# Portable Gas Chromatography Standard Operating Procedures

## 1.0 Purpose

This document outlines the procedures for the operation of a Portable Gas Chromatograph (GC) for in the field gas measurement. The portable gas chromatograph separates and measures the individual gas components in a natural gas mixture. The following properties can be determined from this measurement:

- Composition
- Specific gravity
- Heating value
- Hydrocarbon liquids, gallons per 1,000 cubic feet of gas (GPM)
- Liquid petroleum gases (LPG), gallons per 1,000 cubic feet of gas (propane and butane)
- Compressibility

This Standard Operating Procedure (SOP) requires the use of a historical verification software program for validating sample results to ensure an accurate and representative sample was collected before the analyst leaves the location.

This SOP utilizes the following industry guidance standards:

- GPA Standard 2166 - Obtaining Natural Gas Samples for Analysis by Gas Chromatography
- API Manual of Petroleum Measurements Standards Chapter 14.1 - Natural Gas Fluids Measurement - Collecting and Handling of Natural Gas Samples for Custody Transfer
- GPA Standard 2261 - Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography
- GPA Standard 2145 - Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas Industry
- GPA Standard 2172 - Calculation of Gross Heating Value, Relative Density, Compressibility and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for Custody Transfer
- GPA Standard 2198 - Selection, Preparation, Validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends
- GPA Standard 2198 - Selection, Preparation, Validation, Care and Storage of Natural Gas and Natural Gas Liquids Reference Standard Blends

This SOP contains the following sections:

## 2.0 Portable GC Checklist

### 2.1 Daily Responsibilities:

1. Ensure Helium carrier gas is of adequate pressure for model of gas chromatograph and the regulator is functioning properly. (No lower than 200 psig cylinder pressure). (Refer to Section 3.0 Attaching the Helium Carrier Gas).
2. Purge the sample hose with sample gas, standard gas, or UHP Helium prior to analyzing the first samples of the day and prior to analyzing the first sample at each location (between 16 and 20 psig for a minimum of 2 minutes). A multi-port valve at the sample / calibration gas inlets of the chromatograph will allow for purging the sample line without detaching it from the instrument, thus reducing the potential for ambient infiltration.
3. Ensure the sampling system is heated to a minimum of 30º F above hydrocarbon dewpoint of the gas being sampled.
4. Keep a cap or plug on the sampling end of the heated line and the filter/regulator assembly when they are not in use to ensure foreign objects do not enter the system.
5. Do not lie anything on top of the heated hose while being stored. Keep it loose, coiled, and free from chafing. Do not kink the hose which will break the heat tape and pinch the sample tubing within.
6. Discard the first run of the day.
7. Check the un-normalized totals (should be between 97.0% and 103.0%) and verify the heating value, specific gravity, and individual mole% concentrations with historical data prior to accepting and processing any and all analyses into the measurement accounting system and/or entering values into the meter (refer to Section 6.0 In the Field Sample Analysis).
8. When analyzing high $H_2S$ wells, it is recommended that the sample system be purged with UHP Helium in-between locations (this will help clear the system of $H_2S$ contamination).

### 2.2 **Weekly Responsibilities**:

1. Perform validation / calibration procedures, ensure the all required documentation is saved and maintained in accordance with company's best practices (refer to Section 7.0 Calibration and Validation).
2. Monitor the calibration gas pressure and temperature.
    a. All calibration gases shall be maintained in accordance with GPA 2198.
    b. The temperature of each cylinder should be maintained at a minimum of 30º F above hydrocarbon dewpoint.
        i. Each cylinder should be heated for a minimum of 24 hours prior to use.
3. Check for leaks in the entire system (do not use leak detection liquids on the Helium fitting on the the back of the GC).
4. Ensure integrity of the heated hose (inspect for cuts, cold spots, kinks, etc.). Replace as necessary.

### 2.3 **Monthly Responsibilities**:

1. Verify the cleanliness of the sampling system by flowing UHP Helium through the entire sampling system and analyzing it on the chromatograph, clean as necessary (refer to Section 9.0 Sampling System Validation).
    a. More frequent cleaning of the sampling system may be required depending on the locations sampled. Monitor the types of field gas sampled throughout the month and increase cleaning frequency as necessary.

### 2.4 **Annual Responsibilities**:

1. Update historical sample verification database from the Measurement Validation and Accounting system.
    a. More frequent updates may be required, depending on the variability of the samples being analyzed.

## 3.0 Attaching the Helium Carrier Gas

**<u>Note</u>**:
It is recommended that Helium carrier gas cylinders be mounted inside the cab of the vehicle due to the extreme temperature fluctuations the cylinder may be exposed to during the winter and summer months. Super cooling and super heating can cause a wide range of chromatographic issues and irregularities. The chromatograph should always be <u>OFF</u> when carrier gas is not flowing (full Shut-Down and Start-Up procedures should be followed when installing a new carrier gas bottle)**.**

1. Verify the carrier gas being used is Ultra High Purity (UHP) Helium. UHP is defined as 99.999% pure.
2. Ensure any regulators and tubing being used for carrier gas are clean and dedicated. Never use regulators or tubing that has been used for any other purpose.
   a. A 2um in-line filter should be installed between the chromatograph and carrier gas tubing to ensure no particulate enters the instrument. Contaminants and/or particulate in the carrier gas can cause chromatographic issues and potentially damage the instrument.
   b. A moisture trap can also be installed between the chromatograph and carrier gas tubing to ensure no moisture enters the instrument. Moisture vapor in the carrier gas can cause chromatographic issues and potentially degrade the columns.
3. Check the Helium carrier gas bottle for proper operating pressures. The cylinder pressure should be above a minimum of 200 psig.
4. Prior to attaching the carrier gas tubing to the chromatograph, the regulator and tubing should be purged. With the tubing disconnected from the instrument, open the Helium cylinder and increase (clockwise) the pressure to approximately 5 psig. Allow the Helium to bleed into the atmosphere for approximately 60 seconds.
5. With the Helium still flowing at approximately 5 psig, connect the carrier gas tubing to the inlet port of the instrument. <u>Tighten the fitting but do not use a liquid leak detector to test for leaks on the GC</u>.
6. Very slowly increase (clockwise) the regulator pressure setting from 5 psig to the manufacturer recommended setting. This process should take an average of 1-2 minutes to perform. Check the regulated pressure setting daily. As it bounces down the road in the vehicle, the setting can change.
   a. Each Helium carrier gas cylinder regulator shall be designed for the proper pressure range. UHP Helium cylinders typically have 2200 to 2600 psig when new. Portable gas chromatographs typically require between 55 and 95 psig. The delivery side of the regulator should have a max setting of no more than 300 psig. Regulators with higher settings are not as accurate at 95 psig and below. Delivering too much pressure can severely damage the instrument.
7. In order to avoid the build up of potentially hazardous Helium concentrations within the cab of the vehicle, the carrier gas cylinder valve should be closed when the GC is to remain unused for an extended period of time, such as nights and weekends.
8. Validation of Helium carrier gas is to be performed prior to new cylinder attachment to the GC.

   a. Verify that there are no gas components trapped within the GC prior to the verification process by running the Ultra High Purity Helium validation gas through the GC several times to establish a base line.
   b. Use a piece of clean or new nylon 11 tubing with clean or new fittings and a clean regulator for connection between the GC and cylinder, not the heated sample line and/or filter/regulator assembly.
   c. Purge the tubing and regulator to clear the system of Oxygen and Nitrogen (thoroughly purge the regulator several times), prior to attaching them to the instrument.
   d. Regulate the Helium gas inlet pressure to the GC between per manufacturer specifications.
   e. Perform several analyses until it is verified that the GC has no residual components (refer to Section 9.0 Sampling System Validation). Un-normalized concentrations for each component should be non-detectable.
   f. Once the GC is verified to be free of residual components, connect the new Helium carrier gas cylinder.
   g. Purge the tubing and regulator to clear the system of Oxygen and Nitrogen (thoroughly purge the regulator several times), prior to attaching them to the inlet of the instrument.
   h. Regulate the Helium gas inlet to the GC between per manufacturer recommendations.
   i. Perform 3 analyses. Un-normalized concentrations for each component should be non-detectable.
   j. Another GC may be used for confirmation purposes, running the same test and using the same parameters as listed above
9. If the new cylinder is not within the specified limits, notify the vendor for replacement.
10. If the carrier gas passes, it may be placed in service using the connection procedures at the beginning of this section, Steps 1-7.
    a. Do not use leak detection liquids on the Helium carrier gas system.

## 4.0 Start-Up

1. Ensure the verified UHP Helium carrier gas is attached and on. Carrier gas should always be turned on prior starting the instrument (refer to Section 3.0 Attaching the Helium Carrier Gas).
    a. Carrier gas should always be the first thing on and the last thing off.
2. Ensure the appropriate communication cable is plugged into both the chromatograph and computer.
3. Turn the gas chromatograph power on.
4. Turn on the heated sampling system.
5. Power up the computer (computer can be powered up prior to powering up the chromatograph).
6. Launch the GC operation software.
7. Launch the historical verification software.
8. Download/initiate the appropriate analytical method as necessary.
9. Allow the gas chromatograph to stabilize for approximately 45 minutes prior to first analysis.
10. It is recommended that the first analysis of the day be discarded.

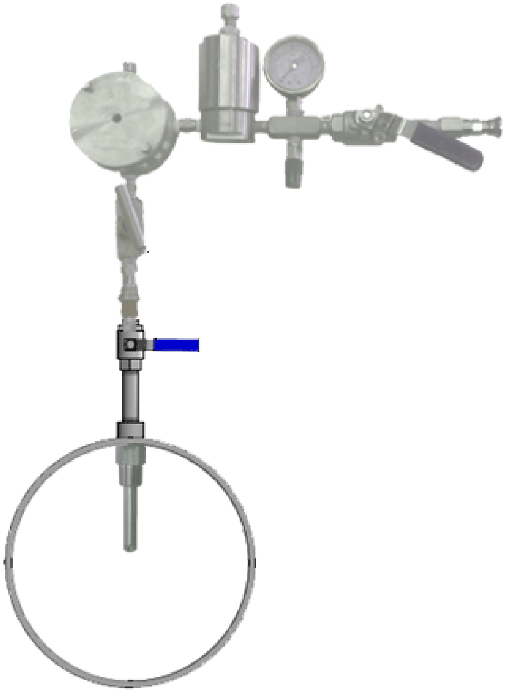
## 5.0 Shut-Down

1. When finished for the day, the power switch of the chromatograph can simply be turned off and software can be closed.
2. If the chromatograph is enclosed in a vehicle, the carrier gas should be turned off to reduce the potential for hazardous level build up.

## 6.0 In the Field Sample Analysis

***Note** - Never analyze a sample stream which is not flowing. A sample stream should flow a minimum of 2 hours prior to sample analysis. If that is impossible (such as in plunger lift applications), allow as much time as practicable prior to sample analysis.*

1. Vent the location sample point to ensure there are no standing liquids built up in the probe or valve.
2. Once the sampling point is free and clear of liquids, attach the filter/regulator assembly.
   a. The following picture is an example filter/regulator assembly.
   b. The assembly should be heated and/or insulated in a manner which ensures it is maintained at least 30º F above hydrocarbon dewpoint of the gas stream being analyzed.
      i. Heat should be maintained on the system when traveling between sampling locations.
   c. The filter/regulator assembly should be stored in a location which minimizes the opportunity for damage.

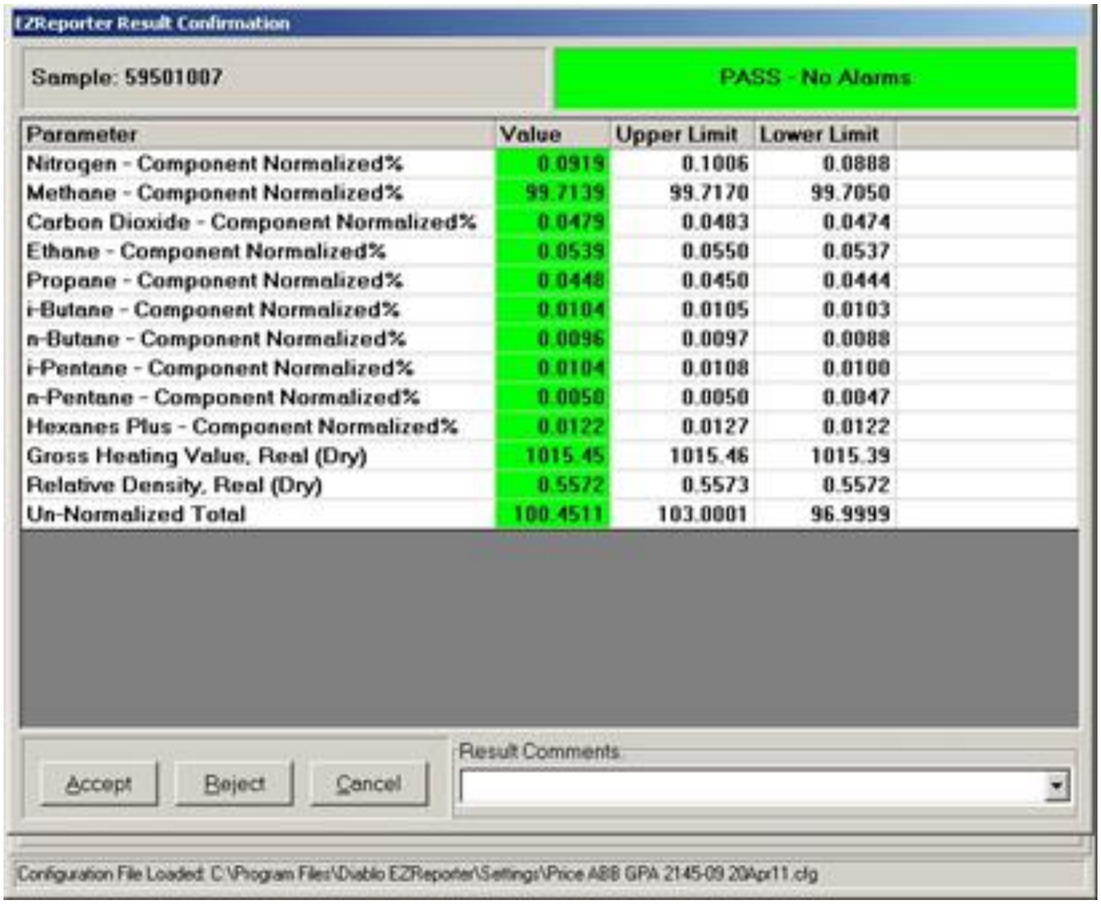


**Example Filter/Regulator Assembly**

3. Set the regulator to deliver the sample gas to the gas chromatograph at the same pressure at which it was calibrated (refer to Section 7.0 Calibration and Verification).
4. Attach the heated line to the filter/regulator assembly.
    a. Ensure the entire sampling system has reached at least 30º F hydrocarbon dewpoint prior to sampling.
    b. When possible, suspend the heated line to keep it off the ground (the cold ground pull heat from the line rapidly).
5. Turn the sample valve at the chromatograph to the vent position. Vent sample gas through the sampling system for a sufficient period of time to ensure a representative sample prior to starting analysis.
6. Turn the sample valve at the chromatograph to the sample inlet position.
7. Start the injection and analytical process on the gas chromatograph.
    a. When prompted, enter the appropriate identification into the system for sample tracking.
    b. Enter all other relevant information as necessary and available. This may include, but is not limited to, the following:
        i. Meter Number
        ii. Meter Name
        iii. Description
        iv. Flowing Temperature
        v. Flowing Pressure
8. If this was the first run of the day, discard and return to Step 7.
9. Upon completion of the analysis, the historical verification software data entry page will prompt the entry of additional information.
    a. Ensure the location identification number transferred correctly into the ‘Sample Name’ field.
        i. The location identification number will need to be identical to that used in the historical database to accurately compare the data.
    b. Enter all relevant data. This may include, but is not limited to, the following:
        i. Meter Name
        ii. Sample Date
        iii. Laboratory
        iv. Atmospheric Pressure
        v. Analyzer Type
        vi. Analyzer Make and Model
        vii. Last Verification/Calibration Date
        viii. Sampling Flow Rate
        ix. Ambient Temperature
        x. Sampling System Heat Tracing
        xi. Type of Sample (Spot or Composite)
        xii. Sampling Method
        xiii. Company Collecting Sample
        xiv. Hexanes Plus Split Ratio (if applicable)
        xv. Water Vapor Concentration (lbs/MMscf)
        xvi. Injection Date
        xvii. Report Date

   c. If $H_2S$ concentrations are collected by an analyzer or colorimetric tubes, enter the concentration in parts per million by volume (ppmv) into the appropriate '$H_2S$' field.
   d. If water vapor concentrations are collected by an analyzer, enter the concentration in pounds per million cubic feet (lbs/mmcf) into the 'Water Vapor' field.

10. Process the sample results through the historical data verification software system.
   a. The historical data verification software will verify the sample's individual component concentrations, gross heating value, and relative density against historical results for that sample location. Any results which fall within the preset acceptance windows (typically two sigma) will be highlighted green. Any results which fall outside the preset acceptance windows will be highlighted red. It will also validate the un-normalized total is between 97.0% and 103.0%
      i. The following is an example verification window with passing results.



EZReporter Result Confirmation

Sample: 59501007

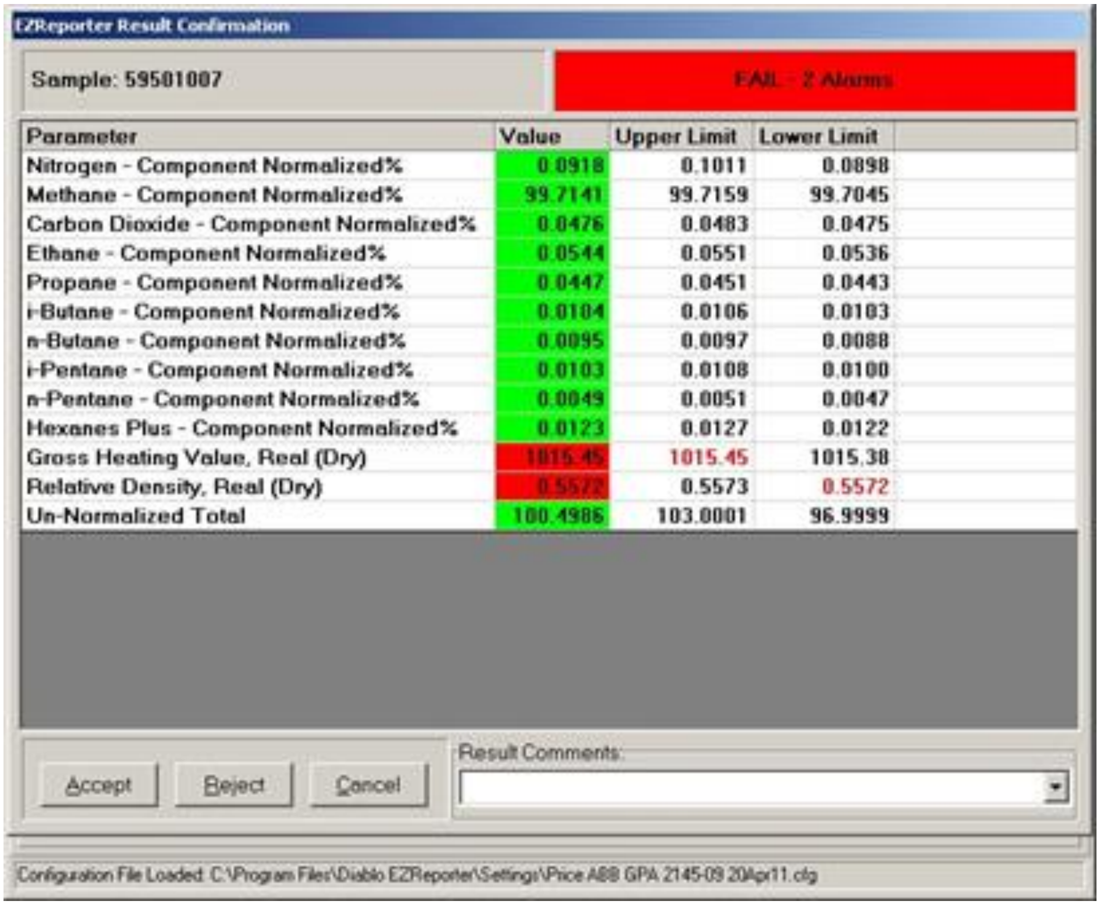
PASS - No Alarms

| Parameter | Value | Upper Limit | Lower Limit |
|---|---|---|---|
| Nitrogen - Component Normalized% | 0.0919 | 0.1006 | 0.0888 |
| Methane - Component Normalized% | 99.7139 | 99.7170 | 99.7050 |
| Carbon Dioxide - Component Normalized% | 0.0479 | 0.0483 | 0.0474 |
| Ethane - Component Normalized% | 0.0539 | 0.0550 | 0.0537 |
| Propane - Component Normalized% | 0.0448 | 0.0450 | 0.0444 |
| i-Butane - Component Normalized% | 0.0104 | 0.0105 | 0.0103 |
| n-Butane - Component Normalized% | 0.0096 | 0.0097 | 0.0088 |
| i-Pentane - Component Normalized% | 0.0104 | 0.0108 | 0.0100 |
| n-Pentane - Component Normalized% | 0.0050 | 0.0050 | 0.0047 |
| Hexanes Plus - Component Normalized% | 0.0122 | 0.0127 | 0.0122 |
| Gross Heating Value, Real (Dry) | 1015.45 | 1015.46 | 1015.39 |
| Relative Density, Real (Dry) | 0.5572 | 0.5573 | 0.5572 |
| Un-Normalized Total | 100.4511 | 103.0001 | 96.9999 |

Configuration File Loaded: C:\Program Files\Diablo EZReporter\Settings\Price ABB GPA 2145-09 20Apr11.cfg

**Example Historical Data Verification Window – All Parameters Passing**

   b. If all results fall within the acceptance parameters, they can be accepted and processed into the Measurement Accounting and Validation System.
      i. The following is an example verification window with failing results.



Sample: 59501007

| Parameter | Value | Upper Limit | Lower Limit |
|---|---|---|---|
| Nitrogen - Component Normalized% | 0.0918 | 0.1011 | 0.0898 |
| Methane - Component Normalized% | 99.7141 | 99.7159 | 99.7045 |
| Carbon Dioxide - Component Normalized% | 0.0476 | 0.0483 | 0.0475 |
| Ethane - Component Normalized% | 0.0544 | 0.0551 | 0.0536 |
| Propane - Component Normalized% | 0.0447 | 0.0451 | 0.0443 |
| i-Butane - Component Normalized% | 0.0104 | 0.0106 | 0.0103 |
| n-Butane - Component Normalized% | 0.0095 | 0.0097 | 0.0088 |
| i-Pentane - Component Normalized% | 0.0103 | 0.0108 | 0.0100 |
| n-Pentane - Component Normalized% | 0.0049 | 0.0051 | 0.0047 |
| Hexanes Plus - Component Normalized% | 0.0123 | 0.0127 | 0.0122 |
| Gross Heating Value, Real (Dry) | 1015.45 | 1015.45 | 1015.38 |
| Relative Density, Real (Dry) | 0.5572 | 0.5573 | 0.5572 |
| Un-Normalized Total | 100.4986 | 103.0001 | 96.9999 |

Configuration File Loaded: C:\Program Files\Diablo EZReporter\Settings\Price ABB GPA 2145-09 20Apr11.cfg

**Example Historical Data Verification Window – Parameter Failure**

a. If any results which fall outside the preset acceptance parameters, the following Steps should be followed:
   i. Individual parameter failures, with the exception of un-normalized totals, do not automatically indicate a bad sample. Failures indicate a potential issue and further evaluation and investigation should be performed to verify if the sample is good or bad.
      (1) If sample has high Nitrogen, turn the sample valve at the chromatograph to vent and vent sample gas through the sampling system again. Return to Step 6.
         (a) If Nitrogen concentrations do not decrease to expected levels, inspect the sampling system for leaks. Repair or replace as necessary.
      (2) If C6+ concentrations are high, it may be an indication of a contaminated sampling system.
         (a) Re-analyze the sample to verify concentration. Return to Step 6.
            (i) If C6+ concentrations remain higher than the acceptance limits, and it is due to contamination in the sampling system, clean the sampling system prior to performing any further analyses (Refer to Section 9.0 Sampling System Validation).
   ii. If the un-normalized totals are outside of the 97.0% to 103.0% acceptance window, return to Step 9.

(1) If after several analyses the un-normalized totals remain outside of the acceptance window, re-calibrate the instrument before proceeding (refer to Section 7.0 Calibration and Validation).
(2) Note that ambient pressure and altitude can also affect un-normalized totals.

iii. If individual component concentrations, heating value, and/or specific gravity values do not fall within the preset acceptance criteria, return Step 6.

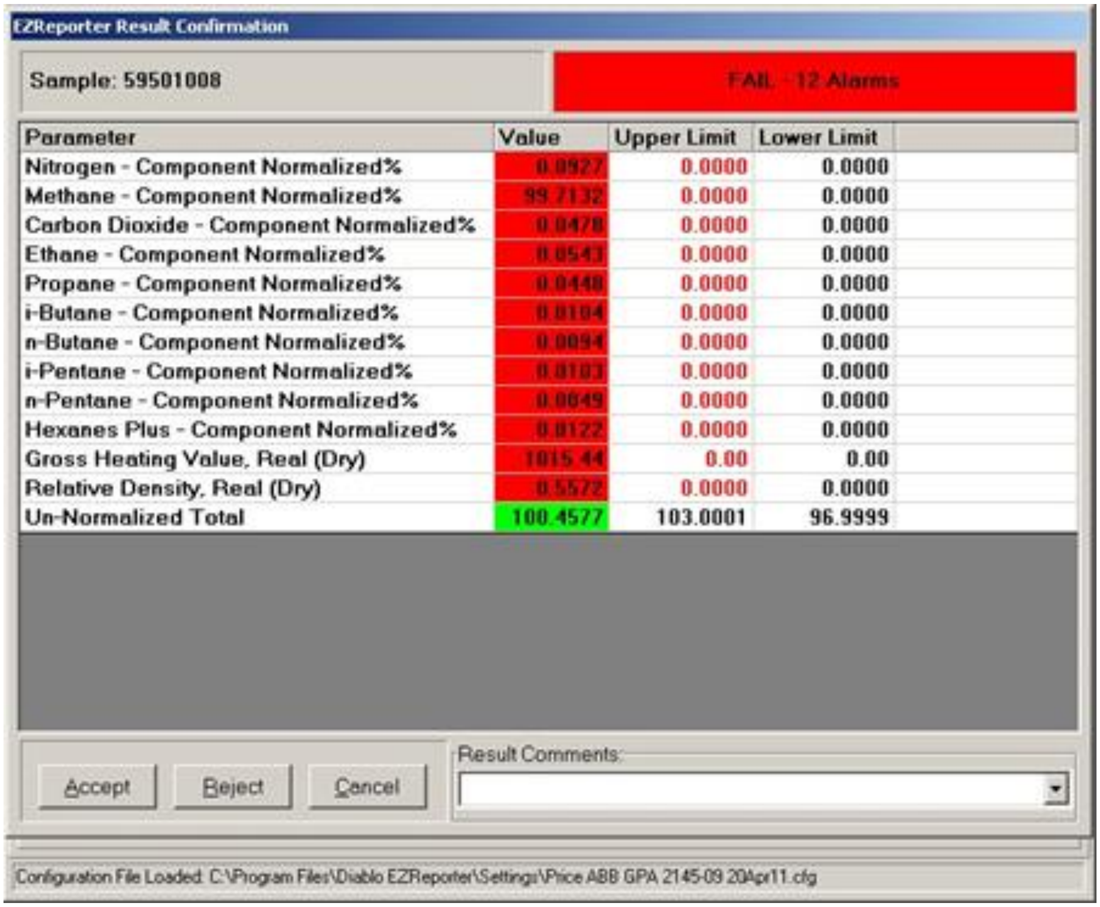
(1) If the results do not come within the preset acceptance criteria on the secondary analysis, determine if there are circumstances which would make that sample from that location different from past analyses. Such circumstances may include, but are not limited to, the following:
  (a) Difference in ambient temperatures between current and past analyses.
  (b) Well has not had flow in quite some time prior to analysis.
    (i) Remember; never analyze a well that is not flowing.
  (c) Multiple wells flow into the stream being tested and each turns on and off at various times.

Note - There are many other circumstances which may lead to differences from past analyses.

(2) If there are circumstances which explain the failure, enter any explanation into the comments field and accept the results.
  (a) It is very important to enter the explanations for any failures into the comments field because that information accompanies the data into the Measurement Accounting and Validation System and can be used for further validating and auditing. In addition, it will reduce the need for editors to contact technicians for confirmation.

iv. Most Historical Data Verification Software Systems require a minimum of 3 samples in the historical database to validate analyses. If there are less than 3 samples in the historical database, each individual result, with the exception of un-normalized totals, will be highlighted red.

(1) The following is an example verification window with failing results due to insufficient sample history.



Sample: 59501008

FAIL - 12 Alarms

| Parameter | Value | Upper Limit | Lower Limit |
|---|---|---|---|
| Nitrogen - Component Normalized% | 0.0927 | 0.0000 | 0.0000 |
| Methane - Component Normalized% | 99.7132 | 0.0000 | 0.0000 |
| Carbon Dioxide - Component Normalized% | 0.0478 | 0.0000 | 0.0000 |
| Ethane - Component Normalized% | 0.0543 | 0.0000 | 0.0000 |
| Propane - Component Normalized% | 0.0448 | 0.0000 | 0.0000 |
| i-Butane - Component Normalized% | 0.0104 | 0.0000 | 0.0000 |
| n-Butane - Component Normalized% | 0.0094 | 0.0000 | 0.0000 |
| i-Pentane - Component Normalized% | 0.0103 | 0.0000 | 0.0000 |
| n-Pentane - Component Normalized% | 0.0049 | 0.0000 | 0.0000 |
| Hexanes Plus - Component Normalized% | 0.0122 | 0.0000 | 0.0000 |
| Gross Heating Value, Real (Dry) | 1015.44 | 0.00 | 0.00 |
| Relative Density, Real (Dry) | 0.5572 | 0.0000 | 0.0000 |
| Un-Normalized Total | 100.4577 | 103.0001 | 96.9999 |

Configuration File Loaded: C:\Program Files\Diablo EZReporter\Settings\Price ABB GPA 2145-09 20Apr11.cfg

**Example Historical Data Verification Window – Not Enough History**

(2) If the un-normalized totals are within the 97.0% to 103.0% acceptance criteria, enter “Not Enough History” into the comments field and accept the results.

## 7.0 Calibration and Validation

**Note:**

Validation, and if necessary calibration, of the portable GC shall be done on a weekly basis, unless no samples are to be analyzed during a given week.

The calibration and validation procedures within this document utilize the GPA 2261-13 acceptance criteria for repeatability and reproducibility (see Table 1). Acceptance can be determined through the use of spreadsheets or though built-in comparisons within the historical verification software system.

| Compound | Range | Repeatability | Reproducibility |
|---|---|---|---|
| **Nitrogen** | .02 – 15 | $0.039x^{1/4}$ | $0.158x^{1/2}$ |
| **Methane** | 50 – 100 | $0.0079x^{1/3}$ | $91000x^{-3}$ |
| **$CO_2$** | .02 – 15 | $0.0042x^{1/3}$ | $0.12x^{1/3}$ |
| **Ethane** | .02 – 15 | $0.0124x^{1/3}$ | $0.0315x^{1/3}$ |
| **Propane** | .02 – 15 | $0.0084x^{1/8}$ | $0.026x^{1/2}$ |
| **iso-Butane** | .02 – 8 | $0.01x^{1/5}$ | $0.018x^{1/2}$ |
| **n-Butane** | .02 – 8 | $0.0117x^{2/5}$ | $0.033x^{1/2}$ |
| **iso-Pentane** | .02 – 4 | $0.009x^{1/4}$ | $0.025x^{1/4}$ |
| **n-Pentane** | .02 – 4 | $0.01x^{1/5}$ | $0.026x^{1/3}$ |
| **Hexanes Plus** | .02 – 2 | $0.0135x^{1/4}$ | $0.051x^{1/2}$ |

**Table 1: GPA 2261-13 Acceptance Criteria**

Individual compound concentrations for the samples analyzed by a given gas chromatograph should be within ±50% of the certified standard concentrations used for calibration of that GC. If individual compound concentrations for the samples analyzed by a given gas chromatograph exceed ±50%, a multi-point calibration or multiple single-point calibrations shall be performed. Refer to manufacturer specification for multi-point calibrations.

## 7.1 Prior to Validation/Calibration:

1. The UHP carrier gas cylinder should be above a minimum of 200 psig pressure. Verify the carrier gas delivery pressure is set per manufacturer recommendations **(**refer to Section 3.0 Attaching the Helium Carrier Gas).
2. Ensure the calibration gas cylinder is above a minimum of 20 psig, or roughly 10% of the initial pressure of the cylinder at delivery to the asset.
    a. If not, a new cylinder should be used. Ensure it has been heated for a minimum of 24 hours prior to use and has been verified per GPA 2198 (refer to Section 8.0 Calibration Gas Standard Specifications).
3. Attach the filter/regulator assembly to the regulator of the calibration standard.
    a. Set the regulator to deliver the calibration sample at the manufacturer recommended pressure.
4. Attach the heated sample line to the filter/regulator assembly.
    a. Ensure the entire system is at least 30º F above hydrocarbon dewpoint prior to performing any analyses.
    b. Suspend the heated line to keep it off the ground (the cold ground will pull heat from the line rapidly).

## 7.2 As-Found Verification:

Note: The As-Found validation procedures assume that an initial calibration has already been performed. If it has not, skip the As-Found verification and proceed to section 7.3 Calibration.

1. Turn the sample valve at the chromatograph to vent. Vent calibration gas through the sampling system for sufficient time to ensure a representative sample is delivered to the gas chromatograph.
2. Turn the sample valve at the chromatograph to the sample inlet.
3. Analyze the calibration standard in duplicate.
4. Evaluate the compound concentrations of the two analyses against one another using the GPA 2261-13 repeatability acceptance criteria.
   a. If the analyses do not pass the repeatability acceptance criteria, analyze a third sample and compare the second and third analyses.
      i. Note – Do not pick and choose analyses, only consecutive analyses should be compared for repeatability.
   b. If the second and third analyses do not pass the repeatability acceptance criteria, inspect the gas chromatograph, sampling system, and calibration standard for discrepancies.
   c. If an issue is found, repair as necessary and return to Step 1.
   d. In no issue is found, repeat Steps 1 through 4.
      i. If the problem persists, remove the gas chromatograph and sampling system from service until the issues are determined and resolved, and the instrument can pass for repeatability.
5. If the two analyses pass the repeatability acceptance criteria, evaluate the compound concentrations of the second analysis against the certified concentrations of the calibration standard using the GPA 2261-13 reproducibility acceptance criteria.
   a. If the analyses pass the reproducibility acceptance criteria, the gas chromatograph can be placed into service after completing Step 6.
   b. If the analyses do not pass the reproducibility acceptance criteria, repeat Steps 1 through 5.
   c. If the analyses still do not pass the reproducibility acceptance criteria, document as such and move on to instrument calibration.
6. Retain all documentation from the As-Found verification necessary to meet all contractual obligations, regulatory compliance, and company best practices.

| Run | 2 | 1 | Average | Repeatability | Repeatability | Test |
|---|---|---|---|---|---|---|
| **Compound** | **Mole %** | **Mole %** | **Mole %** | **Deviation** | **Limits** | |
| **Nitrogen** | 0.9570 | 0.9610 | 0.9590 | 0.0040 | 0.04 | PASS |
| **Methane** | 85.5090 | 85.5100 | 85.5095 | 0.0010 | 0.04 | PASS |
| **Carbon Dioxide** | 1.4480 | 1.4460 | 1.4470 | 0.0020 | 0.01 | PASS |
| **Ethane** | 5.8650 | 5.8630 | 5.8640 | 0.0020 | 0.03 | PASS |
| **Propane** | 2.9630 | 2.9650 | 2.9640 | 0.0020 | 0.01 | PASS |
| **Isobutane** | 0.7940 | 0.7940 | 0.7940 | 0.0000 | 0.01 | PASS |
| **n-Butane** | 0.7920 | 0.7900 | 0.7910 | 0.0020 | 0.02 | PASS |
| **Isopentane** | 0.5900 | 0.5910 | 0.5905 | 0.0010 | 0.01 | PASS |
| **n-Pentane** | 0.5890 | 0.5900 | 0.5895 | 0.0010 | 0.01 | PASS |
| **Hexanes+** | 0.4930 | 0.4900 | 0.4915 | 0.0030 | 0.02 | PASS |
| **TOTAL** | 100.0000 | 100.0000 | | | | |

According to GPA 2261-13

| Standard | Reproducibility | Reproducibility | Test |
|---|---|---|---|
| **MOLE %** | **Deviation** | **Limits** | |
| 0.9690 | 0.0120 | 0.16 | PASS |
| 85.4200 | 0.0890 | 0.15 | PASS |
| 1.4710 | 0.0230 | 0.14 | PASS |
| 5.9240 | 0.0590 | 0.06 | PASS |
| 2.9560 | 0.0070 | 0.05 | PASS |
| 0.7880 | 0.0060 | 0.02 | PASS |
| 0.7980 | 0.0060 | 0.03 | PASS |
| 0.5910 | 0.0010 | 0.03 | PASS |
| 0.5910 | 0.0020 | 0.03 | PASS |
| 0.4920 | 0.0010 | 0.04 | PASS |
| 100.0000 | | | |

**Table 2: Example As-Found Verification**

## 7.3 Calibration:

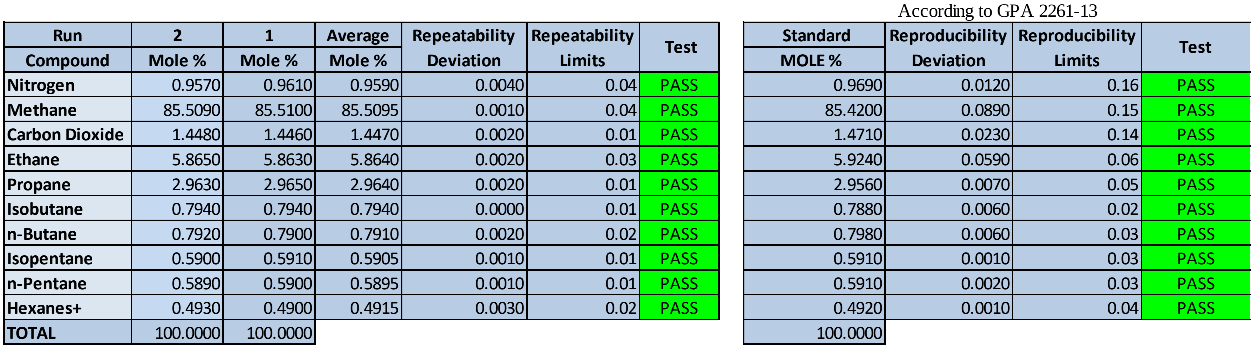
1. Turn the sample valve at the chromatograph to vent. Vent calibration gas through the sampling system for sufficient time to ensure a representative sample is delivered to the gas chromatograph.
2. If the gas chromatograph has a separate calibration stream, turn the sample valve to calibration gas input. If it does not, turn the sample valve at the chromatograph to the sample inlet.
3. If a different calibration gas cylinder is being used from the one the chromatograph was calibrated previously, the new certified values will need to be entered into the chromatograph and the historical verification software.
4. Process or re-process the calibration analysis as the chromatograph calibration.
5. Upon completion, verify the calibration results.
    a. The normalized mole% values should match exactly those values on the calibration gas certification sheet.
        i. If so, proceed to the As-Left verification after completing Step 6.
        ii. If not, return to Step 1.
        iii. If it still does not match, contact support.
6. Retain all documentation from the calibration necessary to meet all contractual obligations, regulatory compliance, and company best practices.

## 7.4 As-Left Validation:

1. Leave the sample valve at the chromatograph to calibration gas input or sample inlet, as appropriate for the instrument.
2. Analyze the calibration standard in duplicate.
3. Evaluate the compound concentrations of the two analyses against one another using the GPA 2261-13 repeatability acceptance criteria.
    a. If the analyses do not pass the repeatability acceptance criteria, analyze a third sample and compare the second and third analyses.
        i. Note – Do not pick and choose analyses, only consecutive analyses should be compared for repeatability.
    b. If the second and third analyses do not pass the repeatability acceptance criteria, inspect the gas chromatograph, sampling system, and calibration standard for discrepancies.
    c. If an issue is found, repair as necessary and return to Step 1 of Calibration.
    d. In no issue is found, repeat Steps 1 through 4.
        i. If the problem persists, remove the gas chromatograph and sampling system from service until the issues are determined and resolved, and the instrument can pass for repeatability.
4. If the two analyses pass the repeatability acceptance criteria, evaluate the average compound concentrations of the two analyses against the certified concentrations of the calibration standard using the GPA 2261-13 reproducibility acceptance criteria.

   a. If the analyses pass the reproducibility acceptance criteria, the gas chromatograph can be placed into service.
   b. If the analyses do not pass the reproducibility acceptance criteria, repeat Steps 1 through 5.
   c. If the analyses still do not pass the reproducibility acceptance criteria, return to Step 1 of Calibration.
      i. If the problem persists, remove the gas chromatograph and sampling system from service until the issues are determined and resolved, and the instrument can pass for reproducibility.

5. Retain all documentation from the As-Left verification necessary to meet all contractual obligations, regulatory compliance, and company best practices.



According to GPA 2261-13

| Run | 2 | 1 | Average | Repeatability | Repeatability | Test |
|---|---|---|---|---|---|---|
| **Compound** | **Mole %** | **Mole %** | **Mole %** | **Deviation** | **Limits** | |
| **Nitrogen** | 0.9570 | 0.9610 | 0.9590 | 0.0040 | 0.04 | PASS |
| **Methane** | 85.5090 | 85.5100 | 85.5095 | 0.0010 | 0.04 | PASS |
| **Carbon Dioxide** | 1.4480 | 1.4460 | 1.4470 | 0.0020 | 0.01 | PASS |
| **Ethane** | 5.8650 | 5.8630 | 5.8640 | 0.0020 | 0.03 | PASS |
| **Propane** | 2.9630 | 2.9650 | 2.9640 | 0.0020 | 0.01 | PASS |
| **Isobutane** | 0.7940 | 0.7940 | 0.7940 | 0.0000 | 0.01 | PASS |
| **n-Butane** | 0.7920 | 0.7900 | 0.7910 | 0.0020 | 0.02 | PASS |
| **Isopentane** | 0.5900 | 0.5910 | 0.5905 | 0.0010 | 0.01 | PASS |
| **n-Pentane** | 0.5890 | 0.5900 | 0.5895 | 0.0010 | 0.01 | PASS |
| **Hexanes+** | 0.4930 | 0.4900 | 0.4915 | 0.0030 | 0.02 | PASS |
| **TOTAL** | 100.0000 | 100.0000 | | | | |

| Standard | Reproducibility | Reproducibility | Test |
|---|---|---|---|
| **MOLE %** | **Deviation** | **Limits** | |
| 0.9690 | 0.0120 | 0.16 | PASS |
| 85.4200 | 0.0890 | 0.15 | PASS |
| 1.4710 | 0.0230 | 0.14 | PASS |
| 5.9240 | 0.0590 | 0.06 | PASS |
| 2.9560 | 0.0070 | 0.05 | PASS |
| 0.7880 | 0.0060 | 0.02 | PASS |
| 0.7980 | 0.0060 | 0.03 | PASS |
| 0.5910 | 0.0010 | 0.03 | PASS |
| 0.5910 | 0.0020 | 0.03 | PASS |
| 0.4920 | 0.0010 | 0.04 | PASS |
| 100.0000 | | | |

**Table 3: Example As-Left Verification**

# 8.0 Calibration Gas Standard Specifications and Validation

## 8.1 Calibration Gas Standard Specifications:

1. Calibrations shall be performed using a Certified Natural Gas Reference Standard.
2. Standards shall be verified and handled in accordance with GPA 2198.
3. Verify the new cylinders have no loss of pressure during transport and storage.
   a. Contact manufacturer for initial pressures.
   b. In the event of pressure loss, do not put the cylinder into use. Contact the manufacturer.
4. Calibration gas standard cylinders shall be heated to a minimum of 30º F above hydrocarbon dewpoint. They shall be heated a minimum of 24 hours prior to use and stored in a vertical position. NEVER PULL GAS FROM A COLD CYLINDER.
   a. The temperature should be monitored on a regular basis, and especially prior to pulling any gas from the cylinder for calibrations and validations.
   b. Approved heating devices should be used, such as heating blankets with hoods and pads, heating cabinets, etc. Make sure all electrical codes and classifications are followed. Ensure any and all applicable safety guidelines are followed.
5. Install a two-stage regulator to regulate the calibration gas to the manufacturer recommended pressure for the inlet of the GC being used.

6. All fittings attached to the calibration cylinder should be leak tested initially and then periodically to maintain integrity of the calibration blend. The cylinder valve and the valve downstream of the regulator should be closed when the standard is not in use.
7. Each technician's heated sample line may be used for calibrations and validations. Be aware that a contaminated line can bias calibration and/or validation results (refer to Section 9.0 Sampling System Validation).

### 8.2 <u>Calibration Gas Standard Validation</u>:

Calibration cylinders on occasion can be prepared incorrectly by the manufacturer. All new calibration standards should be verified for accuracy prior to being put into service.

1. Perform the full 'As Found', 'Calibration', and 'As Left' procedures (see Section 7 Calibration and Validation) using the almost depleted cylinder which is being replaced.
    a. Ensure the almost depleted cylinder has met all GPA 2198 specifications prior to use.
2. Analyze the new calibration cylinder as an unknown. Make sure it has been heated to at least 30º F above hydrocarbon dewpoint for a minimum of 24 hours prior to use and stored vertically (refer to Section 8.0 Calibration Gas Standard Specifications).
3. Set the regulator to the manufacturer recommended pressure for the sample inlet.
4. Attach heated line. Ensure the heated line is at least 30ºF above hydrocarbon dewpoint before sampling.
5. Suspend the heated line to keep it off the ground (the cold ground will pull heat from the line rapidly).
6. Turn the sample valve at the chromatograph to vent. Vent calibration gas through the sampling system for sufficient time to ensure a representative sample is delivered to the gas chromatograph.
7. Turn the sample valve at the chromatograph to the sample inlet.
8. Analyze the calibration standard in duplicate.
9. Evaluate the compound concentrations of the two analyses against one another using the GPA 2261-13 repeatability acceptance criteria.
    a. If the analyses do not pass the repeatability acceptance criteria, analyze a third sample and compare the second and third analyses.
        i. Note – Do not pick and choose analyses, only consecutive analyses should be compared for repeatability.
    b. If the second and third analyses do not pass the repeatability acceptance criteria, attempt verification of the calibration cylinder on a different gas chromatograph.
        i. If the cylinder does not pass the criteria on a second instrument, contact the calibration standard manufacturer.
10. If the two analyses pass the repeatability acceptance criteria, evaluate the average compound concentrations of the two analyses against the certified concentrations of the calibration standard using the GPA 2261-13 reproducibility acceptance criteria.
    a. If the analyses pass the reproducibility acceptance criteria, the calibration gas cylinder can be placed into service after completing Step 11.

  b. If the analyses do not pass the reproducibility acceptance criteria, repeat Steps 1 through 5.
  c. If the analyses still do not pass the reproducibility acceptance criteria, attempt verification of the calibration cylinder on a different gas chromatograph.
    i. If the cylinder does not pass the criteria on a second instrument, contact the calibration standard manufacturer.

11. Retain all documentation from the cylinder verification necessary to meet all contractual obligations, regulatory compliance, and company best practices.

## 9.0 Sampling System Validation

1. Attach the filter/regulator assembly to the regulator on the UHP Helium cylinder (it may require an adaptor fitting).
2. Set the regulator to the manufacturer recommended pressure for the sample inlet.
3. Attach the heated line to the filter/regulator. Ensure the entire sampling system is hot.
    a. Although the UHP Helium has no hydrocarbon dewpoint, the heat is necessary to ensure any residual hydrocarbons are liberated from the sampling system.
4. Turn the sample valve at the chromatograph to vent. Vent calibration gas through the sampling system for sufficient time to ensure ambient air and any gases are purged from the system.
5. Turn the sample valve at the chromatograph to sample input.
6. Perform several analyses until it is verified that the sampling system has no residual components.
    a. Continue analyses until the un-normalized concentrations for each component are non-detectable.
        i. If un-normalized Nitrogen concentrations remain detectable, there may be a leak in the sampling system (see note below).
            (1) Disconnect the sample system from the chromatograph (sample system includes heated sample hose and filter/regulator assembly).
            (2) Cap the end of the heated line and pressurize the system to 50 psig and check for leaks. Liquid leak detector may be used to check this part of the system.
            (3) Repair leaks as necessary.
            (4) Re-assemble the system and return to Step 1.

    **Note:**

    If using Helium of lesser quality than chromatographic Ultra High Purity (UHP) grade, 99.999% purity, trace amounts of Methane and/or Nitrogen may be present on the chromatogram. This will cause sampling system validations to not pass. In addition, the GC will be misstating Methane and/or Nitrogen concentrations on all field analyses and will fail Nitrogen concentration values during an audit.

    b. If the sampling system shows residual hydrocarbons after several analyses and purging, the sampling system will need to be cleaned.
        i. Replace the membrane element as necessary.
        ii. Use wet steam or an alcohol to clean the membrane filter body. Thoroughly dry all components before assembly and use, using Helium or Nitrogen.

  iii. Replace the inner tubing in the sample line if it is designed to do so.
  iv. If the sample line does not clean up and does not have a replaceable inner line, a light soapy solution in warm water can be used.
    (1) Pump the solution through the entire sample line, with the sample line on and warm, for 2 to 4 hours (the solution should not be pumped through the filter/regulator assembly or any part of the chromatograph).
    (2) Pump clean water through the sample line, with the sample line on and warm, for approximately 4 hours.
    (3) Pump air through the line for approximately 8 hours. Ensure the line is completely dry prior to re-attaching it to the chromatograph.
    (4) Do not use any type cleaner or solvent to clean any part of the sampling system that contains petroleum distillates, toluene, or benzene.
  v. Return to Step 1.

7. Validate the cleanliness of the sampling system at least monthly. Inspect membrane element at least monthly for holes and discoloration. Replace membrane element as necessary.
   **Note:**
   Inspection and replacement of the membrane may be required more frequently depending on the type of field gas sampled. It would not be an uncommon practice to replace the membrane filter on a weekly or daily basis if needed in order to keep the sampling system free of contamination.
8. Keep the end connection of the heated line and filter/regulator assembly capped when not collecting samples. This will keep dust and other contaminants from entering the line when not in use.

## 10.0 Miscellaneous

1. By using the filter/regulator assembly, contamination to the hose and GC will be held to a minimum.
2. If the sampling system (filter/regulator assembly or heated line) become contaminated during field-testing, remove them from service, clean, and then validate. Discontinue the use of the sampling system until clean. If contaminated, not only the GC is at risk, but the validity of any samples analyzed can be compromised and biased.
3. The heated line and heated filter/regulator assembly are integral parts of the inlet system to the GC. They are necessary to keep the sample gas in single phase. If at any time, these items cease to function properly, remove them from service and replace the affected parts.
4. It is recommended to purge the sample line with sample gas, standard gas, or UHP Helium regulated to the manufacturer recommended pressure for at least 2 minutes, to ensure the sampling system is dry and conditioned, before the initial sampling each day.