Enthalpy Analytical
Standard Operating Procedure

Methane Analysis of Canister Samples Collected Near Upstream Oil and Gas Production Facilities

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Laboratory Director/designee Approval: _____ Approval Date: _____

Quality Control Coordinator /designee Review: _____ Review Date: _____

Effective Date: _____

1.0 Scope and Application:

This document describes the analysis of canister samples for Methane using Gas Chromatography/Flame Ionization Detector (GC/FID) by gas loop injection technique. It is the responsibility of the employee performing Methane analysis on canisters collected during remote measuring efforts near upstream oil and gas production facilities to follow the procedures set forth in this SOP.

2.0 Summary of Method:

Samples are collected in specially cleaned and evacuated canisters as prescribed by each test plan. The canister samples are pressurized and analyzed for Methane using GC/FID. Results are reported in ppmv after a pressurization dilution factor is applied

3.0 Definitions:

3.1 GC – Gas Chromatograph
3.2 FID – Flame Ionization Detector
3.3 LOQ – Limit of Quantitation
3.4 MDL – Method Detection Limit
3.5 CCV – Continuing Calibration Verification
3.6 LCS – Laboratory Control Sample
3.7 UHP – Ultra High Purity Gas ≥99.999% pure
3.8 Batch – Up to 20 samples per 24 hour period

4.0 Safety:

All samples should be considered hazardous material and should be handled in an appropriate manner. Any sample that poses a specific health hazard to Enthalpy Analytical, Inc. personnel must be pre-approved by the Laboratory Director. All personnel who will come in contact with such sample(s) must be notified of appropriate safety measures to be taken. The client must also provide any information, i.e., a material safety data sheet (MSDS), which would enable Enthalpy Analytical, Inc. to take the required safety precautions.

5.0 Equipment and Supplies

5.1 An Agilent Series 5890, 6890, 7890 or equivalent GC in good working order equipped with a gas sampling valve outfitted with a 0.25mL loop.

5.2 Restek Rtx-1 capillary column 30m x 0.32mm ID 4.0µm film thickness or equivalent
5.3 Methane cylinder standard – ppmv concentration certified to ±2% accuracy.
5.4 Environics 4000 series gas dilution system or equivalent
5.5 Entech Instruments 1.4L sample canister or equivalent
5.6 Peristaltic Pump set to draw 50-150 cc/min through sample loop
5.7 Digital pressure gauge capable of reading from -760mmHg to 1000mmHg (gauge) with 0.1mmHg resolution and accurate to 2% of scale
5.8 Calibrated Weather Station
5.9 Metering valve to control flow from pressurized canister
5.10 Rotometer 100cc full scale used to indicate positive sample flow

6.0 Reagents and Standards:

6.1 Certified cylinder(s) containing Methane in ppm concentrations
6.2 UHP Nitrogen, or equivalent, to dilute standards and pressurize canisters

7.0 Sample Preservation, Storage, and Handling:

7.1 Samples are stored in the secure ambient storage area prior to and after analysis.
7.2 VOCs are stable in the canisters for at least 30 days after collection.

8.0 Calibration

8.1 Prior to initial calibration, a system blank is analyzed to confirm the absence of a positive or negative Methane bias.
8.2 The initial calibration consists of a minimum of a three points bracketing the sample concentrations. The lowest point in the calibration must be 1.0 ppmv or lower.
8.3 The curve must be prepared from a certified cylinder blend containing methane at ppmv concentrations certified to ± 2% accuracy. The multi-point calibration is prepared by using an Environics gas diluter. Each level is injected in duplicate with the Methane peak areas of the individual chromatograms being no more than 5% from the mean of the two areas.
8.4 A linear regression analysis is performed using the average of the two injections for each data point. Quadratic weighting is used to ensure accuracy at the low end of the curve. Each point must calculate within 10% of the theoretical value when analyzed against the resulting curve.
8.5 The absolute value of the intercept of the resulting curve must be no greater than 50% of the slope.
8.6 A CCV is analyzed, in duplicate, at the beginning of each workday, after a maximum of 10 samples and at the end of an analytical sequence. All CCV results must be within 10% of the theoretical value. If a CCV falls outside this range, all samples analyzed after the last passing CCV must be reanalyzed.
8.7 If a calibration fails, check for errors and recalibrate if necessary.

9.0 Procedure:

9.1 Instrument setup:
9.1.1 Establish appropriate instrument conditions in order to achieve baseline resolution of Methane and Ethylene. See example conditions below:

Inlet
Injection type: Split
Inlet Temp: 160°C
Valve Temp: 100°C
Initial Pressure: 5.12 psi

Gas: Hydrogen
Flow: 2.1mL/min – Constant

Oven

Initial Temp: 35°C
Initial Time: 2.20 min
Rate 1: 15°C/min to 70°C hold 0.7min
Rate 2: 30°C/min to 250°C hold 1.00min
Run Time: 11.60 min

9.1.2 Attach a peristaltic pump to the vent line of the gas sampling valve

9.1.3 Attach a tee to the sample inlet with one leg going to vent and the other to the sample/standard to be analyzed.

9.2 Standard Analysis:

9.2.1 Blended standards are introduced to the sample inlet line dynamically allowing excess flow to go to vent to avoid pressurizing the sample loop.

9.2.2 Allow the peristaltic pump to flush the sample loop for at least 10 seconds

9.2.3 Data collection begins when the gas sampling valve is actuated to the inject position introducing the contents of the loop to the GC column.

9.2.4 The gas sampling valve is returned to the load position once the loop has been completely flushed with carrier gas (e.g. 10-30sec).

9.3 Sample Analysis:

9.3.1 After sample receipt, canister pressures are measured and recorded to the nearest mmHg. Barometric pressure and temperature is also recorded.

9.3.2 Each canister then is pressurized to ~760mmHg using UHP Nitrogen and final pressure is recorded to the nearest mmHg along the with ambient pressure and temperature.

9.3.3 Once pressurized, each sample canister is connected to the sample inlet with a metering valve in the closed position between the tee and canister.

9.3.4 When analyzing samples a 100cc/min rotometer, or digital equivalent, is attached to the vent line after the tee to indicate excess flow.

9.3.5 The canister valve is opened first, then the metering valve is opened until positive flow is observed on the rotometer.

9.3.6 The sample loop is flushed for at least 10 seconds making sure the rotometer indicates positive flow for the duration.

9.3.7 The gas sampling valve is actuated in the same manner as the standards.

9.3.8 Sample areas are analyzed against the initial calibration and a report created with raw data calculated in ppmv.

10.0 Quality Control:

10.1 A Nitrogen blank is analyzed per batch. A blank will be acceptable if Methane is not detected above the MDL.

10.2 An LCS must be analyzed for each sample batch. The LCS will be considered acceptable if Methane recovery is 85%-115%.

11.0 Data Analysis and Calculations:

11.1 When the canister is pressurized prior to analysis, a tank dilution factor is calculated and included in the calculation with the final concentrations. The following formula is used to calculate tank dilution factors:

$$\frac{(GPF + PbarF)}{(TempF + 460)}$$

$$\left(\frac{GPI + PbarI}{TempI + 460}\right) - \left(\frac{GPP + PbarP}{TempP + 460}\right)$$

Where:

GPF = Final Gauge Pressure, mmHg
PbarF = Final Barometric Pressure, mmHg
TempF= Final Temperature, degrees F
GPI = Initial Gauge Pressure, mmHg
PbarI = Initial Barometric Pressure, mmHg
TempI = Initial Temperature, degrees F
GPP = Pretest Gauge Pressure, mmHg
PbarP = Pretest Barometric Pressure, mmHg
TempP = Pretest Temperature, degrees F

12.0 Method Performance:

Method performance is demonstrated through MDL studies and demonstrations of capability performed by the analyst. Follow procedures detailed in SOP ENT027, "Detection Limits and Limits of Quantification" for determining MDLs. Follow the procedures detailed in SOP ENT005, "Training" for performing demonstrations of capability.

13.0 Pollution Prevention and Waste Management:

Sample canisters are purged and vented under a laboratory fume hood or using a manifold vented to outdoors.

14.0 References:

NA

15.0 Tables, Diagrams, and Flow Charts:

NA

Revision History:

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0	June 6, 201	David M. Berkowitz