


Figure 4-46. Summer storage tank HC mass balance vs. well cycle start time.

Figure 4-47 presents the same data with $T_{\text{tank bottom}}$ on the x-axis. The mass balances improved as the tank liquid temperature increased. These results suggest a "quenching" of flash gas generation when the tank liquid is relatively cold; that is, less flash gas was measured when the tank liquids were colder in the morning than in the late afternoon. Separator dump fluids are a mix of liquid and gas, and adiabatic flash calculations and estimates of the underground separator-to-tank pipeline temperature suggest these dump fluids are colder than the tank bottom liquid temperature. The measured flash gas generation is thought to be primarily the sum of the dump fluids gas and "secondary" flash gas that evolves as the dump liquid temperature increases as the dump liquid mixes with warmer tank liquid. Relatively cooler tank liquid in the morning would be expected to reduce such secondary flash gas generation. A second consideration is that colder morning tank liquid may be under-saturated after cooling overnight (without any condensate production) and absorb some of the flash gas from the separator dump. To preserve well pressure for testing, the well was shut in after the last test each day until the first test the next morning. Thus, light HCs (e.g., C1-C5) were not added to the tank oil as it cooled over-night. The data in Figure 4-47 suggest that, for this testing and this temperature range, the absolute tank bottom temperature was less of an influence on the mass balance than the morning to afternoon temperature change. For example, during the HP well cycles, the temperature increased about 6°F and the mass balance improved from about 20% to 100%. During the MP well cycles, the temperature increased about 2°F and the mass balance improved from about 60% to 100%, and during the LP well cycles about a 3°F temperature increase improved the mass balance from about 50 to 120%. Mass balances greater than 100% are likely due to the contribution of heavy HCs from breathing losses, and this is discussed below. These trends support the idea that tank liquid becomes under-saturated as it cools in the tank overnight.

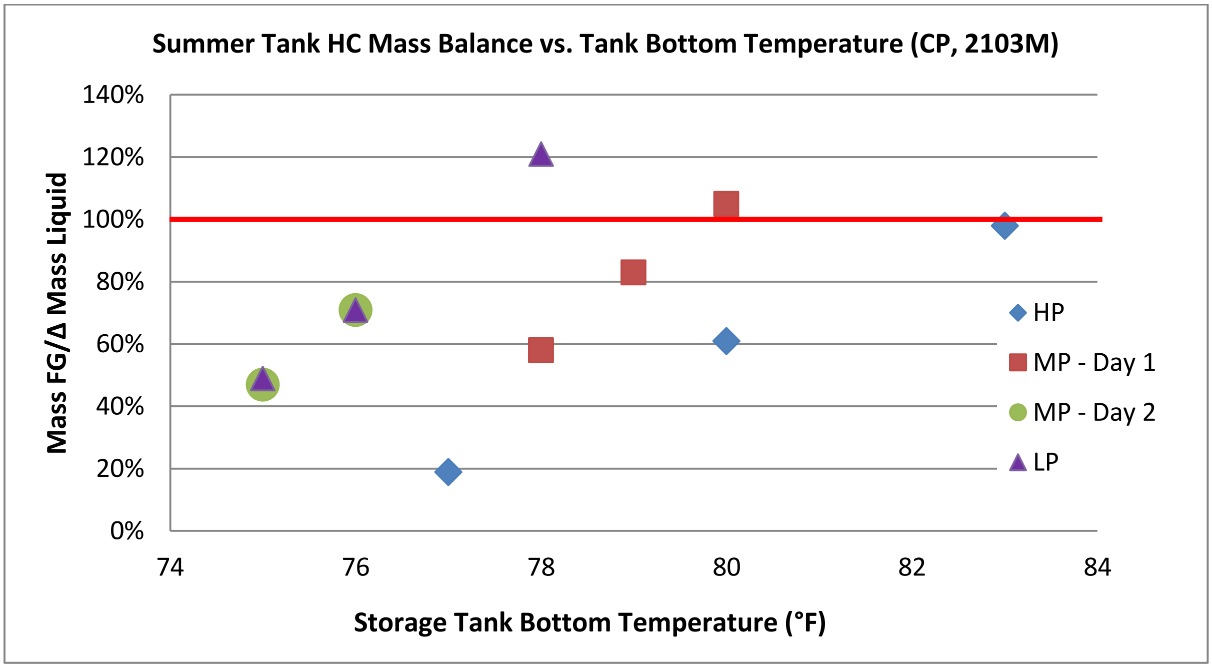


Figure 4-47. Summer storage tank HC mass balance vs. tank bottom temperature.

Storage Tank Mass Balances for C1–C5

Table 4-15 presents storage tank mass balances for total HCs and C1 to C5 HC species for the summer testing well cycles. Measured FGORs are also listed. The 95% level of confidence values for these calculated values, based on the uncertainties of the volume and composition measurements for the condensate and tank headspace gas process streams, are shown in parentheses. The data for well cycle S-MP3 are illustrative. The overall mass balance closure for S-MP3 was 105%. Mass balances for methane, ethane, and propane ranged from 74% to 96%, and the mass balances for the heavier HCs butanes and pentanes were 120% and 260%, respectively. Methane, ethane, and propane are volatile compounds and a review of the post-flash condensate composition for this well cycle shows that about 100% of C1, 99% of C2, and 85% of C3 would be expected to flash in the tank. Butanes and pentanes are less volatile and a review of the post-flash condensate composition for this well cycle indicates that about 50% of C4s and 10% of C5s would be expected to flash in the tank. Mass balances greater than 100% for butanes and pentanes suggest these HCs are volatilizing in the tank as breathing losses. Mass balances less than 100% for C1–C3 suggest these HCs are displacing some breathing loss gases in the tank headspace (recall that the tank gas composition is measured downstream of the tank in the tank-to-burner pipeline).

The total mass balance greater than 100% supports the interpretation that lighter flash gas components are displacing heavier breathing losses in the tank headspace. Similar trends were observed for the other well cycles with the pentanes mass balance having the highest value and usually greater than 100% (albeit typically with a large uncertainty). Even if relatively cold liquid in the tank interior was “quenching” flash gas emissions, hot tank wall temperatures from solar radiation were still driving heavier HCs into the gas phase. An implication for storage tank vapor control system design is that the composition of the actual gas that goes from the tank to the burner can be heavier (i.e., have a higher heat content) than flash gas estimated by PSM/EOS calculations, and this should be considered for the design.

Table 4-15. Summer Three-Pressure Testing FGORs and Storage Tank Mass Balances for HCs and C1–C5 (CP, 2103)

Well Cycle	Measured Value (95% Level of Confidence)						
	FGOR (scf/bbl)	Tank HC MB (FG/ΔL)[A]	Tank C1 MB (FG/ΔL)	Tank C2 MB (FG/ΔL)	Tank C3 MB (FG/ΔL)	Tank C4 MB (FG/ΔL)	Tank C5 MB (FG/ΔL)
S-HP1	78 (+/- 9.0)	19% (+/- 3.6%)	14% (+/- 1.7%)	14% (+/- 1.7%)	17% (+/- 2%)	23% (+/- 2.3%)	77% (+/- 27%)
S-HP2	184 (+/- 8)	61% (+/- 12%)	32% (+/- 2.0%)	34% (+/- 1.7%)	43% (+/- 2.2%)	60% (+/- 3%)	190% (+/- 61%)
S-HP3	328 (+/- 74)	98% (+/- 28%)	69% (+/- 16%)	65% (+/-15%)	80% (+/- 18%)	110% (+/- 20%)	290% (+/- 87%)
S-MP1	172 (+/- 14)	58% (+/- 13%)	53% (+/- 5.0%)	41% (+/- 3.5%)	47% (+/- 4.1%)	67% (+/- 5.2%)	160% (+/- 47%)
S-MP2	256 (+/- 13)	83% (+/- 17%)	77% (+/- 5.2%)	57% (+/- 3.3%)	66% (+/- 3.8%)	91% (+/- 5.1%)	180% (+/- 37%)
S-MP3	327 (+/- 14)	105% (+/- 23%)	96% (+/- 6.0%)	74% (+/- 3.7%)	84% (+/- 4.2%)	120% (+/- 6.0%)	260% (+/- 62%)
S-MP4	156 (+/- 8.4)	47% (+/- 10%)	50% (+/- 3.4%)	36% (+/- 2.1%)	39% (+/- 2.2%)	55% (+/- 3.4%)	160% (+/- 55%)
S-MP5	228 (+/- 26)	71% (+/- 16%)	70% (+/- 8.4%)	51% (+/- 5.8%)	53% (+/- 6.1%)	71% (+/- 6.7%)	150% (+/- 34%)
S-LP1	149 (+/- 28)	49% (+/- 14%)	63% (+/- 12%)	43% (+/- 8.0%)	39% (+/- 7.4%)	49% (+/- 7.5%)	150% (+/- 53%)
S-LP2	193 (+/- 18)	71% (+/- 19%)	88% (+/- 9.1%)	59% (+/- 5.7%)	53% (+/- 5.2%)	64% (+/- 5.2%)	140% (+/- 33%)
S-LP3	277 (+/- 17)	121% (+/- 35%)	110% (+/- 7.8%)	84% (+/- 5.4%)	84% (+/- 5.6%)	110% (+/- 7.0%)	300% (+/- 96%)

A. FG/ΔL = mass of flash gas generation measured during Well Cycle/change in mass of HC liquids during Well Cycle (= pre-flash - post-flash HC liquids mass).

PSM/EOS Dead Oil Model Results

PSM/EOS calculations were conducted to simulate the effects of mixing fresh oil/condensate from a separator dump with “dead” (i.e., weathered) oil/condensate in the storage tank. PSM/EOS storage tank models were modified to add a dead oil stream to mimic the mixing of fresh and dead oil in a storage tank. The volume of the dead oil stream was adjusted until the PSM/EOS calculations matched the measurements of storage tank HC mass balance (i.e., the results in Table 4-15). Figure 4-48 summarizes the results of the dead oil process simulation modeling, and shows a trend of increasing dead oil volume (x-axis) to simulate lower measured storage tank HC mass balances (y-axis). These simulations lend support to the theory that mixing of cold, unsaturated tank oil with separator dump fluids suppresses flash gas generation.

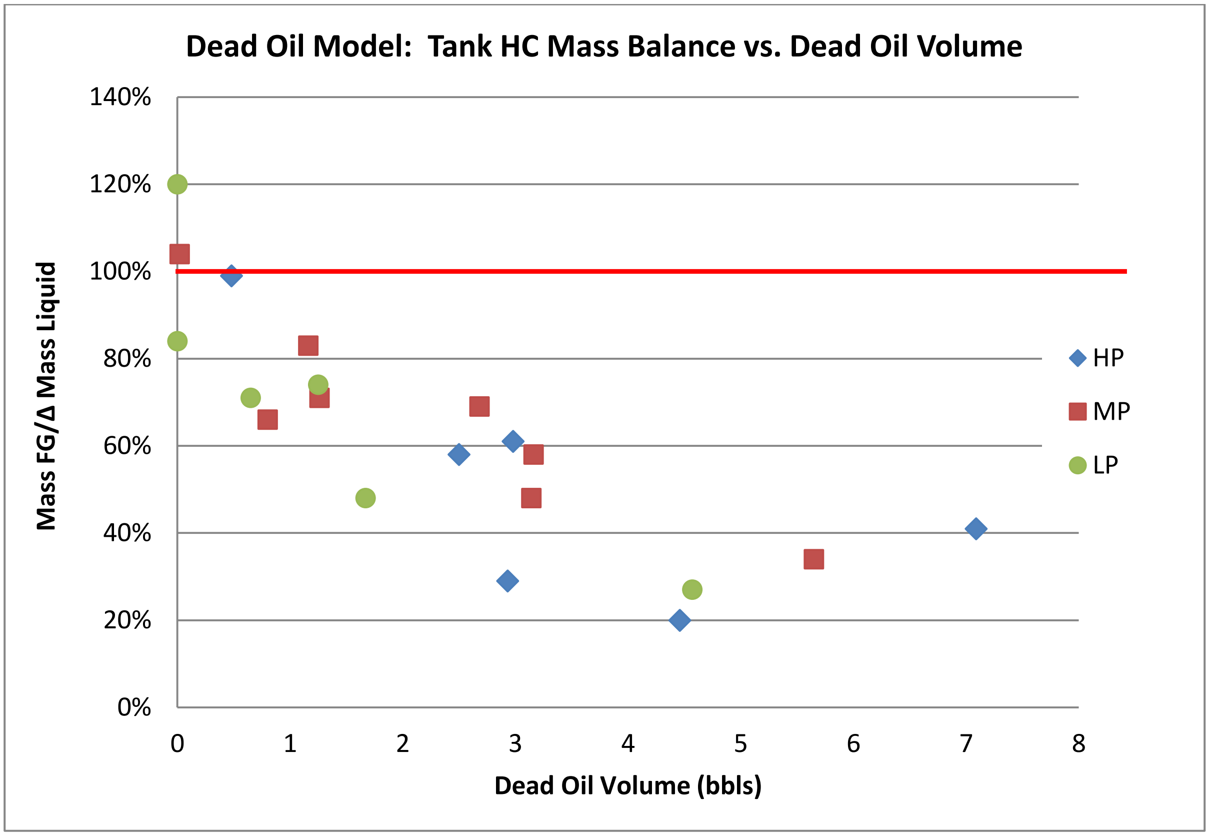


Figure 4-48. Summer testing PSM/EOS dead oil model results: measured storage tank HC mass balance vs. dead oil volume.

Impact of GPA 2186M Analysis on Storage Tank Mass Balance

Figure 4-49 includes the same storage tank mass HC balance data as presented in Figure 4-47 and adds mass balances based on GPA 2186M analysis of the CP cylinder pressurized condensate samples. The only difference between the GPA 2103M mass balance data and the GPA 2186M mass balance data is the pressurized condensate sample analysis method. The GPA 2186M mass balances are consistently greater than the corresponding GPA 2103M mass balances. This is because GPA 2186M calculates the C10+ fraction SG, and this SG was, for this testing, always less than the GPA 2103M SG which is directly measured (refer to Section 4.2). This translates to a lower pre-flash oil SG for GPA 2186M, a smaller $Mass_{pre\text{-}flash\text{-}oil}$ value in Equation 4-1, and calculation of a higher mass balance. The mass balances based on the GPA 2103M analyses, using a direct measurement of C10+ SG, are believed to be more accurate than the mass balances based on the GPA 2186M analyses. As shown in Section 4.2 (refer to Figure 4-10), GPA 2103M C10+ SG measurements are more accurate than GPA 2186M C10+ SG calculations.

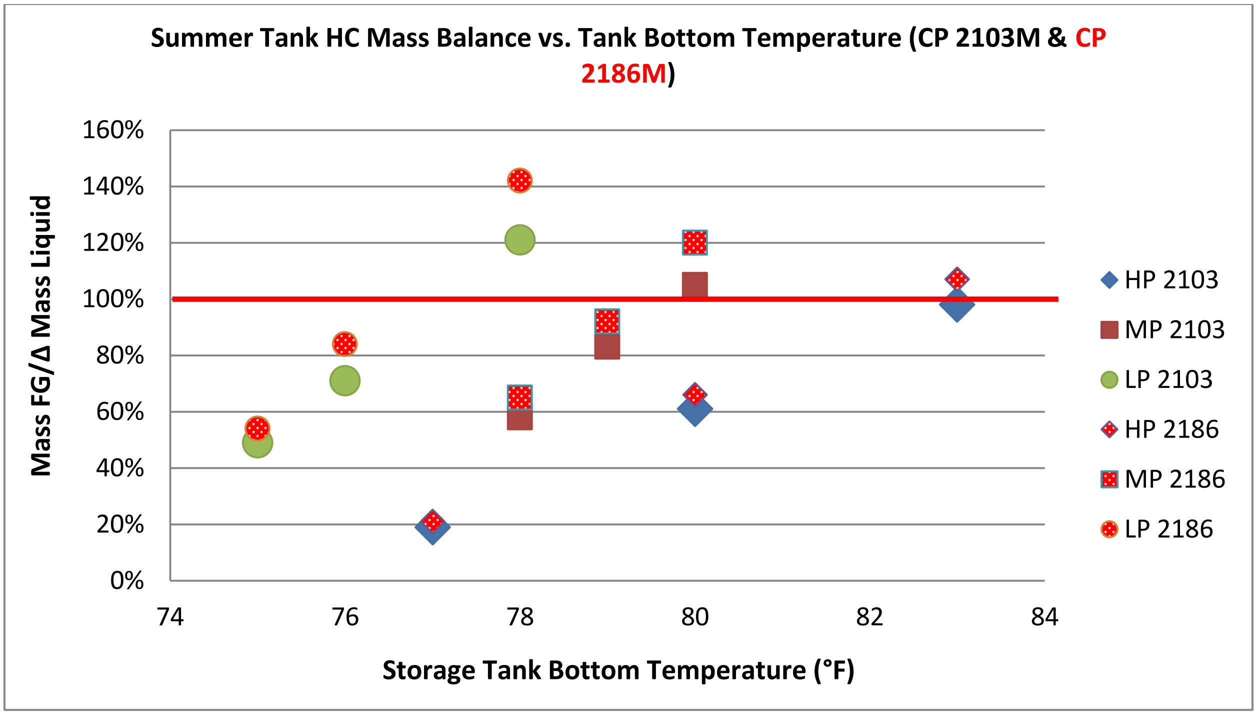


Figure 4-49. Summer measured storage tank HC mass balance vs. tank bottom temperature for GPA 2103M and GPA 2186M analyses.

Flash Gas-to-Oil Measurements

Equation 4-2 is used to calculate the FGOR for a well cycle.

$$\mathrm{FGOR} = \frac{\mathrm{Vol}_{\mathrm{FG}}}{\mathrm{Vol}_{\mathrm{post\text{-}flash\ oil}}} \qquad \text{Eqn. 4-2}$$

Where:

FGOR = flash gas-to-oil ratio for a well cycle (scf/bbl)

$\mathrm{Vol}_{\mathrm{FG}}$ = volume of flash gas generated during a well cycle (scf)

$\mathrm{Vol}_{\mathrm{post\text{-}flash\ oil}}$ = volume of post-flash HC liquids produced during a well cycle (bbl)

Appendix IV provides more detailed FGOR equations. Figure 4-50 shows the FGOR for the summer testing well cycles. The y-axis is the measured FGOR for the well cycle (i.e., Equation 4-2), and the x-axis is the well cycle start time. Figure 4-51 shows the same FGOR values as a function of tank bottom liquid temperature (x-axis). Results are shown for HP, MP, and LP well cycles. Similar to the mass balances, it is evident that the FGOR increased as each day progressed and the tank liquid temperature increased. In Figure 4-50 the vertical bars through the data points indicate the 95% level of confidence for the calculated FGORs based on the uncertainties of the volume measurements for the condensate and tank headspace gas process streams. The vertical lines with the “PSM/EOS” labels indicate the 95% level of confidence for PSM/EOS FGOR calculations that used a Monte Carlo (MC) simulation to estimate the FGOR calculation uncertainty. The PSM/EOS FGOR calculations were conducted for the HP, MP, and LP well cycles with HC mass balances closest to 100%. The PSM/EOS calculated FGORs agree within the 95% level of confidence limits for the HP and MP well cycles. For the LP well cycle, the PSM/EOS calculated FGOR is slightly lower than the measured FGOR. However, the mass balance for this well cycle (S-LP3) was about 120% (refer to Figure 4-46) suggesting the flash gas generation measurement may have been biased high.

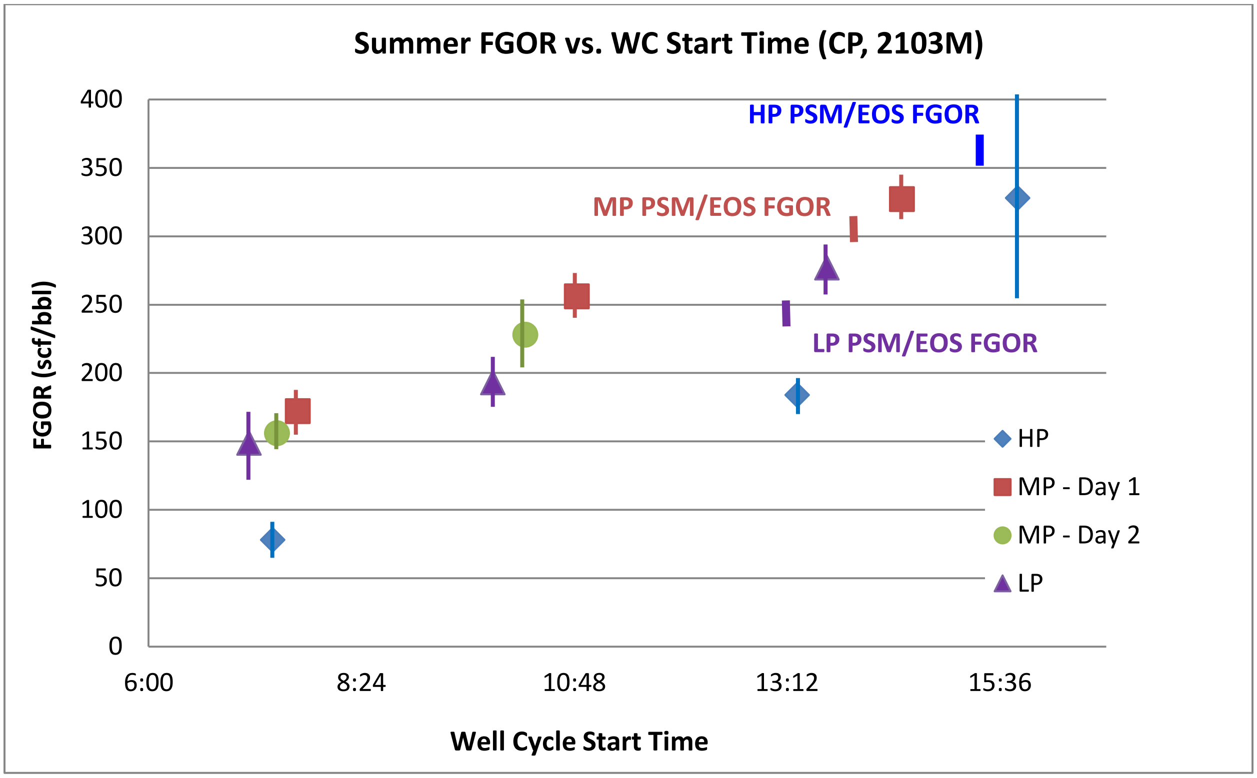


Figure 4-50. Summer measured FGOR vs. well cycle start time.

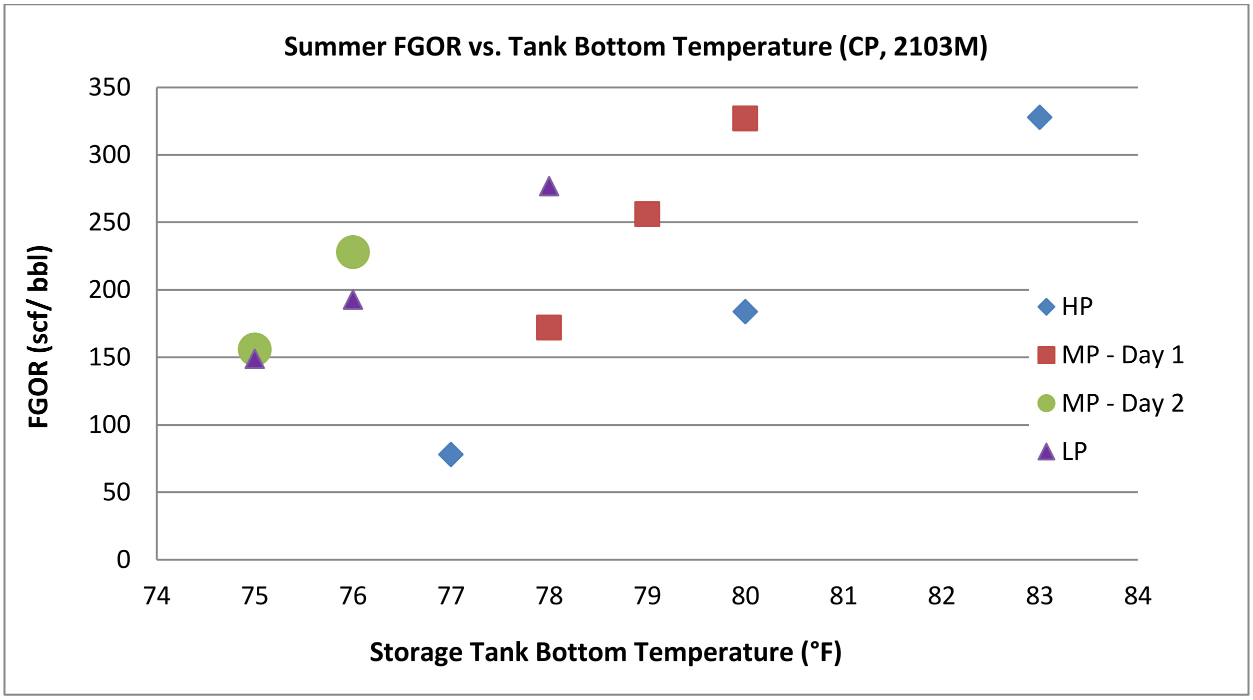


Figure 4-51. Summer measured FGOR vs. tank bottom temperature.

An observation from the testing was that actual maximum gas flowrates during a well cycle were significantly less than a theoretical PPIVFR. Table 4-16 compares calculated PPIVFRs for the four well cycles with the largest FGORs and the maximum measured tank-to-burner gas flowrates during the well cycle. The actual maximum gas flowrates during the well cycles were significantly less than (e.g., about 60 to 70% of) the PPIVFR. Most of the separator dump fluids entered the tank through the downcomer and then migrated through the tank liquid to the top of the tank, and this would be expected to dampen peak flowrates. In addition, it is hypothesized that when separator dump fluids that are colder than the tank liquids enter the tank there is “secondary” flash as the separator dump fluids mix with the tank oil, warm up, and release gas. The time for this process would further dampen peak flowrates. Storage tanks with side-fill or downcomer fill and lower liquid levels could have higher measured tank-to-burner flowrates, closer to the PPIVFR.

Table 4-16. PPIVFR vs. Measured Tank-to-Burner Pipeline Gas Flows

WC	WC Flash Gas + Breathing Losses + Working Losses	Σ Separator Dumps Duration	PPIVFR	Total Duration of Tank-to-Burner Gas Flow During WC	Maximum Measured Gas Flowrate During WC	
	scf	sec	scf/sec	sec	MSCFD	scf/sec
S-LP3	110	58.5	1.87	138	116	1.34
S-MP2	162	74.9	2.16	183	129	1.49
S-MP3	144	55.0	2.62	160	138	1.59
S-HP3	132	45.6	2.90	131	165	1.91

Impact of Separator Pressure on FGOR

The data presented in Figure 4-50 and Figure 4-51 indicate that storage tank temperatures impact FGORs. In addition, the separator temperature impacts the separator pressurized condensate composition and the FGOR. Because the tank and separator temperatures varied for each well cycle, the effect of separator pressure on FGOR for this testing could not be completely isolated. A comparison of the measured FGORs for the well cycles with near 100% HC mass balance suggest similar FGORs for the HP and MP well cycles (i.e., separator pressures from about 230 to 265 psig), and lower FGORs for the LP well cycles (i.e., separator pressures about 175 psig). However, PSM/EOS calculated FGORs were higher for the near 100% mass balance HP well cycle than for the near 100% mass balance MP well cycle (refer to Figure 4-50).

4.7.3 Winter Three-Pressure Testing Results

Table 4-17 lists the winter testing well cycles and a summary of primary operating parameters. Three tests were conducted during well cycles at the MP and LP separator operating conditions.

Four tests were conducted at the HP separator operating condition. The samples from well cycle W-HP2 were not analyzed because the separator pressure and temperature were in flux before and during the well cycle, and testing at a fourth HP well cycle, W-HP4, was completed. Similar to Table 4-14, the operating parameters listed in the table include the sample collection pressure and temperature, the separator pressure and temperature during the well cycle, and storage tank bottom liquid and headspace gas and temperatures during the well cycle. The sample collection pressure and temperature were recorded during sample collection, which was initiated within 30 minutes of the end of the well cycle.

Table 4-17. Winter Three-Pressure Testing Summary

Well Cycle	Date	WC Start Time	Separator, Tank, and Sample Collection Temperatures & Pressures, Average During Well Cycle			
			P_{sep} / P_{SC} (psig)	T_{sep} / T_{SC} (°F)	$T_{tank\ gas}$ (°F)	$T_{tank\ bottom}$ (°F)
W-HP1	3/7/2016	9:30	262 / 250	85 / 69	66	46
W-HP3	3/8/2016	8:06	246 / 247	59 / 59	49	47
W-HP4	3/8/2016	13:30	263 / 262	58 / 57	70	45
W-MP1	3/9/2016	8:39	235 / 232	81 / 78	57	45
W-MP2	3/9/2016	12:45	227 / 223	92 / 87	74	44
W-MP3	3/9/2016	15:57	229 / 224	85 / 78	57	46
W-LP1	3/10/2016	13:14	178 / 174	87 / 83	85	45
W-LP2	3/10/2016	15:26	179 / 173	90 / 85	79	46
W-LP3	3/11/2016	8:17	180 / 178	85 / 85	60	47

Most sample collection pressures were within 5 psig of the average separator pressure during the well cycle, and sample collection temperatures were generally within 5°F of the average separator temperature during the well cycle. With the exception of W-HP1, these pressure and temperature measurements suggest that the sampled condensate had a composition similar to the condensate that flowed to the tank during the well cycle. For well cycle W-HP1, the sample collection pressure and temperature are noticeably lower than the well cycle conditions. W-HP1 was the first test, and separator heater and pressure control procedures were enhanced after this test and the difficulties encountered during well cycle W-HP2 testing. For well cycle W-HP1, the separator pressure decreased from the end of the well cycle to sample collection and this would be expected to cause light HCs to volatize. However, the separator temperature also decreased from the well cycle end to sample collection and this would be expected counteract the pressure drop (i.e., effect would be to help light HCs remain in solution). These pressure and temperature changes were thought to be less severe than the operational fluctuations observed during well cycle W-HP2, and the W-HP1 results were retained.

Mass Balance Measurements

Figure 4-52 shows the storage tank HC mass balances for the winter testing well cycles based on GPA 2103M analysis of pressurized condensate samples collected with CP cylinders. The y-axis is the measured mass balance during the well cycle (i.e., Equation 4-1). The x-axis is the well cycle start time and results are shown for HP, MP, and LP well cycles. The vertical bars indicate the 95% level of confidence for the calculated mass balances based on the uncertainties of the volume and composition measurements for the condensate and tank headspace gas process streams. The uncertainties for the winter mass balances were larger than for the summer testing, and a primarily reason was because the tank-to-burner gas flowrates during the winter testing were measured with two flow meters, as opposed to three flowmeters in the summer. The statistical uncertainty for the average of two replicate measurements is greater than the statistical uncertainty for the average of three replicate measurements. In addition, flash gas flowrates during the winter testing were generally a factor of about two lower than during the summer testing. Thus, a smaller fraction of the gas flow was measured in the flowmeters optimum range, and a larger fraction of the gas flow was during severe flowrate transients that impact measurement accuracy. Similar to the summer testing, the mass balances generally improved (i.e., were closer to 100%) as the day progressed.

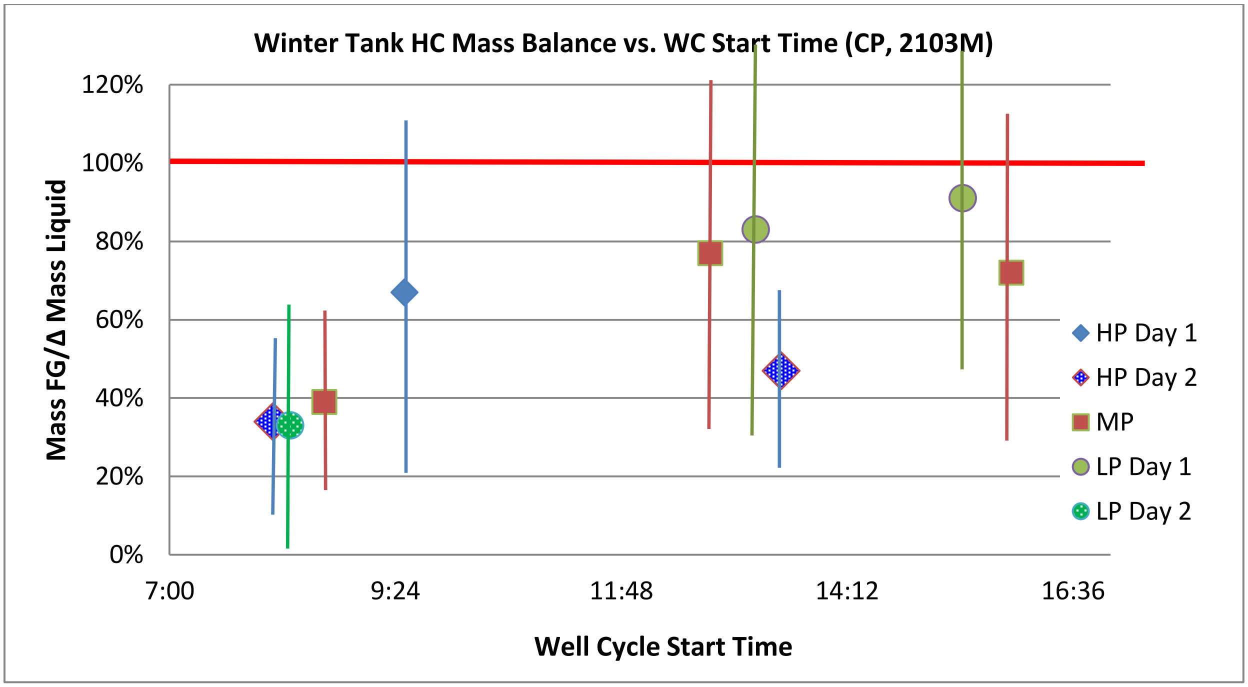


Figure 4-52. Winter storage tank HC mass balance vs. well cycle start time.

Figure 4-53 presents the same data with $T_{\text{tank bottom}}$ as the x-axis. For the winter testing, the trend of increasing mass balance with increasing tank bottom temperature was not as pronounced as observed during the summer testing. After the testing was completed, water was drained from the bottom of the tank, and it was suspected that the water may have influenced and biased the tank bottom temperature instrument; thus, these temperature measurements may not be reliable. Figure 4-54 presents the same data with the tank headspace temperature as the x-axis, and the general mass balance/temperature relationship discussed above is generally more apparent.

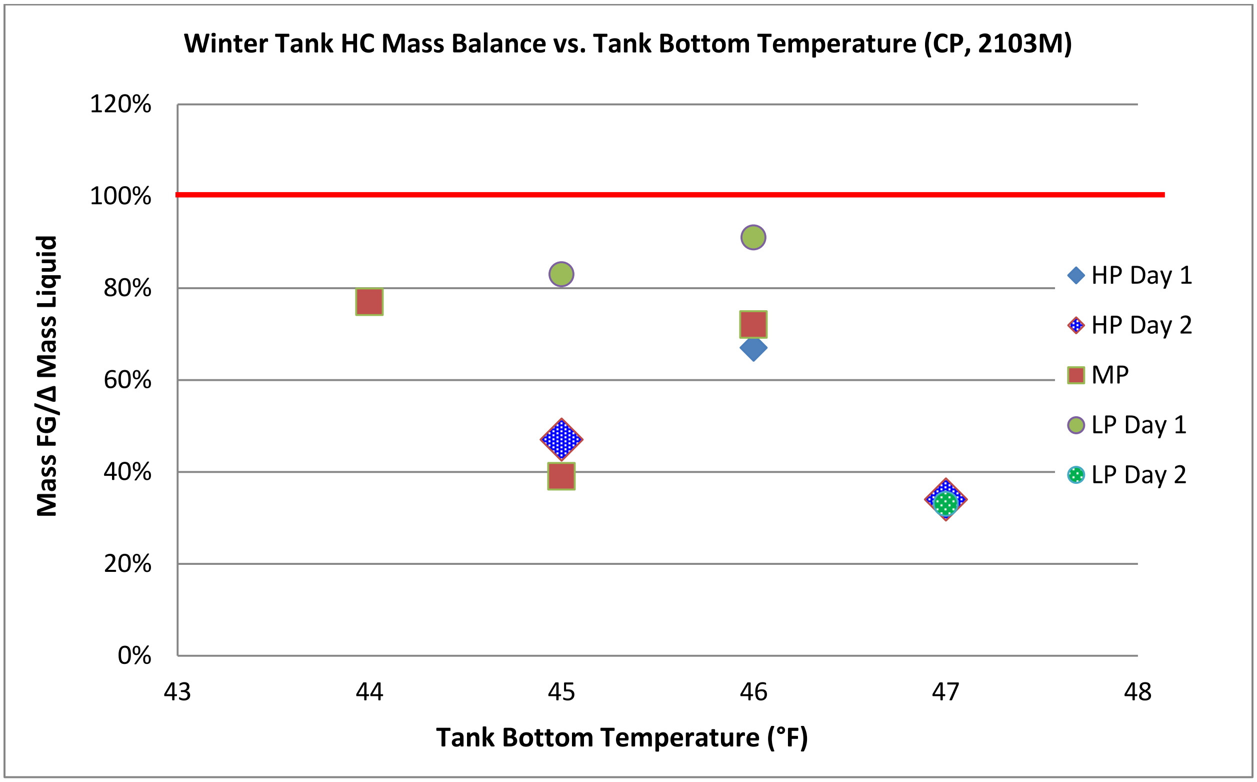


Figure 4-53. Winter storage tank HC mass balance vs. tank bottom temperature.

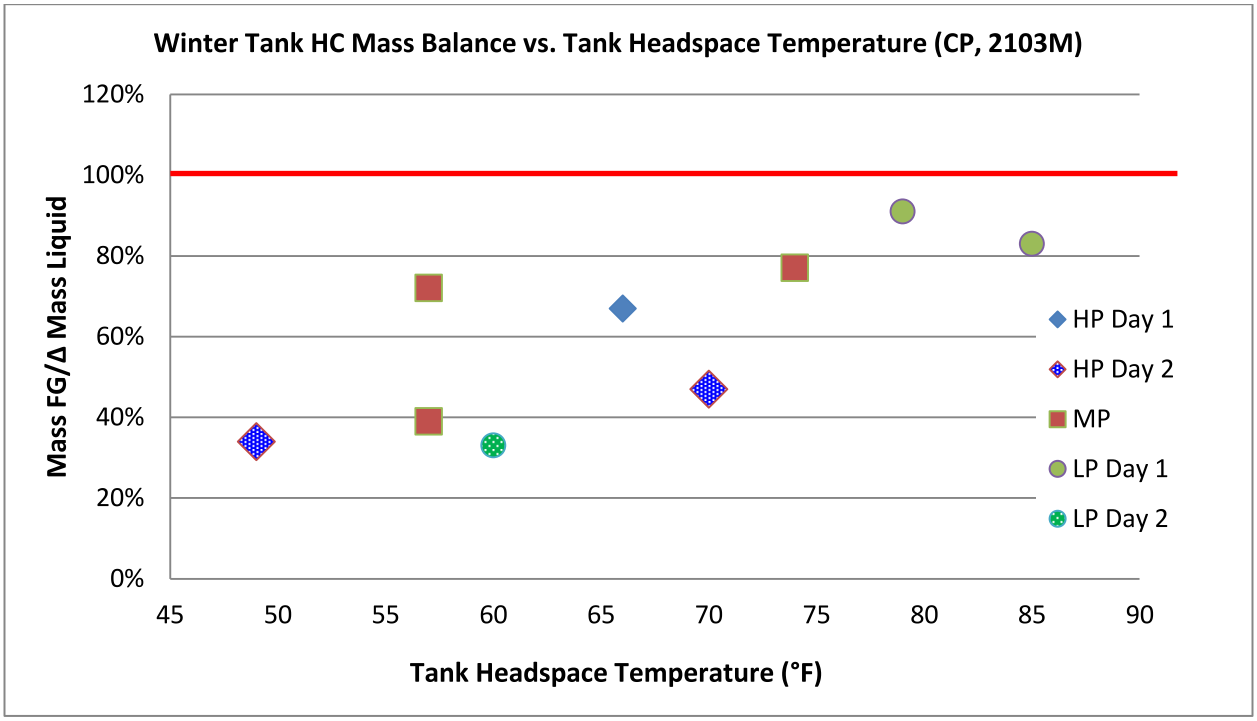


Figure 4-54. Winter storage tank HC mass balance vs. tank headspace temperature.

Storage Tank Mass Balances for C1 – C5

Table 4-18 presents storage tank mass balances for total HCs and C1 to C5 HC species. The 95% level of confidence values for these calculated values, based on the uncertainties of the volume measurements for the condensate and tank headspace gas process streams, are shown in parentheses. A difference between the summer and winter mass balance profiles is that the summer testing had higher mass balances for butanes and pentanes, indicating higher breathing rates during the summer. This is not surprising considering the higher temperatures and solar radiation.

Table 4-18. Winter Three-Pressure Testing FGORs and Storage Tank Mass Balances for HCs and C1–C5 (CP, 2103M)

Well Cycle	Measured Value (95% Level of Confidence)						
	FGOR (scf/bbl)	Tank HC MB (FG/ΔL)[A]	Tank C1 MB (FG/ΔL)	Tank C2 MB (FG/ΔL)	Tank C3 MB (FG/ΔL)	Tank C4 MB (FG/ΔL)	Tank C5 MB (FG/ΔL)
W-HP1	120 (+/- 61)	67% (+/- 46%)	40% (+/- 20%)	50% (+/- 25%)	48% (+/- 24%)	38% (+/- 14%)	73% (+/- 33%)
W-HP3	114 (+/- 70)	34% (+/- 22%)	39% (+/- 24%)	38% (+/- 23%)	35% (+/- 21%)	31% (+/- 14%)	-250% (+/- 350%)
W-HP4	174 (+/- 75)	47% (+/- 22%)	46% (+/- 20%)	46% (+/- 20%)	46% (+/- 20%)	33% (+/- 10%)	40% (+/- 13%)
W-MP1	115 (+/- 64)	39% (+/- 24%)	50% (+/- 28%)	41% (+/- 23%)	35% (+/- 19%)	26% (+/- 11%)	55% (+/- 27%)
W-MP2	140 (+/- 53)	77% (+/- 44%)	62% (+/- 22%)	57% (+/- 22%)	52% (+/- 20%)	33% (+/- 10%)	30% (+/- 8.6%)
W-MP3	169 (+/- 75)	72% (+/- 44%)	77% (+/- 34%)	75% (+/- 33%)	71% (+/- 31%)	55% (+/- 18%)	130% (+/- 69%)
W-LP1	122 (+/- 42)	83% (+/- 52%)	71% (+/- 25%)	65% (+/- 22%)	63% (+/- 22%)	51% (+/- 14%)	150% (+/- 88%)
W-LP2	167 (+/- 44)	91% (+/- 42%)	94% (+/- 25%)	94% (+/- 25%)	92% (+/- 25%)	70% (+/- 14%)	150% (+/- 62%)
W-LP3	61 (+/- 51)	33% (+/- 31%)	35% (+/- 30%)	35% (+/- 30%)	31% (+/- 26%)	24% (+/- 15%)	60% (+/- 46%)

A. FG/ΔL = mass of flash gas generation measured during Well Cycle/change in mass of HC liquids during Well Cycle (= pre-flash - post-flash HC liquids mass).

Flash Gas-to-Oil Measurements

Figure 4-55 shows the FGOR for the winter testing well cycles. The y-axis is the measured FGOR for the well cycle (i.e., Equation 4-2), and the x-axis is the well cycle start time. Figure 4-56 shows the same FGOR values as a function of tank bottom liquid temperature (x-axis), and Figure 4-57 shows the same FGOR values as a function of tank headspace temperature (x-axis). Results are shown for HP, MP, and LP well cycles. Similar to the storage tank HC mass balances, it is evident that the FGOR increased as each day progressed; however, an impact of tank temperatures on FGOR (shown in Figures 4-56 and 4-57) is not observed. These FGORs are significantly lower than the FGORs measured during the summer testing (refer to Figure 4-50), generally a factor of 2 lower.

In Figure 4-55 the vertical bars through the data points indicate the 95% level of confidence for the calculated FGORs based on the uncertainties of the volume measurements for the condensate and tank headspace gas process streams. The vertical lines with the "PSM/EOS" labels indicate the 95% level of confidence for PSM/EOS FGOR calculations that used a MC simulation to estimate the FGOR calculation uncertainty. The PSM/EOS calculated FGORs agree within the 95% level of confidence limits for the LP well cycle, although the PSM/EOS calculated FGOR was about 30 scf/bbl lower than the measured FGOR.

For the MP and HP well cycles, the PSM/EOS calculated FGORs were significantly greater than the measured FGORs, above the 95% level of confidence for the measured values. The storage tank HC mass balances for the well cycles associated with the PSM/EOS calculated FGORs were all less than 100%. For example, for well cycle W-HP4 that is the basis for the HP PSM/EOS FGOR = 342 shown on Figure 4-55, the mass balance closure was about 50%. Dividing the measured FGOR by the mass balance for the well cycle (i.e., calculating a "mass balance-corrected" FGOR) results in an FGOR of about 370 scf/bbl (refer to Table 4-19), which is in agreement with the HP PSM/EOS FGOR. Mass balance-corrected FGORs for the LP and MP well cycles produce much better agreement with the PSM/EOS calculations. The better agreement between the mass balance-corrected measured FGORs and the PSM/EOS calculated FGORs than between the as measured FGORs and the PSM/EOS calculated FGORs can be at least partially explained by the dead oil mixing effect. The measured FGORs appeared to be reduced by the dead oil effect, whereas the PSM/EOS calculated FGORs do not include the dead oil mixing effect.

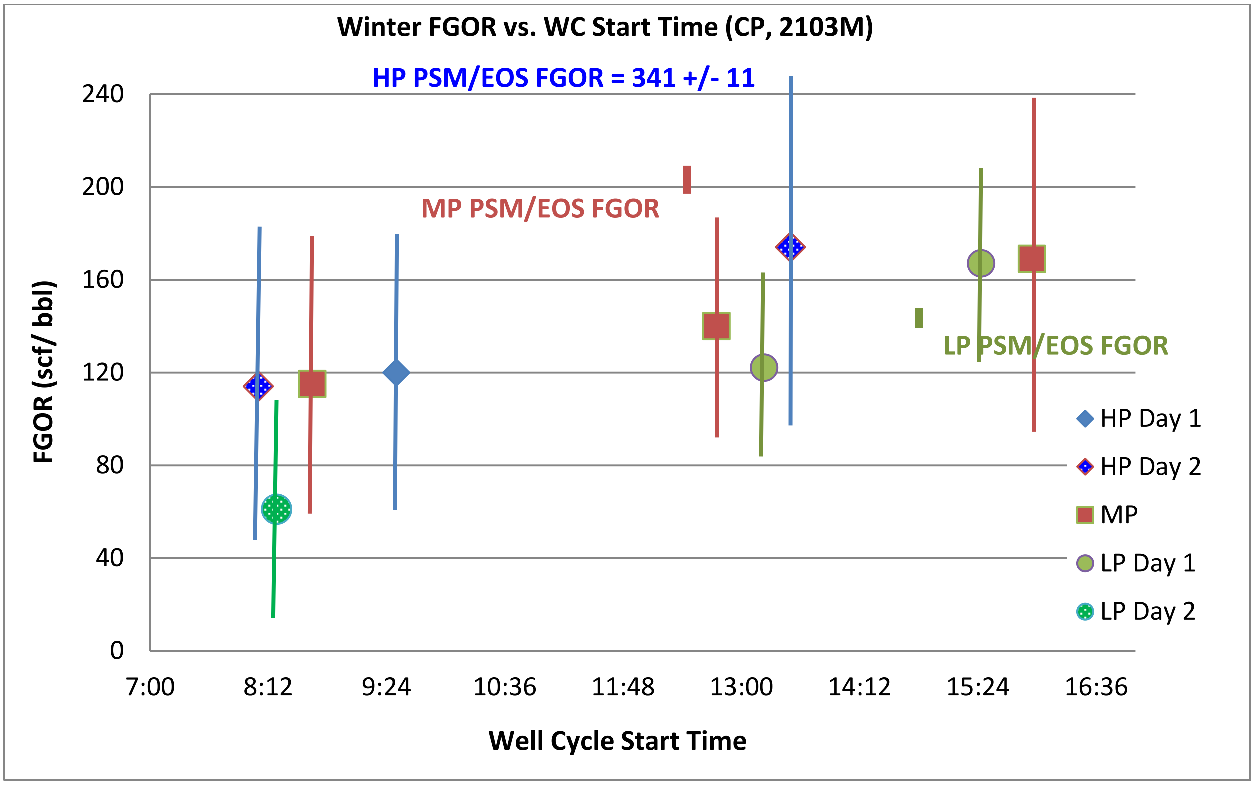


Figure 4-55. Winter measured FGOR vs. well cycle start time.

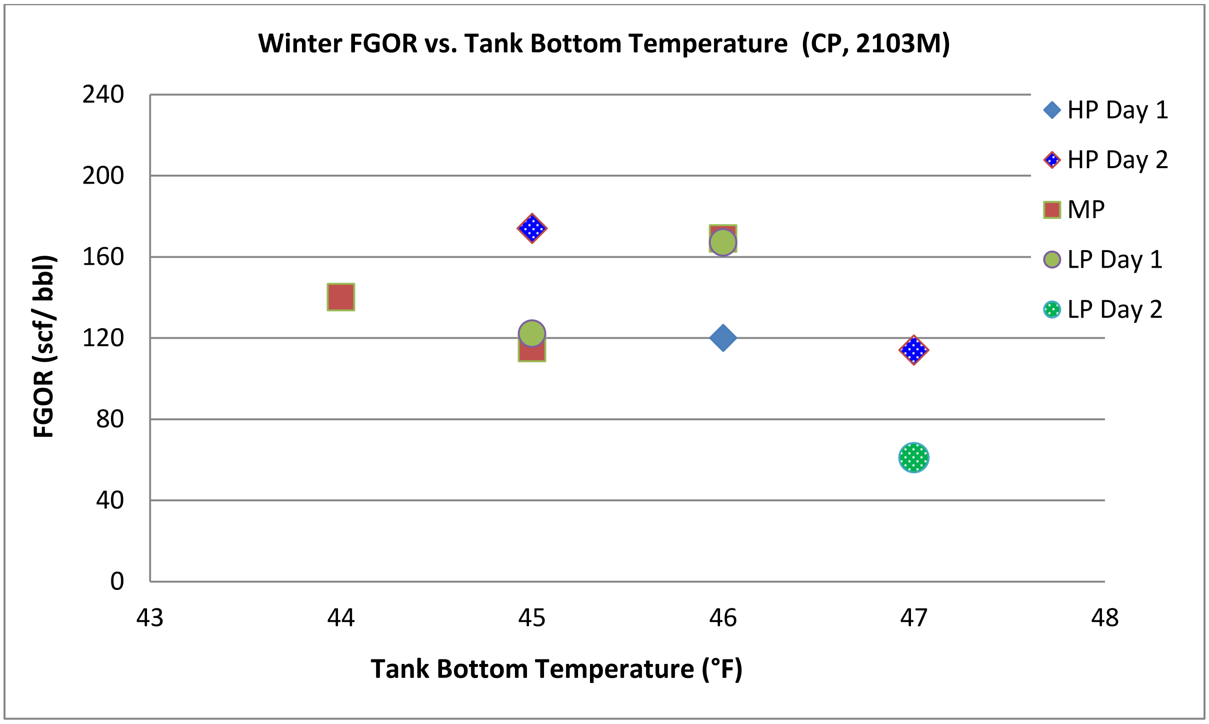


Figure 4-56. Winter measured FGOR vs. tank bottom temperature.

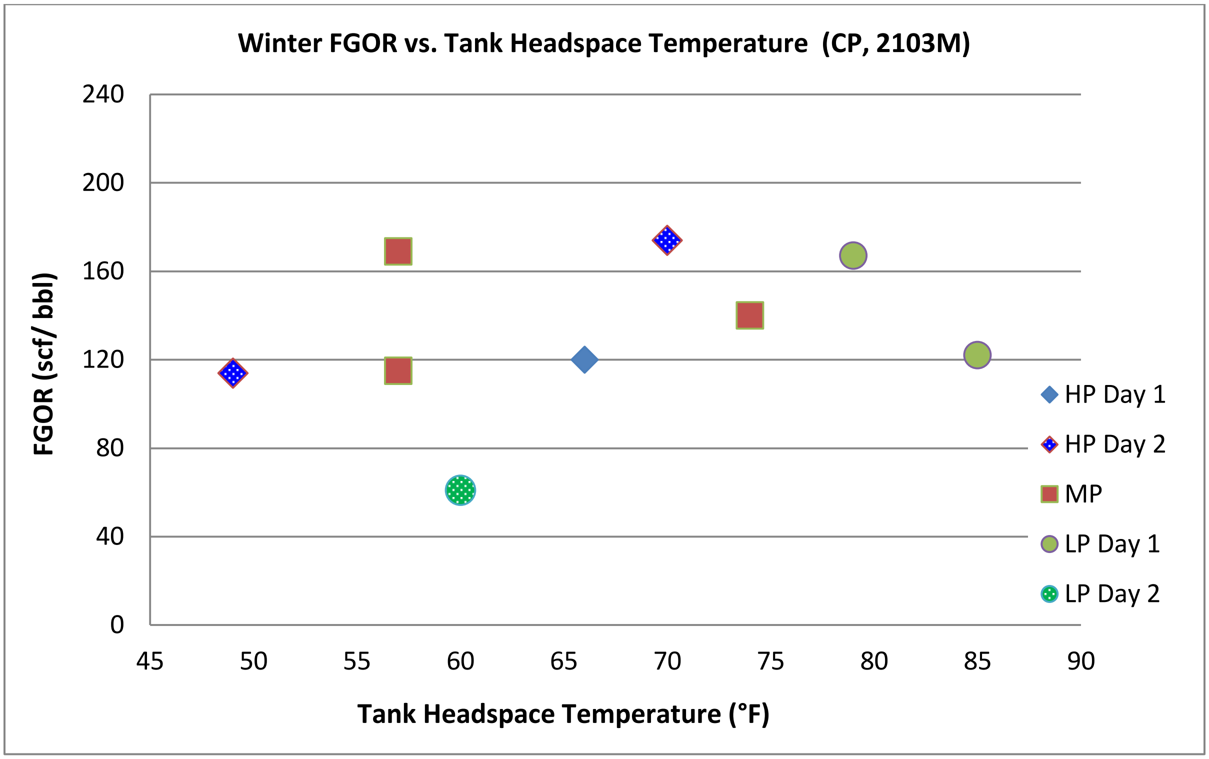


Figure 4-57. Winter measured FGOR vs. tank headspace temperature.

Table 4-19. Winter Storage Mass Balance-Corrected FGORs (CP, 2103)

Well Cycle	Measured Value (95% Level of Confidence)		
	FGOR (scf/bbl)	Tank HC MB (FG/ΔL)[A]	FGOR at 100% MB (scf/bbl)[B]
W-HP1	120 (+/- 61)	67% (+/- 46%)	180 (+/- 140)
W-HP3	114 (+/- 70)	34% (+/- 22%)	330 (+/- 290)
W-HP4	174 (+/- 75)	47% (+/- 22%)	370 (+/- 230)
W-MP1	115 (+/- 64)	39% (+/- 24%)	290 (+/- 240)
W-MP2	140 (+/- 53)	77% (+/- 44%)	180 (+/- 120)
W-MP3	169 (+/- 75)	72% (+/- 44%)	230 (+/- 160)
W-LP1	122 (+/- 42)	83% (+/- 52%)	150 (+/- 100)
W-LP2	167 (+/- 44)	91% (+/- 42%)	180 (+/- 100)
W-LP3	61 (+/- 51)	33% (+/- 31%)	180 (+/- 230)

A. FG/ΔL = mass of flash gas generation measured during Well Cycle/change in mass of HC liquids during Well Cycle (= pre-flash - post-flash HC liquids mass).

B. FGOR at 100% MB = FGOR /Tank HC MB.

The very high uncertainties for the measured FGORs and the poor agreement between the measured and PSM/EOS calculated FGORs suggest that strong conclusions should not be based on the winter testing. The summer testing results, which were completed after some operations and measurement procedures were refined, are more reliable.

Impact of Separator Pressure on FGOR

Separator and tank temperatures, which impact separator pressurized condensate composition and the FGOR, varied for each well cycle during the winter testing. Thus, the effect of separator pressure on FGOR for this testing could not be completely isolated. A comparison of mass balanced-corrected FGORs, shown in Table 4-19, suggest that FGORs, in the absence of the dead oil effect, generally increase with separator pressure. As noted above, these data have very high uncertainties and strong conclusions based on the winter testing are not recommended.

4.7.4 PSM/EOS FGOR Calculations and Sensitivity Analysis

Appendix V provides the guidelines, input and output parameters, and results of the PSM/EOS calculations conducted for the PHLSA Study (Section 3.3 provides an overview of the PSM/EOS calculations). Comparing calculations of FGOR, shrinkage factor and bubble point pressure between the four software simulation packages (SIM1, SIM2, SIM3, and SIM4) showed:

- SIM 1, 2 and 3 FGOR calculations agreed in within +/- 2% for about 93% (97 of 104) of the modeled well cycles; and
- SIM 4 FGOR calculations were within +/- 15% of the SIM 1, 2 and 3 calculations for about 83% (86 of 104) of the modeled well cycles. The SIM 4 calculated FGORs were closer to the SIM 1, 2 and 3 calculations for the winter testing than for the summer testing. As discussed in Section 2.4, SIM 4 does not have the design flexibility of SIM 1, 2, and 3, and this is likely a key contributor to the difference in the results.

For the January 2016 testing (Task 8), the GPA 2103M analyses were run with two modifications. One modification used analysis through C10+, and the second modification used analysis through C100+. PSM/EOS calculated FGORs and P_{BP}s using the C10+ and C100+ analytical results agreed within less than 1%. These results indicated that, for this particular fluid, more analytical detail (i.e., C100+ vs. C10+) had negligible impact on PSM/EOS calculations and did not warrant the additional analytical cost. Thus, pressurized condensate samples collected during subsequent tests were only analyzed through C10+.

PSM/EOS calculated FGORs and P_{BP}s based on GPA 2103M analytical results and GPA 2186M analytical results were compared. PSM/EOS calculated FGORs based on GPA 2103M analytical results were on average about 5% closer to measured directly FGOR values corrected to 100% mass balance (i.e., the best estimate of the true FGOR) than PSM/EOS calculated FGORs based on GPA 2186M analytical results. PSM/EOS calculated P_{BP}s based on GPA 2103M analytical results were on average about 2% closer to the measured separator pressure during sample collection than PSM/EOS calculated P_{BP}s based on GPA 2186M analytical results. These apparently more accurate PSM/EOS calculations using GPA 2103M analytical results are likely due, at least in part, to measured (and more accurate) C10+ SG and MW values for GPA 2103M as opposed to calculated (and less accurate) values for these C10+ properties for GPA 2186M.

PSM/EOS calculated FGOR values based on samples collected in summer were 20-40% higher than PSM/EOS calculated FGOR values based on samples collected in winter. This is primarily due to higher tank temperatures, which increase flash gas generation, in summer. Also, higher separator temperatures in winter reduced the FGOR potential of the separator liquids. The results of the PSM/EOS calculations sensitivity study, summarized below, support these observations (i.e., FGOR formation is highly sensitive to separator and tank temperatures). For more information regarding the sensitivity of PSM/EOS calculated FGORs to key process parameters, refer to Appendix V.

It is likely that the PSM/EOS calculations over-predict FGOR due to a volume translation bias. The EOS models used in this study over-estimate liquid density, which under-predicts liquid volume when mass is converted to volume. No correction was made for this bias in this study. This effect was observed in the Separator Balance portion of the study (refer to Appendix V, Appendix V.3), where PSM/EOS calculated gas volumes were within about +/- 2% of measured values but PSM/EOS calculated liquid volumes were typically about 7% less than measured values. Because FGOR is the ratio of flash gas volume to post-flash HC liquids volume, a low bias in the denominator would cause the FGOR value to be over-estimated.

The uncertainty of PSM/EOS calculations of FGOR, resulting from the uncertainty of input parameters, was evaluated using two approaches using data from six well cycles: three from winter tests (a HP, MP, and LP) and three from summer (a HP, MP, and LP). Well cycles with good storage tank HC mass balance results were selected. Results for both GPA 2103M and GPA 2186M analysis of CP cylinder samples were used, with samples collected at 20 ml per minute less than 30 minutes after the completion of the well cycle. The two FGOR uncertainty estimation approaches were:

1. A Monte Carlo simulation that produced a distribution of possible outcome results by performing thousands of calculations. The MC simulations ran about 3,000 PSM/EOS

calculations and each calculation used a different set of random input values based on their probability functions, and achieved outputs with normal distributions.

2. A numerical approximation approach which isolated and varied calculation input variables to determine the sensitivity of the calculation to the parameter. This numerical approximation solution, or "dither method" described in API MSPS 13.3 5.6.2, iterates input values over the range of uncertainty for the variable to determine the sensitivity of the dependent variable (e.g., FGOR) to this variable. Combining these results for all the input variables provides a reasonable estimate of the overall FGOR uncertainty. In the numerical approximation approach, analytical variation was limited to two components which showed the highest sensitivity in the MC simulation. The numerical approximation approach covered a wider range of SPH values than the MC simulation (0-100% vs. 4-8%).

The results were evaluated and compared. Figure 4-58 and Figure 4-59 show the uncertainty budgets for both evaluation methods. Separator temperature and pressure, and tank bottom temperature are the measured process parameters that have a large influence upon FGOR uncertainty. SPH fraction also contributes to FGOR uncertainty, and a larger impact was observed for the numerical approximation approach because a wider range of SPH flow fraction was assumed for the calculations. For the MC simulation, the light HCs ethane and propane were the pressurized condensate components that had the most significant effect on FGOR uncertainty.

Tables 4-20 through 4-23 show uncertainty estimates for FGOR, shrinkage factor, P_{BP}, and flash gas MW, respectively. As shown in Table 4-20, both approaches estimated FGOR relative uncertainties of 3-5%. The MC approach is considered to be a more rigorous uncertainty estimation procedure, and good agreement between the two approaches provides confidence in the numerical approximation results.

In sum, PSM/EOS calculations of FGOR are most sensitive to tank bottom temperature, separator pressure and temperature, and assumptions regarding the fraction of separator dump fluids flowing through the SPH. These parameters, and HC liquids components with high analytical uncertainty, are the largest potential sources of uncertainty in assessing flashing losses.

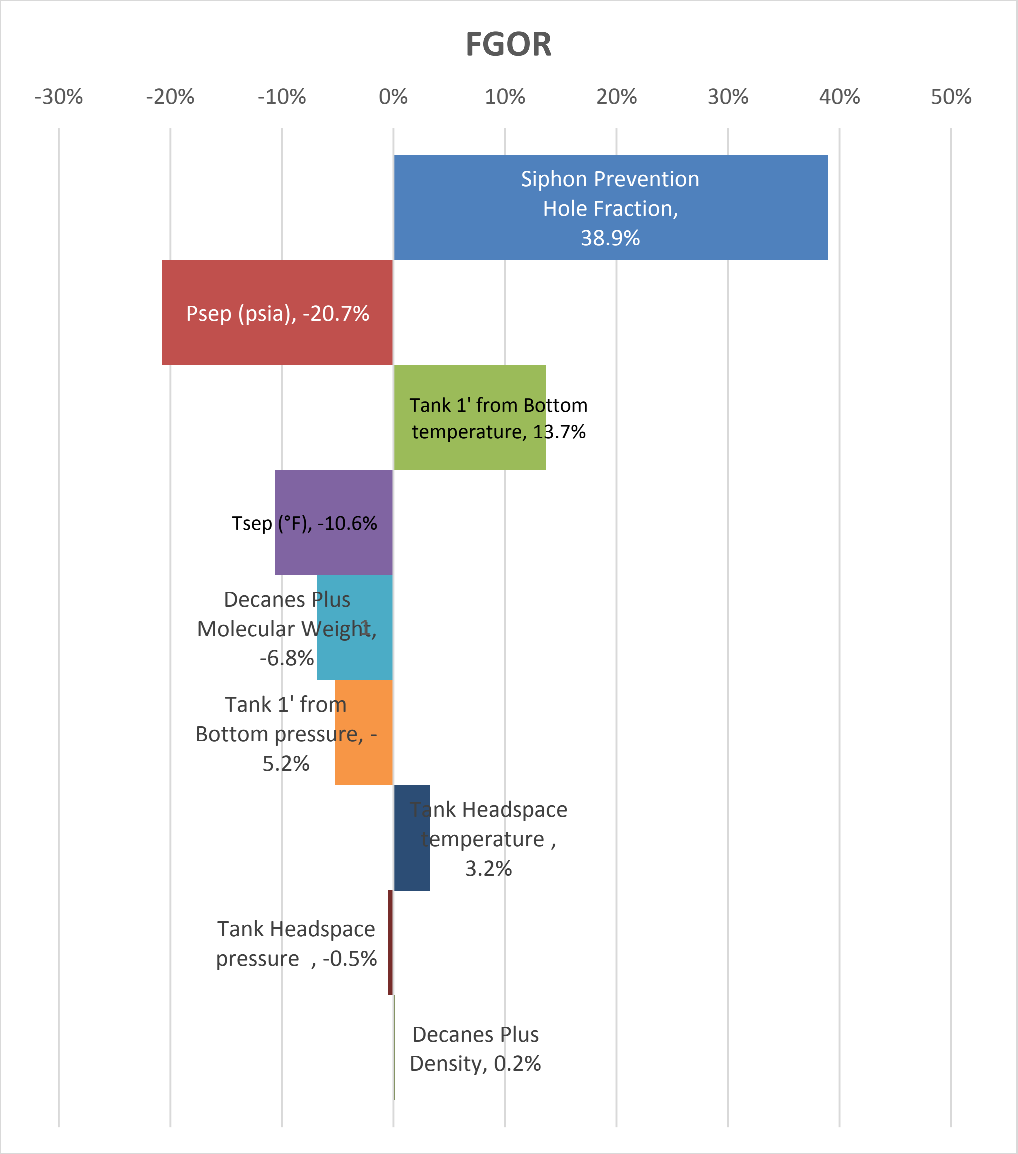
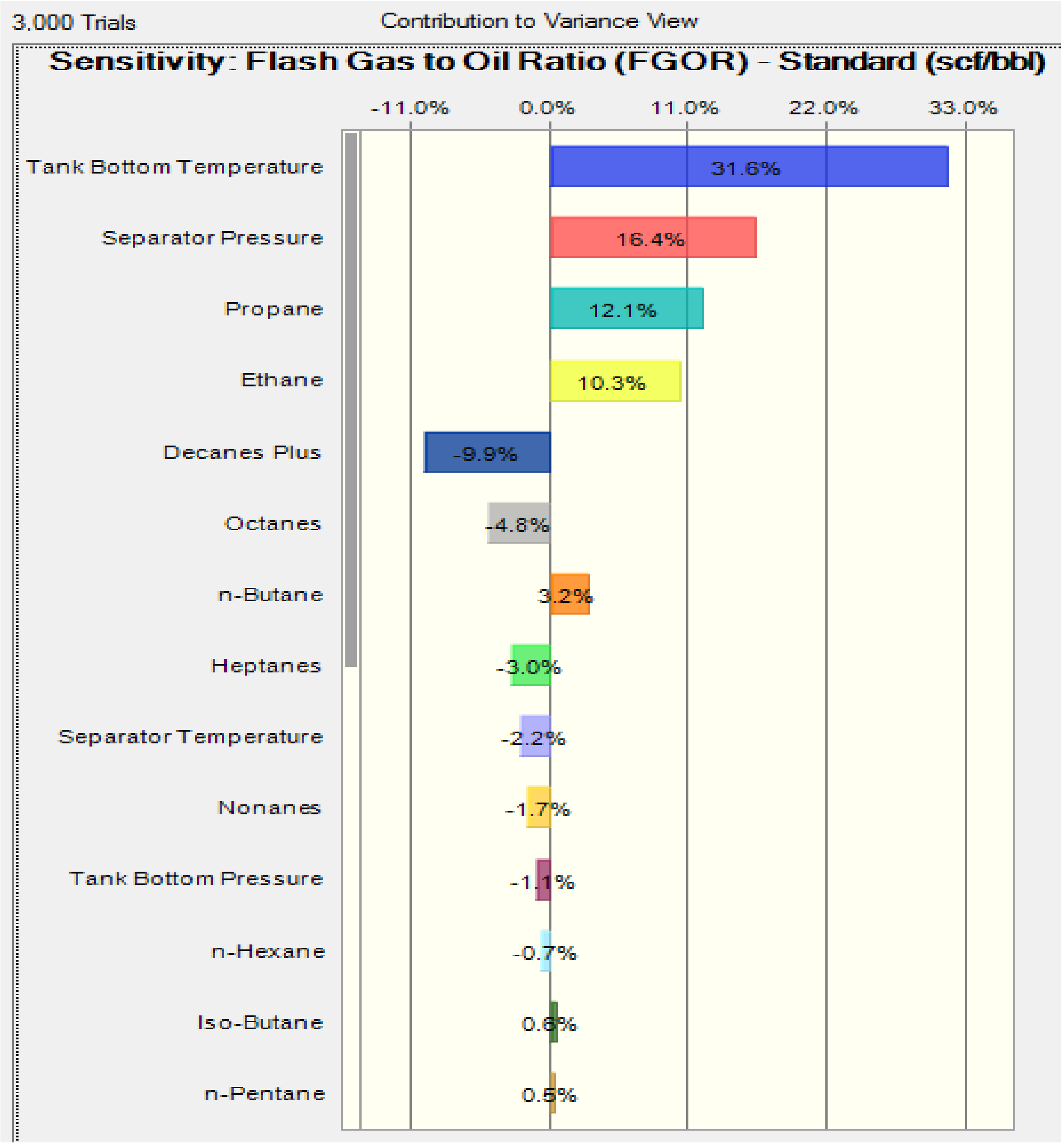


Figure 4-58. FGOR sensitivity to key parameters from numerical approximation approach.



*Note that sensitivity to octanes based on preliminary analytical uncertainty estimates that included a higher analytical uncertainty for octanes than the final estimates.

Figure 4-59. FGOR sensitivity to key parameters from Monte Carlo simulation.

Table 4-20. Estimated Uncertainty for FGOR Calculated by PSM/EOS Using Two Approaches

FGOR Relative Uncertainty (%U)					
SEASON	SAMPLE	2103M		2186M	
		Numerical Approximation	Monte Carlo Simulation	Numerical Approximation	Monte Carlo Simulation
SUMMER	LP	3.8%	3.0%	4.0%	3.3%
SUMMER	MP	2.8%	2.8%	3.1%	3.0%
SUMMER	HP	2.8%	2.7%	3.7%	2.9%
WINTER	LP	4.9%	3.8%	4.7%	3.8%
WINTER	MP	3.8%	3.3%	3.7%	3.3%
WINTER	HP	3.3%	3.1%	3.0%	3.1%

Table 4-21. Estimated Uncertainty for Shrinkage Factor Calculated by PSM/EOS Using Two Approaches

Shrinkage Factor Relative Uncertainty (%U)					
SEASON	SAMPLE	2103M		2186M	
		Numerical Approximation	Monte Carlo Simulation	Numerical Approximation	Monte Carlo Simulation
SUMMER	LP	0.5%	0.4%	0.5%	0.4%
SUMMER	MP	0.6%	0.5%	0.5%	0.5%
SUMMER	HP	0.6%	0.6%	0.7%	0.5%
WINTER	LP	0.4%	0.3%	0.4%	0.3%
WINTER	MP	0.4%	0.4%	0.4%	0.4%
WINTER	HP	0.6%	0.5%	0.5%	0.5%

Table 4-22. Estimated Uncertainty for Bubble Point Pressure Calculated by PSM/EOS Using Two Approaches

Bubble Point Pressure Relative Uncertainty (%U)					
SEASON	SAMPLE	2103M		2186M	
		Numerical Approximation	Monte Carlo Simulation	Numerical Approximation	Monte Carlo Simulation
SUMMER	LP	1.1%	2.2%	1.0%	2.9%
SUMMER	MP	1.1%	2.2%	1.0%	2.9%
SUMMER	HP	1.1%	2.2%	1.2%	2.9%
WINTER	LP	1.2%	3.0%	0.8%	3.0%
WINTER	MP	1.2%	3.0%	0.8%	3.0%
WINTER	HP	0.9%	3.1%	0.7%	3.1%

The uncertainty for flash gas MW was only estimated with the MC simulation.

Table 4-23. Estimated Uncertainty for Flash Gas Molecular Weight Calculated by PSM/EOS Using Monte Carlo Simulation

Flash Gas Molecular Weight Relative Uncertainty (%U)			
Season	**Pressure**	**GPA 2103M**	**GPA 2186M**
SUMMER	LP	0.9%	0.9%
SUMMER	MP	0.8%	0.8%
SUMMER	HP	0.9%	0.8%
WINTER	LP	1.3%	1.2%
WINTER	MP	1.1%	1.1%
WINTER	HP	0.9%	0.9%

4.8 Produced Water Hydrocarbon Content

Supporting data for the information in this sub-section is in Appendix III.

Table 4-24 and Table 4-25 summarize the results of the analysis of pressurized produced water samples. The flash gas content of the produced water was very low, less than 3 scf/bbl, and the primary components were CO_2 and methane.

Table 4-24. Analytical Results for Pressurized Produced Water Samples, Summer Testing

Well Cycle:	**S-LP1**
FGWR (scf/bbl):	2.4
Component	**Mole %**
Carbon Dioxide	0.0088
Nitrogen*	0.0002
Methane	0.0169
Ethane	0.0039
Propane	0.0013
Iso-Butane	0.0001
n-Butane	0.0004
Iso-Pentane	0.0001
n-Pentane	0.0001
C6+	0.0001
Water	99.9680

Table 4-25. Analytical Results for Pressurized Produced Water Samples, Winter Testing

Well Cycle:	**W-LP1**	**W-MP1**	**W-HP3**
Component	**Mole %**		
Nitrogen*	0.000	0.000	0.000
Methane	0.014	0.022	0.019
Carbon Dioxide	0.007	0.010	0.009
Ethane	0.003	0.004	0.003
Propane	0.000	0.000	0.000
Butanes	0.000	0.000	0.000
Pentanes	0.000	0.000	0.000
C6+	0.000	0.000	0.000
Water	99.976	99.964	99.969

* Results reported on an air-free basis.

5.0 Summary of Findings and Recommendations

This section provides:

- a summary of the primary findings for the PHLSA Study (Section 5.1);
- a list of recommended best practices for pressurized HC liquids sample collection and analysis, and associated PSM/EOS calculations of FGOR estimates (Section 5.2); and
- a list of the factors unique to the PHLSA Study that inherently limit the applicability of the PHLSA Study findings (Section 5.3).

5.1 Summary of Primary PHLSA Study Findings

The following are the primary findings of the PHLSA Study.

1. Nitrogen/air measured in pressurized condensate samples was determined to be a sampling artifact. High N_2 concentrations were more prevalent in CV cylinder samples than in CP cylinder samples, and it appears that it is more difficult to purge a CV cylinder sampling system prior to sample collection than to purge a CP cylinder system. Because nitrogen will readily volatilize, sample contamination with air can bias PSM/EOS calculations of FGOR and P_{BP} for pressurized HC liquids samples, and can also bias direct measurements of P_{BP}. Nitrogen has a much larger impact on P_{BP} than on FGOR. For a sample with about 0.15 wt% N_2, the with-N_2 P_{BP} was about 21% greater than the without-N_2 P_{BP}, whereas the associated FGOR only increased about 3%.

2. The evaluation of analytical methods for pressurized HC liquids included an internal SPL study and a multi-laboratory study:

   a. The SPL study generally determined that SPL GPA 2103M analyses had better accuracy and precision than the SPL GPA 2186M and SPL flash liberation methods for measuring individual HCs. Correspondingly lower analytical method uncertainty and bias estimates were calculated for SPL GPA 2103M than for SPL GPA 2186M and SPL flash liberation, and SPL GPA 2186M generally demonstrated better performance than SPL flash liberation.

   b. For the multi-laboratory study, accuracy and precision of the analytical results for individual HCs varied by method and by laboratory, and this suggests O&G producers would benefit from a means to compare the performance of different laboratories and analytical methods.

   c. The multi-lab study had a limited scope and was not intended to be a comprehensive and robust Inter-laboratory study to estimate the reproducibility of the methods. The multi-lab study results are specific to the participating laboratories and analyzed CRMs, should not be considered representative of the industry-wide performance for these analytical methods.

   d. GPA 2103M directly measures C10+ SG and MW, and demonstrated better accuracy for the measurement of these parameters than GPA 2186M and flash liberation for both the SPL study and the multi-lab study. GPA 2186M and flash liberation calculate C10+ SG and MW based on GPA methodologies, and GPA 2186M in particular had poor accuracy for C10+ MW.

   e. Errors in reported analytical results were not common but several were identified. Examples include outdated report templates (i.e., lab reports included parameters that were not measured), results with an apparent systematic bias (e.g., the multi-lab study results for Lab 1), incorrect presentation of results (e.g., sample A results reported as sample B results), sum of species not totaling 100%, and data transcription errors. Three of the four participating labs reported anomalous results. Rather than fundamental analytical problems, these appear to primarily result from human error, inflexible data handling systems, and insufficient data review.

3. Evaluation of laboratory sample handling procedures determined that sample mixing and pressure prior to GC injection impacted analytical results. Sample collection cylinder type (CP or CV) was found to influence the carbon dioxide and nitrogen, and have a borderline statistically significant influence on methane.

4. Sample collection parameters that impacted pressurized condensate sample results included sample collection initiation time (after the end of well cycle), sample cylinder type (CV vs. CP), sample collection location, and, to a lesser extent, sample collection rate.

   a. Samples with collection initiated 90 minutes and 150 minutes after the end of a well cycle had lower P_{BP}/P_{SC} and methane than samples with collection initiated during the well cycle or within 30 minutes of the end of the well cycle. Gas flow from the separator to the gathering pipeline between the collection of the less than 30-minute and 90-minute samples is a suspected cause, at least in part, of the change in HC liquids composition. Based on these results, a project guideline to collect samples within 30 minutes of the well cycle end was adopted. These samples were collected under controlled separator conditions (i.e., efforts were made to maintain a stable separator pressure and temperature), and the impact of sample initiation time on the pressurized condensate sample composition would likely be exacerbated if the separator pressure and/or temperature were changing; for example, due to changes in sales line pressure and/or use of separator headspace gas as heater fuel. Thus, collecting a pressurized HC liquids sample soon after a well cycle increases the probability that the sample composition will be the same as or very similar to the liquids that flowed from the separator to the storage tank.

b. Pressurized condensate samples collected with CV cylinders had, on average, about 10% less CO_2 and about 5% less methane than simultaneously collected CP cylinder samples, and the data suggest that some CO_2 and methane were transferred from the condensate samples to the water in the CV cylinders. This effect appears to be more pronounced at lower temperatures, possibly because the solubility of CO_2 and methane in water is inversely proportional to temperature. PSM/EOS calculated values of sample P_{BP} and FGOR were, on average, about 5% lower for CV cylinder samples than for CP cylinder samples. The mechanisms of the transfer of CO_2, methane, and other components from the HC liquids to the water in CV sample cylinders are not fully understood.

c. CP cylinder samples simultaneously collected from the separator oil box sight glass and a sample probe had P_{BP}/P_{SC} that differed by 5% or less with no consistent bias, and sample location had no apparent impact on the pressurized condensate sampling and analysis results. The results for CV cylinder samples simultaneously collected from the separator oil box sight glass and a sample probe were different. For the two of the four well cycles, P_{BP}/P_{SC} for the sight glass sample was more than 20% greater than P_{BP}/P_{SC} for the paired probe sample, and the P_{BP}/P_{SC} values for the two CV sight glass samples, 1.09 and 1.16, were the highest measured for the entire study. It is not understood why the CV sight glass sample results differed from the probe sample results.

d. Sample collection rates from 20 to 180 ml/min had no discernible effect on sample P_{BP}/P_{SC}. Samples collected at a rate of 180 ml/min showed minor shifts in C10+ concentration, SG, and MW. It should be noted that these samples were collected from sample probes installed about two feet below the separator gas/liquid interface, and were pressurized in the lab to 1,100 psi prior to GC injection. Such a pressure is expected to dissolve any gas that evolved (i.e., flashed) during sample collection. Sample collection rate may have a larger impact under different conditions, such as samples collected closer to the gas/liquid interface. For example, the gas/liquid interface could only be a few inches above the sample connection at an oil box sight glass, and a rapid sample rate could entrain gas. For the remainder of the study, conservative sample collection rates of 60 ml/min or less were used.

5. The primary results and findings of the OPC evaluations were:

a. Due to practical considerations and apparent measurement anomalies, two OPCs were found to be unreliable during the study: 1) densitometer measurement of sample P_{BP}, and 2) comparing HC liquids density measurements conducted at the production facility by a Coriolis meter and in the lab with a densitometer.

b. Bubble point pressures are strongly impacted by nitrogen (i.e., air) and methane, and PSM/EOS calculated FGOR estimates are much less dependent on the concentrations of these volatile compounds in pressurized HC liquids samples. Thus, 1) air contamination (e.g., caused by incomplete purging of sample collection equipment), or 2) a non-equilibrium methane concentration for a sample (e.g., loss during sample collection, transport and handling, and/or sample collection from a non-equilibrium separator) may cause an anomalous P_{BP} estimate when an associated FGOR and flash gas composition are reliable for estimating flash gas VOC generation and/or flash gas mass generation for tank vapor control system design.

    i. PSM/EOS calculations show that a 20% reduction in the methane concentration in a typical condensate sample results in about a 16% change in P_{BP} but only about a 5% change in FGOR.

    ii. For a sample with about 0.15 wt% N_2 (~ 0.48 mole %), the with-N_2 P_{BP} was about 21% greater than the without-N_2 P_{BP}, whereas the associated FGOR only increased about 3%.

    iii. PSM/EOS calculations should be based on a without-N_2 sample composition if the nitrogen in a sample is determined to be air contamination. PSM/EOS calculations estimate a N_2 concentration of about 0.003 wt% for Test Facility condensate at 260 psig and 60°F (i.e., high pressure/low temperature operation).

c. FGOR and P_{BP} are not strongly correlated, and this suggests that P_{BP}/P_{SC} may not be an optimal OPC if the ultimate goal of HC liquids sample collection and analysis is to estimate FGOR and flash gas composition (e.g., data for storage tank vapor control system design and/or flash gas VOC generation estimates).

d. The study results indicate that an IPT P_{BP} measurement would not be an optimal OPC if the ultimate goal of HC liquids sample collection and analysis is to estimate FGOR. This is because, while an IPT P_{BP} measurement checks the sample after collection and transport, it does not evaluate the analytical results (i.e., an IPT is conducted prior to lab analysis), and FGOR and IPT P_{BP}/P_{SC} are not strongly correlated. In addition, air contamination can bias an IPT P_{BP} measurement, but air in a sample is not necessarily a reason for sample rejection.

6. The summer and winter three-pressure testing measurements showed trends of improved storage tank HC mass balance and higher FGOR as the testing progressed from morning to afternoon. The summer high-pressure separator testing results were typical, with tank mass balance improving from 20% during early morning testing to about 100% during late afternoon testing. The measured FGOR increased from about 80 to about 330 scf/bbl.

These results suggest a “quenching” of flash gas generation when the tank liquids are relatively cold; that is, less flash gas was measured when tank liquids were colder in the morning than in the afternoon. Separator dump fluids are a mix of liquid and gas, and adiabatic flash calculations and estimates of the underground separator-to-tank pipeline temperature suggest these dump fluids are colder than the tank bottom liquids temperature. The measured flash gas generation is thought to be primarily the sum of the dump fluids gas and “secondary” flash gas that evolves as the dump liquids temperature increases as the dump liquids mix with warmer tank liquids. Relatively cooler tank liquids in the morning would be expected to reduce such secondary flash gas generation. A second consideration is that colder morning tank liquids may be under-saturated after cooling overnight (without any condensate production) and absorb some dump fluids flash gas.

Other primary summary observations from these measurements and associated PSM/EOS calculations include:

a. When storage tank mass balance closures were close to 100% (suggesting reliable measurements and minimal quenching of flash gas formation in the tank), measured FGOR values generally agreed with associated PSM/EOS calculated FGOR values within a 95% confidence interval.

b. Measured FGORs generally increased with separator pressure, decreased with separator temperature, and increased with tank temperature. For similar separator operating conditions, summer FGORs were about twice the winter FGORs. This was primarily a result of colder tank temperatures in the winter suppressing flash gas generation. Because the separator heater was fired during the winter, separator temperatures were generally higher in the winter than in the summer, and this would be expected to contribute to lower FGORs in the winter.

c. Actual maximum tank-to-burner pipeline gas flowrates during well cycles were significantly less than (e.g., ~ 60 to 70% of) calculated PPIVFRs. Contributing factors to this observation include: 1) there is a dynamic relationship between tank headspace pressure and gas flow to the burner, 2) the actual duration of flash gas generation in the tank is longer than the separator dump cycle (e.g., cold separator dump liquid must heat up in the tank before all flash gas is generated), 3) most of the separator dump fluids entered the tank through the downcomer and then migrated through the tank liquid to the top of the tank, and this would be expected to dampen peak flowrates, and 4) some “flash gas” components may be emitted later as breathing losses rather than emitted immediately as flash gas during the well cycle.

d. A PSM/EOS “dead oil” model, which simulated the effects of mixing fresh oil from a separator dump with dead (i.e., weathered) oil in the storage tank, showed a trend of increasing dead oil volume to simulate lower measured storage tank mass balances. These simulations lend support to the theory that mixing of cold, unsaturated tank oil with separator dump fluids suppresses flash gas generation.

7. PSM/EOS calculations of flash gas generation are most sensitive to tank bottom and headspace temperatures and pressures, separator pressure and temperature, assumptions regarding the fraction of separator dump fluids flowing through a SPH (estimated to be a small fraction), and HC liquids components with high analytical uncertainty. These are the largest potential sources of uncertainty in flash gas generation estimates. Imperfections in the EOS used for the equilibrium calculations may also contribute to the uncertainty.

8. Recent separator operating history may impact understanding and interpretation of pressurized HC liquids sampling and analysis results. The implication for sample collection is to attempt to maintain a steady separator temperature and pressure for one or more well cycles prior to sample collection.

   Pressurized HC liquids samples collected after a well cycle are a mixture of new HC liquids (i.e., HC liquids produced during the well cycle) and residual HC liquids (i.e., HC liquids in the separator from previous well cycles). The proportion of these two HC liquids in the sample is not known, and this proportion would be expected to impact the equilibrium pressure and temperature of the sample if the new and residual HC liquids have different compositions. Reasonable estimates of the true sample equilibrium pressure and temperature are needed to evaluate a sample's validity (i.e., conduct OPCs) and for PSM/EOS calculations of flash gas generation. The equilibrium pressure and temperature are typically assumed to be the separator operating pressure and temperature during the pressurized HC liquids sample collection. This assumption could have a large error if the residual HC liquids equilibrium pressure and temperature differ from these separator operating conditions; that is, the true HC liquids sample equilibrium pressure and temperature could be quite different than the separator operating conditions during sample collection. Attempting to maintain a steady separator temperature and pressure for one or more well cycles prior to sample collection is thus recommended, although this may not be practical at some production facilities (e.g., if the sales gas pipeline pressure is changing and/or if separator gas is used to fuel the separator heater during cold weather operation).

9. Considerations for collecting pressurized HC liquids samples during cold weather (i.e., winter sample collection) include:

   a. The separator heater may be fired during cold weather to prevent separator fluids from freezing, and associated implications include:

        i. Separator temperatures may be higher than during warm weather operation, and this will result in lower volatility HC liquids than during summer operations;
        ii. Production fluids remaining in a flowline between well cycles will get cold in winter, and when these cold fluids enter the separator transient temperature, non-equilibrium conditions could result, particularly if the separator heater fires in response.
        iii. A corollary to the recent separator operating history consideration discussed above is that if the separator headspace gas is used to fuel the heater, the separator pressure can decrease below the well cycle pressure and the residual separator HC liquids will likely lose light HCs. When these residual HC liquids mix with new HC liquids during a well cycle, the composite HC liquids equilibrium pressure and temperature could be quite different than the pressure and temperature measured during sample collection.
    b. The sample collection line and/or container can heat up (if the HC liquids coming in are warmer than the ambient and the sample container) or cool down (due to cold weather) during the sample collection. Such heating or cooling could complicate the measurement of the HC liquids sample temperature.
    c. If samples get too cold, paraffins can form solids in the sample cylinder.
    d. For CV samples, the solubility of CO_2 and methane in water increases as the temperature decreases and increases the potential for a bias in the measurement of these two volatile species.

10. Siphon prevention holes are installed in the downcomers of most, if not all, storage tanks. Separator dump fluids that flow through a SPH into the tank headspace may generate different flash gas than separator dump liquids that enter the bottom of the tank through the downcomer. This is because the tank headspace temperature and pressure can be different from the tank bottom temperature and pressure. Based on conversations with operations personnel, it does not appear that there is a uniform size and shape for these holes.

11. Storage tank pressure data indicate that breathing losses are minimal or non-existent during many nights, especially during the winter. This suggests that, if a directly measured breathing rate is used to estimate annual breathing losses, the time factor (e.g., hours per year) should be consistent with the data used to develop the breathing loss rate. For example, if a breathing rate was measured during the afternoon of a hot sunny day, this breathing rate should not be applied to 8,760 hours per year. Breathing losses also depend

on HC liquids production rate and HC liquids weathering (i.e., time in the tank), amongst other factors.

12. Measured compositions of gas that flowed from the tank to the burner were often heavier than flash gas estimated by PSM/EOS calculations, likely due to the contribution of heavy HCs generated as breathing losses, and this has implications for storage tank vapor control system design.

5.2 Recommended Best Practices for Protocols

Based on the PHLSA Study results, some generally applicable best practice guidelines for protocols for pressurized HC liquids sample collection, laboratory sample handling, and analysis were developed and can be recommended. These include:

1. When high concentrations of nitrogen (e.g., higher than PSM/EOS calculated equilibrium estimates) are measured in pressurized HC liquids samples, air contamination caused by a sampling artifact should be investigated (e.g., determine if nitrogen is in the sales gas (nitrogen will primarily partition to the gas phase); compare nitrogen concentrations to historical samples and samples from other wells in the vicinity).

   If nitrogen in a pressurized HC liquids sample is determined to be from air contamination, it is recommended that PSM/EOS FGOR and P_{BP} calculations be conducted using a HC liquids composition with the nitrogen mathematically removed.

2. It is recommended that analytical laboratory reports include uncertainty estimates for reported parameters, and that these uncertainty estimates be based on an ISO-based or similar uncertainty estimate methodology that is audited and verified by an accredited third party. For example, ISO Standard 17025 “General requirements for the competence of testing and calibration laboratories“ specifies general requirements for the reporting of uncertainties for analytical results. Accreditation bodies for calibration laboratories can require labs to participate in Proficiency Tests to validate their claimed uncertainty, and some laboratories regularly participate in Proficiency Tests to assess performance and confirm reported uncertainty.

   Further, it is recommended that data users review analytical laboratory reports for errors and anomalies (e.g., sum of species should equal 100%, compare results to similar historical samples).

3. Recommended laboratory sample handing procedures include a pre-injection sample pressure that is a minimum of 300 psi greater than the sample collection pressure, and the

number of mixing rocks for sample homogenization should be 18 or more. Heavier and more viscous HC liquids than evaluated for this study may require more mixing.

4. Use calibrated and highly accurate pressure gauges and temperature sensors during all sample collection and laboratory procedures. Existing instruments on separators may not provide accurate measurements and sample collection personnel are advised to use dedicated equipment.

   Separator temperature should be based on liquid temperature measurement. Gas temperature measurements are likely more susceptible to wall effects (e.g., cold separator walls in the winter could cause gas temperature stratification). A separator HC liquids temperature measurement during sample collection, in the vicinity of the sample collection location if possible, is recommended for P_{BP}/P_{SC} calculations.

5. Collect pressurized HC liquids samples as soon as possible after a well cycle, this increases the probability that the sample composition will be the same as or very similar to the liquids that flowed from the separator to the storage tank. Document, as able, that the separator temperature and pressure have been fairly stable since the well cycle *prior to* the sample collection well cycle. This increases the probability that the collected HC liquids sample and separator gas are at or near equilibrium at the measured temperature and pressure, and that the collected sample is representative of these conditions.

6. Other pressurized HC liquids sample collection recommendations include:
   a. Collect the sample from a location (e.g., sample probe, sight glass fitting) with routine oil circulation (e.g., avoid collecting stagnant HC liquids from the bottom of the separator HC liquids layer).
   b. Use a sample collection rate of 60 ml/min or less.
      i. Rule of thumb is a higher pressure causes a higher volatility sample and a slower sampling collection rate may be warranted to preclude flashing across the sample cylinder valve.
      ii. A faster sample collection rate may be preferred if the separator pressure and/or temperature is rapidly drifting after a well cycle; but faster sampling rates increase the chance of sample flashing and/or mass discrimination biasing the sample (e.g., heavy C10+ HCs biased low).
   c. Record the sample collection pressure and temperature at the start, middle, and conclusion of sample collection, and monitor these parameters throughout the sample collection. Note any anomalous changes in these measurements.

   d. Start sample collection at a slow rate and then increase to target sampling rate.
   e. Be aware of potential biases in samples collected using a CV cylinder.

7. When collecting a pressurized HC liquids sample to estimate flash gas generation for atmospheric storage tank vapor control system design, collect the sample during high pressure/low temperature separator operation that is expected to produce HC liquids with close to a maximum FGOR.
   a. Considerations for associated PSM/EOS calculations of flash gas generation (i.e., breathing and working losses are determined separately) for storage tank vapor control system design include:
      i. Use the maximum anticipated tank temperature (tank liquids for tanks that use a downcomer and/or tank headspace gas temperature for tanks that employ side-fill and/or may have flow through a downcomer SPH);
      ii. Use the minimum anticipated tank pressure; for example, assume a low liquid level in tanks that use a downcomer; and
      iii. Use conservative assumptions regarding separator dump-to-tank fluids flow through a SPH (e.g., use high-end estimates of parameters that impact SPH flow estimates). Appendix V provides an example calculation of estimated separator fluids flow through a SPH.
      iv. Due to the contribution of heavy HCs generated as breathing losses, gas that flows from the tank to the burner can be heavier (i.e. have a higher heating value) than flash gas estimated by PSM/EOS calculations. Thus, it is recommended that this be considered during the design of storage tank vapor control systems.
   b. Rather than using a theoretical PPIVFR to determine atmospheric storage tank vapor control system capacity requirements, a dynamic model approach is recommended.

8. When collecting a pressurized HC liquids sample to estimate an annual flash gas generation volume and composition (e.g., to develop an emission factor for emission inventory purposes), collect the sample during average pressure/average temperature separator operation that is expected to produce HC liquids with close to an annual average FGOR.
   a. Considerations for associated PSM/EOS calculations of flash gas generation (i.e., breathing and working losses are determined separately) volume include:
      i. use an annual average tank temperature (tank liquids for tanks that use a downcomer and/or tank headspace gas temperature for tanks that employ side-fill and/or may have flow through a downcomer SPH);

        ii. use an annual average tank pressure; for example, assume an average liquid level in tanks that use a downcomer; and
        iii. use average assumptions regarding separator dump-to-tank fluids flow through a SPH.

9. Avoid, if possible, collecting samples during very cold weather and when separator heater operation may be changing the separator pressure and HC liquids composition, mixing of cold well cycle fluids and hot residual separator fluids may be incomplete, and/or sample collection could be compromised (e.g., paraffin deposition on cold sample cylinder walls).
10. Suggested OPC guidelines for pressurized HC liquids samples include:
    a. Measure sample pressure and temperature during sample collection and during lab analysis with highly accurate, calibrated instruments.
    b. Determine an IPT P_{BP}/P_{SC} and/or a PSM/EOS calculated P_{BP}/P_{SC} to identify potential anomalies with the sample, and flag anomalous results for further scrutiny.
    c. As appropriate, adjust N_2 levels in HC liquids compositions prior to PSM/EOS calculations (e.g., if sample N_2 is determined to be sample collection artifact air, set N_2 level to zero).
    d. Acceptance of pressurized HC liquids composition results should depend on the ultimate data use and engineering judgment.
        i. The study data suggest that PSM/EOS calculated FGOR and flash gas composition could be an appropriate OPC for samples collected to estimate FGOR and flash gas composition (e.g., data for storage tank vapor control system design and/or flash gas VOC generation estimates). Acceptance criteria could be based on comparing the FGOR and flash gas composition to historical trends for similar production facilities.

           Lacking appropriate historical FGOR and flash gas composition data to determine sample acceptance criteria, PSM/EOS calculated P_{BP}/P_{SC} could be used as a conservative OPC for samples collected to estimate FGOR and flash gas composition. For this study, P_{BP}/P_{SC} ranged from about 0.73 to 1.16, and this range could be a minimum for OPC acceptance criteria, although the applicability of these findings to other production facilities cannot be determined. The issues discussed in Section 5.3 "Applicability and Limitations of PHLSA Study Findings" should be considered prior to applying this OPC acceptance criteria. In addition, during the PHLSA Study the pressurized condensate samples were collected from a single source by experienced personnel using dedicated equipment under controlled conditions (e.g., the separator pressure and temperature history were controlled and monitored), and all the samples were analyzed by the same lab by experienced analysts. These optimized sample collection and analysis procedures, and controlled separator operation may have produced a tighter P_{BP}/P_{SC} range than is practical under real-world conditions.

ii. Because pressurized condensate methane content and P_{BP} are strongly correlated, P_{BP}/P_{SC} could be an effective OPC for samples collected to estimate flash gas methane generation.

5.3 Applicability and Limitations of PHLSA Study Findings

The results and findings of the PHLSA Study for pressurized HC liquids sample collection and analysis, and subsequent PSM/EOS calculations apply to the Test Facility production equipment, operating conditions, and process streams. The applicability of these findings and conclusions to other O&G production locations has not been determined. That is, while study findings have broader applicability, and some general recommendations are provided in Section 5.2, the applicability of these results and findings to other O&G production liquids (e.g., different API gravity), different equipment (e.g., separator design), equipment operating conditions (e.g., separator operating pressure and temperature, tank temperatures), sample collection and analysis methods, and PSM/EOS calculation approaches has not been determined. Specifically, it should be noted that:

1. The pressurized HC liquids sample collection and analysis was conducted on fluids from a single well (with an API gravity of about 60°), and HC liquids with different API gravities/compositions were not sampled or analyzed as part of this study.

2. The PHLSA Study attempted to tightly control the separator pressure and temperature, and maintain constant conditions from before the well cycle through the completion of pressurized HC liquids sample collection. The separator pressure was isolated from the sales gas pipeline pressure with a back-pressure regulator, and during the winter testing the separator heater was fired using instrument gas from other separators such that the test separator pressure would not be reduced. This approach was used to isolate the impacts of test matrix parameters of interest (e.g., sample collection parameters, separator pressure). Such operational controls do not exist at separators during “real-world” HC liquids sample collection, and the effects of separator pressure changes (e.g., from sales gas pipeline pressure changes and/or separator heater firing separator headspace gas) and/or temperature changes (e.g., from ambient temperature changes and/or separator heater firing) on separator HC liquids composition change with time are not understood.

3. For the PHLSA Study, the majority of the separator fluids entered the condensate storage tank through the downcomer and mixed with weathered tank liquid. During tank side-fill

operation, separator dump fluids enter the tank headspace, which, during sunny days, can be at a higher temperature than the liquid temperature. The results of this project and the literature suggest that, under certain conditions, higher flash gas generation rates occur from a tank with side-fill.

4. Water production was very low during the PHLSA Study and associated flash gas generation was negligible; however, HCs, including VOCs, dissolved in water could potentially be emissions of interest for large water producers (e.g., some shale production areas).

5. There is currently no published standard or consensus method (e.g., a GPA or ASTM method) for flash liberation analyses, and for the data collected for this study, flash liberation analytical results generally had poorer accuracy and precision than GPA 2103M and GPA 2186M. It is understood that analytical laboratories have in-house flash liberation procedures, and the limited number of labs participating in the study may not have included the breadth of flash liberation methodologies. Thus, the performance of flash liberation analysis observed during the PHLSA Study may not represent the performance of different flash liberation methodologies used throughout the industry.

6. It was not possible to directly measure the two-phase fluid flow through the downcomer SPH inside the tank during separator dumps, and this flow was estimated using an engineering approximation of undetermined accuracy. Based on discussion with operators, it is understood that SPHs do not have a uniform size and shape, and the applicability of the engineering approximation used for this study to other storage tanks is not known. A better understanding of two-phase flow through SPHs would likely require a controlled lab study (e.g., vary parameters such as SPH size and shape, and fluid pressure, temperature, and composition).

7. A practical limitation of collecting and analyzing pressurized HC liquids to conduct PSM/EOS calculations is that the separator may not be operating at the desired conditions at the time when it is practical to collect the sample. For example, a pressurized HC liquids sample collected for the purpose of storage tank vapor control system design should ideally be collected at the maximum possible separator pressure and minimum possible separator temperature. These operating conditions are expected to produce HC liquids with a maximum FGOR. However, it may not practical to collect samples at these extreme conditions (e.g., sales gas line (and separator) pressures are typically not controlled by the production facility). Some PSM/EOS software packages claim the ability to extrapolate FGOR calculations from actual separator conditions to different (e.g., storage tank vapor control system design) conditions, and the additional uncertainty in FGOR estimates associated with such extrapolations may be of interest to control system designers. Under

such circumstances, it would be recommended that control system designers consult with the PSM/EOS software package vendors.

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