# QUANTIFICATION OF A PRECISION POINT SOURCE FOR GENERATING CARBON DIOXIDE EMISSIONS

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## ABSTRACT

This study provides an analysis of the uncertainty of carbon dioxide ($CO_2$) emissions from an 8 MW natural gas burner. A precise and accurate point source for industrial quantities of carbon dioxide can be used to evaluate the performance of stack gas carbon dioxide measurement equipment. Uncertainties of individual measurement components were considered and their contribution to the overall carbon source uncertainty was evaluated to show where greatest improvements could be achieved. It was demonstrated that less than one percent carbon dioxide generation measurement uncertainty was possible using readily available components, facilitating the use of the fire laboratory as a test-bed for precision point source exhaust stack measurements.

## 1. INTRODUCTION

Concerns of climate change due to carbon emissions attributed to human activity demand accurate industrial carbon emission measurement techniques. Existing $CO_2$ accounting methods include fuel consumption based carbon emission calculations and continuous emission monitoring (CEM) measurements. With both techniques there are indications that significant uncertainty (up to approximately 16 %) in emission reporting exist [1]. This study evaluates the uncertainty of $CO_2$ emissions from a large non-premixed natural gas burner. The objective of this study is to reduce, to as low as practicable, the uncertainty of the carbon dioxide emissions produced by a natural gas burner so that it can be used as precision source for evaluating carbon emission measurement equipment.

Precise measurement of the fuel mass flow and chemical composition can be used to predict the amount of carbon dioxide that is emitted from a natural gas fire. Each of the measurement components required for this prediction has an uncertainty that affects the overall emission rate uncertainty. This paper will present a detailed accounting and analysis of the uncertainty of each individual measurement component. The propagation of measurement uncertainty analysis

shows how each measurement can affect the accuracy of the determination of the rate of carbon dioxide production. The results can be used to target systematic improvements to the measurement system.

## 2. EXPERIMENTAL DESCRIPTION

The facility used for this study was the Large Fire Laboratory (LFL) located on the Gaithersburg, Maryland campus of the National Institute of Standards and Technology (NIST). A 1.2 m × 1.5 m turbulent non-premixed flame natural gas tube burner is used at the LFL as a reference fire source for oxygen consumption calorimetry measurements [2]. The natural gas burner and natural gas supply system in the LFL can operate at heat release rates up to 8 MW (see Fig. 1). When operating the burner at full capacity the natural gas fire produces approximately 0.5 kg/s of $CO_2$.

In order to evaluate the heat release rate of the natural gas burner, the pressure, temperature, volumetric flow and component makeup of the delivered natural gas are measured. From the composition and flow of the gas it is a simple matter to predict the heat release rate from the burner. The burner can be used to simulate steady-state and transient combustion processes from a moderate to large $CO_2$ source such as an industrial plant. Large fire exhaust hoods are used to capture burner combustion products. The fire hood exhaust ducts are instrumented for measurement of temperature, velocity and gas species. The maximum exhaust flow capacity is approximately 50 kg/s air and the operating pressure in the duct is slightly below atmospheric.

**Figure 1.** Photograph of natural gas burner operating at 8 MW.

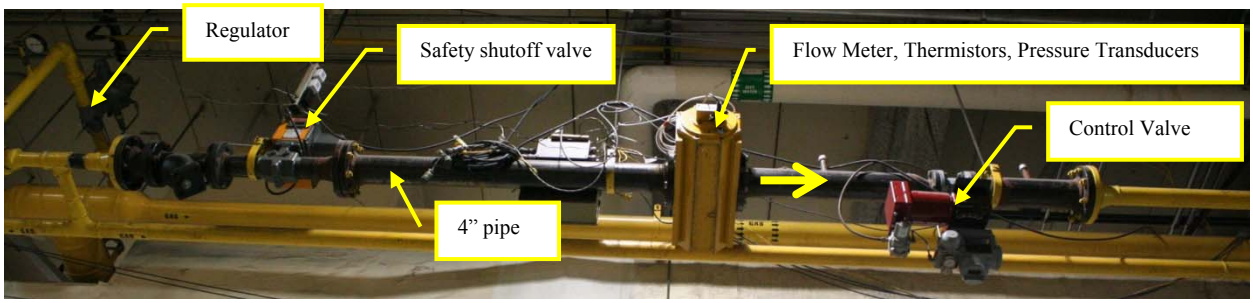


**Figure 2.** Photograph of natural gas fuel delivery system.

The natural gas measurement system consists of a positive displacement flow meter (see Fig. 2), three thermistor temperature probes, two pressure transducers and a gas chromatograph to analyze the natural gas composition. Knowing the composition of the natural gas from the gas chromatograph also makes it possible to establish the molar mass, compressibility factor, and the molecular carbon fraction of the fuel. The carbon fraction of a typical natural gas sample was 4 % to 6% greater than the carbon fraction of pure methane.

## 3. UNCERTAINTY ANALYSIS

A detailed uncertainty analysis was performed for the carbon dioxide emissions while the burner was operating at 2 MW. This case was chosen because the burner can be operated for extended periods of time without significant radiant heating of the environment. This case was also used for a related study of the exhaust duct flow profile. Table 1 below shows the components of standard uncertainty for the carbon emissions calculation. The expanded ($k$ = 2) relative uncertainty of $CO_2$ mass flow rate was 0.80 % for the given conditions. The largest components of uncertainty in the measurement were the fuel carbon content and the volumetric flow rate measurement. The expression for carbon dioxide emission mass flow rate, $\dot{m}_{CO_2}$, is given below and the parameters are defined in Table 1.

$$\dot{m}_{CO_2} = \frac{\dot{V}_{ng} \cdot P_{ng} \cdot X_{c,ng} \cdot \eta_b \cdot MW_{co_2}}{R \cdot T_{ng} \cdot Z_{ng}}$$

The conversion of carbon mass in the fuel source to carbon dioxide in the exhaust plume was assumed to be ideal ($\eta_b$=1) and it was assumed that all combustion products were captured by the canopy exhaust hood. Exhaust stream measurement of $CO_2$, CO, total hydrocarbons and soot were performed in order to verify the burner conversion efficiency assumption. The accuracy and detection limits of the exhaust measurements were used to determine the uncertainty of the conversion efficiency value.

**Table 1.** Standard uncertainty budget for $CO_2$ emissions from a 2 MW natural gas fire.

| **Measurement Component ($x_i$)** | **Units** | **Value $x_i$** | **Std. Unc. $u_c(x_i)$** | **Rel. Std. Unc. $u_c(x_i)/ x_i$** |
|---|---|---|---|---|
| Gas Volume Flow Rate ($\dot{V}_{ng}$) | $m^3/s$ | 0.0298 | 0.000057 | 0.19 % |
| Gas Pressure ($P_{ng}$) | Pa | 197719 | 319 | 0.16 % |
| Gas Temperature ($T_{ng}$) | K | 290.65 | 0.507 | 0.17 % |
| Gas Compressibility ($Z_{ng}$) | -- | 0.9958 | 0.0005 | 0.050 % |
| Gas Carbon Fraction ($X_{c,ng}$) | mol/mol | 1.04 | 0.00213 | 0.20 % |
| Molar Mass of $CO_2$ ($MW_{CO2}$) | g/mol | 44.0095 | 0.0001 | 0.0002 % |
| Ideal Gas Constant (R) | J/mol/K | 8.314472 | 0.000015 | 0.0002 % |
| Burner Conversion Efficiency ($\eta_b$) | -- | 1.00 | 0.015 | 0.15 % |
| **Burner $CO_2$ Emission Rate ($\dot{m}_{CO_2}$)** | g/s | 112.4 | 0.45 | **0.40 %** |

***Uncertainty Methods***

The uncertainty of the measurement components was determined using standard statistical methods [3]. The analysis requires the determination of all significant error components and the functional relationship between measurement parameters. The combined standard uncertainty $u_c x_i$ includes type A and type B components. The type A uncertainty is determined by statistical methods such as the standard deviation of a noisy signal or measurement repeatability. The type B uncertainty is determined by other means such as a tolerance or accuracy given by the equipment manufacturer. The uncorrelated components of uncertainty were combined as a simple root-sum-of-square or RSS $u_c(x_i)=(u(x_{i,A})^2+ u(x_{i,B})^2)^{1/2}$. The combined standard uncertainty values $u_c(x_i)$ have a confidence level of 68 % and the expanded uncertainty ($U_c(x_i)$) has a coverage factor of two (i.e., $k = 2$) and a confidence level of approximately 95 %.

When the functional relationship of measurement components was known, a propagation of uncertainty analysis was performed. In this work the correlated uncertainty components are negligible and are taken to be zero.

$$y = f(x_1, x_2, \ldots . x_i)$$

$$u_y = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)^2 u_{x_i}^2}$$

***Data Acquisition***

A modular data acquisition system was used for the voltage signal measurements in this study. Transducer inputs to the data acquisition system were connected through manufacturer supplied terminal block modules. The terminal blocks carry the input signal into a signal conditioner also referred to as the input module. The analog signal was converted to digital though a 16 bit A/D converter. The terminal blocks were connected directly to a signal conditioner and the signal then passes from the signal conditioner through a multiplexer card before passing to the analog to digital converter. The signal conditioner and analog to digital convertor each add uncertainty to the voltage signal measurement. The signal conditioner is subject to offset errors, temperature drift and noise while the analog to digital convertor exhibits the same type errors and is also subject to an additional gain error. The data acquisition hardware components are listed in Appendix A.

***Gas Volume Flow Rate***

The volumetric flow rate of natural gas delivered to the burner was determined using a positive displacement rotary piston flow meter. The positive displacement flow meter was calibrated [4] in dry air using a combination of seven critical flow venturi working standards mounted in parallel in a common plenum. The expanded uncertainty of the mass flow for these seven venturis was 0.11 % of the reading. The meter was calibrated at steady state conditions. The meter was calibrated over nine different flow rates with each calibration point being the average of six or more individual calibration measurements. The average expanded ($k = 2$) uncertainty of the meter frequency factor, $K_m$, for all points was 0.14 % and the uncertainty for the flow rate nearest that required for the 2 MW heat release fire was also 0.14 %. The pulse/frequency counting device and voltage data acquisition system were not used while the meter was calibrated, therefore the uncertainty of these devices must be considered separately. The volume flow equations and uncertainty components are given in Table 2 below.

$$\dot{V}_{ng} = \frac{f}{K_m} \quad , \quad f = \frac{k_p \cdot V_p}{R_p}$$

**Table 2.** Uncertainty budget for gas flow measurement.

| **Measurement Component ($x_i$)** | **Units** | **Value** | **$u_c(x_i)$** | **$u_c(x_i)$/Value** |
|---|---|---|---|---|
| Flow meter frequency factor ($K_m$) | pulses/$m^3$ | 507.5 | 0.36 | 0.070 % |
| Pulse Frequency Voltage ($V_p$) | V | 0.9422 | 0.0015 | 0.163 % |
| Precision Resistor ($R_p$) | Ω | 249.0 | 0.125 | 0.050 % |
| Pulse Frequency (*f*) | Hz | 15.136 | 0.027 | 0.178 % |
| Pulse Counter Sensitivity ($k_p$) | Hz/mA | 4.000 | 0.0020 | 0.050 % |
| **Volume Flow Rate ($\dot{V}_{ng}$)** | $m^3$/s | 0.0298 | 0.000057 | **0.19 %** |

***Natural Gas Temperature and Pressure***

Temperature measurements were performed by three thermistor probes located in the gas flow stream. Two were located at the inlet to the flow meter and one at the outlet. Pressure measurements were performed at the center of the flow meter body and at the outlet of the flow meter. The thermistor resistance was converted to a temperature through use of the Steinhart-Hart Equations and curve fit coefficients for the particular calibration of thermistor.

$$T = \frac{1}{a + b\ln(\Omega) + c\,[\ln(\Omega)]^3}$$

Where a = 1.468E-03, b = 2.383E-04 and c = 1.007E-07 are the curve fit Steinhart-Hart coefficients for the 2252 thermistor used in this study and Ω is the measured resistance. A 100 μA current source was applied to each thermistor to determine the resistance. The voltage drop across the thermistor is measured and recorded by the data acquisition system. The manufacturer stated uncertainty associated with the specified coefficients is 0.05 °C. An additional 0.03 °C of temperature uncertainty was included to account for resistive heating of the temperature probe. The resistive heating error was approximated by assuming 32 μW of power from the probe was dissipated by natural convection in still air.

The natural gas pressure was measured by two precision pressure transducers with a 4-20 mA output. A 500 Ω precision resistor was used to convert the pressure transducer output to a voltage signal and recorded using the data acquisition system.

**Table 3.** Uncertainty budget for gas temperature and pressure.

| **Measurement Component ($x_i$)** | **Units** | **Value** | **$u_c(x_i)$** | **$u_c(x_i)$/Value** |
|---|---|---|---|---|
| Thermistor voltage | V | 0.31553 | 0.00083 | 0.26 % |
| Thermistor resistance | Ω | 3155.3 | 8.49 | 0.27 % |
| Excitation Current | A | 0.000100 | $5.0 \times 10^{-8}$ | 0.050 % |
| Thermistor temperature | K | 290.64 | 0.083 | 0.028 % |
| **Gas Temperature ($T_{ng}$)** | K | 290.6 | 0.51 | **0.17 %** |
| Pressure Voltage | V | 6.601617 | 0.0055 | 0.083 % |
| Precision Resistor | Ω | 500.00 | 0.050 | 0.010 % |
| Pressure Sensitivity | Pa/mA | 21483.62 | 13.0 | 0.061 % |
| Pressure Gage Reading | Pa | 197719 | 248 | 0.13 % |
| **Gas Pressure ($P_{ng}$)** | Pa | 197719 | 319 | **0.16 %** |

The uncertainties of the natural gas temperature and pressure measurements include both the transducer uncertainty and the effect of non-uniform spatial distributions on the flow meter housing. The pressure used for the flow calculation was located at the center of the flow meter housing and the thermistor probe for the gas temperature was located at the centerline inlet to the flow meter. The additional temperature and pressure probes were used to estimate the non-uniformities in the meter.

During the initial setup and installation, the thermistor and pressure transducer measurement systems were tested to insure they were operating within specifications. These performance tests were conducted within one month of the data collected for this study. For the thermistor system the current source, data acquisition system and thermistors were tested individually for function. Several channels from the current source were checked with a precision bench type digital multi-meter and found to be within 0.02 μA of the nominal 100 μA output. A bank of precision resistors representing temperatures from approximately -1 °C to approximately 83 °C was connected to the data acquisition system to test both measured resistance as well as resolved temperature. Recorded resistance and resolved temperature errors were all within one standard uncertainty. The thermistors were evaluated using a 0 °C ice bath and a dry block precision temperature source for temperatures at (30, 50, 70 and 100) °C. The expanded uncertainty of the

physical reference temperatures was less than ± 0.1 °C. The measurement system temperature agreed with the reference temperature values within the expanded uncertainty limits.

Following installation the recorded output data from the pressure transducers was validated against a dead weight pressure tester. Precision weights were applied to the tester to achieve pressures of (5, 10, 13, 15, 17 and 20) psi above atmospheric pressure. The typical natural gas pressure is near 15 psi above ambient when operating. Uncertainty of the dead weight tester was half of the uncertainty of the pressure transducer, not including additional uncertainty incurred by the data acquisition system. The measured pressures including uncertainties incurred by both the transducers and data acquisition system agreed with the reference pressure values within the standard uncertainty limits. The pressure and temperature measurement hardware components are listed in Appendix A.

***Carbon Content:***

The chemical composition of natural gas was used to determine the compressibility, molar mass and carbon molecular fraction using standard methods [5]. A gas chromatograph (GC) was used to measure each individual gas constituent. The GC used two separated injection, column and detector modules. A helium carrier gas and thermal conductivity detectors (TCD) were used for these measurements. The species identified and quantified are listed in Table 4. The GC specifications are given in Appendix A. Gas species measurements were attained at intervals of 3.5 minutes. The natural gas molecular carbon fraction, $X_{c,ng}$ and molar mass $MW_{ng}$ are calculated using the gas component volume fractions, $X_i$ and carbon numbers, $Cn_i$. The gas compressibility, $Z_{ng}$ was determined by importing the component fractions, pressure and temperature into REFPROP [6].

$$X_{c,ng} = \sum X_i \cdot Cn_i$$

$$MW_{ng} = \sum X_i \cdot MW_i$$

**Table 4.** Uncertainty budget for gas composition and physical properties.

| **Measurement Component ($x_i$)** | **Units** | **Value** | **$u_c(x_i)$** | **$u_c(x_i)$/Value** |
|---|---|---|---|---|
| Methane Volume Fraction, Cn=1 | % | 94.15 | 0.0019 | 0.20 % |
| Ethane Volume Fraction, Cn=2 | % | 3.089 | 0.00039 | 1.26 % |
| Propane Volume Fraction, Cn=3 | % | 0.530 | 0.000111 | 2.03 % |
| i-Butane Volume Fraction, Cn=4 | % | 0.0594 | 0.000022 | 3.78 % |
| n-Butane Volume Fraction, Cn=4 | % | 0.101 | 0.000022 | 2.23 % |
| i-Pentane Volume Fraction, Cn=5 | % | 0.0235 | 0.000022 | 9.54 % |
| n-Pentane Volume Fraction, Cn=5 | % | 0.0197 | 0.000022 | 11.42 % |
| C6-C8 Volume Fraction, Cn=6.7 | % | 0.0293 | 0.000022 | 7.66 % |
| Nitrogen Volume Fraction, Cn=0 | % | 0.710 | 0.00014 | 2.02 % |
| Carbon Dioxide Volume Fraction, Cn=1 | % | 1.287 | 0.00016 | 1.25 % |
| Balance Species Volume Fraction, Cn=0 | % | 0.00 | 0.001 | 0 |
| Natural Gas Molecular Weight ($MW_{ng}$) | g/mol | 17.184 | 0.038 | 0.22 % |
| Natural Gas Compressibility ($Z_{ng}$) | -- | 0.99582 | 0.0005 | 0.050 % |
| Natural Gas Carbon Fraction ($X_{c,ng}$) | mol/mol | 1.0426 | 0.0021 | 0.20 % |

The gas chromatography has two main sources of uncertainty including uncertainties in the standard calibration gas, and uncertainties from the measurement method or instrument. According to manufacturer's specifications, assuming a normal distribution and 95 % confidence, instrument uncertainty for any component measured by the GC should be less than or equal to 0.4 %. The instrument detection limits (minimum area count) were also considered as a source of uncertainty. The greatest improvement in uncertainty can be made by obtaining a carefully prepared calibration gas. For this study the calibration gas had 1 % relative standard uncertainty for all listed components with the exception methane. The calibration standard lists methane as the remaining balance from all other gasses, therefore both the concentration and the uncertainty must be calculated from information on the gas certification sheet.

An independent analysis of natural gas composition was performed to validate the GC methodology. A gas sample was acquired from the fuel delivery line by flowing gas though a sample bottle with at least 10 volume changes. The results of the blind comparison are given in

Table 5 below. The sample was analyzed using the identical method for the results given above (Standard Method) and also independently analyzed by the NIST Gas Metrology Group (Control Method). The resulting carbon fraction from the two independent methods agreed well with the measurement uncertainty and had a difference of less than 0.1 %.

**Table 5.** Quality control comparison for natural gas composition measurement.

| Natural Gas Component | Standard Method (%) | Expanded Uncertainty (%) | Control Method (%) | Expanded Uncertainty (%) |
|---|---|---|---|---|
| Methane | 93.75309 | 0.380 | 93.859 | 0.2190 |
| Ethane | 3.443241 | 0.087 | 3.410 | 0.0210 |
| Propane | 0.598382 | 0.024 | 0.570 | 0.0030 |
| i-Butane | 0.060604 | 0.0046 | 0.054 | 0.0006 |
| n-Butane | 0.105941 | 0.0047 | 0.103 | 0.0009 |
| i-Pentane | 0.02429 | 0.0046 | 0.023 | 0.0006 |
| n-Pentane | 0.020559 | 0.0047 | 0.054 | 0.0002 |
| C6-C8 | 0.031816 | 0.0049 | 0.006 | 0.0001 |
| Nitrogen | 0.818137 | 0.033 | 0.78 | 0.0039 |
| Carbon Dioxide | 1.143937 | 0.029 | 1.167 | 0.0604 |
| Helium | 0 | 0.0001 | 0.026 | 0.0009 |
| Natural Gas Carbon Fraction ($CF_{ng}$) | 1.0468 | 0.0041 | 1.0461 | 0.0022 |

## SUMMARY

An accurate and precise method to establish a point source for carbon dioxide emissions was demonstrated. The expanded uncertainty of the $CO_2$ mass flow rate varied from 0.75 % at the 8 MW upper limit of the burner to 0.97 % when the burner is operating at 1 MW. The components of uncertainty for the $CO_2$ generated by a 2 MW fire are show in Figure 3.

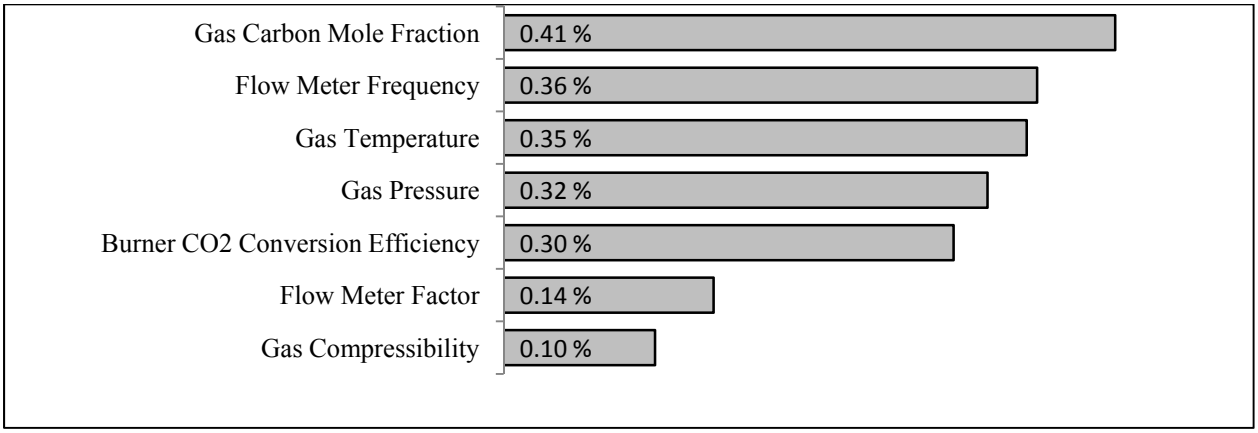


**Figure 3.** Components of measurement uncertainty ($k$ = 2, 95 % confidence level) in natural gas carbon emission source.

The largest source of uncertainty is the fuel carbon mole fraction which is derived from the gas composition measurement. The previous generation of this measurement system had an expanded relative uncertainty of 2.5 %. Significant error reductions were achieved by improving the temperature and pressure measurement, volume flow calibration and gas compressibility estimate. Additional improvements could be achieved by attaining a more precise natural gas calibration gas standard and improving the method for measuring the gas meter pulse frequency.

## 4. CONCLUSIONS

An accurate and precise method to establish a source for carbon dioxide was demonstrated using a natural gas burner. The advantage of this technique over direct injection of $CO_2$ is that there is continuous supply of source material and large mass flow rates can be attained. All known and reasonably expected sources of measurement uncertainty were included in this analysis. The uncertainty of the carbon dioxide source mass flow rate was less than 1 % and is sufficiently low to serve and a standard reference for evaluating continuous emission monitoring methods.

## 5. AKNOWLEDGEMENTS

A number of individuals made significant contributions to this project. Gina Kline performed the flow meter calibration. Jennifer Carney provided the natural gas quality control analysis. Equipment and installation was performed by Laurean DeLauter and Anthony Chakalis. Data system installation and collection was performed by Doris Rinehart. Data programming for compressibility was performed by Artur Chernovsky.

## 6. REFERENCES

[1] R.P. Borthwick, J. Whetstone, J. Yang, and A. Possolo, "Examination of United States Carbon Dioxide Emission Databases," *to appear- EPRI CEM User Group*, Chicago, IL: 2011.

[2] R.A.Bryant, T.J.Ohlemiller, E.L.Johnsson, A.Hamins, B.S.Grove, A.Maranghides, G.W.Mulholland, and W.F.Guthrie, *The NIST 3 Megawatt Quantitative Heat Release Rate Facility - Description and Proceedure,*, NIST IR 7052, 2004.

[3] B.N. Taylor and C.E. Kuyatt, *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*, NIST/TN-1297, Gaithersburg, MD: National Institute of Standards and Technology, 1994.

[4] A. Johnson and G. Kline, *REPORT OF CALIBRATION FOR A POSITIVE DISPLACEMENT FLOW METER*, Gaithersburg, MD: National Institute of Standards and Technology, 2010.

[5] ASTM D 1945-03, *Standard Test Method for Analysis of Natural Gas by Gas Chromatography*, West Conshohocken, Pennsylvania: ASTM International, 2003.

[6] E. Lemmon, M. Huber, and M. McLinden, *NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP*, Gaithersburg, MD: National Institute of Standards and Technology, 2010.

## APPENDIX A

LIST OF MEASUREMENT EQUIPMENT[1]

| **Description** | **Make** | **Model** |
|---|---|---|
| Multifunction 16-Bit DAQ Card | National Instruments | PXI-6220 |
| DAQ Signal Conditioner Module | National Instruments | SCXI-1102 |
| Data Acquisition Terminal Block | National Instruments | TC-2095 |
| Excitation Current Supply Module | National Instruments | SCXI-1581 |
| Gas Flow Meter | Instrumet | IRMA15M125-4BFI |
| Frequency Pulse Counter | Pepperl&Fuchs | KFD2-UFC-Ex1.D |
| Thermistor Probe | Omega | ON-403-PP |
| Pressure Transducer | Honeywell | TJE |
| Gas Chromatograph<br>2 channel 3000A Micro GC | Agilent | G2801A |
| GC Column, 8m x 0.32mm | Agilent | Plot U |
| GC Column, 8m, 0.15mmx2.0um | Agilent | UV-1 |
| Dry Block Temperature Source | Omega | CL121-4 |
| Dead Weight Pressure Tester | Ametek | RK-100 |

[1] Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.