PHLSA Study Final Report

Appendix II

Uncertainty Analysis

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Abbreviations, Acronyms, and Symbols

a	Slope constant of first order regression (dimensionless)
b	Ordinate to origin or intercept constant of first order regression (dimensionless)
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
BAM	Bundesanstalt für Materialforschung
bbl	barrel
BTEX	benzene + toluene + ethyl benzene + xylenes
BIPM	Bureau International des Poids et Measures
Bz	Weight of Benzene for Cryoscopy Analysis (g)
C1	methane
CH_4	methane
C5	pentanes
C6+	hexanes and heavier hydrocarbons
C7+	heptanes and heavier hydrocarbons
C8+	octanes and heavier hydrocarbons
C10+	decanes and heavier hydrocarbons
c_i	Sensitivity coefficient
CI	confidence interval
CO_2	carbon dioxide
CP	constant pressure
CRM	Certified Reference Material
Cv	Certified value of component for multi-laboratory study (regression dependent variable)
CV	constant volume
D	Knob adjustment of cryoscope
d	density (g/mL)
DoF	degrees of freedom
°F	degrees Fahrenheit
FGOR	flash gas-to-oil ratio
g	gram
G	relative density
GC	gas chromatography

gmol	gram-mole
GPA	Gas Processors Association
GUM	Guide to the expression of Uncertainty in Measurement
HP	High pressure (well cycle)
IPT	initial pressure test
ISO	International Organization for Standardization
JCGM	Joint Committee for Guides in Metrology
K	Kelvin
k	Number of data sets with different n elements
$\%L$	Component liquid volume percent (*% liquid*)
L	Cryoscope reading of an unknown sample (dimensionless)
lb	pound
LP	Low pressure (well cycle)
LV%	liquid volume percent
m_i	Component mass in 1 g of CRM (mass fraction) (g)
min	minute
ml	milli-liter
MW	Molecular Weight (g/gmol)
MPMS	Manual of Petroleum Measurement Standards
MWs	Standard Molecular Weight (128.22 for n-Nonane) (g/gmol)
n	Total number of elements or components of a data set
N_2	nitrogen
NGLs	natural gas liquids
NIST	National Institute of Standards and Technology
NPL	National Physical Laboratory
OPC	operational performance check
P_{BP}	bubble point pressure
P_{sep}	Separator pressure
P_{SC}	Separator pressure during pressurized hydrocarbon sample collection
psia	pounds per square inch absolute
psig	pounds per square inch gauge
PSM/EOS	process simulation modeling/ equation of state

P_{tank}	tank pressure
PVT	pressure-volume-temperature
R	Cryoscope reading for n-nonane
R	ideal gas constant
R	correlation coefficient (e.g., for linear regression equation)
Rv	Reported value in multi-laboratory study, regression independent variable
s	Standard deviation
scf	standard cubic feet
s_p	Pooled standard deviation
s_{eff}	Estimated standard deviation of test result
Sd	Sample Standard Deviation
SW	Sample weight for Cryoscopy Analysis (g)
SG	Specific gravity at 60 °F/60 °F (*dimensionless*)
SHP	summer high-pressure
SLP	summer low-pressure
SMP	summer mid-pressure
SPL	Southern Petroleum Laboratories
SWs	Weight of standard (n-Nonane) for Cryoscopy Analysis (g)
t	Critical value of *t* distribution (i.e., for n-1 degrees of freedom)
TCD	thermal conductivity detector
T_{sep}	Separator temperature, typically during pressurized hydrocarbon sample collection
T_{tank}	tank temperature
u	Standard uncertainty (units of related variable)
U	Expanded uncertainty (units of related variable)
$\%u$	Relative standard uncertainty (%)
$\%U$	Relative expanded uncertainty (%)
UK	United Kingdom
WMP	winter mid-pressure
wt%	weight percent
WSRT	Wilconxan Sign-Rank Test
Z	compressibility factor

%	percent
Δ	difference or change
α	significance level, is the probability of rejecting the null hypothesis when it is true
Δ	Density at 60 °F (g/mL)
Δ_i	Density of component i at 60 °F (g/mL)
Δ_w	Density of water at 60 °FD, 0.999017 (g/mL)

References.

1. API Manual of Petroleum Measurement Standards Chapter 13—Statistical Aspects of Measuring and Sampling Section 1—Statistical Concepts and Procedures in Measurements reaffirmed, March 2016.
2. API Manual of Petroleum Measurement Standards Chapter 13.3 —Measurement Uncertainty. First Ed. May 2016.
3. ASTM D6300 − 16 Standard Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants
4. ASTM E691 − 16 “Standard Practice for Conducting an Inter-laboratory Study to Determine the Precision of a Test Method”
5. JCGM 100:2008. GUM 1995 with minor corrections. Evaluation of measurement data — Guide to the expression of uncertainty in measurement.
6. JCGM 101:2008 Evaluation of measurement data — Supplement 1 to the “Guide to the expression of uncertainty in measurement” — Propagation of distributions using a Monte Carlo method
7. ISO 5725-2. Accuracy (trueness and precision) of measurement methods and results - Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method
8. ISO/TS 29041 (E) Gas mixtures - Gravimetric preparation - Mastering correlations in composition.
9. ISO 6142-1 (E) Gas analysis - Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures.
10. ISO 14912 Gas analysis -- Conversion of gas mixture composition data
11. ISO 6974 - 1 Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 1: General guidelines and calculation of the composition.
12. ISO 6974-2 Natural gas - Determination of composition and associated uncertainty by gas chromatography - Part 2: Uncertainty calculations.
13. ISO 6976:2016 Natural gas - Calculation of calorific values, density, relative density and Wobbe Index from composition.
14. ISO 80000-1 First edition 2009-11-15 Quantities and units Part 1: General
15. GPA Standard 2261-13. Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography.
16. GPA Midstream Standard 2145-16. Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas and Natural Gas Liquids Industries.
17. GPA Standard 2103-03 “Tentative Method for the Analysis of Natural Gas Condensate Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography”

18. GPA Standard 2177-13 “Analysis of Natural Gas Liquid Mixtures Containing Nitrogen And Carbon Dioxide By Gas Chromatography“

19. GPA 2186-14“Tentative Method for the Extended Analysis of Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Temperature Programmed Gas Chromatography”

1. Introduction

Many variables impact estimates of flash gas generated in atmospheric oil storage tanks and contribute to complex uncertainty calculations. Integrating data from multiple components, procedures, operators, environmental conditions, instruments, maintenance and calibrations is required to estimate the uncertainty of oil tank flash gas generation.

Assessing the influence of each contributing parameter to a measured or calculated result is critical and necessary for confidence in the estimated uncertainty of the result. This assessment must be accomplished by detailed procedures based upon recognized practices or standards. Detailed documentation of data sources such as calibration reports, experimental data and other published sources contribute to support trustworthiness of results.

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

For some critical measurement components, such as chromatographic analytical methods or Certified Reference Materials 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. This report includes the following sections that document the approach and results for primary uncertainty estimates.

2.0 Preparation of Certified Reference Materials

3.0 Multi-laboratory Study

4.0 SPL Analytical Methods Evaluation

5.0 Sample Handling and Sample Collection Perturbation Studies

6.0 Process Measurement

7.0 Operational Performance Checks

8.0 Storage Tank Mass Balance and FGOR Measurements

9.0 PSM/EOS FGOR Calculations Uncertainty Analysis

The O&G production facility used for this testing produces HC liquid that is classified as condensate, and the terms HC liquid, condensate, and oil are used interchangeably in this document.

2. Certified Reference Material

Supporting data and calculations for the information presented in this section can be found in Annex 1.

Condensate Certified Reference Materials (CRM) were prepared in accordance with common American industry practices and gravimetrically blended from high purity feedstocks of C1 – C5 hydrocarbons and characterized heavy ends (depentanized C6+) condensate obtained from the test site storage tank. There were two target CRM compositions (i.e., “CRM1” and “CRM2”), and about 30 CRM1 sample cylinders were prepared and about 30 CRM2 sample cylinders were prepared.

CRM composition confirmation and associated uncertainty calculations were performed applying API Chapter 13.3 and ISO International Standards ISO/TS 29041, ISO 6142-1 and ISO 14912. Sources of uncertainty identified through these standards are schematically presented in Figure 1-1 and include:

- Feedstocks purity;
- Balance linearity, minimum division, repeatability, and bias;
- Buoyancy;
- Published values of component molecular weights and densities;
- C6+ fraction density and specific gravity; and
- Other sources: vacuum residues, cylinder expansion by pressure, volume shrinkage for liquid volume units.

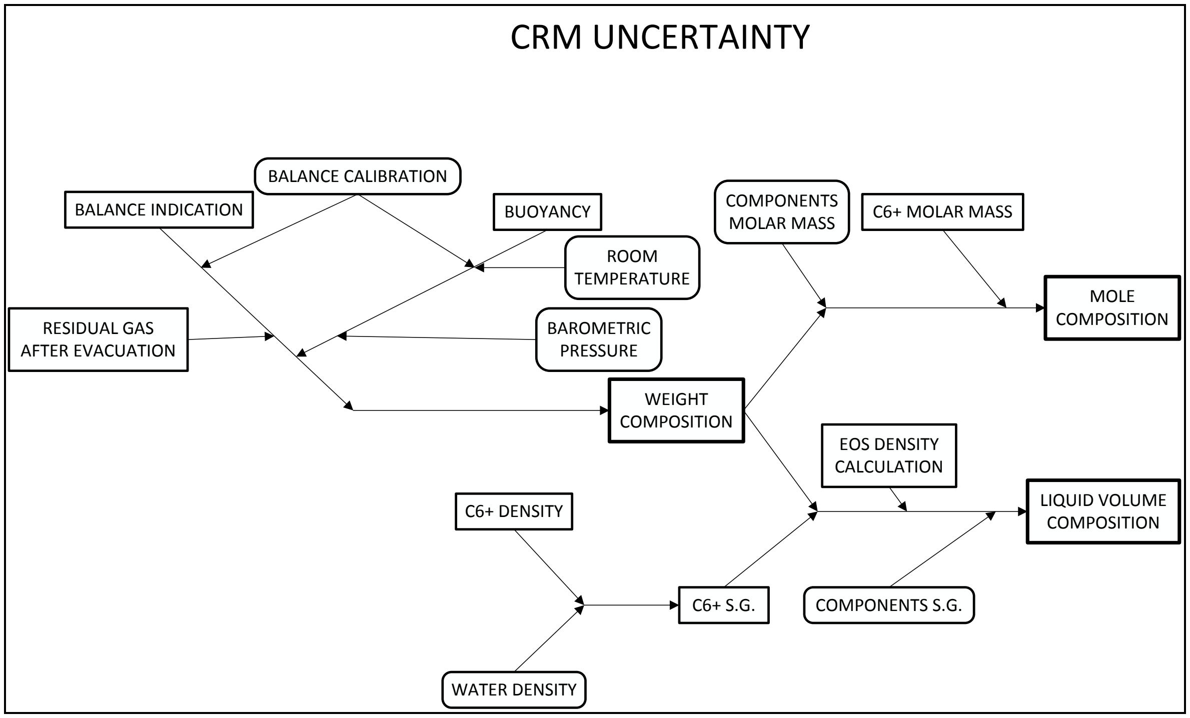

Figure 2-1. CRM sources of uncertainty. Rounded square boxes represent type B uncertainties.

Three different engineering units are needed for CRMs' composition. CRMs were gravimetrically blended and the composition was initially reported as a weight percentage or fraction basis, and then calculations were performed to obtain mole percent and liquid volume percent (LV%).

CRM composition conversion from weight percent to liquid volume percent (which is impacted by mixing rules discussed in section 2.1.6) is necessary because the general method for gas chromatographs (GCs) calibration is by liquid volume. This is because the instrument has a fixed volume valve for handling the samples and calibration materials (i.e., CRM's). For process simulation modeling/equation of state (PSM/EOS) calculations, mole fraction or percent values are used.

Weight and mole percent uncertainty calculations

GravCalc2 from NPL (National Physical Laboratory from United Kingdom) was used to perform ISO 6142 compliant calculations for uncertainty in mole and weight/mass fractions. While the method is designed for natural gas, most calculations are applicable to condensates. Input variables are the weight and composition (assay and impurities) of each component in the blend and their associated standard uncertainty (from balance's calibration certificates), and barometric pressure and room temperature for buoyancy calculations. The temperature and pressure were obtained from the databases of meteorological stations close to the Reference Materials Producer laboratory. A detailed explanation of the calculation model can be found in ISO 6142.

Liquid volume uncertainty calculations

In absence of an International Standard for liquid volume uncertainty calculations, these calculations were performed following API 13.3 and BIPM GUM guidelines JCGM 100:2008. Densities from Refprop by National Institute of Standards and Technology (NIST), rather than GPA 2145, were used. Refprop provides a generic uncertainty for density of around 0.02%, or higher (up to 0.2%), for almost all the components in the CRMs. Differences in densities between the two data sources (i.e., Refprop and GPA 2145) are small compared to related uncertainty levels. Refer to Annex 2 for input data (type B).

2.1 Description of Uncertainty Sources

2.1.1 Weighing

The weighing process uncertainty considers the weight without tare zeroing uncertainty and uncertainty at range of balance. The weight amount of substance is the weight of substance plus vessel minus the tared vessel weight. The uncertainty of the net weight measurement is approximately 40% (square root of 2 minus 1) greater than the balance uncertainty because the mathematical operation includes two similar weight readings.

The uncertainty contribution from the balance is around 0.001 %, and the balance uncertainty provides a very low contribution to the CRM uncertainty.

2.1.2 Buoyancy

Buoyancy, which accounts for the air displaced by the weighing vessel, is a variable for high accuracy weighing. Even when the buoyancy correction is almost cancelled in net weight calculations, its effect on uncertainty is not cancelled and it must be included in uncertainty calculations. The contribution of buoyancy is only a small fraction of the overall weight uncertainty.

2.1.3 Molecular weight

The contribution of the C1 – C5 feedstocks molecular weight uncertainties to the overall CRM molecular weight uncertainty is very small. The feedstocks molecular weight uncertainties result from impurities and associated uncertainties of published molecular weights of components. For CRM components molecular weights, ISO 6976-2016 data are used instead of GPA 2145 because the ISO method includes uncertainties for molecular weights.

The C6+ fraction molecular weight was obtained from cryoscopy analysis prior to mixing with the lighter components. Cryoscope molecular weight measurements have a relative uncertainty of approximately 0.3%, and this value is the greatest contribution to the CRM mole composition uncertainty. It is two orders of magnitude larger than uncertainties obtained from molecular weight tables for the C1 – C5 feedstocks. The molecular weight by cryoscopy uncertainty calculation is detailed in Section 2.4.

2.1.4 C6+ Density

Densities of C1 – C5 feedstocks components were obtained from Refprop. The C6+ fraction density and specific gravity were determined by an oscillating tube method (i.e., densitometer) with an ASTM D4052 compliant procedure. Repeatability of this method is around 0.1 %, and a relative uncertainty obtained from Toluene quality control samples was used to estimate sample uncertainties. An example detailed calculation can be found in Section 2.5.

2.1.5 Other minor sources

Uncertainty calculations included additional sources such as vacuum residues and cylinder expansion by effect of pressure. These were considered negligible.

2.2 Software Validation

Even though the software used for uncertainty calculations are from trusted sources, the calculations were validated using example input and output data from ISO 6142.

2.2.1 GravCalc2 (version 2.3.0), by NPL (National Physical laboratory, UK National Metrology Institute) calculates mole fractions and associated uncertainties for mixtures of gases prepared gravimetrically from known data of added mass, relative molecular mass of each component, and the purity of the components based upon ISO 6142. The software was validated using an example from Annex B of ISO 6142.

2.2.2 CONVERT (version 1.0) by BAM (Bundesanstalt für Materialforschung und -prüfung, German National Metrology Institute) was used to calculate uncertainties associated with weight to mole percent conversions, including correlation matrix calculation of molecular weight components updated to latest ISO 6976 version, and uncertainty of weight percent values. CONVERT is compliant with ISO 14912, furthermore, this software is indicated in the standard. Results of CONVERT were validated with examples of Annex D of ISO 14912.

2.2.3 The uncertainties of the CRM mass fractions (i.e., weight percent) were directly calculated as described below. Converting the CRM weight percent values to mole % and LV% required application of unit conversion constants. Calculating the uncertainty in the CRM mole % and LV% values requires consideration of the uncertainty in the conversion factors. An Excel calculation for liquid volume conversions and associated uncertainty calculations was developed by Movilab and validated by confirmation of the same model with GUMsim 2.0.0 from Quodata.

2.3 Input data for calculations

2.3.1 Molecular weights of compounds and associated uncertainties.

Table 2-1 lists molecular weights and associated uncertainties for pertinent compounds from ISO 6976:2016 (E). Note that the production facility used for this project does not produce sulfur compounds at detectable levels and H_2S was not a target analyte.

Table 2-1. Molecular Weight and Uncertainty ISO 6976:2016 (E)

Component	**Molecular weight (g/gmol)**	**Standard Uncertainty (g/gmol)**
Methane	16.04246	0.00042379
H2	2.01588	0.00007
H20	18.0153	0.00016553
CO	28.0101	0.0004272
N2	28.0134	0.0002
C2H4	28.05316	0.00081216
NO	30.0061	0.00018028
Ethane	30.06904	0.0008271
O2	31.9988	0.0003
C3H6	42.07974	0.00121824
CO2	44.0095	0.0005
Propane	44.09562	0.00123223
NO2	46.0055	0.00031623
i-C4	58.1222	0.00163783
n-C4	58.1222	0.00163783
SO2	64.0638	0.00251794
i-C5	72.14878	0.00204362
neo-C5	72.14878	0.00204362
n-C5	72.14878	0.00204362
n-C6	86.17536	0.00244951
n-C7	100.20194	0.00285545
n-C8	114.22852	0.00326143
n-C9	128.2551	0.00366742
n-C10	142.28168	0.00407344
C_6+*	Refer to Section 2.4	Refer to Section 2.4

*Note: C6+ molecular weight and uncertainty were obtained by Cryoscopy (UOP 103-58)

2.3.2 Elemental molecular weights and associated uncertainties.

Table 2-2 lists elemental molecular weights and associated uncertainties from ISO 6976:2016 (E).

Table 2-2. Elemental Molecular Weight and Uncertainty ISO 6976:2016 (E)

Element	Molecular Weight (g/gmol)	Standard Uncertainty (g/gmol)
Carbon	12.0107	0.0004
Hydrogen	1.00794	0.000035
Nitrogen	14.0067	0.0001
Oxygen	15.9994	0.00015
Sulfur	32.065	0.0025
Helium	4.002602	0.000001
Neon	20.1797	0.0003
Argon	39.948	0.0005

2.3.3 Density of compounds and associated uncertainties.

Table 2-3 lists densities (ρ) and associated uncertainties for compounds from NIST REFPROP.

Table 2-3. Density and Uncertainty (NIST REFPROP)

Component	ρ (g/ml)	%U (g/ml)	U (g/ml)	u (g/ml)
C6+	0.7589	0.005	0.00004	0.00002
n-C5	0.6300217	0.2	0.00126	0.0006
i-C5	0.6244784	0.2	0.0012	0.0006
n-C4	0.5836279	0.02	0.00012	0.00006
i-C4	0.5622760	0.02	0.00011	0.00006
Propane	0.5066873	0.010	0.000051	0.000025
Ethane	0.3559346	0.039	0.00014	0.00007
Methane*	0.2997	0.15	0.00045	0.0002
Nitrogen	0.8069000	0.02	0.0002	0.00008
Carbon Dioxide	0.8163591	0.049	0.0004	0.0002
Toluene	0.8709451	0.05	0.0004	0.0002
Isooctane	0.6955658	0.05	0.0003	0.00017
Water	0.9990171	0.0001	0.000001	0.000005

*Note: Methane was calculated from 0.3 relative density (to water) at 60 °F (Source GPA 2145). Methane is a gas at analytical temperatures and pressures, and an uncertainty of four times the other uncertainties was assigned based on engineering estimate.

2.3.4 CRM liquid volume percent uncertainty

Because GravCalc 2 does not calculate liquid volume percent conversions, additional uncertainty calculations were required:

Liquid volume percent formula is:

$$\%LV_i = \frac{\frac{m_i}{\rho_i}}{\sum_1^n \frac{m_i}{\rho_i}} \cdot 100 = \frac{\frac{m_i}{\rho_i}}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} + \cdots + \frac{m_n}{\rho_n}} \cdot 100 \qquad (2.1)$$

Where:

%LVi liquid volume percent of component i

m_i component mass in 1 g of CRM (mass fraction) (g)

ρi density of component I (g/ml)

n number of components in the CRM blend.

Then $u\%LV_i$, the standard uncertainty of the liquid volume percent of component i, is:

$$u^2\%LV_i = \sum_{j=1}^{n} \left[\left(100 \cdot \frac{\frac{\sum_1^n \frac{m_i}{\rho_i}}{\rho_j} - \frac{m_j}{{\rho_j}^2}}{\left(\sum_1^n \frac{m_i}{\rho_i} \right)^2} \cdot um_j \right)^2 + \left(100 \cdot \frac{\frac{\sum_1^n \frac{m_i}{\rho_i}}{{\rho_j}^2} - \frac{{m_j}^2}{{\rho_j}^3}}{\left(\sum_1^n \frac{m_i}{\rho_i} \right)^2} \cdot u\rho_j \right)^2 \right] \qquad (2.2)$$

Where:

um_i standard uncertainty of the component mass in 1 g of CRM (mass fraction) (g)

$u\rho_i$ standard uncertainty of the density of component i (g/ml)

2.4 C6+ Molecular Weight Uncertainty

This section describes the procedure used to estimate the uncertainty of the molecular weight of the C6+ material used to blend the CRM. The C6+ material was depentanized liquids collected from the Bernhardt facility storage tank. GPA Method 2103 clause 3.4.3 prescribes Cryoscopy molecular weight determination using UOP 103-58 method, and the principle of operation is the property of colligative solutions for depression of freezing point. The calibration procedure uses a pure substance with known molecular weight, in this case n-nonane. A small amount of standard is dissolved in a known quantity of benzene. Samples are similarly prepared.

Several sources of uncertainty were identified and these included weighing of materials, purity of standards, assigned molecular weight uncertainty, and accuracy or stability of instrument response (which considers the initial instrument adjustment).

The following assumptions were made for reasonable uncertainty calculations:

- For the molecular weight of n-nonane standard, the impurities composition was assumed to be a triangular distribution between octane and decane molecular weights.
- For the n-Nonane nominal molecular weight, UOP Method 103-58 lists a n-nonane molecular weight of 128.22, while ISO 6976-16 reports 128.25510. The ISO standard was selected because it contains stated molecular weight uncertainties. The difference between the UOP and ISO molecular weights was combined with uncertainty as bias.
- For cryoscope reading adjustment, a triangular distribution at center position of 0.001 cryoscope reading was assumed.
- For weight measurements, an uncertainty corresponding to the proportional uncertainty of the interval between nearest calibration points was assigned.
- The calculation procedure includes sensitivity coefficient calculations based on calculation models (equations) of instrument response adjustment and molecular weight calculation formulas.
- Stability or precision in reproducibility conditions of Instrument Reading were calculated using the pooled standard deviation of two sets of observations of quality control samples as prescribed in GUM JCGM 100:2008 clause 4.2.4.
- Final combined uncertainty was obtained from the standard uncertainties of Cryoscope Adjustment and Sample Molecular weight calculations.
- Coverage factor for expanded uncertainty is 1.96 (95% confidence interval (CI)).

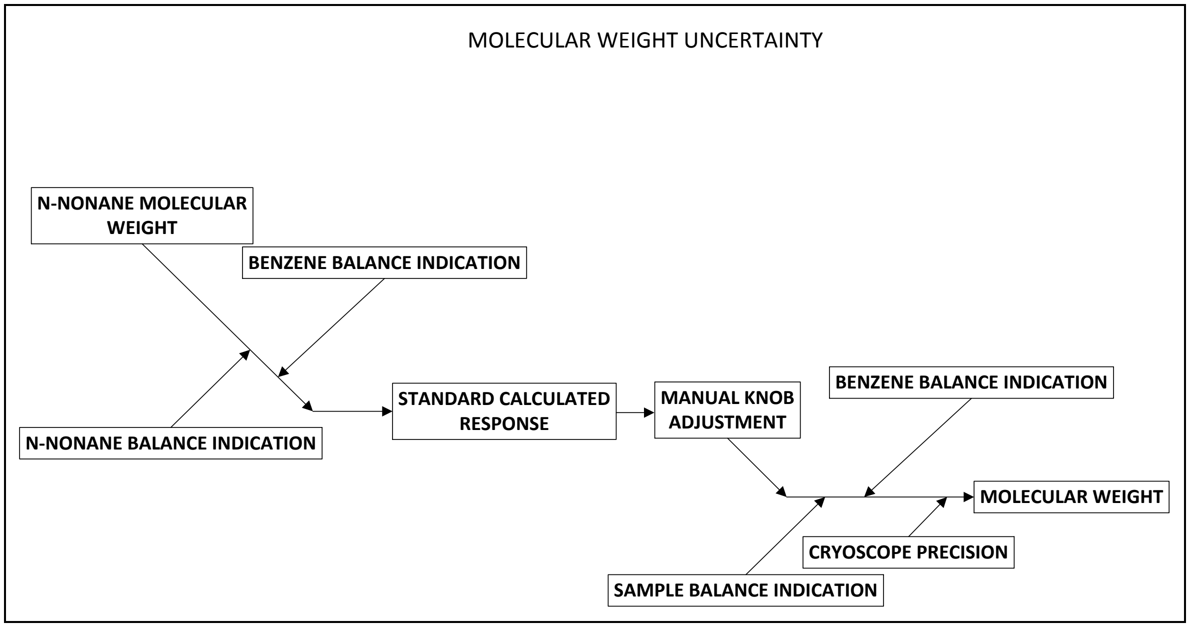

Figure 2-2. Sources of uncertainty for molecular weight measurements

2.4.1 Cryoscope Response Adjustment (reading adjustment) Uncertainty

The initial calibration of the cryoscope requires the calculation of the target instrument response to a known mass of standard dissolved in a known amount of benzene. The instrument is adjusted to this target reading.

$$R = \frac{5.12 \cdot 1000 \cdot SWs}{MWs \cdot Bz} \tag{2.3}$$

Where:

R	adjusted cryoscope reading for n-nonane (K)
5.12	conversion constant in UOP-103-58.
1000	unit conversion
Bz	weight of benzene for cryoscopy analysis (g)
MWs	standard molecular weight (128.22 for n-nonane) (g/gmol)
SWs	weight of standard (n-nonane) (g)

After sensitivity coefficients calculations (i.e., partial derivatives), the combined standard uncertainty for the cryoscope calibration reading is:

$$u^2(R) = \left(\frac{5.12 \cdot 1000}{MWs \cdot Bz}\right)^2 u^2(Ss) + \left(\frac{5.12 \cdot 1000 \cdot SWs}{MWs^2 \cdot Bz}\right)^2 u^2(MWs) + \left(\frac{5.12 \cdot 1000 \cdot SWs}{MWs \cdot Bz^2}\right)^2 u^2(Bz) \qquad (2.4)$$

The following calculation example is based on the instrument verification values:

Variable	**Units**	**Value**	**Standard Uncertainty**	**Comments**
SWs	g	0.5082	0.00005936	
MWs	g/gmol	128.22	0.017929	Includes bias related to ISO 6976
Bz	g	23.8085	0.00005936	

Note: The molecular weight for n-nonane is 128.25510 g/gmol with 0.00366742 g/gmol standard uncertainty. The difference in the n-nonane molecular weights listed in the UOP and ISO methods is 0.03510 g/gmol, and half of this difference is added as additional standard uncertainty (square root of the sum of the squares).

Substituting the example data in equation 2.4:

$$R = \left(\frac{5.12 \cdot 1000 \cdot 0.5082}{128.22 \cdot 23.8085}\right) = 0.85235\ K \qquad (2.5)$$

$$u^2(R) = \left(\frac{5.12 \cdot 1000}{128.22 \cdot 23.8085}\right)^2 0.00005936 + \left(\frac{5.12 \cdot 1000 \cdot 0.5082}{128.22^2 \cdot 23.8085}\right)^2 0.017929 + \left(\frac{5.12 \cdot 1000 \cdot 0.5082}{128.22 \cdot 23.8085^2}\right)^2 0.00005936 = 2.4\ x10^{-8}\ K^2$$

$$u(R) = (2.4\ x10^{-8})^{½} = 0.00016\ K = 0.026\ g \cdot gmol^{-1} \qquad (2.6)$$

Note: 0.001 units of temperature depression are equivalent to 0.16 molecular weight units, obtained by substitution of equation; 2.10. Standard uncertainties must be expressed in final measurand units (g·gmol^{-1}).

2.4.2 Uncertainty of the reading adjustment (triangular)

Instrument reading adjustment (D) has an uncertainty related to lower scale reading, in this case 0.001. A triangular distribution was selected to calculate an uncertainty with a ±0.0005 range.

$$u(D) = \frac{0.0005}{\sqrt{6}} = 0.00020\ K = 0.033\ g \cdot gmol^{-1} \tag{2.7}$$

Note: 0.001 units of temperature depression are equivalent to 0.16 molecular weight units, obtained by substitution of equation 2.10.

2.4.3 Instrument reading stability under reproducibility conditions.

A pooled standard deviation was calculated from quality control samples (Annex 1), and used to estimate the reproducibility uncertainty:

$$s_L = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \cdots + (n_k - 1)s_k^2}{n_1 + n_2 + \cdots + n_k - k}} \tag{2.8}$$

Where:

s_L	standard deviation of L
L	cryoscope reading of an unknown sample
n_i	total number of elements or components of data set i
s_i	standard deviation of data set i
k	number of data sets with different n elements

Table 2-4 lists the cryoscope readings used for the repeatability uncertainty calculation. “L” differs from “R” introduced above in that L is a cryoscope reading for an unknown or quality control sample and *R* is an adjusted instrument response for a known mass of standard (i.e., nonane) dissolved in benzene.

Table 2-4. Cryoscope Readings for Repeatability Uncertainty Calculation.

	Set 1	Set 2
$SW_s(g)$	0.5060	0.5082
$B_z(g)$	23.6345	23.8085
L_1	0.845	0.846
L_2	0.861	0.848
L_3	0.857	0.846
L_4	0.862	0.849
L_5	0.857	0.849
L_6	0.862	0.853
L_7	0.855	0.852
L_8	0.854	0.854
L_9	0.855	—
L_{10}	0.862	—
Average	0.857	0.850
s (standard deviation)	0.0053	0.0031
n (number)	10	8
Pooled standard deviation	0.0033	
Standard uncertainty	0.0008	

$$s_L = \sqrt{\frac{(10-1)0.0053^2 + (8-1)0.0031^2}{10+8-2}} = 0.0045$$

$$u(L) = \frac{s_L}{\sqrt{n}} = \frac{0.0045}{\sqrt{18}} = 0.0011\ K \tag{2.9}$$

2.4.4 Uncertainty of molecular weight measurement by cryoscopy

Molecular Weight Calculation from UOP 103

$$MW' = \frac{5.12 \cdot 1000 \cdot SW}{Bz \cdot L} \tag{2.10}$$

Where:

MW' Calculated Molecular Weight (g/gmol)

SW Sample weight for Cryoscopy Analysis (g)

Calculated molecular weight uncertainty:

$$u^2(MW') = \left(\frac{5.12 \cdot 1000}{Bz \cdot L}\right)^2 u^2(SW) + \left(\frac{5.12 \cdot 1000 \cdot SW}{Bz^2 \cdot L}\right)^2 u^2(Bz) + \left(\frac{5.12 \cdot 1000 \cdot SW}{Bz \cdot L^2}\right)^2 u^2(L) \qquad (2.11)$$

Substitution:

Variable	Units	Value	Standard Uncertainty	Comments
SW	g	0.5082	0.00005936	
L	°K	0.849	0.0011	Equation 2.9
Bz	g	23.8085	0.00005936	

$$u^2(MW') = \left(\frac{5.12 \cdot 1000}{23.8085 \cdot 0.849}\right)^2 \cdot 0.00005936^2 + \left(\frac{5.12 \cdot 1000 \cdot 0.5082}{23.8045^2 \cdot 0.849}\right)^2 \cdot 0.00005936^2 + \left(\frac{5.12 \cdot 1000 \cdot 0.5082}{23.8045 \cdot 0.849^2}\right)^2 \cdot 0.0011^2 = 0.025\ (g \cdot gmol^{-1})^2$$

$$u(MW') = 0.00023^{½} = 0.16\ g \cdot gmol^{-1} \qquad (2.12)$$

MW' uncertainty of calculated molecular weight

2.4.5 Combined C_6+ molecular weight uncertainty

Combined uncertainty of C6+ MW from equations 2.12, 2.6 and 2.7

$$u^2(MW) = u^2(MW') + u^2(R) + u^2(Sd) \qquad (2.13)$$

$$u^2(MW) = 0.16^2 + 0.026^2 + 0.033^2 = 0.027\ (g \cdot gmol^{-1})^2$$

$$u(MW) = 0.027^{½} = 0.17\ g \cdot gmol^{-1} \qquad (2.14)$$

$$U(MW) = 1.96 \cdot 0.17 = 0.3\ g \cdot gmol^{-1} \qquad (2.15)$$

2.4.6 Observations

Molecular weight should be expressed to the nearest 0.1 g/gmol, in accordance with ISO 80000-1, instead of limitations of ASTM E29 rules and similar good laboratory practice standards. This is important because rounding to the nearest integer number increases standard uncertainty by 0.29 g/gmol, doubling uncertainty (i.e., rounding to 1 implies 1 ±0.5, with rectangular distribution. u=0.5//3=±0.29).

The uncertainty of 0.3 g/g-mole is adequate for producing low uncertainties in CRM composition.

2.5 CRM and C6+ Specific Gravity Uncertainty Calculations

GravCalc 2 is limited to gas density and composition calculations. Liquid density and liquid specific gravity (SG) are not determined. An alternative calculation of SG uncertainty is thus required.

Densities of most CRM components at 60 °F and their associated uncertainties were obtained from Refprop by NIST. These values are almost identical to those reported by GPA 2145.

Methane liquid density at 60 °F, 0.2997 g/ml was obtained from GPA 2145, and standard uncertainty was assumed to be 0.0002248 g/ml based on engineering estimation. This is a 0.15 % expanded relative uncertainty.

2.5.1 CRM Specific Gravity Uncertainty Calculation

$$SG = \frac{1}{\sum_1^n \frac{m_i}{\rho_i}} = \frac{1}{\frac{m_1}{\rho_1} + \frac{m_2}{\rho_2} + \cdots + \frac{m_n}{\rho_n}} \tag{2.16}$$

Where:

m_i Component mass in 1 g of CRM (mass fraction) (g)

Δ_i Density of component i at 60 °F (g/ml)

Then $u^2(SG)$ is:

$$u^2(SG) = \sum_{i=1}^{n} \left[\left(\left(\frac{m_i}{\rho_i}\right)^2 + 1 \right) \left(\frac{1}{\rho_i \left(\sum_1^n \frac{m_i}{\rho_i}\right)^2} \right) \right] \tag{2.17}$$

2.5.2 C6+ specific gravity uncertainty calculation

The density of the C6+ material was measured using a Digital Density Meter. The Digital Density Meter measurement uncertainty was calculated from the analysis of ten quality control samples of toluene. Inference of uncertainty from Toluene Quality Samples under reproducibility conditions to samples was considered adequate. Since each weight and density measurement was independent, no correlation was assumed.

Standard uncertainty for a set of samples is determined from the standard uncertainty of the mean:

$$u(\bar{\rho}) = \frac{s}{\sqrt{n}}$$

$$\bar{\rho} = \frac{1}{n}\sum_{i=1}^{n} \rho_i$$

(API 13.3 4.12)

$$s^2 = \sum_{i=1}^{n} \frac{(\rho_i - \bar{\rho})^2}{n-1}$$

Mathematical model for Specific Gravity is:

$$SG = \frac{\rho_s}{\rho_w} \tag{2.18}$$

Where:

Δ_s	Density of sample at 60 °F (g/mL)
Δ_w	Density of water at 60 °FD, 0.999017 (g/mL)

Standard Uncertainty for *SG* is:

$$u^2(SG) = \left(\frac{1}{\rho_w}\right)^2 u^2\rho_s + \left(\frac{\rho_s}{\rho_w^2}\right)^2 u^2\rho_w \tag{2.19}$$

$$U\ (SG) = t \cdot u(SG) \tag{2.20}$$

Where:

t Student t distribution value for n-1 degrees of freedom

Table 2-5 lists the toluene quality control samples used for the uncertainty calculations.

Table 2-5. Quality Control Toluene Samples

	Toluene (g/mL)
1	0.8710
2	0.8710
3	0.8710
4	0.8710
5	0.8710
6	0.8711
7	0.8710
8	0.8709
9	0.8709
10	0.8710
mean (x)	0.87099
std.dev. (s)	0.000057
DoF (degrees of freedom)	9
t=	2.3198
$u\ (s\theta n^{-½})$	0.000018
$\%u = std.\ u \cdot mean^{-1}$	0.0021%
$U = t \cdot s\theta n^{-½}$	0.000042
$\%U = 100 \cdot U \cdot mean^{-1}$	0.0048%

Table 2-6 lists densities of water and toluene and associated uncertainties used for toluene specific gravity uncertainty calculations.

Table 2-6. Input Variables for Specific Gravity of Toluene Standard Uncertainty Calculation

Δ_w (g/ml)	$u\Delta_w$ (g/ml)	Δ_s (g/ml)	$u\Delta_s$ (g/ml)
0.999017	4.9951E-07	0.87099	0.000018

Note: Data from Tables 2-2 and 2-5

$$u^2(SG) = \left(\frac{1}{0.999017}\right)^2 0.000018^2 + \left(\frac{0.87099}{0.999017^2}\right)^2 0.000005^2 = 3.4\text{ x}10^{-10}$$

$$u(SG) = 0.00002 \tag{2.21}$$

$$U(SG) = 0.00004\ g \cdot gmol^{-1}$$

$$\%U(SG) = 4\text{ x}10^{-7}\% \tag{2.22}$$

A similar procedure was applied to C6+ samples with unknown SG.

2.6 Summary of CRM Uncertainty Calculations

Table 2-7 provides an example CRM sample composition and the estimated uncertainty for each of the components, and these results are representative of the uncertainties of all the CRM samples. The relative uncertainty for each CRM hydrocarbon component was less than 0.5% (i.e., for components C1 – C6+), and the contribution of CRM uncertainty to the total uncertainty of analytical results was small.

Table 2-7. CRM 101259 Composition and Uncertainty Estimates[A]

Component	Concentration (mole fraction)	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%
i-Butane	2.222	0.428%
n-Butane	6.428	0.362%
i-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

Supporting information and calculations can be found in Annex 1.

3. Multi-laboratory Study

Supporting data and calculations for the information presented in this section can be found in Annex 2.

3.1 Introduction

This report section presents the results of the uncertainty analysis of the multi-laboratory study. This study consisted of four different analytical labs analyzing samples of certified reference materials with two different target compositions (I.e., CRM1 and CRM2) using three different analytical methods: GPA 2103M, GPA 2186M, and flash liberation, where "M" indicates lab-specific method modifications (i.e., participating labs were asked to use their "best practice" methods and document any modifications.). The four laboratories that analyzed the CRM condensate samples reasonably represent the skills of analytical resources available in the U.S. market. Table 3-1 summarizes the number of samples analyzed by each laboratory in the study. The labs were not informed of the CRM compositions. Certified value and laboratory analytical results were compared to determine analytical uncertainty. This procedure provided an assessment of method performance.

Table 3-1. Number of Samples Analyzed for the Multi-laboratory Study

Lab	Test Method and Number of Samples Analyzed[A]		
	GPA 2103	GPA 2186	Flash Liberation
1	6	-	6
2	6	6	-
3	-	6	6
4	6	6	6

A. Each lab was sent three CRM1 sample cylinders and three CRM2 sample cylinders.

3.2 Background

Regardless of the calibration procedure, which in the case of GPA 2103 and GPA 2186 is performed with the response factor from a single point calibration with an inherent extrapolation, the net uncertainty effect of laboratory analysis depends upon ruggedness of method and random errors impacted by laboratory performance skills. Multi-laboratory round-robin testing studies provide an evaluation of analytical methods uncertainty.

Available International standards for method precision assessment based on an Inter-Laboratory Study are ISO 5725 series and ASTM D6300. For an Inter-Laboratory Study, 30 or more laboratories are recommended (ASTM E691, Clause 9.1.1), but when this is not practical, 8 laboratories could be enough. Under no circumstances should the final statement of precision of a test method be based from fewer than 6 laboratories (ibidem Clause 9.1.2). In any case, it is necessary to obtain at least 30 degrees of freedom (ASTM D6300, Clause 6.4.2) for determinations of both repeatability and reproducibility. For repeatability, this means obtaining a total of at least 30 pairs of results in the program.

Because the number of laboratories and sample pairs for the multi-lab study are not compliant with these recommendations, the referenced methods limit any statistical deductions to a general conclusions statement. Thus, uncertainty calculations were performed similar to the practice of individual laboratories analysis of reference materials as stated in ISO 6974 series (for natural gas analysis). These include calculating uncertainty using errors in a linear regression analysis, which is appropriate for single point calibration methods.

3.3 Approach

The data set was first evaluated for outliers, and then a linear regression model was used to analyze the multi-laboratory results and conduct an uncertainty analysis to evaluate:

- Relative performance of the three analytical methods by estimating each method’s uncertainty for each CRM compound; and
- Relative performance of the four analytical labs.

3.3.1 Outliers

The GPA 2103 CRM analysis data reported by Laboratory 1 appeared to be very different from the reference values and the results of the other laboratories. To determine if rejection of outliers was statistically supported, outlier identification procedures were conducted in accordance with two techniques, Mandel's h statistic and API MPMS 13.1.8.1.2 through Dixon's Q test. Complete statistical treatment used for outlier identification was performed in accordance with the ISO 5725-2 method.

Dixon´s Q test results for n-hexane results are presented in Table 3-2. The average of three results of the levels was used to preclude masking effects from multiple outliers. The Q test critical value for three results is 0.941 for 90% and 0.970 for 95%. For this data, only the 4th result from Laboratory 1 is greater than the Q critical value and could be rejected; however, some of the other values are very close to the outlier rejection criteria (0.97).

Table 3-2. Q test for n-Hexane by GPA 2103 average values

Level	1	2
Lab 1	8.670	10.102
Lab 2	6.084	7.105
Lab 4	6.224	7.152
Q	0.946	**0.984**
Critical value	0.97	0.97

Mandel's h statistic method identified the entire data set from Laboratory 1 is as outlier. As shown in Figure 3-1, this method identified that Laboratory 1 exhibited patterns of results that were highly different from the others in the study. When this occurred, the specific laboratory was contacted to try to ascertain the cause of the discrepant behavior; however, the cause of the biased analyses was not resolved.

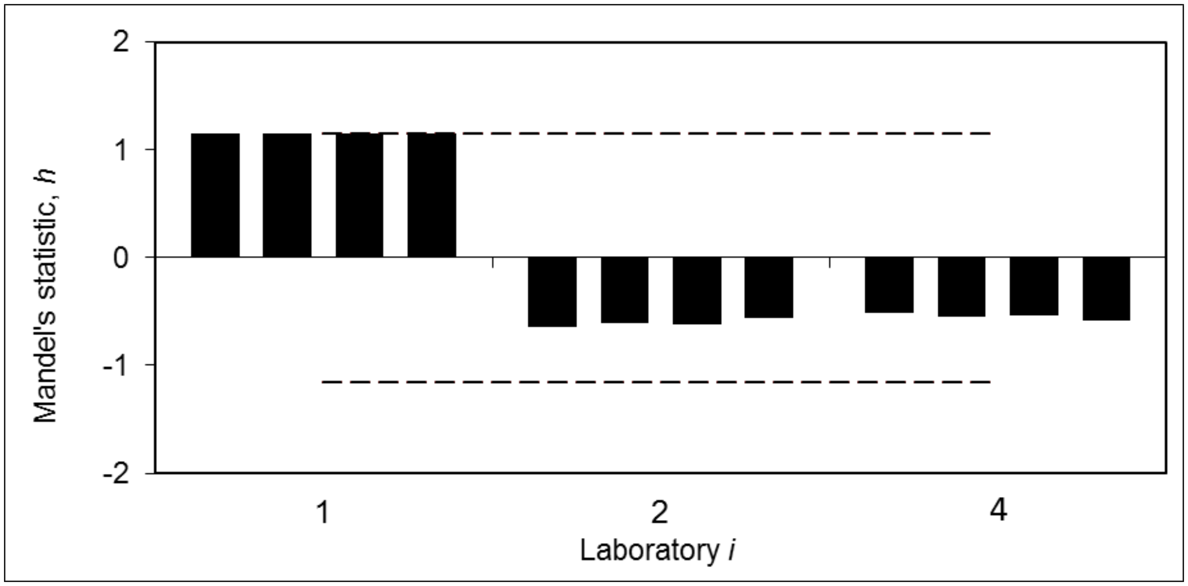

Figure 3-1. Mandel's statistic for laboratories 1, 2 and 3. n-Hexane by GPA 2103

The conclusion of the outlier analysis was that there is significant statistical evidence showing that results from Laboratory 1 are biased; thus, these results are not valid for uncertainty analyses and reproducibility determinations. Due to the normalization procedure, other CRM components had similar bias and this outlier rejection is applicable to the other components. The entire outlier analysis is presented in Annex 1.

Rejection of Lab 1 results reduced the average bias, and the remaining data were determined to be suitable for laboratory bias performance assessment.

3.3.2 Overview of the uncertainty calculations

Uncertainty calculations were performed following methodology from API MPMS 13.3 "Measurement Uncertainty". The procedure compared the CRM reference composition and the analytical results from each lab to estimate the associated analytical uncertainty. For each pressurized condensate component, a first order regression model was developed using CRM values as independent variables and associated lab results as dependent variables, and the uncertainties of analytical results were estimated from the uncertainties in the slopes and y-intercepts of the linear regression models. This approach is in accordance with NIST Engineering Statistic Handbook, 2.3.6.7.3, and was used because much relevant information regarding calibration and traceability was not available from all participant laboratories, and a black box model can overcome this issue. Additionally, a Monte Carlo simulation was performed for procedure validation and provided similar results.

Section 3.4 presents the general equations for uncertainty calculations. The n-hexane calculation is presented in section 3.5 as an example of the general procedure for uncertainty calculations. The same uncertainty analysis model and procedure, based on experimental data, was applied to all components of analytical methods.

Finally, overall results of components and/or methods are compared using graphical representation and associated uncertainties are identified. These evaluations may be used to select a preferred method for a given application.

3.4 General Equations for Uncertainty Calculations

3.4.1 Measurement model

The measurement model was developed considering the reported data as the dependent variable and the CRM value as the independent variable, and a first order linear regression was found appropriate to represent behavior of analytical methods. Evaluation with a second order function did not show significant improvement.

Analytical data assessment was based on the following function:

$$Rv = a\,Cv + b \tag{3.1}$$

Where:

a	Slope constant of first order regression (dimensionless)
b	Ordinate to origin or intercept constant of first order regression (dimensionless)
Cv	Reference (CRM) value of component for multi-laboratory study, independent variable in linear regression
Rv	Reported analytical value in multi-laboratory study, dependent variable in linear regression

If the analytical results equaled the CRM values, then the results of the linear regression would be “a” = 1.0 and “b” = zero.

Sensitivity Coefficients determination:

Sensitivity coefficients quantify the effect of the uncertainty of a component on the total uncertainty estimate. The sensitivity coefficient of x with respect to y is defined by the first derivative of y evaluated with the given x_i value. Figure 3.2 presents the entire hexane results data set (i.e., includes the Lab 1 data identified as outliers) and Figure 3.3 presents the hexane results excluding the Lab 1 outliers. The two groups of data represent CRM1 samples and CRM2 samples.

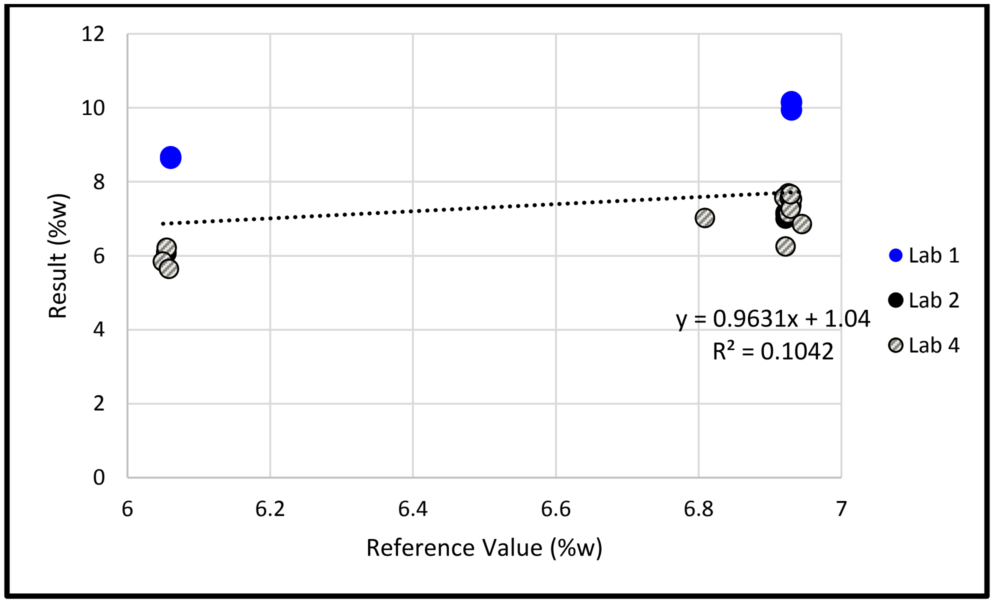

Figure 3.2. GPA 2103 n-Hexane data with outliers

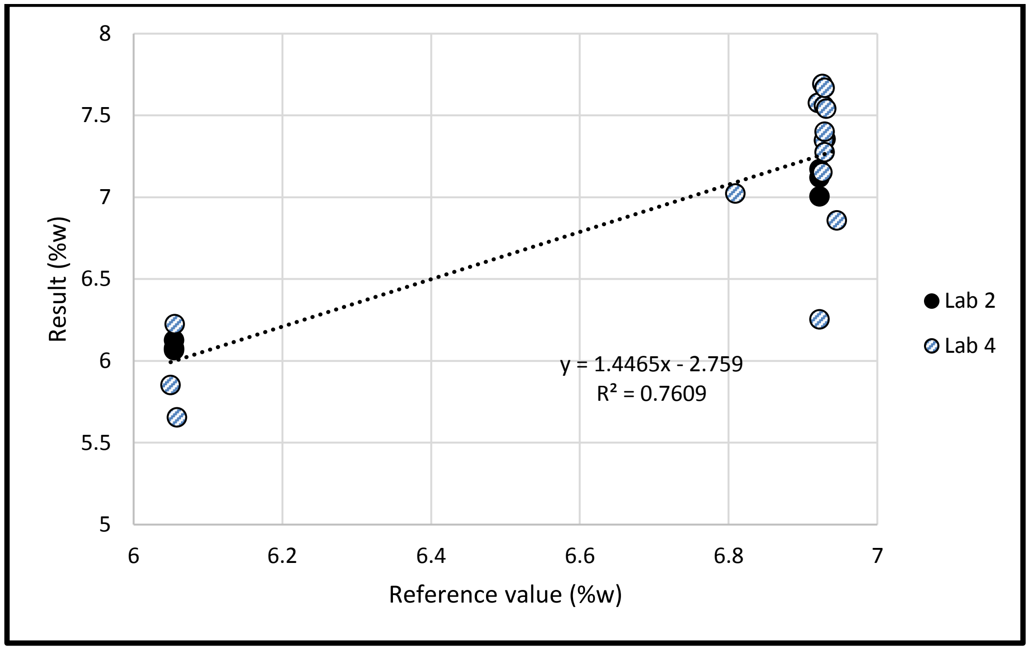

Figure 3-3. GPA 2103 n-Hexane data after removal of outliers

3.4.2 Linearity Check

Suitability of first and second order regressions were evaluated for analytical methods modeling. A second order regression does not provide significant improvement over a first order regression and does not reflect the limitation of single point calibration employed for GPA 2103 and GPA 2186. Thus, a first order regression model was used, and this mathematical model for performance assessment is defined in equation 3.1

3.4.3 Uncertainty calculation

According to API MPMS Chapter 13.3 equation 7, uncertainty of a mathematical model is defined by:

$$u_y = \sum_{i=1}^{n} c_i^2 u_i^2 + 2 \sum_{i-1}^{n-1} \sum_{j=i+1}^{n} r_{(i,j)} c_i c_j u_i u_j \qquad (3.2)$$

Where:

u_y standard uncertainty of y

y_i: the measurand of interest (i.e., Rv = reported molar fraction)

x_i: The input quantity (i.e., Cv = CRM value)

c_i:	Sensitivity coefficient of the input quantity (x_i)
u_i	The standard uncertainty of input x_i
$r_{(x,j)}$:	Correlation coefficient of x_i to x_j
n:	Total number of elements in the measurement model equation

Correlation is the degree of relationship between two variables. It is assumed that correlation coefficients quantify the intensity and direction of a linear relationship between elements in two sets of measurements, and is defined by the following equation (API MPMS Chapter 13.3 equation 6):

$$r_{(x_i,j_i)} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(x_i - \bar{j})}{\sum_{i=1}^{n}(x_i - \bar{x})^2 \sum_{i=1}^{n}(j_i - \bar{j})^2} \qquad (3.3)$$

Where:

$r_{(xi, ji)}$: Correlation coefficient

Based on this approach, uncertainty calculation of the first order linear regression model is equation 3.4:

$$u_y = c_a^2 u_a^2 + c_b^2 u_b^2 + 2r_{(a,b)} c_a c_b u_a u_b \qquad (3.4)$$

Where:

c_a:	Slope sensitivity coefficient
u_a:	Slope uncertainty (a regression standard error)
c_b:	Ordinate to the origin sensitivity coefficient
u_b:	Ordinate to the origin uncertainty (b regression standard error)
$r_{(a,b)}$:	Correlation coefficient of Slope and Ordinate to the origin

The standard error of estimates of slope and intercept were used to estimate the uncertainty of these variables (NIST Engineering Statistic Handbook, 2.3.6.7.3.).

Sensitivity coefficients are derived from the first order linear regression and correlation element.

$$c_{\mathrm{x}} = \frac{\partial y}{\partial \mathrm{x}} \qquad (3.5)$$

Where:

$\frac{\partial y}{\partial \mathrm{x}}$ is the partial derivative of y with respect to x

Calculations for regression, covariance and correlation matrices were performed with R Code (R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.) Examples code and calculation results are included in Annex 2. Validation of uncertainty calculations using GUM procedure was performed with GumSim. This also provides a Monte Carlo simulation result with a confirmed value equal to the GUM procedure calculations due to normal distribution assumptions.

3.4.4 Example

Continuing with the GPA 2103 n-Hexane example, we obtained the following result:

Using the full data including Lab 1 outlier data, the calculated result for a 6.06 %LV (liquid volume) reference material is 6.9 %LV, with an expanded uncertainty of 0.7 %LV. These correspond to a positive bias of 13.4% relative and a relative expanded uncertainty of 10%.

After rejecting the Lab 1 data as outliers, the same calculated value (i.e., for a 6.06 %W reference material) is 6.00 %LV, with an expanded uncertainty of 0.27 %W.; These correspond to a negative bias of 1 % relative and a 4.5% relative expanded uncertainty. Table 3-3 presents the R Code linear regression results for the data without the Lab 1 outliers and additional calculations follow:

Table 3-3. R Code Calculation of Slope and Intercept for n-Hexane

a = 1.451	u_a = 0.1820
b = -2.79	u_b = 1.2190
$r(x_i,x_j)$ = -0.9983	

Using 6.06 mole% as the x value, the linear regression equation yields:

$$y = (1.4510 \cdot 6.060) - 2.7900 = 6.0031\ \%W \tag{3.6}$$

Sensitivity Coefficients are calculated using Equation 3.5:

Original model: $y = ax + b$

$$c_a = \frac{dy}{da} = \frac{\partial(ax_i + b)}{\partial a} = x_i \tag{3.7}$$

$$c_b = \frac{dy}{db} = \frac{\partial(ax_i + b)}{\partial b} = 1 \tag{3.8}$$

Uncertainty is obtained by substituting these values into Equation 3.4:

$$u_y^2 = (x * 0.1820)^2 + (1 * 1.2190)^2 + 2(x * 1 * 0.1820 * 1.9190 * -0.9983) \tag{3.9}$$

Uncertainty result:

Table 3-4. GPA 2103 Analysis, n-Hexane Uncertainty

Variable	Value
Y	*6.003 %W*
u^2_y	*0.0180 %W*
u_y	*0.1346 %W*
U_y	*0.27 %W*
$\%U_y$	*4.5%*

This method performance analysis (i.e., uncertainty calculation) considers both data dispersion/precision (i.e., uncertainty of slope “a” of the linear model) and zero offset/bias (i.e., uncertainty of y-intercept “a” of the linear model.

Limitations. This uncertainty estimate is only valid for the range of data points included in the calculation; however, some samples collected during the testing included values outside this data range and extrapolation using the relative uncertainty estimate was required.

API 13.1.8.1.6.3 has provisions to adjust analytical results for bias; however, bias adjustment is not addressed in the GPA methods and uncorrected analytical results are reported and used for calculations in this study. This approach is consistent with industry practice.
For this project, Section 4 provides, in addition to analytical methods uncertainty estimates, estimates of biases in analyses conducted by SPL to further assess method performance.

3.5 Measurement Uncertainty of Multi-laboratory Study

Table 3-5a presents the linear regression parameters (i.e., slope “a” and y-intercept “b”) and the relative percent uncertainty for the analytes measured using GPA 2103M during the multi-laboratory study. These results do not include the Lab 1 outliers. Table 3-5b presents these GPA 2103M data for the entire data set (i.e., Lab 1 outliers included). As noted above, If the analytical results equaled the CRM values, then the results of the linear regression would be “a” = 1.0 and “b” = zero. Table 3-6 lists the same information for GPA 2186M analyses and Table 3-7 lists the same information for the flash liberation analyses. Table 3-8 lists these parameters for the decanes plus specific gravity and molecular weight determinations by GPA 2103M, GPA 2186M, and flash liberation. Figure 3-4 graphically presents the data in Tables 3-6 to 3-8.

Table 3-5a. Multi-laboratory Study GPA 2103M Analysis Uncertainty (Lab 1 Outliers Removed)

	C8+	C7+	C6+	Benzene		CO2	C10+	Ethane
a=	0.9265	0.9996	0.8198	1.5335		0.7082	0.7591	0.8711
b=	2.4831	-0.4018	14.2398	-0.3823		0.0599	7.0378	0.2258
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
%U=	1.7	1.2	0.3	7.4		4.5	2.7	2.6
	Ethylbenzene	Heptanes	nC6	iC6	iC4	iC5	Methane	N2
a=	1.4582	0.7511	1.451	0.4942	0.9764	0.4149	1.1255	7.2384
b=	-0.0918	2.8798	-2.79	3.813	0.0309	2.4283	-0.1187	-0.0182
Relative standard uncertainty * coverage factor (95% CI)								
%U=	18.9	4.9	4.5	5.4	0.7	2.5	2.0	40.8
	nC4	nC5	Nonanes	Octanes		Toluene	Xylenes	Propane
a=	1.1096	1.0404	0.0006	0.1812		0.5261	1.3165	1.0764
b=	-0.4139	-0.2154	4.5489	6.1573		1.3722	-0.7613	-0.1721
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
%U=	0.7	0.7	4.9	7.8		2.6	2.8	1.0

Table 3-5b. Multi-laboratory Study GPA 2103M Analysis Uncertainty (Lab 1 Outliers Included)

	C8+	C7+	C6+	Benzene	CO2	C10+	Ethane	
$a=$	1.4642	1.463	1.5044	1.7578	0.977277	1.0184	1.1095	
$b=$	-20.9661	-28.196	-38.8584	-0.6167	0.006146	1.5662	-0.2386	
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
$\%U=$	6.1	6.4	2.2	27	9.1	12	13	
	Ethylbenzene	Heptanes	nC6	iC6	iC4	iC5	Methane	N2
$a=$	1.1	0.75	0.96	1.89	0.87	0.66	1.2	0.79
$b=$	0.02	2.9	1.1	-7.73	0.12	1.1	-0.28	0.0023
Relative standard uncertainty * coverage factor (95% CI)								
$\%U=$	15.3	14.7	11.5	13.2	7.8	8.5	11.3	26.7
	nC4	nC5	Nonanes	Octanes	Toluene	Xylenes	Propane	
$a=$	1.1	1.0	0.0006	0.18	0.53	1.32	1.08	
$b=$	-0.41	-0.22	4.5	6.2	1.4	-0.76	-0.17	
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
$\%U=$	4.5	4.9	9.3	13.3	8.2	5.6	4.7	

Table 3-6. Multi-laboratory Study GPA 2186M Analysis Uncertainty

	C8+	C7+	C6+	Benzene	CO2	C10+	Ethane	
A	1.1154	0.4647	-0.1873	0.5265	2.0004	1.6210	0.8033	
B	-11.2045	33.1645	92.5354	0.3929	-0.1265	-31.1086	0.4234	
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
$\%U$	2.1	0.8	0.4	4.5	20.5	3.4	3.4	
	Ethylbenzene	Heptanes	nC6	iC6	iC4	iC5	Methane	N2
a	1.1941	2.3824	0.8173	0.1162	1.1541	0.1319	0.8008	5.5946
b	-0.0508	-11.8416	1.2141	0.8867	-0.1384	3.8935	0.2639	-0.0136
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
$\%U$	17.3	1.9	5.9	1.5	1.0	2.2	2.7	54.2
	nC4	nC5	Nonanes	Octanes	Toluene	Xylenes	Propane	
a	0.6669	0.5307	3.0003	2.7717	0.6537	1.1195	0.7317	
b	1.4620	3.2220	-7.6430	-10.4915	0.8300	-0.3911	0.8356	
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)								
$\%U$	1.5	1.8	3.2	4.1	0.9	3.0	1.9	

Table 3-7. Multi-laboratory Study Flash Liberation Analysis Uncertainty

	C8+	C7+	C6+	CO2	C10+	Ethane
A	0.3881	0.0040	-0.7793	1.4461	0.4238	1.1344
B	33.8657	66.8641	143.3101	-0.0519	20.9866	-0.0896
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)						
$\%U$	4.5	3.6	1.4	6.4	4.2	6.5

	Heptanes	nC6	iC6	iC4	iC5	Methane	N2
a	0.9311	0.9959	0.3946	0.8979	-0.0855	1.6481	23.6760
b	0.9666	-0.3106	3.0415	-0.0739	3.6950	-0.4276	-0.0513
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)							
$\%U$	2.5	28.3	4.6	13.2	40.4	10.0	47.5

	nC4	nC5	Nonanes	Octanes	Xylenes	Propane
a	-0.0841	0.0921	-0.8911	0.8825	1.3389	-0.0154
b	3.3357	4.2736	10.1220	1.4742	-1.0751	2.6055
Relative standard uncertainty * coverage factor (95% CI for wt% analytical results)						
$\%U$	11.6	8.6	9.3	2.5	5.9	7.9

Table 3-8. C10+ Specific Gravity and Molecular Weight Analyses Uncertainties

	2103M SG	2103M MW	2186M SG	2186M MW	Flash Liberation SG	Flash Liberation MW
a	0.5119	0.6457	0.4820	0.1805	0.4262	0.2589
b	0.4004	82.8025	0.3832	133.3282	0.4513	119.2624
Relative standard uncertainty * coverage factor (95% CI)						
$\%U$	2.2028	6.0614	2.81	7.41	2.9913	10.4455

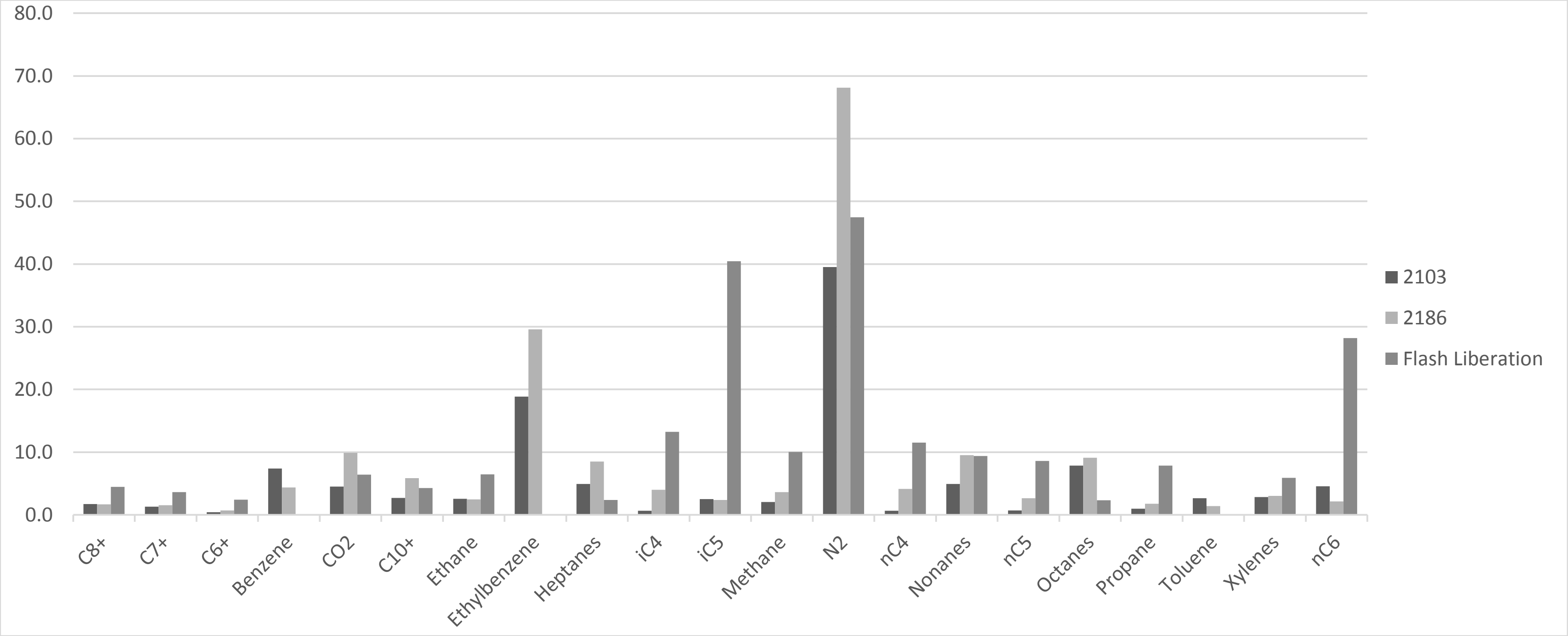

Figure 3-4. Multi-laboratory study analytical method uncertainty analysis results (%U for analytes)

3.6 Summary of Multi-laboratory Study Findings

Primary findings of the multi-lab study include:

- One laboratory has a large bias in its GPA 2103 analytical results of CRM samples. These results were identified as outliers and rejected. Remaining GPA 2103 results have a much better agreement with CRM compositions. These results suggest that pre-qualification of laboratory performance with a blind sample of known composition could be warranted.
- Relative uncertainty for nitrogen analytical results is significant at low concentrations. GPA methods have a lower range limit of 0.01 mole percent nitrogen. For values close to or lower than this concentration, it may be preferable to use nitrogen-free results for subsequent calculations.
- The uncertainties of detailed analysis of pseudo-components from hexane to C10+ are significantly greater than sum of species analytical results (e.g., U(C7) > U(C7+), U(C8) > U(C8+)). The estimated uncertainties for hexanes, heptanes, octanes, nonanes, BTEX, and C10+ are at least four times higher than the uncertainty estimated for total C6+ species. The uncertainty of heptanes is on the order of three to four times greater than the uncertainty of C7+, regardless of the method used. Well characterized lumped or total pseudo-components provide lower uncertainties than the uncertainties of the individual compounds.
- Detailed analysis is performed over multiple peaks nested with low resolution, C6+ can be obtained by difference with C1-C5 low uncertainty results, a more detailed analysis implies compounds with poor resolution, this contributes to larger uncertainty. GPA 2103 analytical results generally had the lowest uncertainties, and had the lowest uncertainties for light end compounds methane, carbon dioxide, and nitrogen.
- Flash Liberation had the highest uncertainties for methane, carbon dioxide, and nitrogen.

4. SPL Analytical Methods Evaluation

Supporting data and calculations for the information presented in this section can be found in Annex 2.

4.1 Introduction and Approach

To assess the performance of the SPL analytical methods for pressurized condensate samples, the SPL analytical results for CRM samples from the method performance task (Task 4 from the Work Plan) and multi-lab study task (Task 3 from the Work Plan and addressed in Section 3) were combined and the data analyzed to evaluate the uncertainty and bias for SPL analyses. This resulted in 16 CRM sample analyses by SPL GPA 2186M, 16 CRM sample analyses by SPL flash liberation, and 26 CRM sample analyses by SPL GPA 2103M. As described in Section 3, analytical results were processed to obtain a regression between reported values and certified values as dependent and independent variables, respectively. The uncertainty of SPL reported results from random errors can be estimated from CRM uncertainty, linearity (linear fit errors) and dispersion (reproducibility and repeatability). Measurement/method bias is defined as an estimate of a systematic measurement error, and was estimated from the difference between reported analytical values and the regression equation estimates of the analytical values based on the associated certified (i.e., CRM) value.

According to international vocabulary of metrology (VIM) measurement bias is an estimate of a systematic measurement error and, measurement uncertainty is a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used.

Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated (API 13.1.8.1.3). As bias correction is not addressed in GPA methods, analysis results are assumed unbiased.

On the other hand, bias cannot be assessed under routine analysis, in the best case this is evaluated for method validation, but also, bias corrections are not applied under proper method execution.

4.2 Summary of SPL Analytical Methods Uncertainty and Bias

Table 4-1 shows a summary of calculated uncertainties by component and method for the SPL analytical results, and Figure 4-1 presents these results graphically. These are the uncertainties used for subsequent uncertainty estimates, such as the uncertainties of directly measured flash gas-to-oil ratios (FGORs) and storage tank mass balance closures. GPA 2103M generally had the lowest uncertainties, with GPA 2186M generally having lower uncertainties than the SPL flash liberation results. It should be noted that here is not a published standard/consensus method (e.g., GPA or ASTM) for flash liberation, and the version used by SPL does not use a PVT (pressure-volume-temperature) cell (i.e., some labs use a PVT cell for flash liberation measurements). A comparison and evaluation of different lab practices and methodologies for flash liberation could lead to improved performance.

Table 4-1. Summary of SPL Analytical Methods Uncertainty Estimates

Compound	Analytical Method		
	SPL GPA 2103M	SPL GPA 2186M	SPL Flash Liberation
	Uncertainty of Wt% Analytical Results (%U, 95% CI)		
CO2	1.70	20.54	8.62
N2	5.73	41.19	16.66
Methane	1.98	2.67	15.95
Ethane	1.26	3.36	9.16
Propane	0.99	1.90	6.68
iC4	0.64	0.99	13.64
nC4	1.09	1.45	13.20
iC5	1.85	2.16	21.56
nC5	0.94	1.83	4.74
iC6	2.95	1.74	4.62
nC6	7.58	5.89	30.84
Heptanes	2.72	1.94	1.13
Octanes	3.54	4.05	1.53
Nonanes	4.40	3.17	2.81
C10+	3.79	3.39	1.44
Benzene	7.88	4.46	—
Toluene	2.64	0.91	—
Ethylbenzene	17.65	17.31	—
Xylenes	3.08	1.52	2.68
C6+	0.24	0.35	0.69
C7+	0.99	0.76	1.85
C8+	1.80	2.09	2.06

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 4-1 and used for subsequent uncertainty calculations, such as for the uncertainties of directly measured flash gas-to-oil ratios (FGORs) and storage tank mass balance closures, do not consider bias. However, in addition to an appropriate method uncertainty, a bias assessment is recommended for a comprehensive method evaluation and selection of the best analytical method for an intended use. Table 4-2 shows a summary of estimated biases by component and method for the SPL analytical results. These data are presented for informational and discussion purposes.

Table 4-2. Summary of Analytical Methods Bias Estimates

Compound	Analytical Method		
	SPL GPA 2103M	SPL GPA 2186M	SPL Flash Liberation
	Wt % Bias		
CO2	7.6%	-16.8%	11.3%
N2	13.4%	-44.1%	87.6%
Methane	0.8%	-3.1%	11.8%
Ethane	1.8%	-9.9%	7.06%
Propane	0.4%	-7.7%	7.94%
iC4	1.1%	-11.0%	14.5%
nC4	0.7%	-8.8%	17.4%
iC5	1.8%	-1.5%	87.7%
nC5	0.4%	-3.9%	21.0%
iC6	0.6%	5.8%	14.7%
nC6	1.0%	-3.0%	5.1%
Heptanes	1.0%	-11.6%	1.3%
Octanes	1.6%	-14.6%	7.0%
Nonanes	5.2%	-19.8%re	31.2%
C10+	4.3%	19.0%	1.8%
Benzene	0.9%	-4.1%	—
Toluene	1.5%	8.3%	—
Ethyl-bz	7.0%	23.1%	—
Xylenes	5.8%	26.5%	2.2%
C6+	0.05%	1.7%	3.0%
C7+	0.7%	3.2%	1.1%
C8+	2.5%	5.9%	3.4%

SPL GPA Method 2103M provided the best overall performance based on the uncertainty and bias estimates. SPL GPA 2103M also provided the best performance for light components such as methane, nitrogen, and carbon dioxide and C2 – C5 which are key compounds for FGOR and pressurized condensate bubble point pressure estimates. For the GPA methods, the lower detection limit for nitrogen in liquid hydrocarbons is 0.01% mol. For concentrations close to or below this limit, high uncertainty and bias were found.

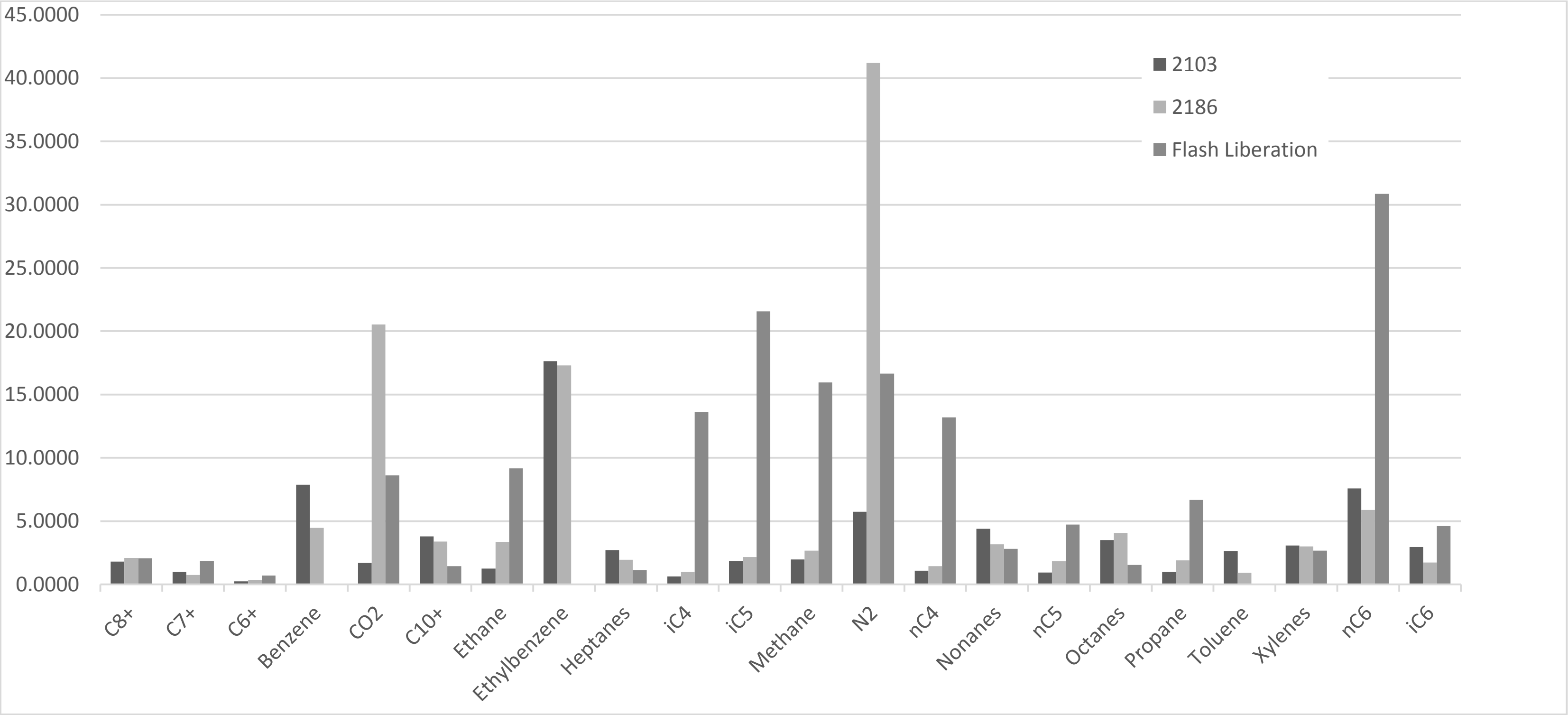

Figure 4-1. SPL study analytical method uncertainty analysis results (%U for analytes).

4.3 Weighted bias

The pressurized hydrocarbon analytical methods evaluated for this project were developed for different applications (e.g., for NGLs (natural gas liquids), light and heavy condensates, or crude oil), and the estimated bias of these methods will depend on the sample properties. The impact of a method bias on an application (e.g., FGOR estimates) can be evaluated for the individual components bias, as an average bias for all the components, and as a weighted average bias. Weighed bias calculation is intended to assign more importance to components with larger concentration than those with lower concentration. A component with a large bias and lower concentration will have less impact on the overall results compared to a component with a large concentration component with low bias.

The average bias of all components may provide a better indication whether an analytical method is appropriate for the sample than the biases of the individual components. An inappropriate analytical method will result in both high bias and uncertainty for certain components, and a high average bias. Thus, a weighted bias calculation may be a better indicator of the impact of the method bias on an application than the average bias. For a weighted bias calculation, the biases of the most abundant components have larger weight in the total bias calculated for the sample. Based on the example sample composition presented in Table 4-3, Table 4-4 provides average and weighted bias estimates for the three SPL pressurized hydrocarbons analytical methods, and shows that weighted bias estimates are generally lower than average bias estimates. This is primarily because low concentration / high bias components such as nitrogen and carbon dioxide have less impact on weighted bias estimates.

Table 4-3. Example Sample for Weighted Bias Calculation

Compound	Weight Percent
CO_2	0.1474
Nitrogen	0.0036
Methane	0.7826
Ethane	1.3794
Propane	2.1769
Iso-Butane	3.0617
n-Butane	3.2978
Iso-Pentane	3.6826
n-Pentane	5.3687
n-Hexane	6.0553
Heptanes	10.4245
Octanes	7.1067
Nonanes	4.0388
Decanes Plus	38.1746
Benzene	0.682
Toluene	3.6357
Ethylbenzene	0.224
m, p-Xylenes	2.7942
C8+	49.3201

Table 4-4. General Method Bias

Analytical Method	Average Bias	Weighted Average Bias
SPL GPA 2103M	1.1%	1.1%
SPL GPA 2186M	3.9%	2.2%
SPL Flash Liberation	8.9%	1.1%

The SPL flash liberation weighted average bias is much lower than the average bias, but is not a good indicator of the method performance for FGOR estimates. This is because the SPL flash liberation has high biases for light end compounds that are flash gas components. This is an example where evaluation of the individual bias, the average bias, and the weighted average bias provides a better indication of the appropriateness of an analytical method for an application. The weighted average bias suggests good performance for SPL flash liberation but the high average bias indicates many compounds must have a high bias, and further investigation determined that many key light hydrocarbon compounds (e.g., C1 – C5) have high biases. Overall, SPL GPA 2103M had the lowest biases of the three methods. Similar to the bias estimates presented in Table 4-2, these data are presented for informational and discussion purposes, and not used for subsequent uncertainty calculations.

4.4 GPA Method 2286

Analysis of gas samples from the tank-to-burner pipeline was conducted with a portable gas chromatograph performing an extended analysis of components up to C6+. This analysis was then combined with the analysis of cylinder samples for heavier hydrocarbons for a compositional analysis to C10+.

4.4.1 Gas composition limitations

The gas samples composition included several main components outside of the GPA 2286 analytical range as shown in Table 4-5. All other components were within the method range.

Table 4-5. GPA 2286 Analytical Range and Sample Composition (mole %)

Component	GPA 2286 Analytical Range	Representative Sample Composition
Methane	50-100	26.4
Ethane	0.02-15	23.4
Propane	0.02-15	21.6

Reproducibility values of GPA 2286 were used to estimate the uncertainty of gas components. Because the methane reproducibility is outside of the analytical range, the ethane reproducibility was assumed. Reproducibility's of ethane and propane were assumed valid in the extended range.[1]

4.4.2 Uncertainties of calculated physical properties

Several physical properties were calculated from the tank-to-burner pipeline gas compositional analysis; for example, real density, relative density, molecular weight; and calorific values are commonly obtained from calculation. Additional, and more complex calculations, like dew point, were performed with commercially available Process Simulation Modeling/Equation of State software programs introduced in Appendix V.

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[1] Refer to GPA 2261 Scope, GPA RR 188 and GPA TP-31.

This section provides the basic uncertainty calculation methodology used for relative density and other properties using a method developed in accordance with ISO 6976-16.

Molecular weight

$$\mathrm{MW} = \sum_{i=1}^{N} MW_i \cdot x_i$$

$$\begin{aligned} u^2(MW) = &\left(\sum_{i=1}^{N}\sum_{j=1}^{N} MW_i \cdot MW_j \cdot u(x_i) \cdot u(x_j) \cdot r(x_i, x_j)\right) \\ &+ \left(\sum_{i=1}^{N}\sum_{j=1}^{N} x_i \cdot x_j \cdot u(MW_i) \cdot u(MW_j) \cdot r(MW_i, MW_j)\right) \end{aligned} \quad (4.1)$$

Compressibility factor

$$u^2(Z) = 4 \cdot S^2 x \left(\left(\sum_{i=1}^{N}\sum_{j=1}^{N} s_i \cdot u(x_i) \cdot r(x_i, x_j) \cdot s_j \cdot u(x_j)\right) + \sum_{i=1}^{N} x_i^2 \cdot u^2(s_i)\right) \quad (4.2)$$

Density

$$\begin{aligned} \left(\frac{u(d)}{d}\right)^2 = &\sum_{i=1}^{N}\sum_{j=1}^{N}\left(\frac{MW_i}{MW} + \frac{2 \cdot s_i \cdot s}{Z}\right) \cdot u(x_i) \cdot r(x_i, x_j) \cdot u(x_j) \cdot \left(\frac{MW_j}{MW} + \frac{2 \cdot s_j \cdot s}{Z}\right) \\ &+ \sum_{i=1}^{N}\sum_{j=1}^{N} \frac{x_i \cdot u(MW_i) \cdot r(MW_i, MW_j) \cdot u(MW_j) \cdot x_j}{MW^2} \\ &+ \frac{4 + s^2 \cdot \sum_{i=1}^{N} x_i^2 \cdot u^2(s_i)}{Z^2} + \left(\frac{u(R)}{R}\right)^2 \end{aligned} \quad (4.3)$$

Relative Density

$$\left(\frac{u(G)}{G}\right)^2 = \sum_{i=1}^{N}\sum_{j=1}^{N}\left(\frac{MW_i}{MW}+\frac{2\cdot s_i\cdot s}{Z}\right)\cdot u(x_i)\cdot r\left(x_i,x_j\right)\cdot\left(\frac{MW_j}{MW}+\frac{2\cdot s_j\cdot s}{Z}\right)\cdot u\left(x_j\right) + \sum_{i=1}^{N}\sum_{j=1}^{N}\frac{x_i\cdot u(MW_i)\cdot r\left(MW_i,MW_j\right)\cdot u(MW_j)\cdot x_j}{MW^2} + \frac{4+s^2\cdot\sum_{i=1}^{N}x_i^2\cdot u^2(s_i)}{Z^2}+\left(\frac{u(MW_{air})}{MW_{air}}\right)^2+\left(\frac{u(Z_{air})}{Z_{air}}\right)^2 \qquad (4.4)$$

Where:

d density (g/mL)

G Relative density (dimensionless)

m Component mass in 1 g of CRM (mass fraction) (g)

MW Molecular Weight (g/gmol)

N Total number of elements or components of a set

$r(x_i,x_j)$ Correlation coefficient of x_i to x_j

R Ideal gas constant

s Standard deviation

u Standard uncertainty (%)

x_i Molar fraction (g/gmol)

Z compressibility factor

Detailed documentation is in ISO 6976. Reported properties are included in extended certificates of analysis included in Annex 2. Table 4-6 and Table 4-7 shows gas compositional analysis and calculated properties with associated uncertainty. Uncertainties were estimated with GPA 2261 reproducibility formulas (Table 4-6) as discussed above.

Table 4-6. GPA 2261-13 Reproducibility

Component	Range (%mol)	Reproducibility	Component	Range (%mol)	Reproducibility
Nitrogen	0.02-15	$0.158x^{1/2}$	Iso-butane	0.02-8	$0.018x^{1/2}$
Methane	50-100	$91000x^{-3}$	N-Butane	0.02-8	$0.033x^{1/2}$
CO_2	0.02-15	$0.12x^{1/3}$	Iso-Pentane	0.02-4	$0.025x^{1/4}$
Ethane	0.02-15	$0.0315x^{1/3}$	N-Pentane	0.02-4	$0.026x^{1/3}$
Propane	0.02-15	$0.026x^{1/2}$	Hexanes Plus	0.02-2	$0.051x^{1/2}$

Table 4-7. Gas Composition for Property Calculation Examples

Component	%mol	Component	%mol	Component	%mol
Nitrogen	3.428	n-Pentane	3.58	n-Heptane	1.288
Methane	26.352	2,2-Dimethylbutane	0.054	Toluene	0.112
CO_2	1.674	2-Methylpentane	0.988	n-Octane	0.312
Ethane	23.171	2,3-Dimethylbutane	0.161	o-Xylene	0.022
Propane	21.622	3-Methylpentano	0.506	n-Nonane	0.008
2-Methylpropane	4.266	Cyclopentane	0.196	n-Decane	0.004
n-Butane	7.544	n-Hexane	1.226		
2-Methylbutane	3.339	Benzene	0.147		

Table 4-8. Gas Properties from Composition

Property	Value	U	%U (95% CI
Molecular Weight $(g{\cdot}gmol)^{-1}$	38.9	0.2	0.6%
Compressibility Factor (dimensionless)	0.9865	0.0009	0.09%
Real density ($kg{\cdot}m^3$ @60°F)	1.662	0.009	0.6%
Specific gravity (Relative density 60/60, dimensionless)	1.359	0.008	0.6%

5. Sample Collection and Sample Handling Perturbation Studies

Procedures for sample collection and sample handling in the laboratory for analysis of condensate applied to the PHLSA project are based on standard methods designed for general purposes. However, these methods do not prescribe provisions for control of all parameters that could be critical for results. For example, sample handling parameters that are not defined include variations in techniques and general procedures, such as the stirring of samples, subject to analyst interpretation.

5.1 Sample Handling Perturbation Study

Supporting data and calculations for the information presented in this section can be found in Annex 3.

Table 5-1 summarizes the sample handling parameters that were evaluated. CRM samples were used to conduct this perturbation study. Only the thermal conductivity detector (TCD) portion of GPA Method 2103 (i.e., measures C1 – C5 and C6+) was used for sample analysis because errors of sampling and sample mishandling generally affect lighter components most prominently. 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 5-1 was conducted for both constant pressure (CP) cylinder CRM samples and constant volume (CV) cylinder CRM samples

Table 5-1. Laboratory Sample Handling Perturbations for CP and CV Cylinders

Parameter	Pert 1	Pert 2	Pert 3	Pert 4	Baseline	Pert 1	Pert 2	Pert 3	Pert 4
Mixing (rocks)	0	6	12	18	**24**				
Purging (ml/sec.)					**1**	**2**	**4**	**8**	**12**
Pressure (psia)	365	415	465	**515**	**1,115**[A]				
Temperature					**55°F**	65°F	70°F	***73***	75

A. Standard liquid injection pressure.

ASTM E1169 “Standard Practice for Conducting Ruggedness Tests” provides tools for assessing the statistical significance of a method parameter (e.g., sample temperature, sample mixing) “effect” over method outcomes. In this discussion, some concepts of ASTM E1169 will be used:

- Ruggedness; the insensitivity of a test method to departures from specified test or environmental conditions.
- Factor: a test parameter that may affect either the result obtained from the use of a test method or the variability of that result.
- Effect: the impact of a factor (method parameter) change upon analytical results.

The effect of a method parameter on analytical results for individual sample components does not necessarily represent the effect of the method parameter over analytical results for composite sample properties. To assess the combined effects of method parameters, the vapor pressure by Raoult's Law was calculated and included in the evaluation.

The ruggedness test procedure consists of the following steps:

- Identification of relevant factors;
- Base line condition definition;
- Selection of appropriate levels to be used in experiment runs;
- Execution of runs in a random order;
- Calculation of High and Low level factors and results from experimental data;
- Statistical analysis to determine the effect of factors on the test method results; and
- Results revision and conclusions

The experimental design shown in Table 5-1 includes more experiments than high and low conditions, and a modification of the ASTM method was needed in order to obtain only two levels. For example, for the mixing factor, with perturbations of 0, 6, 12, 18, and 24 rocks, the low condition factor was assumed to be the average of 0 and 6 rocks and the high condition factor was assumed to be the average of 18 and 24 rocks.

Because the effect of each factor was isolated (i.e., only one factor was changed for each perturbation), there were no factor interactions and direct determination of the effect of each factor was possible. This exceeds the experimental design requirements of ASTM E1169. Also, the number of data points is six to ten times larger than the ASTM method requirements, and the larger data set produces a more robust result.

The statistical significance of a factor is determined by comparing the standard deviation of effect differences caused by changing the factor and the standard deviation of the effect differences from the entire set of factor change experiments.

A half-normal plot is used to present potentially statistical significant factors. Plot construction steps are:

- Construct a results table with analytical results differences against baseline condition result, these data will be at abscissa axis (i.e., x values);
- Sort absolute differences in decreasing order;
    - Ordinates are standard deviations as indicated by ASTM D1169 Table A2.1 or can be calculated applying the normal probability: $\Phi^{-1}(0.5+0.5[e - 0.5]/E)$ (ASTM E1169 – 14 A2.1), excel formula is "=INV.NORM(0.5+0.5*(e-0.5)/E,0,1)" where E is the number of Effects, e is the increasing number from 1 to E, and $\Phi(x)$ is the probability that the standard normal distribution gives a value less than x. Values for five factors correspond to 0.126, 0.385, 0.674, 1.036 and 1.645;
- Calculate one standard deviation for the full data set of differences;
- Plot the standard deviation as solid line up to 2 standard deviations and plot parameter (factors) differences as dots.

Half normal plot interpretation: Method parameters (factors) with greater impact on analytical results are further from the origin than method parameters with lower impact on analytical results. The straight line represents one standard deviation. Method parameters with statistical significant difference are far from the line.

5.1.1 Ruggedness Test Calculations

Conducting a ruggedness test is based on making systematic changes to method parameters, called factors in the ASTM method, and then observing associated effects upon each test result. Factors are features of the test method or of the laboratory environment that can vary across laboratories and can impact the method outcome.

Perturbation factors chosen for ruggedness testing are those believed to have potential to affect results. Identified perturbation factors and corresponding change values listed in Table 5-

1 were performed isolated from other factors; that is, other factors were maintained at the most conservative sample handling condition (base line condition): mixing (24 rocks), pressure (1,100 psig), temperature (55 °F) and purge rate (1 ml/min), and CP sample cylinder.

A statistical analysis to determine the impact of perturbation factors on test method results was conducted and is summarized in section 5.1.5. Possible revisions to the test method and specific guidelines to follow to optimize analytical results are discussed in conclusions.

The standard deviation of the method parameter/factor impact on analytical results was calculated as a pooled standard deviation (ASTM D1169 eq. 1):

$$s = \frac{\sum(x_i - \bar{x})}{n-1}$$

$$s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2 + \cdots + (n_n - 1)s_k^2}{n_1 + n_2 + \cdots + n_k - k}}$$

$$s_{eff} = \sqrt{\frac{4s_p^2}{n}} \tag{5.1}$$

$$t = \frac{|effect\ difference|}{s_{eff}} \tag{5.2}$$

Where:

s	Standard deviation
n	Number of runs or data
x_i	Analytical result
N	Number of effects in the array
r	Number of replicates of the effect
k	Degrees of freedom = Number of data sets (i.e., number of factors)
s_p	Pooled standard deviation
s_{eff}	Estimated standard deviation of test result
t	Critical value of *t* distribution

The student *t* value was calculated by dividing the absolute value of effect difference by s_{eff} and the probability of the *t* score was based on two tails and (Number of effects-1)(replicates-1) degrees of freedom.

Effects with probability lower than 0.05 indicate a statistically significant perturbation (i.e., statistically significant at 95% CI). These effects can be identified in the half-normal plot, where potential significant perturbation effects are those which fall farthest to the right of the line representing the slope of s_{eff}.

5.1.2 Example calculation for Vapor Pressure

This example presents the general calculation procedure followed to identify sample handling parameters that have a statistically significant impact on Vapor Pressure calculated from analytical results using Raoult's Law.

The Vapor Pressure calculated from the Reference Material Certified composition is *203.38 psig*. Table 5-2 lists the Vapor Pressures calculated from the CRM sample associated with the indicated sample handling perturbation (i.e., the indicated "factor" perturbation). Table 5-3 lists the differences between the reference vapor pressure of 203.38 psig and the vapor pressure listed in Table 5-2 (i.e., the "effects" or changing each factor).

Table 5-2. Calculated Vapor Pressures from Compositional Analysis

Parameter	**CP Sampling**				
MIXING (Rocks)	24	18	12	6	0
Vapor Pressure (psig)	201.83	201.73	201.53	201.53	202.05
PURGE RATE (mL/min)	1	2	3	8	12
Vapor Pressure (psig)	202.57	202.63	202.91	202.87	202.89
PRESSURE (psig)	1100	500	450	400	350
Vapor Pressure (psig)	203.05	201.19	201.40	199.08	194.72
TEMPERATURE (°F)	55	65	70	73	75
Vapor Pressure (psig)	202.33	201.18	201.67	202.34	202.40
Parameter	**CV Sampling**				
MIXING (Rocks)	24	18	12	6	0
Vapor Pressure (psig)	200.42	200.27	199.86	199.35	199.42
PURGE RATE (mL/min)	1	2	3	8	12
Vapor Pressure (psig)	202.49	202.64	202.61	201.77	201.18
PRESSURE (psig)	1100	500	450	400	350
Vapor Pressure (psig)	207.31	204.09	203.30	202.83	199.72
TEMPERATURE (°F)	55	65	70	73	75
Vapor Pressure (psig)	206.80	205.47	209.03	204.27	209.03

Table 5-3. Vapor Pressures Differences (Sample Analysis - CRM)

Parameter	CP Sampling				
MIXING (rocks)	24	18	12	6	0
Δ Vapor Pressure (psig)	-1.45	-1.55	-1.75	-1.85	-1.23
PURGE RATE (mL/min)	1	2	3	8	12
Δ Vapor Pressure (psig)	-0.71	-0.65	-0.37	-0.41	-0.39
PRESSURE (psig)	1100	500	450	400	350
Δ Vapor Pressure (psig)	-0.23	-2.09	-1.88	-4.20	-8.56
TEMPERATURE (°F)	55	65	70	73	75
Δ Vapor Pressure (psig)	-0.95	-2.10	-1.61	-0.94	-0.88
Parameter	**CV Sampling**				
MIXING (rocks)	24	18	12	6	0
Δ Vapor Pressure (psig)	-2.86	-3.01	-3.42	-3.93	-3.86
PURGE RATE (mL/min)	1	2	3	8	12
Δ Vapor Pressure (psig)	-0.79	-0.63	-0.67	-1.51	-2.10
PRESSURE (psig)	1100	500	450	400	350
Δ Vapor Pressure (psig)	4.03	0.81	0.02	-0.45	-3.56
TEMPERATURE (°F)	55	65	70	73	75
Δ Vapor Pressure (psig)	3.52	2.19	5.75	1.00	5.75

Table 5-4 presents the calculated differences between analytical results for the low condition factor (i.e., the average of the analytical results for the two lowest perturbation for each sample handling parameter / factor) and the analytical results for the high condition factor (i.e., the average of the analytical results for the two highest perturbations for each sample handling parameter / factor). For example, the average analytical results of mixing 24 and 18 times is the high value while average analytical results of mixing 0 and 6 times is the low value.

Table 5-4. Effect on Vapor Pressures of Low Condition and High Condition Factors

Component **Parameter[a]**	**CO_2**	**N_2**	**Methane**	**Ethane**	**Propane**	**i-Butane**	**n-Butane**	**i-Pentane**	**n-Pentane**	**Hexanes Plus**	**Vapor Pressure**
CP/CV (wt%)	**0.050**	**0.071**	**0.052**	0.019	-0.011	-0.006	-0.023	-0.024	-0.031	0.019	-0.637
Mixing (wt%)	-0.013	0.015	0.014	**-0.100**	0.011	**0.011**	**0.050**	**0.072**	**0.121**	-0.036	-3.831
Purge Rate (wt%)	0.008	0.008	0.013	-0.003	-0.001	0.000	0.002	0.008	0.014	-0.042	0.409
Pressure (wt%)	0.013	0.001	**0.136**	0.038	**0.030**	**0.012**	0.035	0.027	0.040	**-0.345**	**4.825**
Temperature (wt%)	0.001	0.000	-0.007	0.000	-0.001	0.002	-0.006	0.008	0.027	-0.018	-1.596

a: Parameters difference with a statistically significant impact upon results are shown in bold. Additional information is provided in the tables and figures below.

Plotting these data with the s_{eff} slope is:

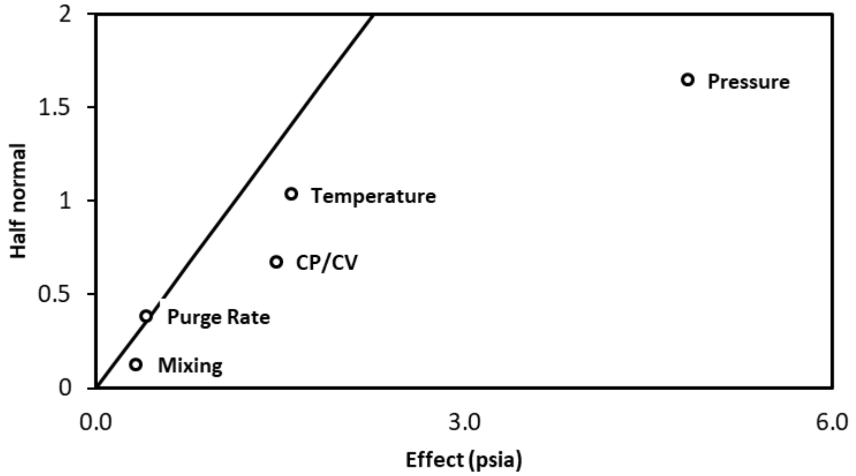

Figure 5-1. Half normal plot of effects over vapor pressure

5.1.3 Assessment of sample handling perturbations

The effects of sample handling parameters on CO_2, N_2, C1-C5, C6+, and vapor pressure calculated with Raoult’s Law were calculated in order to identify the magnitude and statistical significance of these effects. These results are summarized in Table 5-5 and include, for each measurement and parameter/factor, the absolute value of the effect, the Student t-value, and the p-value. P-values less than 0.05 indicate statistically significant factors for the indicated measurement.

Table 5-6 summarizes the results in Table 5-5, by indicating for each measurement and parameter/factor, statistically significant factors.

Table 5-5. Detailed Ruggedness Test Results

Measurement	Parameter	|Effect|	Student's t	p-value
Carbon Dioxide	CP/CV	0.050	3.564	**<0.001**
	Pressure	0.013	0.936	0.357
	Mixing	0.013	0.918	0.366
	Rate	0.008	0.612	0.545
	Temperature	0.001	0.090	0.929
Nitrogen	CP/CV	0.071	2.925	**0.004**
	Pressure	0.015	0.617	0.542
	Temperature	0.008	0.319	0.752
	Mixing	0.001	0.041	0.968
	Rate	0.000	0.000	1.000
Methane	Pressure	0.136	5.103	**<0.001**
	CP/CV	0.052	1.971	0.051
	Mixing	0.014	0.531	0.600
	Rate	0.013	0.479	0.635
	Temperature	0.007	0.254	0.802
Ethane	Mixing	0.100	3.234	**0.003**
	Pressure	0.038	1.248	0.222
	CP/CV	0.019	0.619	0.537
	Rate	0.003	0.097	0.923
	Temperature	0.000	0.008	0.994
Propane	Pressure	0.030	3.912	**<0.001**
	CP/CV	0.011	1.512	0.133
	Mixing	0.011	1.459	0.156
	Rate	0.001	0.133	0.895
	Temperature	0.001	0.099	0.921
i-Butane	Pressure	0.012	2.670	**0.012**

Measurement	Parameter	|Effect|	Student's t	p-value
	Mixing	0.011	2.500	**0.019**
	CP/CV	0.006	1.432	0.154
	Temperature	0.002	0.511	0.613
	Rate	0.000	0.057	0.955
n-Butane	Mixing	0.050	2.833	**0.008**
	Pressure	0.035	1.978	0.058
	CP/CV	0.023	1.295	0.197
	Temperature	0.006	0.313	0.756
	Rate	0.002	0.142	0.888
i-Pentane	Mixing	0.072	3.464	**0.002**
	Pressure	0.027	1.311	0.201
	CP/CV	0.024	1.135	0.258
	Rate	0.008	0.397	0.694
	Temperature	0.008	0.385	0.703
n-Pentane	Mixing	0.121	3.856	**<0.001**
	Pressure	0.040	1.272	0.214
	CP/CV	0.031	0.991	0.323
	Temperature	0.027	0.843	0.407
	Rate	0.014	0.453	0.654
Hexane Plus	Pressure	0.345	5.794	**<0.001**
	Rate	0.042	0.713	0.482
	Mixing	0.036	0.608	0.548
	CP/CV	0.019	0.326	0.745
	Temperature	0.018	0.293	0.771
Vapor Pressure	Pressure	4.825	4.268	**<0.001**
	Temperature	1.596	1.412	0.169
	CP/CV	1.470	1.300	0.195
	Purge Rate	0.409	0.361	0.720
	Mixing	0.332	0.293	0.772

Note: p-values in bold are **less than** statistical significance criterion of 0.05.

Table 5-6. Summary of Results

Parameter / Factor	Component										
	CO2	N2	Methane	Ethane	Propane	i-Butane	n-Butane	i-Pentane	n-Pentane	Hexanes Plus	Vapor Pressure
CP/CV	X	X									
Mixing				X		X	X	X	X		
Purge Rate											
Pressure			X		X	X				X	X
Temperature											

X indicates Parameters that have a statistically significant impact on the CRM component.

5.1.4 Half Normal Plots.

The following half normal plots illustrate method parameters effects upon results for the measurements listed in Table 5-5. Sample handling parameters (factors) with greater impact on analytical results are far from the origin, and method parameters with lower impact on analytical results are closer to origin. The straight line represents one standard deviation. Method parameters with statistical significant difference are far from the line.

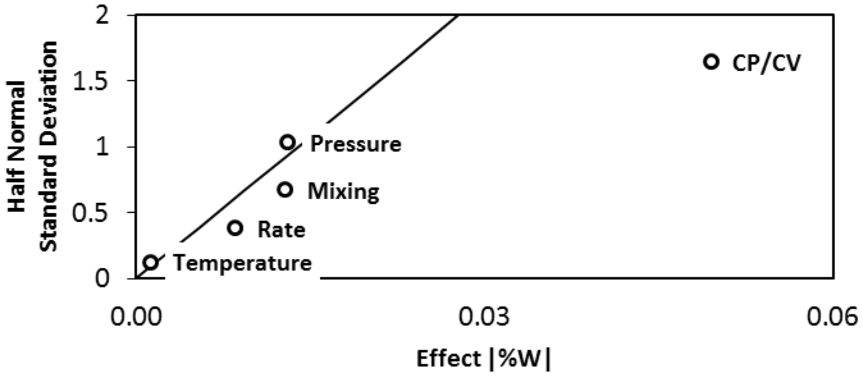

Figure 5-2. Half normal plot of effects over Carbon Dioxide.

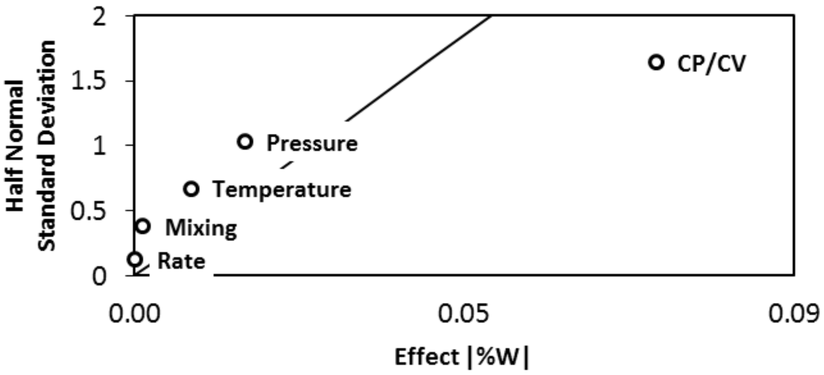

Figure 5-3. Half normal plot of effects over Nitrogen

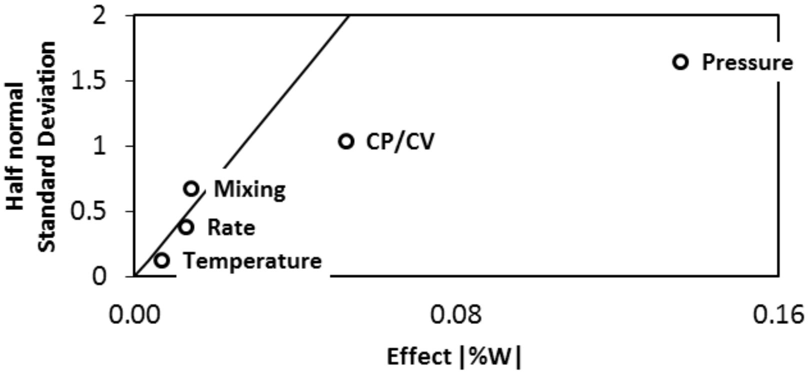

Figure 5-4. Half normal plot of effects over Methane

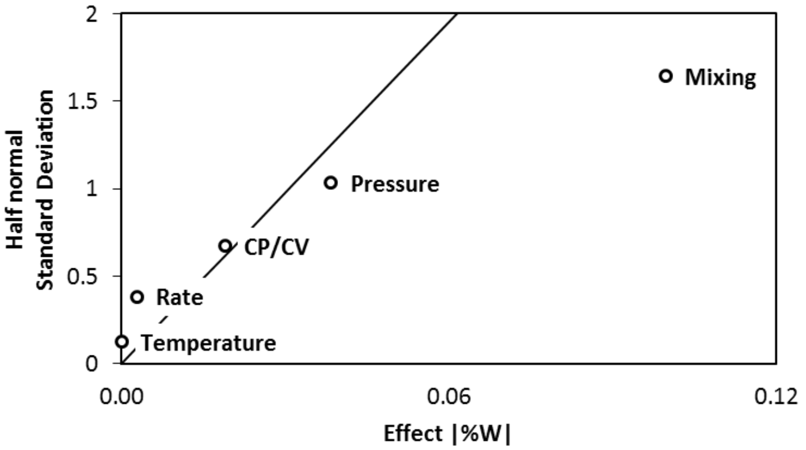

Figure 5-5. Half normal plot of effects over Ethane

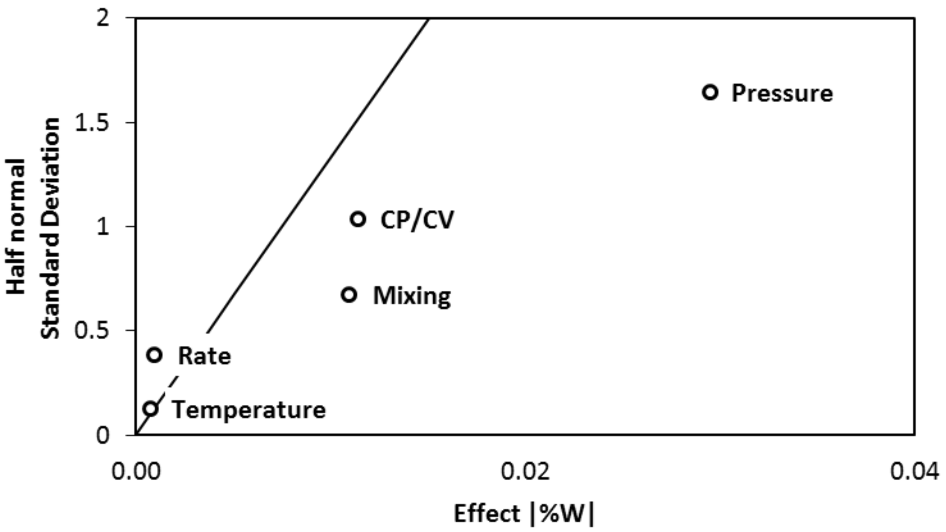

Figure 5-6. Half normal plot of effects over Propane

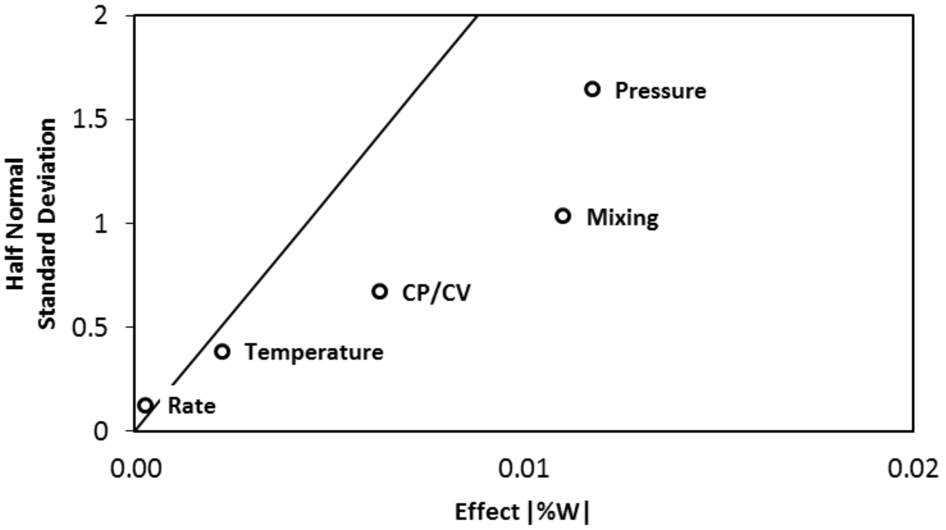

Figure 5-7. Half normal plot of effects over i-Butane

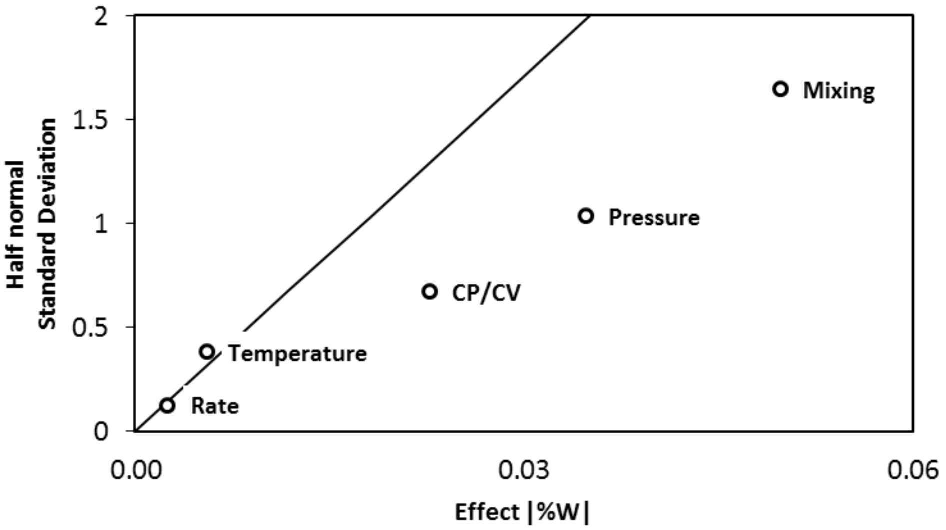

Figure 5-8. Half normal plot of effects over n-Butane

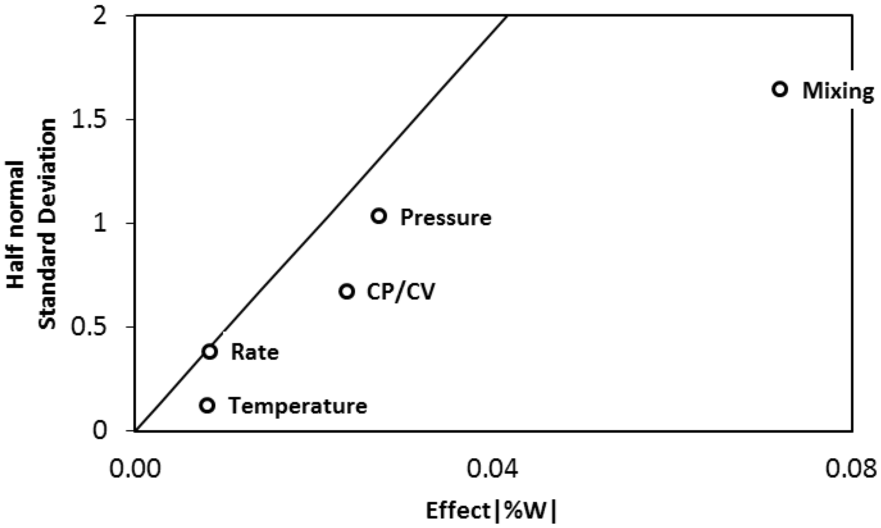

Figure 5-9. Half normal plot of effects over i-Pentane

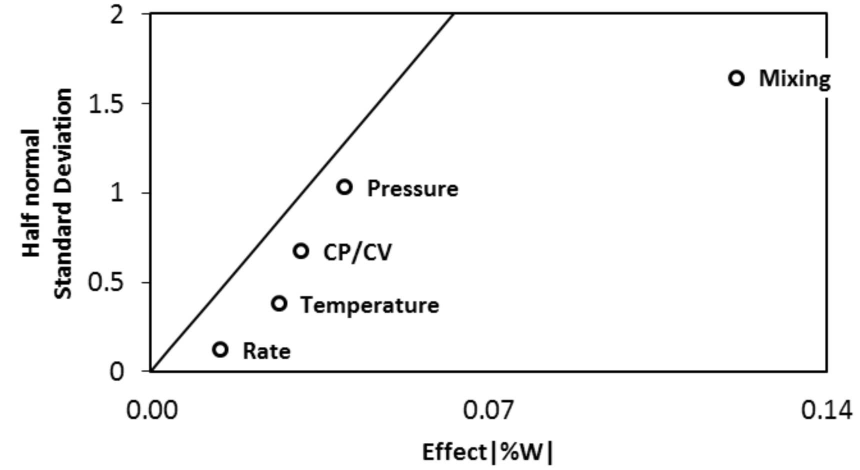

Figure 5-10. Half normal plot of effects over n-Pentane

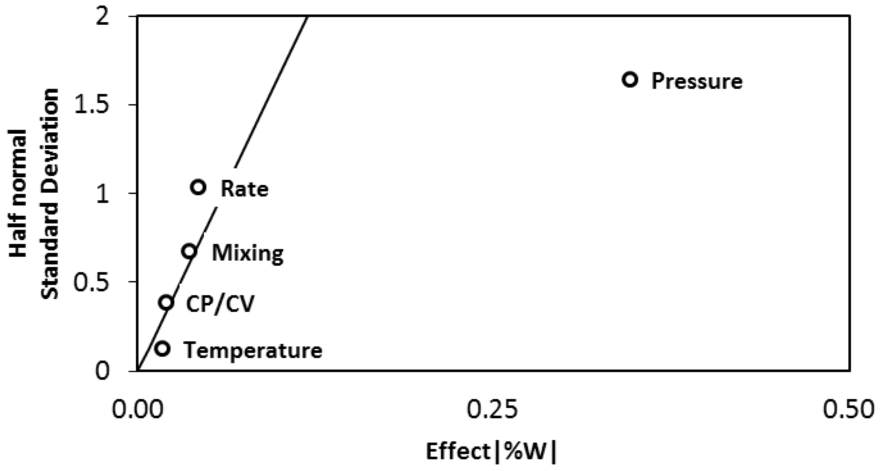

Figure 5-11. Half normal plot of effects over Hexanes plus

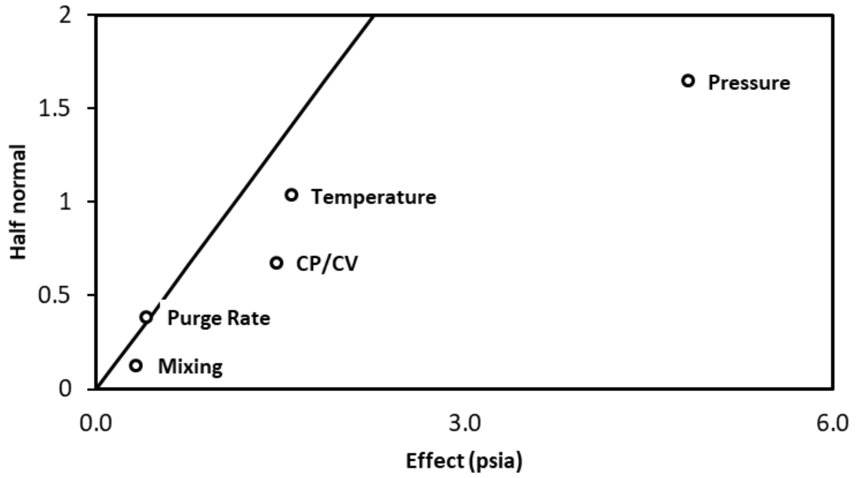

Figure 5-12. Half normal plot of effects over Vapor pressure

5.1.5 Conclusions on sample handling perturbations

- The statistical analysis indicates that the sample handling parameters cylinder pre-charge pressure and number of mixing rocks impact the analytical results for compounds in the pressurized condensate samples. However, there is insufficient statistical evidence to conclude that purge rate and sample temperature have influence over the analytical results of tested samples.

- Sample collection cylinder type (constant pressure cylinder or two valve constant volume cylinder) influences the light end compounds nitrogen and carbon dioxide.

- In order to avoid losses of volatile components, it is recommended that the pressure applied to pre- charge should be a minimum of 300 psi above the simple collection pressure. GPA 2174 guidelines recommend that the pre-charge sample pressure be a minimum of 200 psi greater than the sample vapor pressure at injection valve temperature. The number of rocks for sample homogenization should be between 18 and 24.

5.2 Sample Collection Perturbation Study

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

- Sample cylinder type (constant pressure (CP) cylinder and constant volume (CV) cylinder)
    - Note that Section 5.1 evaluated laboratory sample handling parameters using lab-prepared CRM samples in CP cylinders and CV cylinders, and compared analytical results for these samples. This section evaluates analytical results of CP and CV cylinder samples simultaneously collected from the test facility separator from adjacent sample probes.
- Sample collection rate (20, 40, 60, 100, and 180 ml/min)
- Sample collection initiation time after the end of the well cycle (< 0, < 30, 90, and 150 minutes after well cycle). The well cycle is assumed to start when fluids first begin to flow from the well to the separator and is assumed to end after the last separator-to-tank liquids dump.
- Sample collection location (sample probe and oil box oil level sight glass)

Sample collection perturbations were primarily evaluated by comparing bubble point pressure (P_{BP}) / separator pressure during sample collection (P_{sc}) ratios for all samples. Bubble point pressures (at the sample collection temperature) were calculated by PSM/EOS from the measured pressurized condensate composition, with P_{BP} / P_{sc} ratios greatly deviating from 1.0 being indicative of possible sample collection bias. Operational performance checks (OPC) data analysis and discussion that follow show that P_{BP} is very sensitive to methane and nitrogen (i.e., air) in condensate samples, and that samples that lose some methane or have some air contamination may have anomalous P_{BP}/P_{SC}, but still provide reasonable estimates of flash gas volume and composition. Thus, P_{BP}/P_{SC} is likely a very conservative OPC for sample collection and analysis results.

Supporting data and calculations for the data tables and figures in this section are in the following Excel document in Appendix VI:

PHLSA Study Task 8 Sample Collection Data.xlsm

GPA 2103 analytical results with the nitrogen mathematically removed were used for these evaluations.

5.2.1 Sample cylinder type perturbation study

Overview of data collected and data analysis approach

Paired CV cylinder and CP cylinder pressurized condensate samples were simultaneously collected during sampling events throughout the project 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.

Paired CP cylinder /CV cylinder pressurized condensate samples data were evaluated using the following steps to determine if there were statistically significant differences between the sample collection methods during the PHLSA study.

A. Initial paired data comparisons t-statistic test. A paired data comparisons test was initially used as a screening tool to determine whether CP vs. CV results (e.g., condensate species and parameters calculated based on the condensate composition) were significantly different. This statistical analysis (hypothesis test) applies when evaluating the difference in the value of paired observations/measurements that are not independent.

   For a two-tailed paired data comparisons test, the hypothesis is:

   H_0: $\mu_d = \mu_{md}$ versus H_a: $\mu_d \neq \mu_{md}$

Where:

H_0 = null hypothesis

H_a = alternative hypothesis

μ_d = mean of the paired differences population

μ_{md} = hypothesized mean of paired differences

The t-statistic with n-1 degrees of freedom is:

$$t = \frac{d_{avg} - \mu_{md}}{s_{davg}}$$

Where:

d_{avg} = sample mean difference = $\frac{1}{n}\sum_{i=1}^{n} d_i$

d_i = difference between the i^{th} pair of samples/measurements

s_{davg} = standard error of the mean difference = $\frac{s_d}{\sqrt{n}}$

s_d = sample standard deviation = $\left(\frac{\sum_{i=1}^{n}\left(d_i - d_{avg}\right)^2}{n-1}\right)^{0.5}$

n = number of paired samples

For this analysis, μ_{md}, the hypothesized mean of paired differences, was assumed to be zero.

The t-statistic test is based on data with a normal probability distribution, and step B evaluates this assumption.

B. Normal probability distribution check. Check whether the paired data sets differences can be assumed to have a normal probability distribution. This check was conducted using a goodness-of-fit test based on use of the chi-square distribution, and observed frequencies for sample data categories are compared to the frequencies that would be expected for a population with a normal distribution. Anderson et al[2] summarize the procedure as follows:

I. State the null and alternative hypotheses:

H_0: The population has a normal probability distribution

H_a: The population does not have a normal probability distribution

II. Select a random sample and

a. Compute the sample mean and sample standard deviation

b. Define intervals of values so that the expected frequency is at least five for each interval. Using equal probability intervals is a good approach.

c. Record the observed frequency of data values f_i in each interval defined.

III. Compute the expected number of occurrences e_i for each interval of values defined in II.b. Multiply the sample size by the probability of a normal random variable being in the interval.

IV. Compute the value of the test statistic

$$\chi^2 = \sum_{i=1}^{k} \frac{(f_i - e_i)^2}{e_i}$$

where k is the number of intervals determined in II.b.

V. Rejection rule:

Using test statistic: Reject H_0 if $\chi^2 > \chi_\alpha^2$

Using p value: Reject H_0 if p-value $< \alpha$

Where α is the level of significance and there are k-3 degrees of freedom.

C. Outliers check. Check for data outliers using the Dixon's Q-test and Grubbs test for outliers. Consider data an outlier if identified as an outlier by both tests.

Grubb's test for outliers (one sided test)

Grubb's test identifies a single outlier, and after that outlier is removed from the data set additional outliers can be detected. The general procedure for the Grubb's test is:

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[2] Anderson, Sweeney, & Williams, "Statistics for Business and Economics, 8th Edition". South-Western/Thomson Learning, 2002.

I. Organize sample data from smallest number to largest number.

II. State the null and alternative hypotheses:

H_0: There are no outliers in the data set

H_a: There is at least one outlier in the data set

III. Calculate the Grubb's test statistic

$$G = \frac{X_{avg} - X_{min}}{s} \; or \; \frac{X_{max} - X_{avg}}{s}$$

Where:

s = sample standard deviation

X_{min} = minimum value

X_{max} = maximum value

X_{avg} = sample mean

IV. Reject H_0 if $G > G_{critical}$ at significance level α

Dixon's Q-test

Dixons Q-test identifies a single outlier. After that outlier is removed from the data set, literature guidance varies regarding whether additional outliers can be detected. For this outlier analysis, it was assumed that a second outlier could be identified using the Dixon's Q-test, but outliers were only removed from the data set if detected by both the Grubb's and Dixon's tests (i.e., conservative assumptions regarding outlier removal were used).

The general procedure for the Dixons Q-test is:

I. Organize n sample data from smallest number to largest number (x_1 to x_n), or largest number smallest number (x_1 to x_n) with the suspected outlier the first number (i.e., at the x_1 position).

II. Calculate the test statistic (for data sets larger than 14)

$$Q = r_{22} = \frac{x_3 - x_1}{x_{n-2} - x_1}$$

Where:

n = number of elements in the data set

III. If $Q > Q_{critical}$ at significance level α, then x_1 can be considered an outlier

D. Normal probability distribution check, without outliers. Check whether the paired data sets differences without statistical outliers can be assumed to have a normal probability distribution using the goodness-of-fit test described above in Step B.

E. WSRT test. Use the Wilconxan Sign-Rank Test (WSRT) to test the null hypothesis that two populations are identical. The WSRT can be used when the population cannot be assumed to have a normal distribution. The general procedure is as follows:[3]

I. State the null and alternative hypotheses:

H_0: the difference between paired samples or measurements follows a symmetric distribution around zero

H_a: the difference between paired samples or measurements does not follow a symmetric distribution around zero (i.e., the two populations are not identical)

II. For each sample or measurement pair ($x_{1,i}$ and $x_{2,i}$), calculate $|x_{2,i} - x_{1,i}|$ and the sign (i.e., + or -) of $(x_{2,i} - x_{1,i})$, where i = 1 to N and N = number of sample pairs.

III. Exclude pairs with $|x_{2,i} - x_{1,i}| = 0$ and calculate N_r, where N_r = N – number of pairs with $|x_{2,i} - x_{1,i}| = 0$

IV. Order the N_r pairs from smallest to largest $|x_{2,i} - x_{1,i}|$

V. Rank the pairs from smallest to largest with the smallest $|x_{2,i} - x_{1,i}|$ with a rank of 1. R_i denotes the rank.

VI. Calculate the test statistic W

$$W = \left[\sum_{i=1}^{Nr} sign\left(X_{2,i} - x_{1,i}\right) * R_i \right]$$

VII. Under the null hypothesis, W follows a specific distribution that has an expected value of 0 and a variance of

$$\frac{N_r\left(N_r + 1\right)\left(2N_r + 1\right)}{6}$$

VIII. As N_r increases, the sampling distribution of W converges to a normal distribution and for $N_r > 10$, a z-score can be calculated as

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[3] https://en.wikipedia.org/wiki/Wilcoxon_signed-rank_test

$$z = \frac{W}{\sigma_W}$$, where σ_W = SQRT(variance)

IX. Reject H_0 if $|z| > z_{critical}$

F. Paired data comparisons t-statistic test considering measurement uncertainty. Conduct a paired data comparisons test to determine whether the difference between CP and CV results were significantly greater than the measured or calculated value uncertainty. This test used a single-tailed paired data comparisons test, and the hypothesis is:

H_0: $\mu_d \leq \mu_{md}$ versus H_a: $\mu_d > \mu_{md}$

Where:

μ_d = mean of the paired differences population

μ_{md} = hypothesized mean of paired differences, and assumed to be the analytical uncertainty/ reproducibility

In sum, this analysis evaluated whether the CP/CV differences were greater than the analytical uncertainty at a given statistical significance.

G. Compile additional statistical data and summarize and discuss the results. Additional data includes percent of paired CP/CV samples for which the CP parameter is > the CV parameter, and the ratio of d_{avg} and (CP value + CV value)/2 (i.e., calculate d_{avg} as a percent of the average measured value).

5.2.1.1 Initial paired data comparisons t-statistic test

Table 5-7 lists CP cylinder / CV cylinder paired pressurized condensate samples data for the GPA 2103 analyses, and calculates a t-statistic to test the null hypothesis that the mean of the paired differences population (i.e., d_{avg}) equals 0. The data includes, by column:

Column	Data
A	Measured or calculated compound or parameter. These include condensate compounds and sample bubble point pressure and FGOR calculated by PSM/EOS
B	Engineering units for the compound or parameter.
C	Count – number of paired samples (42)
D	Average CP – average value for all the CP cylinder samples
E	Average CV – average value for all the CV cylinder samples
F	d_{avg} = average difference for the 42 paired samples

G	d_{avg} divided by the average of Average CP and Average CV, expressed as a percentage. Yellow highlighted values are greater than 2%
H	Standard deviation of the paired CP/CV samples differences (d_i values)
I	Standard error of the mean difference
J	t-statistic for the compound or parameter. Red high-lighted t-statistics are greater than the critical t-statistic
K	Critical t-statistic, n-1 degrees of freedom, 95% CI, 2-tailed.

This initial analysis suggests there may be statistically significant differences between CP and CV samples for CO_2, methane, ethane, propane, heptanes, octanes, 2,2,4 trimethylpentane, PSM/EOS bubble point pressure, and PSM/EOS FGOR. 2,2,4 trimethyl pentane concentrations are negligible and further analysis focused on the remaining compounds, with methane data shown in the following subsections as an example.

Table 5-7. CP/CV Cylinders Paired Samples Comparison t-statistic Test Data, H_0: d_{avg} = 0 (GPA 2103 Analysis)

A	B	C	D	E	F	G	H	I	J	K
Compound / Parameter	**Eng. Units**	**Count (n)**	**Average CP**	**Average CV**	**Average difference (d_{avg} =Σdi/n)**	**d_{avg}/ Avg (CP & CV)**	**STDEV (di)**	**Std Error = STDEV(di)/ SQRT(n)**	**ABS(t = d_{avg}/ Std Error)**	**t-critical (95% CI, 2-tailed)**
Carbon Dioxide	mole %	42	0.386	0.347	0.0394	10.74%	0.0361	0.006	7.073	2.021
Nitrogen										
Methane	mole %	42	5.734	5.423	0.3113	5.58%	0.4618	0.071	4.370	2.021
Ethane	mole %	42	5.837	5.750	0.0867	1.50%	0.1374	0.0212	4.091	2.021
Propane	mole %	42	7.529	7.473	0.0562	0.75%	0.1493	0.023	2.439	2.021
Iso-Butane	mole %	42	2.556	2.541	0.0152	0.60%	0.0533	0.008	1.852	2.021
n-Butane	mole %	42	7.863	7.820	0.0427	0.54%	0.1724	0.027	1.607	2.021
Iso-Pentane	mole %	42	5.219	5.196	0.0234	0.45%	0.1119	0.017	1.353	2.021
n-Pentane	mole %	42	7.289	7.257	0.0314	0.43%	0.1693	0.026	1.200	2.021
n-Hexane	mole %	42	5.969	6.020	-0.0508	-0.85%	0.3442	0.053	0.956	2.021
Heptanes	mole %	42	13.116	13.372	-0.2558	-1.93%	0.6699	0.103	2.475	2.021
Octanes	mole %	42	9.980	10.214	-0.2347	-2.32%	0.5902	0.091	2.577	2.021
Nonanes	mole %	42	4.431	4.525	-0.0937	-2.09%	0.3544	0.055	1.714	2.021
Decanes Plus	mole %	42	11.657	11.481	0.1759	1.52%	1.4552	0.225	0.784	2.021
Benzene	mole %	42	0.819	0.826	-0.0072	-0.88%	0.0593	0.009	0.790	2.021
Toluene	mole %	42	2.819	2.866	-0.0464	-1.63%	0.1889	0.029	1.593	2.021
Ethylbenzene	mole %	42	0.207	0.210	-0.0034	-1.61%	0.0117	0.002	1.860	2.021
m, p-Xylenes	mole %	42	2.310	2.348	-0.0374	-1.60%	0.1429	0.022	1.694	2.021
o-Xylene	mole %	42	0.479	0.486	-0.0063	-1.30%	0.0316	0.005	1.286	2.021
2,2,4-Trimethylpentane	mole %	42	0.045	0.046	-0.0011	-2.50%	0.0033	0.001	2.218	2.021
2,2-Dimethylbutane	mole %	42	0.087	0.088	-0.0005	-0.52%	0.0109	0.002	0.268	2.021
2,3-Dimethylbutane	mole %	42	0.340	0.343	-0.0033	-0.96%	0.0321	0.005	0.663	2.021
Cyclopentane	mole %	42	0.418	0.421	-0.0037	-0.88%	0.0395	0.006	0.606	2.021
2-Methylpentane	mole %	42	3.038	3.063	-0.0257	-0.84%	0.2090	0.032	0.796	2.021
3-Methylpentane	mole %	42	1.873	1.886	-0.0124	-0.66%	0.1089	0.017	0.735	2.021
C10+ MW	g/mole	42	215.3	215.5	-0.1695	-0.08%	4.9847	0.769	0.220	2.021
C10+ SG at 60°F		42	0.823	0.824	-0.0008	-0.10%	0.0028	0.000	1.943	2.021
PSM/EOS $P_{Bubble Point}$ @ Tsep	psia	42	221.6	210.9	10.67	4.94%	15.11	2.331	4.579	2.021
PSM/EOS FGOR @ P_{tank}, T_{tank}	scf/bbl	42	261.1	248.5	12.63	4.96%	18.93	2.921	4.325	2.021

5.2.1.2 Normal probability distribution check

Analyses were conducted to determine whether the paired data sets differences can be assumed to have a normal probability distribution. Histograms were developed and a Goodness-of-Fit for Normal Distribution calculation was conducted.

Figure 5-13 is a histogram for the methane CP/CV differences data, and shows a skewed data set. A goodness-of-fit test, shown in Table 5-8 indicted that the methane data set does not have a normal probability distribution.

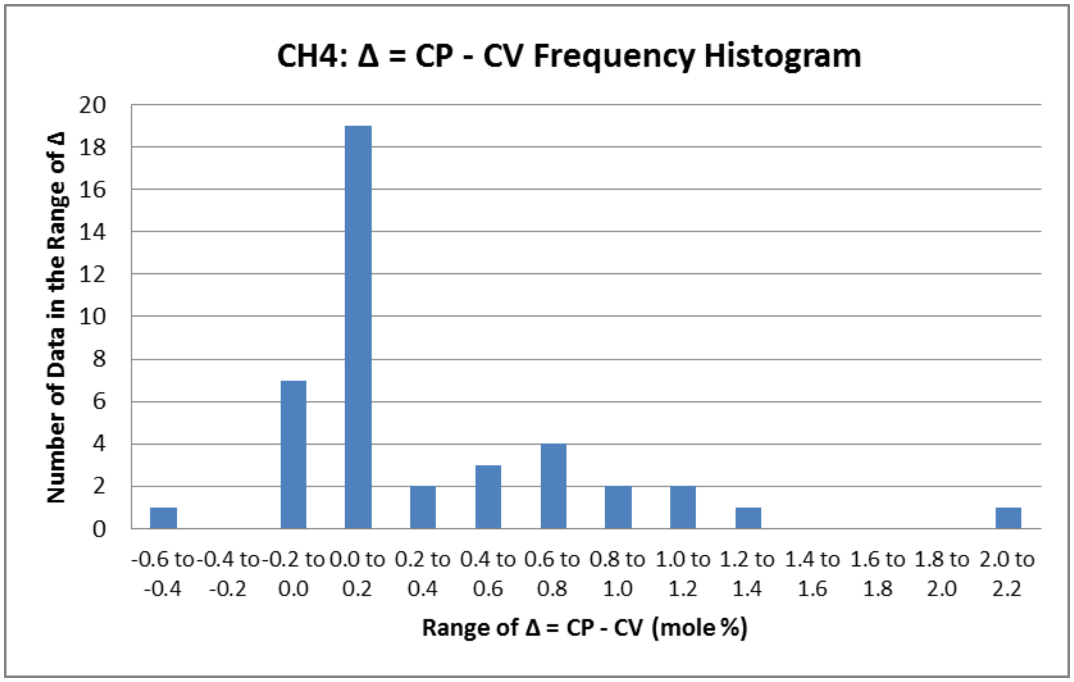


Figure 5-13. Histogram of the CP/CV differences data for methane.

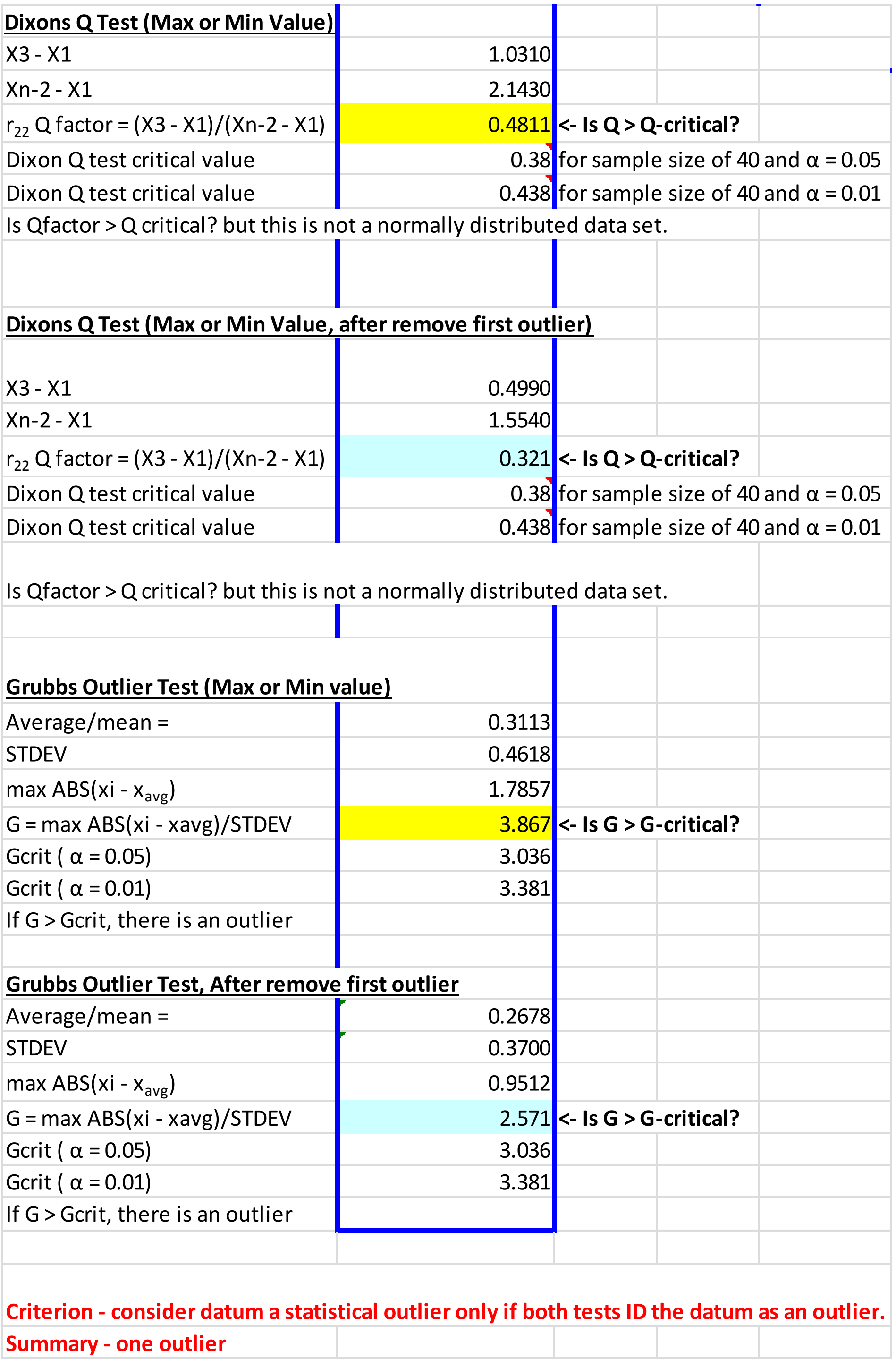
Table 5-8. Goodness-of-fit Test Summary for Methane CP/CV Differences Data

			Z	**Avg-Z*STDEV**	**Expected Frequency (e_i)**	**Observed Frequency (f_i)**	**(fi - ei)**	**(fi - ei)^2**	**(fi - ei)^2/ei**
Avg	STDEV								
0.31135	0.46178				5.25	1	-4.25	18.06	3.44
		Lower 12.5%	1.15	-0.2197	5.25	7	1.75	3.06	0.58
		Lower 25%	0.675	-0.0004	5.25	17	11.75	138.06	26.30
		Lower 37.5%	0.32	0.1636	5.25	3	-2.25	5.06	0.96
		Mid	0.3113	0.3113			0	0.00	
		Upper 37.5%	0.32	0.4591	5.25	3	-2.25	5.06	0.96
		Upper 25%	0.675	0.6231	5.25	1	-4.25	18.06	3.44
		Upper 12.5%	1.15	0.8424	5.25	6	0.75	0.56	0.11
					5.25	4	-1.25	1.56	0.30
								χ^2 = Σ(fi - ei)^2/ei =	36.10
						42		χ_a^2 =	11.07
								d.o.f. =	5
								α =	0.05
				If χ^2 > χa^2; then reject Ho that the population has a normal probability distribution					

5.2.1.3 Outliers check

Table 5-9 summarizes the results of the two outlier tests: Dixons-Q test and Grubb's test for outliers for the methane CP/CV differences data. Both tests identified one outlier, which was the largest CP – CV difference data point.

Table 5-9. Summary of Outlier Tests for Methane CP/CV Differences Data



Dixons Q Test (Max or Min Value)		
X3 - X1	1.0310	
Xn-2 - X1	2.1430	
r_{22} Q factor = (X3 - X1)/(Xn-2 - X1)	0.4811	**<- Is Q > Q-critical?**
Dixon Q test critical value	0.38	for sample size of 40 and α = 0.05
Dixon Q test critical value	0.438	for sample size of 40 and α = 0.01
Is Qfactor > Q critical? but this is not a normally distributed data set.		
Dixons Q Test (Max or Min Value, after remove first outlier)		
X3 - X1	0.4990	
Xn-2 - X1	1.5540	
r_{22} Q factor = (X3 - X1)/(Xn-2 - X1)	0.321	**<- Is Q > Q-critical?**
Dixon Q test critical value	0.38	for sample size of 40 and α = 0.05
Dixon Q test critical value	0.438	for sample size of 40 and α = 0.01
Is Qfactor > Q critical? but this is not a normally distributed data set.		
Grubbs Outlier Test (Max or Min value)		
Average/mean =	0.3113	
STDEV	0.4618	
max ABS(xi - x_{avg})	1.7857	
G = max ABS(xi - xavg)/STDEV	3.867	**<- Is G > G-critical?**
Gcrit (α = 0.05)	3.036	
Gcrit (α = 0.01)	3.381	
If G > Gcrit, there is an outlier		
Grubbs Outlier Test, After remove first outlier		
Average/mean =	0.2678	
STDEV	0.3700	
max ABS(xi - x_{avg})	0.9512	
G = max ABS(xi - xavg)/STDEV	2.571	**<- Is G > G-critical?**
Gcrit (α = 0.05)	3.036	
Gcrit (α = 0.01)	3.381	
If G > Gcrit, there is an outlier		
Criterion - consider datum a statistical outlier only if both tests ID the datum as an outlier.		
Summary - one outlier		

5.2.1.4 Normal probability distribution check, without outliers

Figure 5-14 is a histogram for the methane CP/CV differences data with one statistical outlier removed; the data set is still skewed but to a lesser extent. A goodness-of-fit test with one statistical outlier removed, shown in Table 5-10 still rejects the null hypotheses that the population has a normal probability distribution - although the χ^2 test statistic has been reduced from that in Table 5-9.

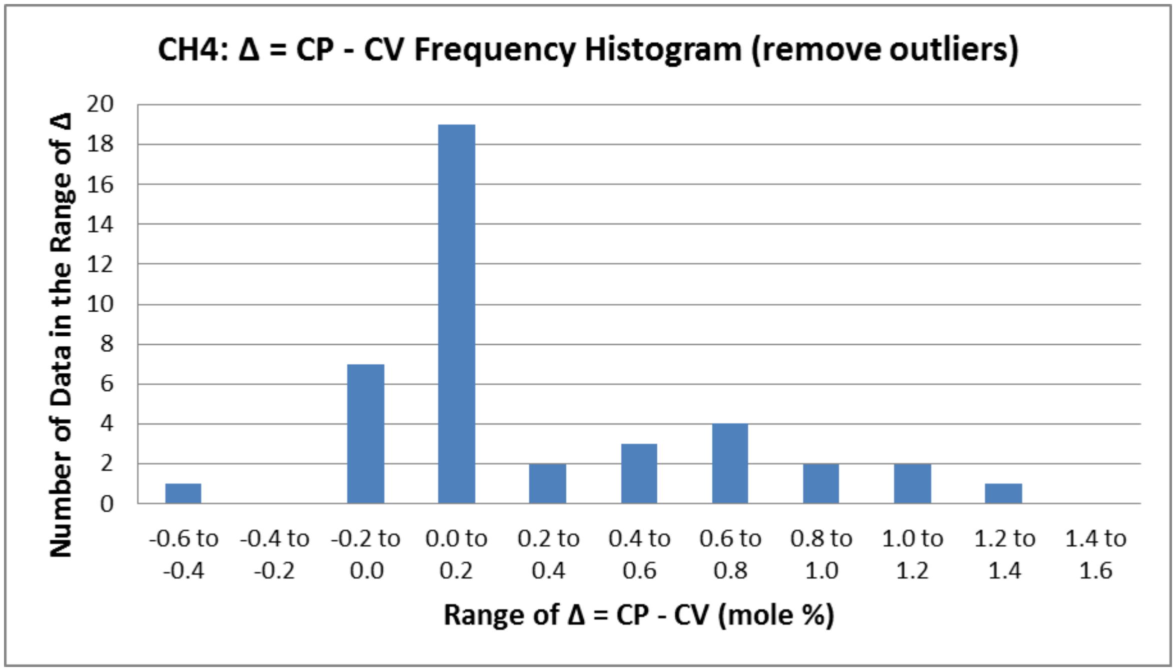


Figure 5-14. Histogram of the CP/CV differences data for methane, with outlier removed.

Table 5-10. Goodness-of-fit Test Summary for Methane CP/CV Differences Data, with Outlier Removed

			Z	Avg-Z*STDEV	Expected Frequency (e_i)	Observed Frequency (f_i)	(fi - ei)	(fi - ei)^2	(fi - ei)^2/ei
Avg	STDEV								
0.26780	0.37002				5.125	1	-4.125	17.02	3.32
		Lower 12.5%	1.15	-0.1577	5.125	9	3.875	15.02	2.93
		Lower 25%	0.675	0.0180	5.125	14	8.875	78.77	15.37
		Lower 37.5%	0.32	0.1494	5.125	3	-2.125	4.52	0.88
		Mid	0.2678	0.2678			0	0.00	
		Upper 37.5%	0.32	0.3862	5.125	2	-3.125	9.77	1.91
		Upper 25%	0.675	0.5176	5.125	3	-2.125	4.52	0.88
		Upper 12.5%	1.15	0.6933	5.125	1	-4.125	17.02	3.32
					5.125	8	2.875	8.27	1.61
								χ^2 = Σ(fi - ei)^2/ei =	30.22
						41		χ_a^2 =	11.07
								d.o.f. =	5
				If χ^2 > χa^2; then reject Ho that the population has a normal probability distribution					

5.2.1.5 Wilconxan Sign-Rank Test (WSRT)

Table 5-11 shows the WSRT analysis of the methane CP/CV differences data. The test statistic is greater than $z_{critical}$ for the data sets with and without the outliers; thus the null hypothesis that the two populations are identical is rejected and it is concluded, that for samples collected for this project, that methane concentrations measured in pressurized condensate collected with a CP cylinder differ from methane concentrations measured in pressurized condensate collected with a CV cylinder.

Table 5-11. Summary of WSRT for Methane CP/CV Differences Data

Methane											
					3.Paste ABS of Δ and sign of Δvalues					6. Calculate Summary Statistics	
1. Paste Δ = CP - CV		2. Calculate ABS of Δ and sign of Δ			4. Sort ABS Δ and sgn Δ data by ABS Δ from smallest to largest					Variance of W = Nr(Nr+1)(2Nr+1)/6 =	25,585
										STDEV W = SQRT(Variance of W) =	160
										Test Statistic (Z) = W/STDEV(W)	4.68
Δ = CP - CV		ABS Δ	sgn Δ		ABS Δ	sgn Δ	Rank	W statistic		Zcritical (95% CI) =	1.96
-0.5450		0.545	-1		0.00017	1	1	1		**If Z > Zcritical, then reject Ho and conclude populations are not identical**	
-0.0540		0.054	-1		0.00200	-1	2	-2			
-0.0460		0.046	-1		0.00200	-1	3	-3			
-0.0190		0.019	-1		0.00500	-1	4	-4		**Remove Outlier(s)**	
-0.0080		0.008	-1		0.00800	-1	5	-5		Variance of W =	23,821
-0.0050		0.005	-1		0.01600	1	6	6		Standard Deviation = SQRT(Variance of W) =	154
-0.0020		0.002	-1		0.01900	1	7	7		Test Statistic (Z) =	4.58
-0.0020		0.002	-1		0.01900	-1	8	-8		Zcritical (95% CI) =	1.96
0.0002		0.00016521	1		0.02000	1	9	9		**If Z > Zcritical, then reject Ho and conclude populations are not identical**	
0.0160		0.016	1		0.04600	-1	10	-10			
0.0190		0.019	1		0.05100	1	11	11			
0.0200		0.02	1		0.05200	1	12	12			
0.0510		0.051	1		0.05400	-1	13	-13			
0.0520		0.052	1		0.06300	1	14	14			
0.0630		0.063	1		0.10216	1	15	15			
0.1022		0.10216449	1		0.11400	1	16	16			
0.1140		0.114	1		0.11500	1	17	17			
0.1150		0.115	1		0.11600	1	18	18			
0.1160		0.116	1		0.12417	1	19	19			
0.1242		0.12417416	1		0.12816	1	20	20			
0.1282		0.12816458	1		0.12900	1	21	21			
0.1290		0.129	1		0.14000	1	22	22			
0.1400		0.14	1		0.14500	1	23	23			
0.1450		0.145	1		0.15000	1	24	24			
0.1500		0.15	1		0.17000	1	25	25			
0.1700		0.17	1		0.17500	1	26	26			
0.1750		0.175	1		0.30000	1	27	27			
0.3000		0.3	1		0.37300	1	28	28			
0.3730		0.373	1		0.44800	1	29	29			
0.4480		0.448	1		0.45000	1	30	30			
0.4500		0.45	1		0.47800	1	31	31			
0.4780		0.478	1		0.54500	-1	32	-32			
0.6800		0.68	1		0.68000	1	33	33			
0.6960		0.696	1		0.69600	1	34	34			
0.7100		0.71	1		0.71000	1	35	35			
0.7300		0.73	1		0.73000	1	36	36			
0.8320		0.832	1		0.83200	1	37	37			
0.8400		0.84	1		0.84000	1	38	38			
1.0090		1.009	1		1.00900	1	39	39			
1.0660		1.066	1		1.06600	1	40	40			
1.2190		1.219	1		1.21900	1	41	41			
2.0970		2.097	1		2.09700	1	42	42			
					5. Calculate W and N_R						
						W= ΣW statistic =		749			
						Count = N_R =		42			
						Remove outlier(s)					
						W= ΣW statistic =		707			
						Count = N_R =		41			

5.2.1.6 Paired data comparisons t-statistic test considering measurement uncertainty.

Table 5-12 lists CP cylinder / CV cylinder paired pressurized condensate samples data for the GPA 2103 analyses, and calculates a t-statistic to test the null hypothesis that the mean of the paired differences population (i.e., d_{avg}) is less than or equal to the analytical method uncertainty for the contract lab. The data includes, by column:

Column	Data
A	Measured compound.
B	Engineering units for the compound.
C	Count – number of paired samples (42)
D	Average CP – average value for all the CP cylinder samples
E	Average CV – average value for all the CV cylinder samples
F	d_{avg} = average difference for the 42 paired samples
G	Standard deviation of the paired CP/CV samples differences (d_i values)
H	Standard error of the mean difference
I	Analytical method uncertainty expressed as a percentage of the measured value
J	Analytical method uncertainty expressed in engineering unit
K	t-statistic for the compound or parameter. Red high-lighted t-statistics are greater than the critical t-statistic for a 99% CI, and blue high-lighted t-statistics are greater than the critical t-statistic for a 95% CI.
L	Critical t-statistic, n-1 degrees of freedom, 99% CI, 1-tailed.
M	Critical t-statistic, n-1 degrees of freedom, 95% CI, 1-tailed.

This analysis suggests that the differences between CP and CV samples for CO_2 and methane are statistically significant, even when the analytical uncertainty is considered. The t-statistics for CO_2 and methane indicate that the null hypothesis is rejected at 99% probability, providing additional support for these conclusions considering that the population of differences for these parameters may not be normally distributed.

Table 5-12. CP/CV Cylinders Paired Samples Comparison t-statistic Test Data, H_0: $d_{avg} \leq$ Analytical Uncertainty (GPA 2103 Analysis)

Compound / Parameter	Eng. Units	Count (n)	Average CP	Average CV	Average difference ($d_{avg} = \Sigma di/n$)	STDEV (di)	Std Error = STDEV(di)/ SQRT(n)	Analytical Uncertainty (95% CI) (% of Average Measured Value)	Analytical Uncertainty (Mole %)	t statistic = [(ABS(d_{avg})- Analytical Uncertainty)/ Std Error] (H_0 : $d_{avg} \leq$ Analytical Uncertainty)	t-critical (99% CI, 1-tail)	t-critical (95% CI, 1-tail)
Carbon Dioxide	mole %	42	0.386	0.347	0.0394	0.0361	0.006	1.70%	0.0062	5.95	2.423	1.697
Nitrogen					0.0000		0.000					
Methane	mole %	42	5.734	5.423	0.3113	0.4618	0.071	1.98%	0.1104	2.82	2.423	1.697
Ethane	mole %	42	5.837	5.750	0.0867	0.1374	0.021	1.26%	0.0730	0.65	2.423	1.697
Propane	mole %	42	7.529	7.473	0.0562	0.1493	0.023	0.99%	0.0743	-0.78	2.423	1.697
Iso-Butane	mole %	42	2.556	2.541	0.0152	0.0533	0.008	0.64%	0.0163	-0.13	2.423	1.697
n-Butane	mole %	42	7.863	7.820	0.0427	0.1724	0.027	1.09%	0.0855	-1.61	2.423	1.697
Iso-Pentane	mole %	42	5.219	5.196	0.0234	0.1119	0.017	1.85%	0.0963	-4.23	2.423	1.697
n-Pentane	mole %	42	7.289	7.257	0.0314	0.1693	0.026	0.94%	0.0684	-1.42	2.423	1.697
n-Hexane	mole %	42	5.969	6.020	-0.0508	0.3442	0.053	7.58%	0.4544	-7.60	2.423	1.697
Heptanes	mole %	42	13.116	13.372	-0.2558	0.6699	0.103	2.72%	0.3602	-1.01	2.423	1.697
Octanes	mole %	42	9.980	10.214	-0.2347	0.5902	0.091	3.54%	0.3574	-1.35	2.423	1.697
Nonanes	mole %	42	4.431	4.525	-0.0937	0.3544	0.055	4.40%	0.1970	-1.89	2.423	1.697
Decanes Plus	mole %	42	11.657	11.481	0.1759	1.4552	0.225	3.79%	0.4384	-1.17	2.423	1.697
Benzene	mole %	42	0.819	0.826	-0.0072	0.0593	0.009	7.88%	0.0648	-6.29	2.423	1.697
Toluene	mole %	42	2.819	2.866	-0.0464	0.1889	0.029	2.64%	0.0750	-0.98	2.423	1.697
Ethylbenzene	mole %	42	0.207	0.210	-0.0034	0.0117	0.002	17.65%	0.0369	-18.56	2.423	1.697
m, p-Xylenes	mole %	42	2.310	2.348	-0.0374	0.1429	0.022	3.08%	0.0717	-1.56	2.423	1.697
o-Xylene	mole %	42	0.479	0.486	-0.0063	0.0316	0.005	3.08%	0.0149	-1.77	2.423	1.697
2,2,4-Trimethylpentane	mole %	42	0.045	0.046	-0.0011	0.0033	0.001	3.54%	0.0016	-0.92	2.423	1.697
2,2-Dimethylbutane	mole %	42	0.087	0.088	-0.0005	0.0109	0.002	3.54%	0.0031	-1.57	2.423	1.697
2,3-Dimethylbutane	mole %	42	0.340	0.343	-0.0033	0.0321	0.005	3.54%	0.0121	-1.78	2.423	1.697
Cyclopentane	mole %	42	0.418	0.421	-0.0037	0.0395	0.006	3.54%	0.0149	-1.83	2.423	1.697
2-Methylpentane	mole %	42	3.038	3.063	-0.0257	0.2090	0.032	3.54%	0.1080	-2.55	2.423	1.697
3-Methylpentane	mole %	42	1.873	1.886	-0.0124	0.1089	0.017	3.54%	0.0665	-3.23	2.423	1.697
		0	0.000	0.000		0.0000	0.000					
C10+ MW	g/mole	42	215.339	215.508	-0.1695	4.9847	0.769	2.20%	4.7393	-5.94	2.423	1.697
C10+ SG at 60°F		42	0.823	0.824	-0.0008	0.0028	0.000	2.20%	0.0181	-40.18	2.423	1.697
		0	0.000	0.000		0.0000	0.000					
PSM/EOS $P_{Bubble Point}$ @	psia	42	221.596	210.922	10.67	15.1058	2.331					
PSM/EOS Bubble Point	psia	42	0.937	0.893	0.0444	0.0593	0.009					
PSM/EOS FGOR @ P_{tank},	scf/bbl	42	261.150	248.517	12.63	18.9276	2.921					

5.2.1.7 Statistical data summary

Table 5-13 summarizes statistics for the CP/CV cylinders paired samples differences data. The table includes data for the compounds and parameters identified in Table 5-7 as having a statistically significant difference between CP and CV samples. In addition to the paired sample t-statistic and WRST results presented previously, this table includes the percent of paired CP/CV samples for which the CP parameter is > the CV parameter, and the ratio of d_{avg} and (CP value + CV value)/2 (i.e., calculate d_{avg} as a percent of the average measured value).

- For 100% of the paired CP/CV cylinder samples, the CP cylinder had a higher concentration of carbon dioxide, and on average this difference was about 10.7% of the CO_2 concentration. These data, and the results of the paired data comparisons t-statistic test considering measurement uncertainty, indicate that the difference between the CP cylinder and CV cylinder measurements of CO_2 in pressurized condensate is statistical significant.
- In 81% of the paired CP/CV cylinder samples, the CP cylinder had a higher concentration of methane, and the overall average difference (CP – CV) was about 5.6% of the methane concentration. These data, and the results of the paired data comparisons t-statistic test considering measurement uncertainty, indicate that there was a statistically significant difference between the CP cylinder and CV cylinder measurements of methane in pressurized condensate.
- For both PSM/EOS bubble point pressure and PSM/EOS FGOR, over 80% of the paired CP/CV cylinder samples had higher calculated values for the CP cylinder and the overall average difference (CP – CV) was about 5% of the calculated value. These data, and the results of the paired data comparisons t-statistic test, indicate that there was difference between the PSM/EOS calculated estimates of P_{BP} and FGOR based on the CP cylinder pressurized condensate samples and the PSM/EOS calculated estimates of P_{BP} and FGOR based on the CV cylinder pressurized condensate samples.

  Both P_{BP} and FGOR are strongly impacted by CO_2 and methane concentrations in the pressurized condensate; thus, these results are consistent with CP/CV results for methane and CO_2.

Table 5-13. 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: ($\lvert d \rvert$ - 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 $P_{Bubble Point}$ @ 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.

5.2.2 Sample initiation time study

To evaluate the impact of sample collection initiation time on measured pressurized condensate composition, a series of samples were collected with sample collection initiated at various intervals after the well cycle end: 0 (i.e., during the well cycle), < 30 (~ 15), 90, and 150 minutes after well cycle). Figure 5-15 shows the impact of sample collection initiation time on P_{BP}/P_{SC} ratio for two sets of sequentially collected samples for two well cycles. The separator temperature changed during the 150 minute sample collection period, therefore all bubble point pressures 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. Figure 5-16 shows the impact of sample collection initiation time on methane for the two well cycles. The data show a decrease in P_{BP}/P_{SC} and methane from the < 30 minute to the 90 minute samples. It should be noted that the separator heater was not firing separator 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 well cycle end. For well cycle 2, gas flow from the separator to the gathering pipeline between the collection of the < 30 minute to the 90 minute samples is a suspected cause, at least in part, of the change in HC liquid composition. Other potential contributing factors to the changes in the bubble point pressure and CH_4 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.

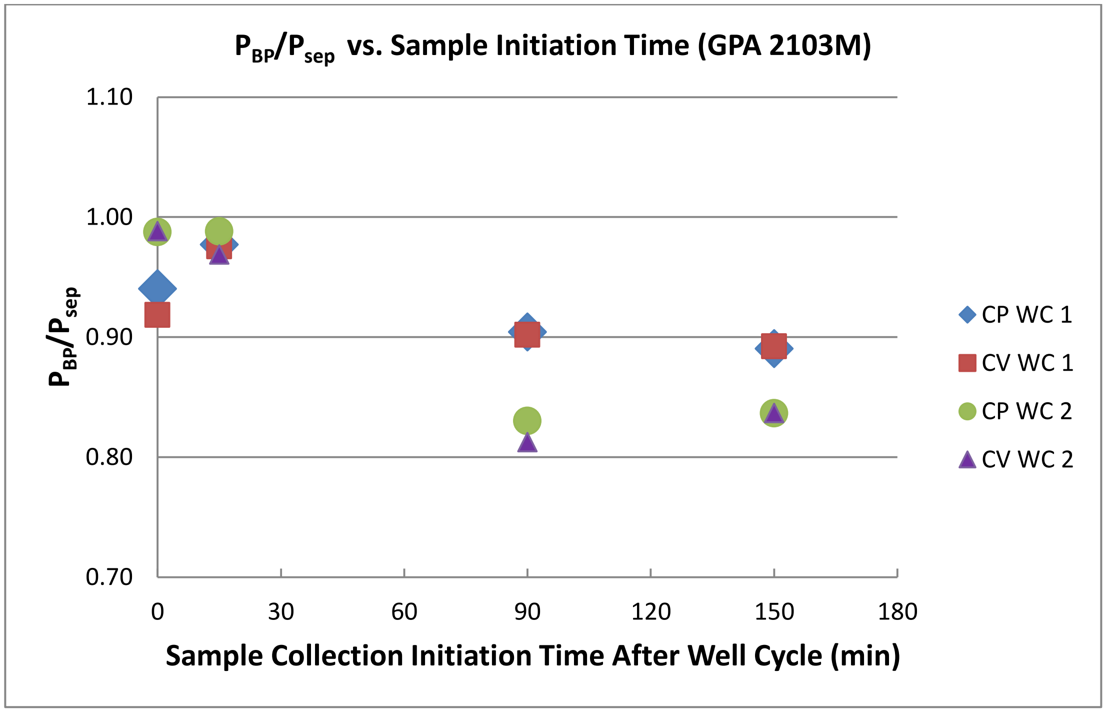


Figure 5-15. Impact of sample collection initiation time on P_{BP}/P_{SC}.

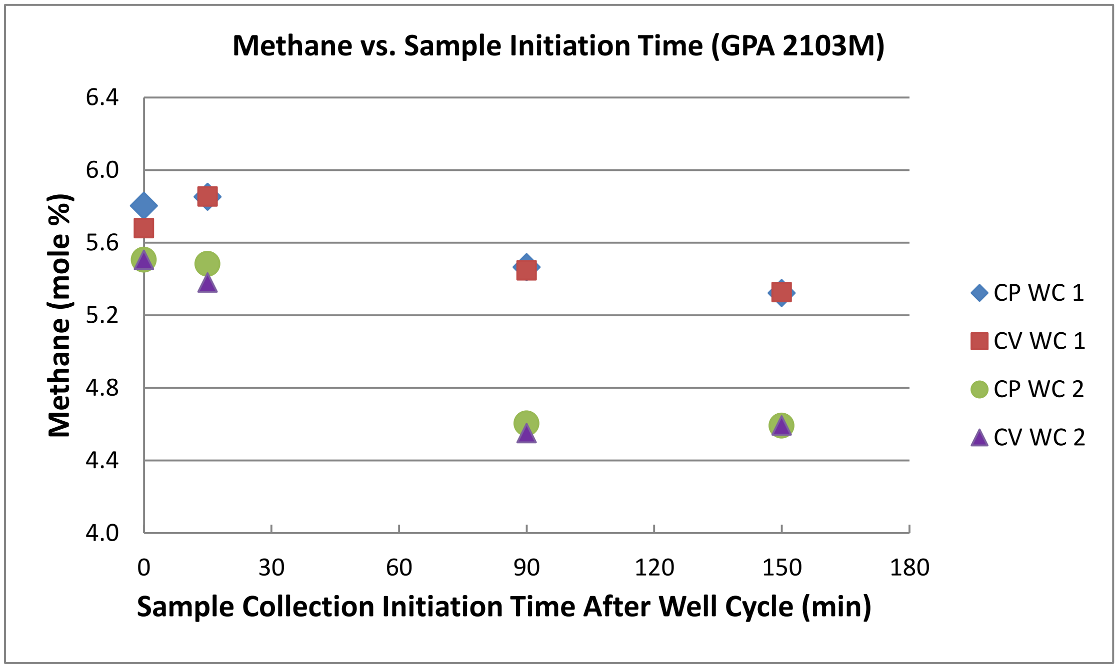


Figure 5-16. Impact of sample collection initiation time on pressurized condensate methane concentration.

The results suggest that samples should be collected soon after the end of a well cycle, and it should be noted that the impact of time on the pressurized condensate sample composition could be exacerbated if the separator pressure and/or temperature was changing; for example, due to changes in sales line pressure and/or use of separator headspace gas as heater fuel. Based on these results, a project guideline to collect samples within 30 minutes of the well cycle end was adopted.

5.2.3 Sample collection rate study

To evaluate the impact of sample collection rate on measured pressurized condensate composition, samples were collected at various rates over the course of the study: 20, 40, 60, 100, and 180 ml/min.

Figure 5-17 includes all the samples collected from the sample probes and shows that, for this project, the sample collection rate had no measurable impact on the P_{BP}/P_{SC} ratio for CP cylinders and for CV cylinders (i.e., the correlation coefficient “R^2” for both linear regression equations is nearly zero). Figure 5-18 includes the samples collected from the sample probes during the mid-pressure well cycles, and the data show the same trend. The data in these figures are based on samples with a sample collection initiation time less than 30 minutes after the end of the well cycle. 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 which is expected to dissolve any gas that evolved 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 this project, a conservative sample collection rate of 60 ml/min or less was used. Most samples were collected at a rate of 20 ml/min.

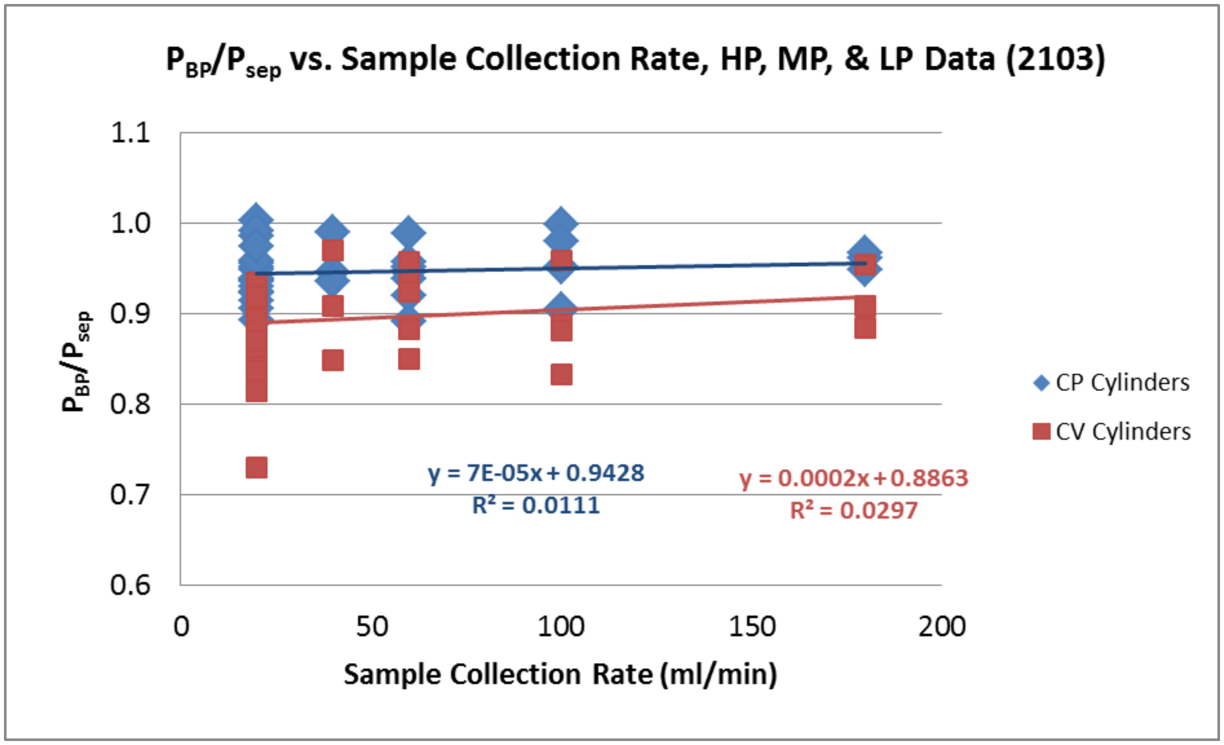


Figure 5-17. Impact of sample collection rate on P_{BP}/P_{SC}, Low-, Mid-, and High-Pressure well cycles.

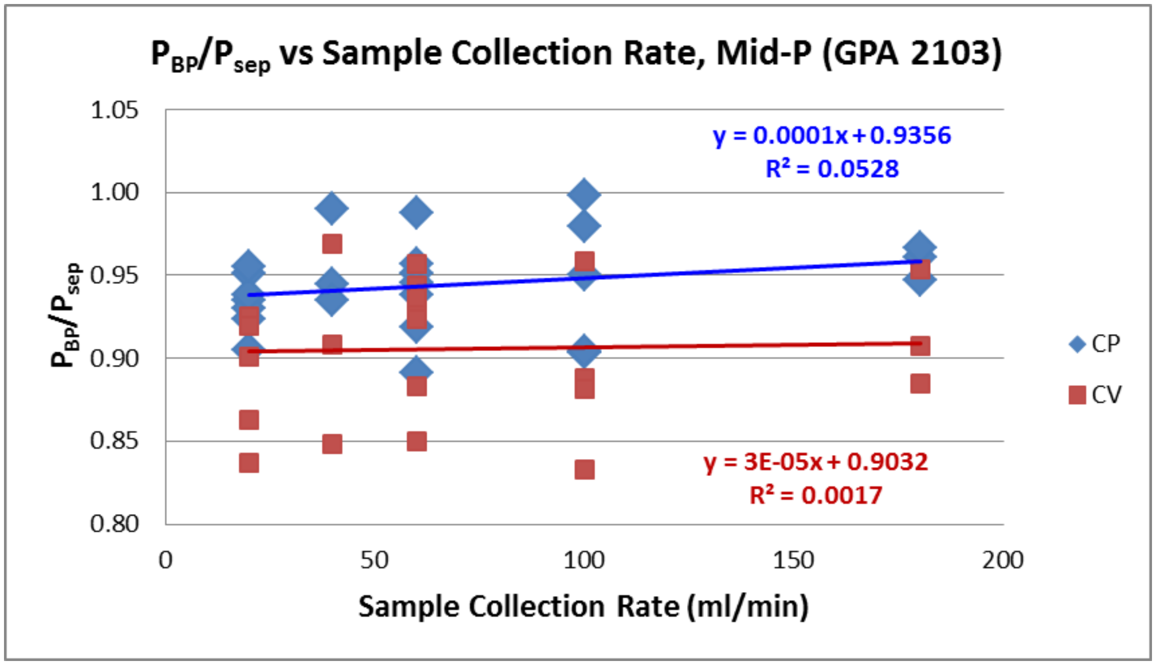


Figure 5-18. Impact of sample collection rate on P_{BP}/P_{SC}, Mid-Pressure well cycles.

More detailed sample collection rate results are in the following figures, and these analyses are based on the mid-pressure well cycles data only (and sample collection initiation times less than 30 minutes after the end of the well cycle) to examine the impact of parameters other than separator pressure on pressurized condensate samples properties:

- Figure 5-19 shows that sample collection rate had negligible impact on condensate concentrations of CO_2 and CH_4. The CO_2 concentrations are multiplied by ten on this graph to scale with the methane data.
- Figure 5-20 shows that condensate concentrations of C10+ decreased with higher sample collection rates. The impact is most pronounced at the highest sample rate, and could be due, at least in part, to mass discrimination at the higher sample collection rates.
- Figure 5-21 shows that condensate C10+ specific gravity 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+ molecular weight. It is not known why the C10+ specific gravity 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 specific gravity C10+ fraction would be anticipated.
- As shown in Figure 5-22, the P_{BP}/P_{SC} ratio increased with separator temperature for CV cylinder samples but decreased with separator temperature for CP cylinder samples.

- Figure 5-23 graphs bubble point pressures for CP and CV cylinders against separator temperature, and these data show that the trends observed in Figure 5-22 are caused by changes in the bubble point pressure rather than the separator pressure. If all other parameters are held constant, then an increase in separator temperature would be expected to drive a larger fraction of the volatile compounds to the gas phase in the separator and reduce the bubble point pressure. This expected trend is observed for the CP cylinders but the opposite trend is seen for the CV cylinders.
- Figure 5-24 graphs CO_2 and methane concentrations for CP and CV cylinders against separator temperature. The general trends observed for CO_2 in CP and CV cylinders, and methane in CP cylinders are as expected, higher separator temperatures result in lower concentrations in the pressurized condensate sample. However, separator temperature has no measureable impact on methane in CV cylinders (i.e., R^2 for the regression equation is essentially zero).

  Higher concentrations of methane at lower separator temperatures are observed, as anticipated, in CP cylinder samples but not in CV cylinder samples; that is, methane concentrations appear to be biased low at lower separator temperatures. An explanation for the low methane concentrations at lower separator temperatures is the increased solubility of methane in water at lower temperatures and methane partitioning to the water fraction in the CV cylinder samples. Such a phenomenon would also help to explain the bubble point pressure / separator temperature trends because methane concentration in pressurized condensate samples has a large impact on PSM/EOS calculations of bubble point pressure.

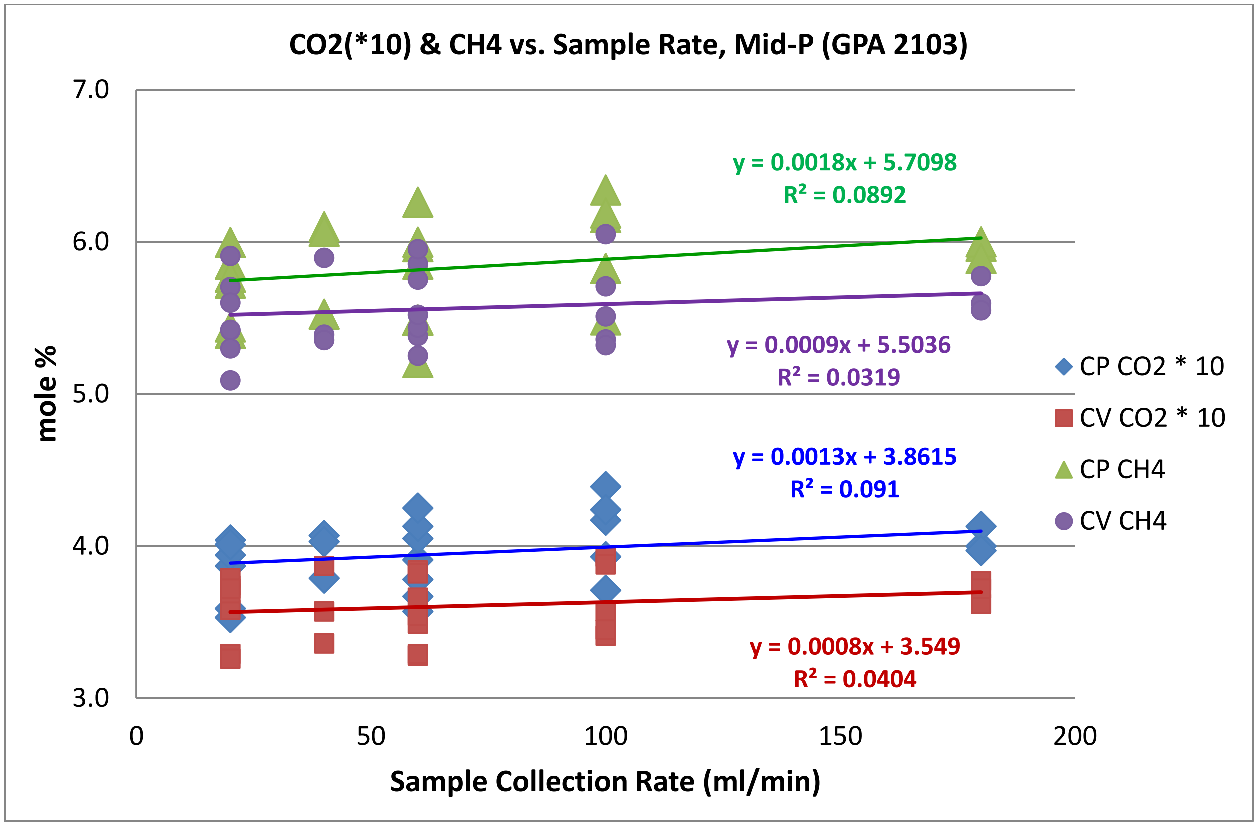


Figure 5-19. Impact of sample collection rate on condensate concentrations of CO_2 and CH_4.

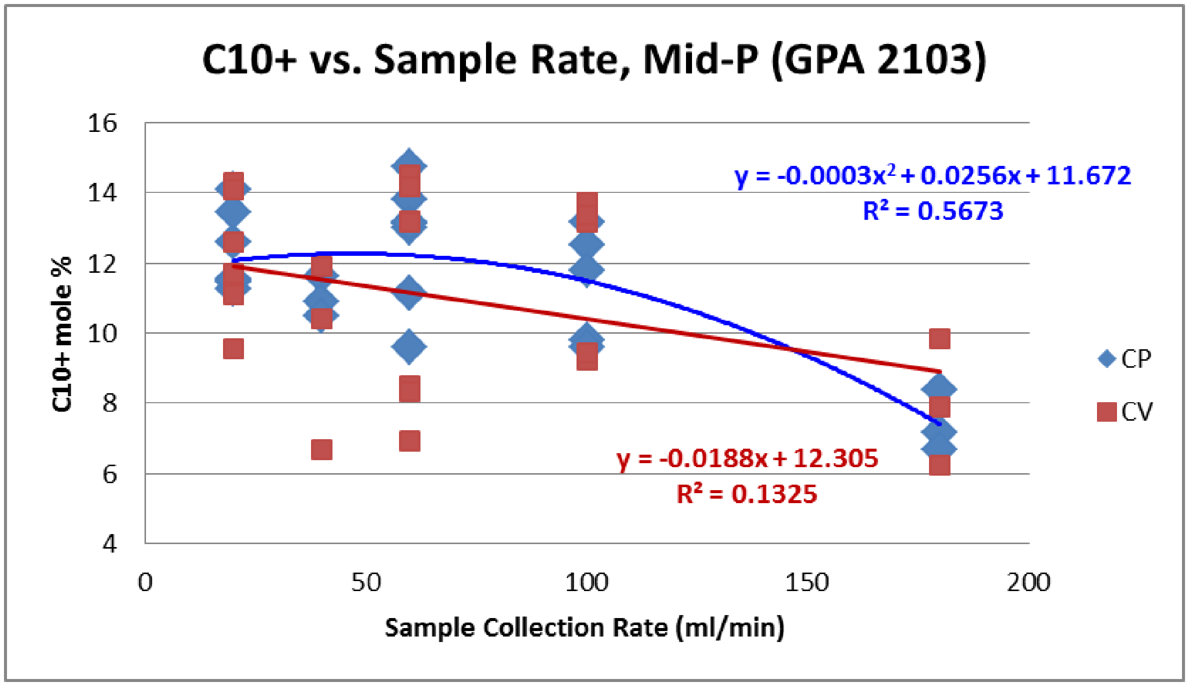


Figure 5-20. Impact of sample collection rate on condensate concentrations of C10+.

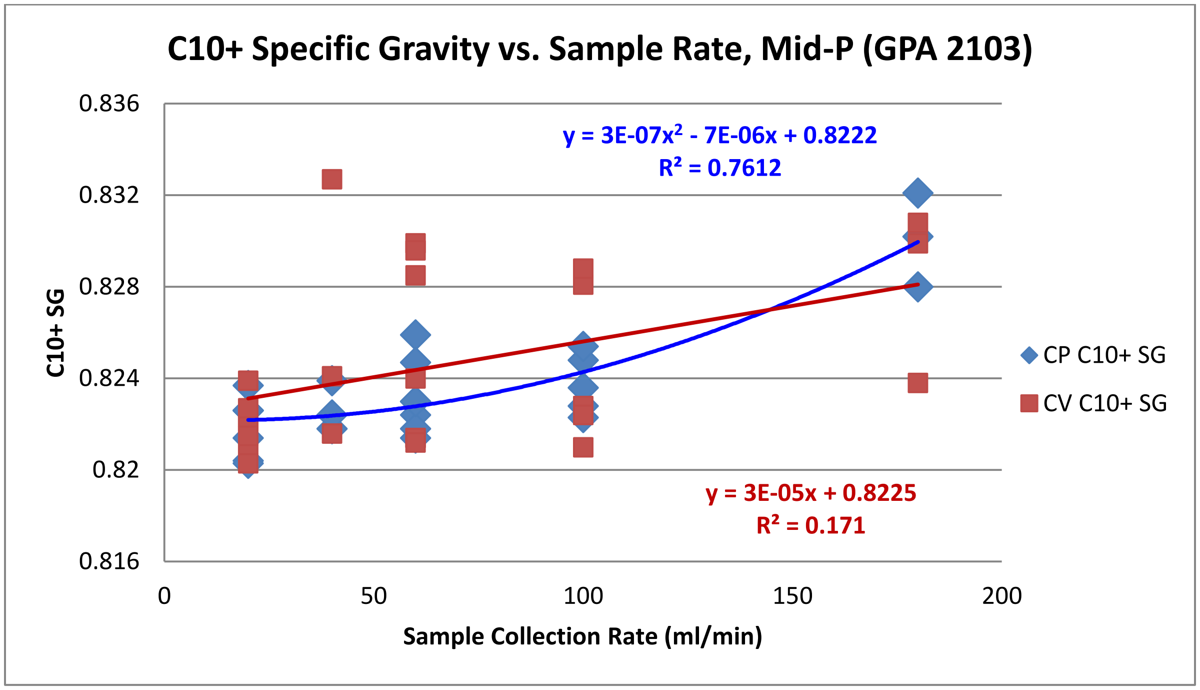


Figure 5-21. Impact of sample collection rate on condensate C10+ specific gravity.

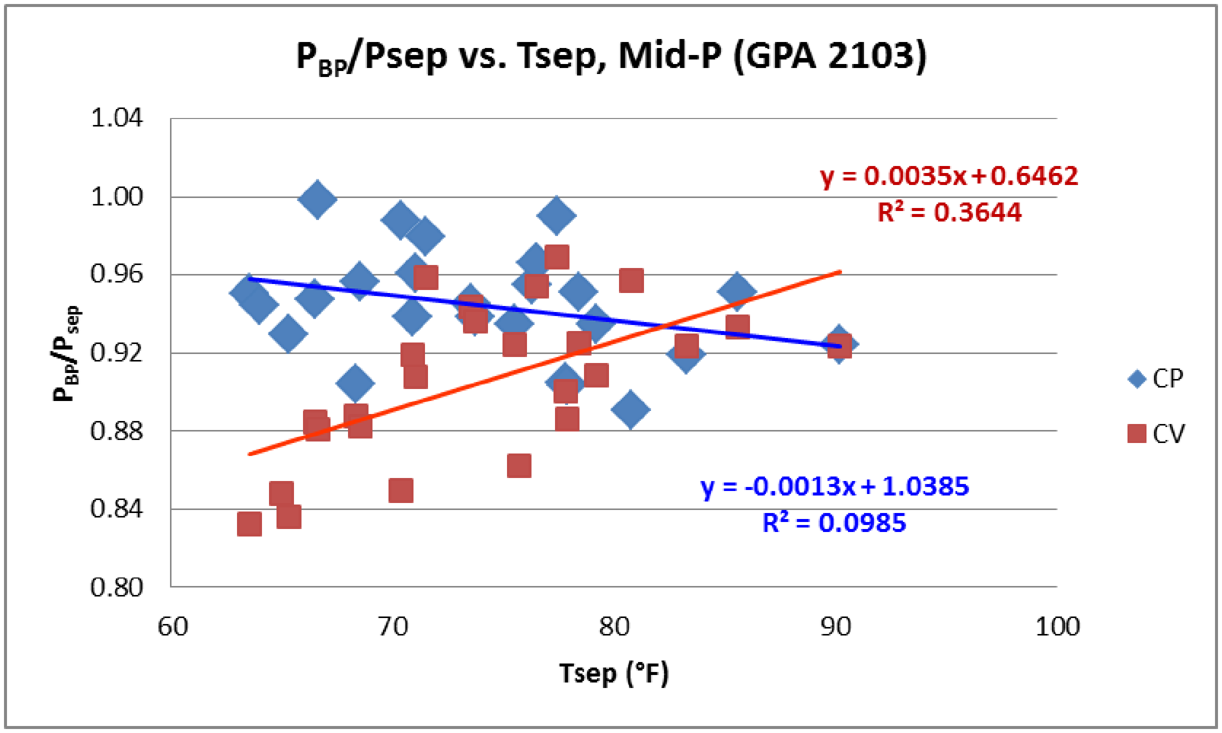


Figure 5-22. Impact of separator temperature on P_{BP}/P_{SC}.

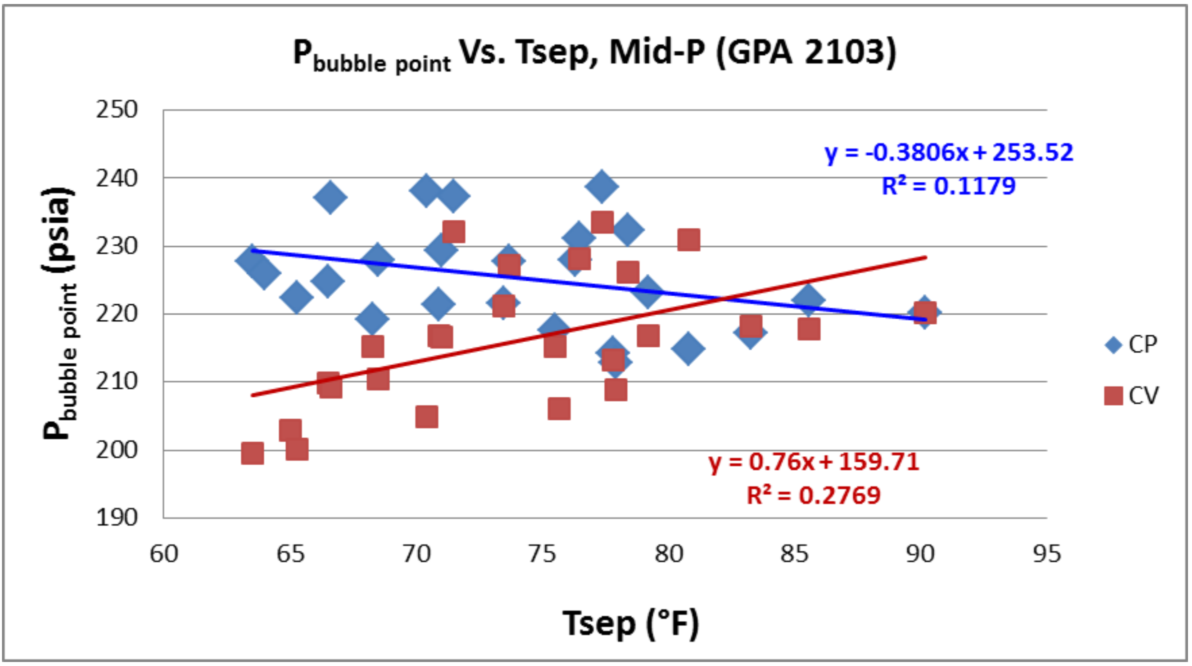


Figure 5-23. Impact of separator temperature on P_{BP}.

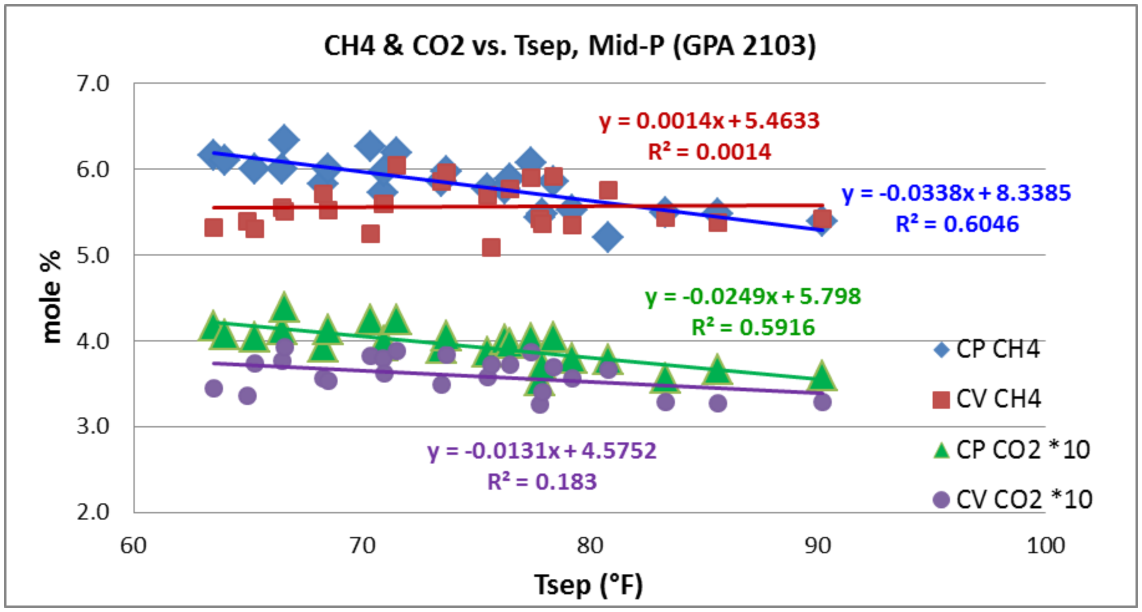


Figure 5-24. Impact of separator temperature on CO_2 and methane.

5.2.4 Oil level sight glass sample collection study

To evaluate the impact of the sample collection location, specifically the separator oil box oil level sight glass which is a practical sampling location for many separators, pressurized condensate samples were simultaneously collected from the two sample probes and the sight glass.

Figure 5-25 compares the P_{BP}/P_{SC} for samples collected from the two sample probes and the sight glass for nine well cycles. 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 5-25 show that for the CP cylinder sampling, the sight glass sample P_{BP}/P_{SC} and sample probe sample P_{BP}/P_{SC} have little difference (i.e., differences range from 1 to 5%). However, for the CV cylinder sampling, the sight glass sample P_{BP}/P_{SC} and sample probe sample P_{BP}/P_{SC} differ by more than 20% for the MP1 and LP2 well cycles.

Paired data comparisons t-statistic test calculations, as described in Section 5.2.1.1, were conducted for the entire sight glass / sample probe samples data set (i.e., included both CP and CV samples, refer to Table 5-14), and for the CP samples (refer to Table 5-15) and CV samples (refer to Table 5-16) only. Table 5-18 provides summary statistics that show:

- For all of the measured condensate compounds, C10+ properties, and PSM/EOS calculated parameters, none of the t-statistics are greater than $t_{critical}$ for a 95% CI
  - This observation applies for the combined CP & CV data, and the CP only and CV only data
  - Although for the CV samples there are some large differences between the sample probe and sight glass results (e.g., for CO_2 and methane as shown in Table 5-17), 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 the complications for CV sampling discussed above may have contributed to the data scatter).
- As show in Table 5-17, the sight glass CV cylinder samples had higher concentrations of CO_2 and methane than the sample probe CV cylinder samples.

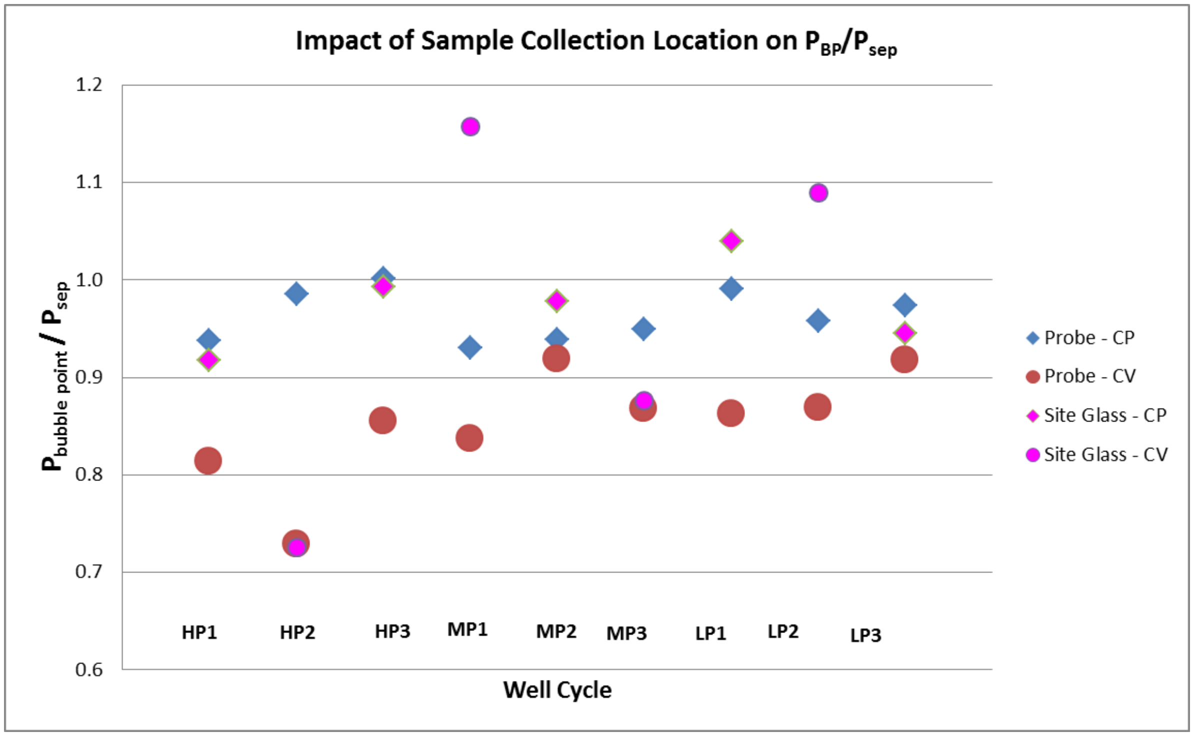


Figure 5-25. Impact of sample collection location on P_{BP}/P_{SC}

Table 5-14. Sight Glass/Sample Probe Paired Samples Comparison t-statistic Test Data, H_0: $d_{avg} = 0$ (GPA 2103 Analysis, CP and CV samples)

A	B	C	D	E	F	G	H	I	J	K
Compound / Parameter	Eng. Units	Count (n)	Average Probe	Average Sight Glass	Average difference ($d_{avg} = \Sigma di/n$)	d_{avg}/ Avg (Pr & SG)	STDEV (di)	Std Error = STDEV(di)/ SQRT(n)	ABS(t = d_{avg}/ Std Error)	t-critical (95% CI, 2-tailed)
Carbon Dioxide	mole %	9	0.356	0.391	-0.0349	-9.35%	0.0631	0.021	1.659	2.306
Nitrogen										
Methane	mole %	9	5.376	5.820	-0.4439	-7.93%	0.8544	0.285	1.559	2.306
Ethane	mole %	9	5.987	5.985	0.0014	0.02%	0.3703	0.123	0.012	2.306
Propane	mole %	9	7.845	7.664	0.1808	2.33%	0.4230	0.141	1.282	2.306
Iso-Butane	mole %	9	2.662	2.583	0.0784	2.99%	0.1470	0.049	1.601	2.306
n-Butane	mole %	9	8.148	7.890	0.2580	3.22%	0.4369	0.146	1.772	2.306
Iso-Pentane	mole %	9	5.220	5.041	0.1783	3.48%	0.2787	0.093	1.920	2.306
n-Pentane	mole %	9	7.304	7.041	0.2633	3.67%	0.4113	0.137	1.921	2.306
n-Hexane	mole %	9	6.140	6.110	0.0301	0.49%	0.4380	0.146	0.206	2.306
Heptanes	mole %	9	13.240	13.589	-0.3487	-2.60%	0.6994	0.233	1.496	2.306
Octanes	mole %	9	10.164	10.429	-0.2656	-2.58%	0.9343	0.311	0.853	2.306
Nonanes	mole %	9	4.451	4.565	-0.1142	-2.53%	0.4713	0.157	0.727	2.306
Decanes Plus	mole %	9	10.739	10.494	0.2449	2.31%	1.5258	0.509	0.482	2.306
Benzene	mole %	9	0.811	0.808	0.0029	0.36%	0.0609	0.020	0.142	2.306
Toluene	mole %	9	2.828	2.843	-0.0146	-0.51%	0.2105	0.070	0.207	2.306
Ethylbenzene	mole %	9	0.189	0.190	-0.0012	-0.64%	0.0098	0.003	0.375	2.306
m, p-Xylenes	mole %	9	2.182	2.204	-0.0224	-1.02%	0.1166	0.039	0.578	2.306
o-Xylene	mole %	9	0.503	0.506	-0.0033	-0.66%	0.0282	0.009	0.355	2.306
2,2,4-Trimethylpentane	mole %	9	0.045	0.046	-0.0016	-3.42%	0.0043	0.001	1.077	2.306
2,2-Dimethylbutane	mole %	9	0.099	0.100	-0.0009	-0.90%	0.0138	0.005	0.193	2.306
2,3-Dimethylbutane	mole %	9	0.334	0.334	-0.0008	-0.23%	0.0346	0.012	0.067	2.306
Cyclopentane	mole %	9	0.410	0.412	-0.0022	-0.54%	0.0416	0.014	0.160	2.306
2-Methylpentane	mole %	9	3.071	3.064	0.0070	0.23%	0.2361	0.079	0.089	2.306
3-Methylpentane	mole %	9	1.902	1.889	-0.1988	-10.49%	0.5605	0.187	1.064	2.306
C10+ MW	g/mole	9	0.823	0.822	0.0005	0.06%	0.0038	0.001	0.426	2.306
C10+ SG at 60°F		9	214.222	212.770	1.4521	0.68%	5.9860	1.995	0.728	2.306
PSM/EOS $P_{Bubble\ Point}$ @ Tsep	psia	9	209.189	222.886	-13.6967	-6.34%	27.6145	9.205	1.488	2.306
PSM/EOS FGOR @ P_{tank}, T_{tank}	scf/bbl	9	309.230	310.399	-1.1686	-0.38%	39.6318	13.211	0.088	2.306

Table 5-15. Sight Glass/Sample Probe Paired Samples Comparison t-statistic Test Data, H_0: d_{avg} = 0 (GPA 2103 Analysis, CP samples only)

A	B	C	D	E	F	G	H	I	J	K
Compound / Parameter	Eng. Units	Count (n)	Average Probe	Average Sight Glass	Average difference (d_{avg} =Σdi/n)	d_{avg}/ Avg (Pr & SG)	STDEV (di)	Std Error = STDEV(di)/ SQRT(n)	ABS(t = d_{avg}/ Std Error)	t-critical (95% CI, 2-tailed)
Carbon Dioxide	mole %	5	0.393	0.390	0.0036	0.92%	0.0105	0.005	0.763	2.776
Nitrogen										
Methane	mole %	5	5.804	5.844	-0.0402	-0.69%	0.2514	0.112	0.357	2.776
Ethane	mole %	5	6.044	5.994	0.0496	0.82%	0.0638	0.029	1.738	2.776
Propane	mole %	5	7.888	7.814	0.0738	0.94%	0.0810	0.036	2.038	2.776
Iso-Butane	mole %	5	2.689	2.660	0.0290	1.08%	0.0306	0.014	2.118	2.776
n-Butane	mole %	5	8.234	8.151	0.0826	1.01%	0.0972	0.043	1.900	2.776
Iso-Pentane	mole %	5	5.262	5.194	0.0678	1.30%	0.0665	0.030	2.280	2.776
n-Pentane	mole %	5	7.371	7.269	0.1022	1.40%	0.0975	0.044	2.343	2.776
n-Hexane	mole %	5	6.078	5.927	0.1514	2.52%	0.4114	0.184	0.823	2.776
Heptanes	mole %	5	12.832	13.317	-0.4858	-3.72%	0.8553	0.382	1.270	2.776
Octanes	mole %	5	9.861	10.475	-0.6138	-6.04%	1.0473	0.468	1.311	2.776
Nonanes	mole %	5	4.356	4.625	-0.2692	-5.99%	0.5949	0.266	1.012	2.776
Decanes Plus	mole %	5	10.979	10.243	0.7356	6.93%	1.5350	0.686	1.072	2.776
Benzene	mole %	5	0.807	0.785	0.0224	2.81%	0.0542	0.024	0.924	2.776
Toluene	mole %	5	2.766	2.731	0.0346	1.26%	0.1751	0.078	0.442	2.776
Ethylbenzene	mole %	5	0.187	0.187	0.0000	0.00%	0.0082	0.004	0.000	2.776
m, p-Xylenes	mole %	5	2.142	2.168	-0.0256	-1.19%	0.0988	0.044	0.579	2.776
o-Xylene	mole %	5	0.496	0.499	-0.0026	-0.52%	0.0259	0.012	0.225	2.776
2,2,4-Trimethylpentane	mole %	5	0.043	0.046	-0.0030	-6.74%	0.0053	0.002	1.268	2.776
2,2-Dimethylbutane	mole %	5	0.098	0.099	-0.0006	-0.61%	0.0168	0.008	0.080	2.776
2,3-Dimethylbutane	mole %	5	0.331	0.330	0.0006	0.18%	0.0394	0.018	0.034	2.776
Cyclopentane	mole %	5	0.406	0.405	0.0010	0.25%	0.0481	0.022	0.046	2.776
2-Methylpentane	mole %	5	3.050	3.001	0.0486	1.61%	0.2396	0.107	0.454	2.776
3-Methylpentane	mole %	5	1.888	1.846	-0.3360	-18.00%	0.7457	0.333	1.008	2.776
C10+ MW	g/mole	5	0.822	0.823	-0.0010	-0.13%	0.0042	0.002	0.558	2.776
C10+ SG at 60°F		5	212.588	212.833	-0.2454	-0.12%	6.9276	3.098	0.079	2.776
PSM/EOS $P_{Bubble Point}$ @ Tsep	psia	5	223.018	223.972	-0.9540	-0.43%	7.6903	3.439	0.277	2.776
PSM/EOS FGOR @ P_{tank}, T_{tank}	scf/bbl	5	325.644	321.484	4.1604	1.29%	13.0172	5.821	0.715	2.776

Table 5-16. Sight Glass/Sample Probe Paired Samples Comparison t-statistic Test Data, H_0: $d_{avg} = 0$ (GPA 2103 Analysis, CV samples only)

A	B	C	D	E	F	G	H	I	J	K
Compound / Parameter	Eng. Units	Count (n)	Average Probe	Average Sight Glass	Average difference (d_{avg} =Σdi/n)	d_{avg}/ Avg (Pr & SG)	STDEV (di)	Std Error = STDEV(di)/ SQRT(n)	ABS(t = d_{avg}/ Std Error)	t-critical (95% CI, 2-tailed)
Carbon Dioxide	mole %	4	0.309	0.392	-0.0830	-23.66%	0.0701	0.035	2.369	3.182
Nitrogen										
Methane	mole %	4	4.841	5.790	-0.9485	-17.84%	1.1185	0.559	1.696	3.182
Ethane	mole %	4	5.915	5.974	-0.0588	-0.99%	0.5928	0.296	0.198	3.182
Propane	mole %	4	7.791	7.476	0.3145	4.12%	0.6523	0.326	0.964	3.182
Iso-Butane	mole %	4	2.628	2.488	0.1403	5.48%	0.2172	0.109	1.292	3.182
n-Butane	mole %	4	8.041	7.564	0.4773	6.12%	0.6172	0.309	1.546	3.182
Iso-Pentane	mole %	4	5.167	4.850	0.3165	6.32%	0.3942	0.197	1.606	3.182
n-Pentane	mole %	4	7.220	6.755	0.4648	6.65%	0.5840	0.292	1.592	3.182
n-Hexane	mole %	4	6.218	6.340	-0.1215	-1.94%	0.4803	0.240	0.506	3.182
Heptanes	mole %	4	13.751	13.928	-0.1773	-1.28%	0.5083	0.254	0.697	3.182
Octanes	mole %	4	10.542	10.372	0.1698	1.62%	0.6407	0.320	0.530	3.182
Nonanes	mole %	4	4.570	4.491	0.0795	1.75%	0.1743	0.087	0.912	3.182
Decanes Plus	mole %	4	10.439	10.807	-0.3685	-3.47%	1.4709	0.735	0.501	3.182
Benzene	mole %	4	0.816	0.837	-0.0215	-2.60%	0.0675	0.034	0.637	3.182
Toluene	mole %	4	2.906	2.982	-0.0760	-2.58%	0.2611	0.131	0.582	3.182
Ethylbenzene	mole %	4	0.192	0.195	-0.0028	-1.42%	0.0126	0.006	0.435	3.182
m, p-Xylenes	mole %	4	2.232	2.251	-0.0185	-0.83%	0.1522	0.076	0.243	3.182
o-Xylene	mole %	4	0.512	0.516	-0.0042	-0.83%	0.0349	0.017	0.243	3.182
2,2,4-Trimethylpentane	mole %	4	0.047	0.047	0.0002	0.54%	0.0022	0.001	0.225	3.182
2,2-Dimethylbutane	mole %	4	0.100	0.101	-0.0013	-1.25%	0.0115	0.006	0.217	3.182
2,3-Dimethylbutane	mole %	4	0.337	0.340	-0.0025	-0.74%	0.0334	0.017	0.150	3.182
Cyclopentane	mole %	4	0.415	0.421	-0.0063	-1.50%	0.0385	0.019	0.325	3.182
2-Methylpentane	mole %	4	3.097	3.142	-0.0450	-1.44%	0.2562	0.128	0.351	3.182
3-Methylpentane	mole %	4	1.917	1.944	-0.0273	-1.41%	0.1605	0.080	0.340	3.182
C10+ MW	g/mole	4	0.824	0.822	0.0025	0.30%	0.0023	0.001	2.203	3.182
C10+ SG at 60°F		4	216.264	212.690	3.5740	1.67%	4.5559	2.278	1.569	3.182
PSM/EOS $P_{Bubble\ Point}$ @ Tsep	psia	4	191.903	221.528	-29.6250	-14.33%	36.6842	18.342	1.615	3.182
PSM/EOS FGOR @ P_{tank}, T_{tank}	scf/bbl	4	288.713	296.543	-7.8298	-2.68%	62.0972	31.049	0.252	3.182

Table 5-17. Sight Glass/Sample Probe Paired Samples Comparison Summary Statistics (GPA 2103 Analysis)

Compound / Parameter	Eng. Units	Avg (Pr-SG)	d_{avg} (Pr - SG) / Avg (Pr & SG)			T-statistic = ABS(d_{avg}/ Std Error)		
		CP & CV	CP & CV	CP	CV	CP & CV	CP	CV
Carbon Dioxide	mole %	0.373	-9.35%	0.92%	-23.66%	1.66	0.76	2.37
Methane	mole %	5.598	-7.93%	-0.69%	-17.84%	1.56	0.36	1.70
Ethane	mole %	5.986	0.02%	0.82%	-0.99%	0.01	1.74	0.20
Propane	mole %	7.754	2.33%	0.94%	4.12%	1.28	2.04	0.96
Iso-Butane	mole %	2.622	2.99%	1.08%	5.48%	1.60	2.12	1.29
n-Butane	mole %	8.019	3.22%	1.01%	6.12%	1.77	1.90	1.55
Iso-Pentane	mole %	5.131	3.48%	1.30%	6.32%	1.92	2.28	1.61
n-Pentane	mole %	7.172	3.67%	1.40%	6.65%	1.92	2.34	1.59
n-Hexane	mole %	6.125	0.49%	2.52%	-1.94%	0.21	0.82	0.51
Heptanes	mole %	13.414	-2.60%	-3.72%	-1.28%	1.50	1.27	0.70
Octanes	mole %	10.297	-2.58%	-6.04%	1.62%	0.85	1.31	0.53
Nonanes	mole %	4.508	-2.53%	-5.99%	1.75%	0.73	1.01	0.91
Decanes Plus	mole %	10.616	2.31%	6.93%	-3.47%	0.48	1.07	0.50
PSM/EOS $P_{Bubble Point}$ @ T_{sep}	psia	216.037	-6.34%	-0.43%	-14.33%	1.49	0.28	1.62
PSM/EOS FGOR @ P_{tank}, T_{tank}	scf/bbl	309.815	-0.38%	1.29%	-2.68%	0.09	0.71	0.25

6. Process Measurement

Supporting data and calculations for the information presented in this section can be found in Annex 5 and Appendix IV.4

6.1 Introduction

Several instruments were used to measure process parameters during the PHLSA study. Manufacturer metrological specifications and calibration data, when available, were typically used for measurement uncertainty calculations.

An integrated operational map, which identifies and codifies each instrument in the process measurement system, may be consulted in Appendix IV.

This section includes two parts. The first refers to general instrumentation, such as temperature, pressure and liquid level transducers. All signals are processed in a Supervisory Control and Data Acquisition (SCADA) system with an Analog-to-Digital (A-D) converter and recorded in a data logger. Total uncertainty for each measurement (i.e., combination of data logger and instrumentation uncertainties) was calculated from transducer and Electronic Flow Computer (EFC) accuracy information. The calculation of uncertainties for measurements based on several instruments, such as tank pressure one foot from the bottom, are discussed at the end of this section.

The second part of this section addresses flow measurements. Liquid process meters were calibrated to accuracies compliant with custody transfer limits for steady-state flow and operate under a metrological confirmation process that includes field proving. The associated uncertainties are the lower feasible for midstream operations. Because the various gas meters used for this project have different operating principles, they require specific uncertainty calculations. A flow computer records readings of flow meters, and because they are digital signals the influence of the data logger on measurement uncertainty is null.

Section 6.2 provides general information regarding calibration and accuracy data for process measurement instruments used for this study, and the methodology used to estimate measurement uncertainty based on this information. Many of these calibrations and accuracy specifications only apply under prescribed conditions (e.g., steady-state flow of a fluid of known composition); thus, for some instruments, engineering assumptions were made regarding instrument/measurement uncertainty for subsequent uncertainty estimation calculations. These engineering estimates are documented in Section 8.

6.2 Uncertainty of General Process Instrumentation

6.2.1 Description of sources of uncertainty[4]

Temperature transducers. Instruments from several manufacturers were used and typical accuracy is in the range of 1.5 to 2 degrees Fahrenheit.

Pressure transducers. Instruments from various manufactures and with differing accuracies were used with +/- 2% of the measured value a typical accuracy specification.

Liquid tank height. Tank ullage is measured by an instrument with a manufacturer stated accuracy of 0.125 inches.

Liquid density. Stabilized condensate (i.e., tank liquids) density was determined using a liquid densitometer with accuracy better than 0.1 %. This measurement was conducted in the laboratory. The Coriolis meter recorded flowing density.

Flow computer. Transducer signals are processed by a flow computer with an ADC with 0.2 % measurement accuracy for analogic transducer signals.

Appendix IV.4 provides additional details regarding the instruments operating principles and calibrations.

6.2.2 General uncertainty model

The signals of some instruments were field verified using a calibration procedure that measured instrument output power or current, because these units do not correspond to the measured property, such as temperature or pressure (e.g. mV output vs. °F measured parameter). Such calibrations only confirm instrument functionality, and manufacturer accuracy specifications were used for uncertainty calculations.

A 95% confidence level (API MPMS 13.1 5.3) was the basis for uncertainty calculations. A rectangular distribution (API MPMS 13.3 4.18.4) was assumed for most instrument calibrations. The 95% CI coverage factor for the standard uncertainty corresponds to 1.65 for rectangular distributions and 1.96 for normal distributions.

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[4] The documentation for the referenced instrument accuracies are in the project Calibration Report, Appendix IV.4.

The standard uncertainty for an instrument with a calibration accuracy defined by ± a and a rectangular probability distribution is defined in equation 6.1.

$$u(Tr_i) = \frac{a}{\sqrt{3}} \tag{6.1}$$

Where:

u(Tr$_i$) is the standard uncertainty for transducer "i"

For a flow computer (FC), the ADC signal standard uncertainty is:

$$u(FC) = \frac{\frac{0.2\%}{100} \cdot FS}{\sqrt{3}} = 0.002 \cdot FS \cdot 3^{-½} \tag{6.2}$$

Where:

FS is the full scale of the instrument

The total standard uncertainty is calculated as follows:

$$u^2(M_i) = u^2(Tri) + u^2(FC) = \left(\frac{a}{\sqrt{3}}\right)^2 + \left(\frac{\frac{0.2\%}{100} \cdot FS}{\sqrt{3}}\right)^2 o \tag{6.3}$$

Where:

u(M$_i$) is the standard uncertainty for measurement M$_i$

Example:

An ambient temperature transducer, instrument #2 identified as RTD7, has manufacturer fixed accuracy of ±2 °F and a scale of 200°C (-25 to 175 °C); for a 74 °F reading equation 6.3 calculates:

$$u^2(M_2) = \frac{2^2 + (0.002 \cdot 200)^2}{\sqrt{3}} = 1.39\ °\mathrm{F}$$

$$u(M_2) = \sqrt{1.39} = 1.18\ °\mathrm{F}$$

$$U(M_2) = 1.18 \cdot 1.65 = 2.56\ \text{°F} \tag{6.4}$$

$$\%U(M_2) = \frac{2.56}{74} = 2.62\% \tag{6.5}$$

Table 6-1 summarizes process instrumentation uncertainties, and relative uncertainties are for information purposes only. For the testing, relative uncertainties were calculated based on actual measurements.

Table 6-1. Process Measurement Standard Uncertainty Algorithm and Example Relative Uncertainty at Half Full Scale

#	Parameter	Instrument	Datalogger ID	Output signal	Range	Accuracy (A)	Units	Square of Combined Standard Uncertainty (u^2)	Relative uncertainty at half FS (%U)
1	Ambient pressure (P_{amb})	Pressure transducer	PIT 4	1-5 vdc	0 – 1 (0 – 14.7)	± 2 % R	atm (psig)	$\frac{(0.02\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.9%
2	Ambient temperature ($T_{ambient}$)	RTD	RTD 7	1-5 vdc	-25 – 175	± 2	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	2.6%
3	Separator Oil Temperature ($T_{sep\ oil}$)	RTD	RTD 1	1-5 vdc	-25 – 175	± 2	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	2.6%
4	Separator Gas Temperature ($T_{sep\ gas}$)	RTD	RTD 2	1-5 vdc	0 – 250	± 2	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	1.6%
5	Separator Pressure (P_{sep})	Pressure transducer	PIT 1	1-5 vdc	0 – 500	± 2% R	psig	$\frac{(0.02\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.9%
6	Vane Meter Velocity	Vane anemometer	Vane Velocity	4-20 mA	0.1 – 70	< 1.5 % FS	m/s	$\frac{(0.015\cdot 70)^2+(0.002\cdot FS)^2}{3}$	1.5%
7	Separator produced gas flowrate ($Q_{sales\ gas}$)	XFC G4 6413	ABB Flow	1-5 vdc	0 – 250 DP 0 – 500 SP	0.05% URL	SMCFD	$\frac{(0.0005\cdot R)^2+(0.002\cdot FS)^2}{3}$	0.4%
8	Separator-to-oil tank pipe gas/liquids pressure Hi ($P_{dump\ flow}$)	Pressure transmitter	PIT 8	4-20 mA	0 – 100	± 0.25 % R (FS @ 75 °F)	psig	$\frac{(0.0025\cdot R)^2+(0.002\cdot FS)^2}{3}$	0.4%
9	Separator oil flowrate to tank (Q_{oil})	Coriolis meter	CM Flow	1-5 vdc	0 – 6 576	± 0.5% R	bbl/d	$\frac{(0.005\cdot R)^2+(0.002\cdot FS)^2}{3}$	0.4%
10	Separator oil to tank density (ρ_{oil})	Coriolis meter	CM Density	1-5 vdc	0 – 3.0	± 0.01	g/cm³ SG	$\frac{0.01^2+(0.002\cdot FS)^2}{3}$	0.7%

11	Separator oil to tank temperature ($T_{CM\ oil}$)	Coriolis meter	CM RTD	1-5 vdc	-40 – 140	± 1 °C ± 0.5 % R	°F	$\frac{1.8^2+(0.002\cdot FS)^2}{3}$	3.5%
12	Coriolis meter drive gain	Coriolis meter	CM DG	1-5 vdc	0 – 100	N/A	Percent	–	
13	Solar Radiation reading	SR05 pyranometer	Solar_Rad	4-20 mA	0 – 1600	20 %	W/m^2	$\frac{(0.2\cdot R)^2+(0.002\cdot FS)^2}{3}$	19%
14	Separator-to-oil tank pipe gas/liquids pressure Post dump valve	Pressure transmitter	PIT 7	4-20 mA	0 – 100	± 0.25 % R (FS @ 75 °F)	psig	$\frac{(0.0025\cdot R)^2+(0.002\cdot FS)^2}{3}$	0.45%
15	Separator Dump leg, Just after dump valve	RTD	RTD 16	1-5 vdc	-25 – 175	± 2	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	2.6%
16	Separator water flowrate to tank (Q_{water})	Coriolis meter	CM W Flow	1-5 vdc	0 – 6 576	± 0.28 % R	bbl/d	$\frac{0.0028\cdot FS}{1.96}$	0.28%
17	Coriolis meter Water drive gain	Coriolis meter	CM DG	1-5 vdc	0 – 100	N/A	Percent	–	–
18	Oil dump valve on/off position & dump time/ duration (τ_{dump}, I_{dump})	Valve position indicator	O Dump Po		0 or 1	NA	0,1,2,3	–	–
19	Separator-to-oil tank pipe gas/liquids temperature ($T_{dump\ flow}$)	RTD	RTD 4	1-5 vdc	0 – 250	± 2 °F	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	1.6%
20	Separator-to-oil tank pipe gas/liquids temperature ($P_{dump\ flow}$)	Pressure transducer	PIT 5	1-5 vdc	0 – 1.5 (0 – 24)	± 2 % R	psig (oz)	$\frac{(0.02\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.9%

21	Separator-to-oil tank pipe gas/liquids pressure Lo ($P_{dump\ flow}$)	Pressure transducer	PIT 9	1-5 vdc	0 – 1.5 (0 – 24)	± 2% R	psig	$\frac{(0.02\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.9%
22	Oil tank headspace gas temperature ($T_{tank\ gas}$)	RTD	RTD 3	1-5 vdc	-25 – 175	± 2 °F	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	2.6%
23	Oil tank gas/liquids temperature ($T_{tank\ 1}$)	RTD	RTD 15	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
24	Oil tank gas/liquids temperature ($T_{tank\ 2}$)	RTD	RTD 14	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
25	Oil tank gas/liquids temperature ($T_{tank\ 3}$)	RTD	RTD 13	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
26	Oil tank gas/ liquids temperature ($T_{tank\ 4}$)	RTD	RTD 12	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
27	Oil tank gas/liquids temperature ($T_{tank\ 5}$)	RTD	RTD 11	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
28	Oil tank gas/liquid temperature ($T_{tank\ 6}$)	RTD	RTD 10	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
29	Oil tank gas/liquids temperature ($T_{tank\ 7}$)	RTD	RTD 9	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
30	Oil tank gas/liquids temperature ($T_{tank\ 8}$)	RTD	RTD 8	1-5 vdc	-40 – 185	± 1.5 °F	°F	$\frac{1.5^2+(0.002\cdot FS)^2}{3}$	0.9%
31	Oil tank liquid level ($H_{tank\ liquids}$)	Tank level sensor	LL1	1-5 vdc	0 – 180	0.125 inch	Inches	$\frac{0.125^2+(0.002\cdot FS)^2}{3}$	0.40%
32	Oil tank headspace gas pressure ($P_{tank\ gas}$)	Pressure transducer	PIT 2	1-5 vdc	0 – 1.5 (0 – 24)	± 2 % R	psig (oz)	$\frac{(0.02\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.9%

33	Oil tank VOC burner line gas temperature ($T_{voc\ pipe}$)	RTD	RTD 6	1-5 vdc	-25 – 175	± 2 °F	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	2.6%
34	Oil tank VOC burner line gas pressure ($P_{voc\ pipe}$)	Pressure transducer	PIT 3	1-5 vdc	0 – 2 (0 – 32)	< ± 0.5 % R (@ 0-1 psig)	psig (oz)	$\frac{(0.005\cdot R)^2+(0.002\cdot FS)^2}{3}$	0.6%
35	Oil tank VOC burner line gas velocity	Thermal flowmeter	Fox1 Velocity	1-5 vdc	TBD	TBD	NMH		–
36	Oil tank VOC burner line gas flowrate ($Q_{tank\ gas\ 1}$)	Thermal flowmeter	Fox1 Flow	1-5 vdc	0 – 500 Two Curves	1 % R + 0.2 % FS	SMCFD	$\frac{(0.01\cdot R)^2+1^2+(0.002\cdot FS)^2}{3}$	1.1%
37	Oil tank VOC burner line gas temp	Thermal flowmeter	Fox1 Temp	1-5 vdc	-40 – 240	1.8	°F	$\frac{1.8^2+(0.002\cdot FS)^2}{3}$	1.8%
38	Oil tank VOC burner line gas flowrate ($Q_{tank\ gas\ 2}$)	Vane anemometer	Vane Anemometer	4-20 mA	0 – 253.2	< 1.5 %	actual m^3/hr.	$\frac{(0.015\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.5%
39	Oil tank VOC burner line gas Velocity	Thermal flowmeter	Fox2 Velocity	1-5 vdc	TBD	TBD	NMH		–
40	Oil tank VOC burner line gas Flowrate ($Q_{tank\ gas}$)	Thermal flowmeter	Fox2 Flow	1-5 vdc	0 – 500 Two Curves	1% R + 0.2 % FS	SMCFD	$\frac{(0.01\cdot R)^2+1^2+(0.002\cdot FS)^2}{3}$	1.1%
41	Oil tank VOC burner line gas Temp	Thermal flowmeter	Fox2 Temp	1-5 vdc	-40 – 240	1.8	°F	$\frac{1.8^2+(0.002\cdot FS)^2}{3}$	1.8%
42	Separator Dump Temp, Just prior to coriolis meter.	RTD	RTD 5	4-20 mA	0 – 200	± 2 °F	°F	$\frac{2^2+(0.002\cdot FS)^2}{3}$	1.9%

43	Separator Dump Pressure, Just prior to coriolis meter.	Pressure transducer	PIT 6	1-5 vdc	0 – 500	± 2 % R	psig	$\frac{(0.02\cdot R)^2+(0.002\cdot FS)^2}{3}$	1.9%
44	Oil tank PRV vent gas flowrate ($Q_{PRV\ gas}$)	Thermal flowmeter	Fox3 Velocity	1-5 vdc	TBD		NMH		–
45	Oil tank PRV vent gas flowrate ($Q_{PRV\ gas}$)	Thermal flowmeter	Fox3 Flow	1-5 vdc	0 – 500 Two Curves	1% R + 0.2 % FS	SMCF	$\frac{(0.01\cdot R)^2+1^2+(0.002\cdot FS)^2}{3}$	1.1%
46	Oil tank PRV vent gas flowrate ($Q_{PRV\ gas}$)	Thermal flowmeter	Fox3 Temp	1-5 vdc	-40 – 240	1.8	°F	$\frac{1.8^2+(0.002\cdot FS)^2}{3}$	1.8%
47	VOC valve on/off position & dump time/ duration (τ_{dump}, I_{dump})	Valve position indicator	BRNvalve/ AUX1		0 or 1	NA	0,1 (logic on/off)	–	–

6.3 Coriolis Liquid Flow Meter

As mentioned before, Coriolis meters are under a metrological control scheme that includes field proving. Calibration reports are in compliance with API MPMS 4, and include repeatability performance as well as uncertainty.

The parameters that influence the flowmeter uncertainty include:

u_{zs}^2: Zero stability uncertainty

u_{Cal}^2: Calibration uncertainty

u_r^2: Repeatability uncertainty

u_T^2: Temperature uncertainty (applied to temperature readings higher than 84.2)

u_P^2: Pressure uncertainty

As condensate flows through the Coriolis meter during a well cycle, zero stability; a zero drift declared by manufacturer (Micro Motion® R-Series Coriolis Flow and Density Meters. Product Data Sheet PS-00363, Rev L May 2017. Emerson Automation Solutions), is applied to calibration and repeatability uncertainty sources. Average uncertainty of calibration and repeatability of calibration certificates are applied to values greater than 1/20 of full scale, lower values are calculated using the formula: accuracy = (zero stability/flow rate) x 100% in accordance with the manufacturer's operation manual.

The total uncertainty for the Coriolis meter oil flow (CM_{oil}) is then expressed as:

$$u^2(CM_{oil}) = u^2{}_{Cal} + u^2{}_r + u^2{}_T \tag{6.6}$$

The calibration uncertainty is based on proving certificates with a correction for low flows, repeatability uncertainty is based on pooled uncertainty from six flow cycles with low flow correction, and temperature is only applied when instrument operation is above temperature range of calibrations.

Example:

A medium separator operating pressure sample was obtained during a summer testing well cycle with a flow of 0.522 bbl/d and 84.2 °F. Since temperature correction does not apply to temperatures below 84.2°F, equation 6.6 is as follows:

$$u^2(CM_{oil}) = (0.522 \cdot 0.00026)^2 + (0.522 \cdot 0.00018)^2 + (|0| \cdot 5/9 \cdot 0.000875)^2)^2$$
$$= 0.00011$$

$$u(CM_{oil}) = \sqrt{1.12x10^{-8}} = 0.00011$$

$$U(CM_{oil}) = 0.00011 \cdot 1.96 = 0.0002$$
$$\%U(CM_{oil}) = 0.021\%$$

(6.7)

This uncertainty is applicable to steady flows, and because steady flow is not feasible under field conditions, an uncertainty of 1.0% of flow, twice the manufacturer specification of 0.5 % of flow, was considered.

7. Uncertainty of Storage Tank Mass Balance and FGOR Measurements

Data and documentation for these calculations are included in the spreadsheets in Appendix IV.2.

8. PSM/EOS FGOR Calculations Uncertainty Analysis

Supporting data and calculations for the information presented in this section can be found in Appendix V.

8.1 Introduction.

The uncertainties of many measurements conducted for this project were estimated using methodologies from international standards; however, this is not the case for PSM/EOS calculations of FGORs.

The uncertainty of results calculated using Equation of State software packages cannot be determined using standard GUM procedures because calculations of sensitivity coefficients and combined calculations are not possible for such black box models. Therefore, the uncertainties of PSM/EOS FGOR calculations were estimated using a numerical approximation method and a Monte Carlo simulation, and the results of these two approaches were compared.

Numerical approximation sensitivity assessment and uncertainty calculation

One approach to estimate the uncertainty of PSM/EOS calculations of FGOR is to isolate and vary 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. This can be a laborious process and additional complexity can result from combining uncertainty sources; for example, some may have a normal distribution while others may have triangular or rectangular distribution.

Monte Carlo simulation sensitivity assessment and uncertainty calculation

Monte Carlo (MC) simulation is another sensitivity and uncertainty calculation approach, but it can be limited by availability of technical resources, software and hardware tools. Monte Carlo simulation produces a distribution of possible outcome results by performing thousands of calculations. Calculation inputs that have an inherent uncertainty are randomly varied for each iteration based on their probability distribution. Each calculation uses a different set of random input values from the probability functions.

Summary of Findings

- Separator temperature and pressure, and tank bottom temperature are the measured process parameters that have a large influence upon FGOR uncertainty. Siphon prevention hole fraction also contributes to FGOR uncertainty. Octanes and methane were the pressurized condensate components that have the significant effect on FGOR. FGOR is sensitive to condensate methane concentration, and octanes influence this analysis because octanes had a very high analytical uncertainty.
- The numerical approximation method and Monte Carlo simulation calculate FGOR uncertainty estimates ranging from 3 to 5 %. In general, the Monte Carlo uncertainty estimates were slightly lower.

8.2 Numerical Approximation Uncertainty Calculation.

The Numerical Approximation approach calculates several PSM/EOS FGOR estimates, or another variable of interest, by changing a critical input parameter in prescribed iterations. FGOR sensitivity to the parameter changes may be calculated from compiled results (i.e., calculate ratio of FGOR change to input parameter change).

If the input variable changes are close to standard uncertainty and the change in the calculated value is proportional to the change in the input variable, then the input variable / calculated value relationship is similar to a sensitivity coefficient multiplied by standard uncertainty as in API MPMS 13.3 equation 7. When these conditions apply, the uncertainty of the PSM/EOS calculated parameter (e.g., FGOR) can be calculated by API MPMS 13.3 equation 7 without correlation.

Limitations of this approach include if the number of input variables/parameters in the measurement model is very large, calculations will be very time consuming and/or only a subset of the input variables can be assessed. In addition, final calculated uncertainties tend to be higher than uncertainties obtained by Monte Carlo simulation because some sensitivities are overestimated.

Another limitation of this approach is the inability to completely isolate the effect of an input parameter (i.e., some input parameters may be correlated). For example, a change to the pressurized condensate methane concentration will proportionally change the concentration of the other condensate components.

8.2.1 Calculation example

A Summer testing, medium separator pressure condensate sample (S-MP3, GPA 2103) was used for PSM/EOS calculations of FGOR values, and the impact of changing the following variables was determined: Tank Headspace temperature, Tank Headspace pressure, Tank 1 foot from Bottom temperature, Tank 1 foot from Bottom pressure, Decanes Plus Molecular Weight, Decanes Plus Density, Separator Pressure, Separator temperature and Siphon Prevention Hole Fraction. For example, Table 8-1 lists the range of Tank 1 foot from Bottom pressures input into the calculations, and associated FGOR values that were calculated. This range is based on the estimated high and low limit values of the parameters that contribute to the tank bottom pressure (i.e., ambient pressure, tank headspace pressure, and liquid head pressure) and their associated uncertainties.

The Numerical approximation calculation was conducted following these steps:

1. Multiple simulations were conducted by changing a variable of interest (e.g., Separator Pressure) by adding and subtracting from the average value one standard uncertainty and one expanded uncertainty (for a total of five simulations) while maintaining the other variables fixed. FGOR, bubble point pressure, and shrinkage factor were calculated during each simulation.
2. Using calculated standard uncertainties, a combined uncertainty of a property such as FGOR was calculated in equivalent form as API 13.1 equation 7, under assumption that sensitivity coefficient and uncertainty square product is equivalent to numerical approximation calculation (API 13.1 5.6.2).

$$u_{FGOR}^2 = \sum_{i=1}^{n-1} c_i^2 \, u_i^2 \tag{8.1}$$

$$u_{FGOR}^2 \approx \sum_{i=1}^{n-1} \left(f_{FGOR}(y_0) - f_{FGOR}(y_i)\right)^2 \tag{8.2}$$

where:

$f_{FGOR}(y_0)$: FGOR calculated value with variables unaffected by uncertainty

$f_{FGOR}(y_i)$: FGOR calculated value with variables affected by uncertainty

3. Expanded uncertainty was calculated applying a coverage factor of 1.96 and relative uncertainty was calculated from the property value without uncertainty.
4. Calculation of the sensitivity of each input variable was performed by calculating the square of property change by sum of squares of property changes

$$S_{P(sep)} = \frac{\left(f_{FGOR}(y_0) - f_{FGOR}(y_{P(sep)})\right)}{\sum_{i=1}^{n-1}\left(f_{FGOR}(y_0) - f_{FGOR}(y_i)\right)^2} \cdot 100 \tag{8.3}$$

where:

$S_{P(SEP)}$: Sensitivity of FGOR to separator pressure changes.

$f_{FGOR}(y_{p(sep)})$: FGOR calculated value with variable Separator Pressure affected by uncertainty

Table 8-1. Tank One Foot from Bottom Pressure (TBP)

Condition	Value	Units	FGOR (scf/bbl)
High value (-)	16.30	psia	376.90
Mid value (-)	16.40	psia	375.77
Central value	16.49	psia	374.78
Mid value (+)	16.57	psia	373.79
High value (+)	16.65	psia	372.69

Linear regressions of input values and FGOR results were calculated (Eq. 8.5), and the regression coefficient of 0.99975 confirms the applicability of the first order model. This means that other FGOR values can be calculated with a first order formula. This allows evaluate standard uncertainties without the need for additional simulations.

$$c_{TBP} \cdot u_{TBP} \approx \frac{(a\,(Ev_{TBP} + u_{TBP}) + b) - (a\,(Ev_{TBP} - u_{TBP}) + b)}{2} \tag{8.4}$$

Where:

c_{TBP}	Reported value of FGOR for the winter testing condition, dependent variable in linear regression
u_{TBP}	Standard uncertainty of Tank Bottom Pressure (TBP)
a	Slope constant of first order regression (dimensionless)
b	Ordinate to origin or intercept constant of first order regression (dimensionless)
Ev_{TBP}	Expected value of Tank Bottom Pressure

A linear regression of the TBP and FGOR values in Table 8-1 produces the following equation:

$$FGOR = -12.46\,TBP + 580.2 \tag{8.5}$$

The Pearson regression coefficient for this equation is -0.99975 and r^2 is 0.9995; thus, the, sensitivity is a negative term, this means that an increase of Tank pressure produces a decrease of FGOR result. FGOR is calculated by adding and subtracting 0.071 psi, the standard uncertainty of tank bottom pressure, to the 16.49 psia central value.

Substituting in Equation 8.1, considering a standard uncertainty of 0.071 psi:

$$c_{TBP} \cdot u_{TBP} \approx \frac{(-12.46\,(16.487 + 0.071) + 580.2) - (-12.46\,(16.487 - 0.071) + 580.2)}{2}$$

$$c_{TBP} \cdot u_{TBP} \approx \frac{(375.67 - 373.90)}{2} \approx -0.885 \; \mathit{(SCF/BBL)} \tag{8.6}$$

An advantage of this solution is that changes in instrumentation or analysis performance can be easily evaluated. After a similar procedure was conducted for all input variables of interest, a quasi-combined uncertainty function could be evaluated and a standard uncertainty of the calculated FGOR or other property may be estimated.

The calculation of uncertainty budget is feasible by sensitivity analysis. Combining the sensitivities for each input quantity and assuming uncorrelated variables (API 13.1 equation 7), the relative sensitivity effects listed in Table 8-2 and graphically presented in Figure 8-1 were obtained. These results indicate that tank Bottom Temperature, methane and Octane, Siphon Prevention Hole Fraction, and Separator Pressure have the largest effect on the PSM/EOS calculated FGOR.

Table 8-2. Relative PSM/EOS FGOR Calculation Sensitivity Effect Determined by Numerical Approximation

Variable	FGOR
Tank 1 foot from Bottom Temperature	26.8%
Methane/-C8	26.2%
Siphon Prevention Hole Fraction	19.7%
Psep (psia)	19.6%
Tsep (°F)	-3.9%
Tank 1 foot from Bottom Pressure	-2.0%
Decanes Plus Molecular Weight	-1.4%
Tank Headspace Temperature	0.3%
Decanes Plus Density	0.0%

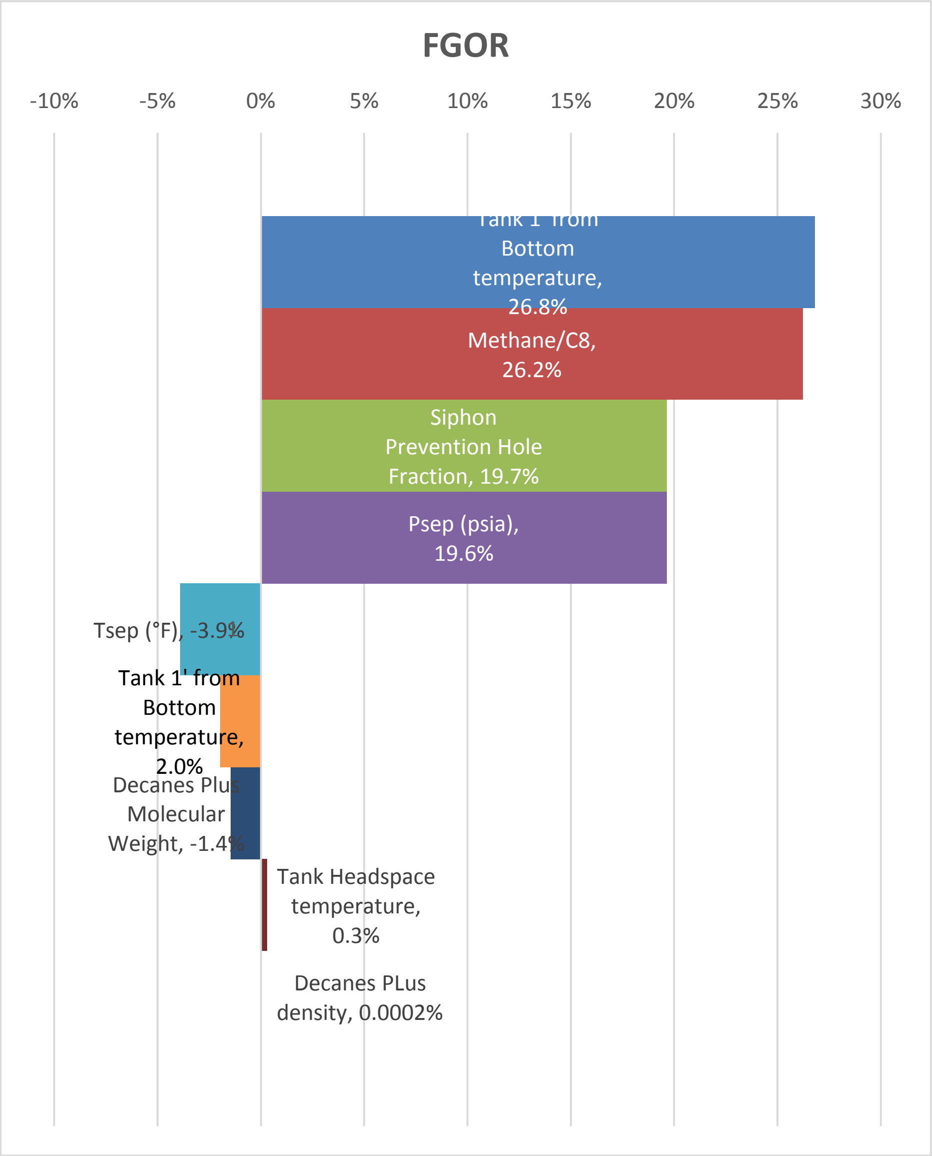

Figure 8-1. Relative PSM/EOS FGOR calculation sensitivity effect determined by numerical approximation

After sensitivity evaluation, a relative expanded uncertainty of 3.3 % was obtained.

8.3 Monte Carlo Simulation.

For FGOR sensitivity analysis and uncertainty calculations, a Monte Carlo simulation using Crystal ball 11.1 and Sim2 for PSM/EOS FGOR calculations (refer to Appendix V), was performed. Input variables were condensate composition and process parameters Oil Flow Rate, Separator Temperature, Separator Pressure, Siphon hole fraction , Tank Headspace

Temperature , Tank Headspace Pressure , Tank Bottom Temperature, and Tank Bottom Pressure and their associated uncertainties.

Uncertainties for pressurized condensate compositional analyses from section 4.0 and process parameter uncertainties from Section 6.0 were used for the MC simulation.

For the winter testing medium separator pressure condensate sample that was used for PSM/EOS calculations of FGOR values in Section 8.2.1, the Monte Carlo simulation estimated an FGOR uncertainty of 2.9% (relative to mean value) based on the MC simulation FGOR output probability distribution standard deviation and 95% confidence level . This is very close to the value estimated with the numerical approximation procedure. Figure 8-2 presents the relative sensitivity effects.

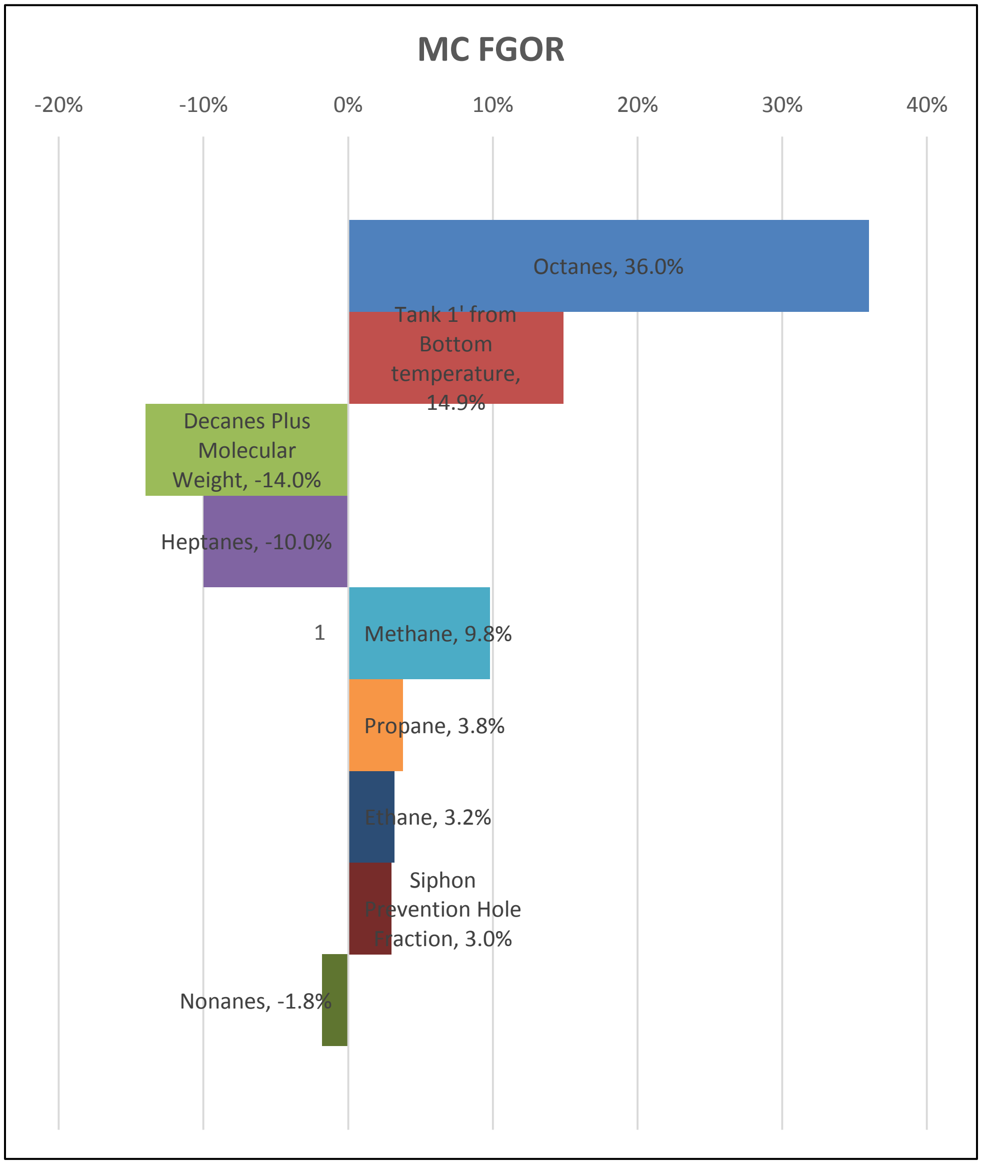

Figure 8-2. Monte Carlo simulation sensitivity study

8.4 Summary of Results

Table 8-3 (FGOR), Table 8-4 (Bubble Point Pressure), and Table 8-5 (Shrinkage Factor) summarize the results for all well cycles for the numerical approximation method and the Monte Carlo simulations.

Table 8-3. Results of FGOR Uncertainty Calculations

Season	Well Cycle Sample	GPA 2103 Analysis		GPA 2186 Analysis	
		Numerical Approximation	Monte Carlo Simulation	Numerical Approximation	Monte Carlo Simulation
SUMMER	LP-3	3.8%	3.0%	4.0%	3.3%
SUMMER	MP-3	2.8%	2.8%	3.1%	3.0%
SUMMER	HP-3	2.8%	2.7%	3.7%	2.9%
WMULTI	LP-1	4.9%	3.8%	4.7%	3.8%
WMULTI	MP-2	3.8%	3.3%	3.7%	3.3%
WMULTI	HP-1	3.3%	3.1%	3.0%	3.1%

Table 8-4. Results of Bubble Point Pressure Uncertainty Calculations

Season	Well Cycle Sample	GPA 2103 Analysis		GPA 2186 Analysis	
		Numerical Approximation	Monte Carlo Simulation	Numerical Approximation	Monte Carlo Simulation
SUMMER	LP-3	1.1%	2.2%	1.0%	2.9%
SUMMER	MP-3	1.1%	2.2%	1.0%	2.9%
SUMMER	HP-3	1.1%	2.2%	1.2%	2.9%
WMULTI	LP-1	1.2%	3.0%	0.8%	3.0%
WMULTI	MP-2	1.2%	3.0%	0.8%	3.0%
WMULTI	HP-1	0.9%	3.1%	0.7%	3.1%

Table 8-5. Results of Shrinkage Factor Uncertainty Calculations

Season	Well Cycle Sample	GPA 2103 Analysis		GPA 2186 Analysis	
		Numerical Approximation	Monte Carlo Simulation	Numerical Approximation	Monte Carlo Simulation
SUMMER	LP-3	0.50%	0.44%	0.47%	0.44%
SUMMER	MP-3	0.57%	0.50%	0.46%	0.49%
SUMMER	HP-3	0.57%	0.57%	0.70%	0.54%
WMULTI	LP-1	0.41%	0.32%	0.36%	0.32%
WMULTI	MP-2	0.42%	0.38%	0.37%	0.38%
WMULTI	HP-1	0.56%	0.55%	0.49%	0.55%