Development of a Tunable Diode Laser Absorption Spectroscopy Moisture Analyzer for Natural Gas

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Abstract
GE Sensing and Inspection Technologies is in the process of developing a hygrometer for measuring water vapor in natural gas by utilizing tunable laser diode absorption spectroscopy (TDLAS). Natural gas is dehydrated and treated prior to transportation and use. The removal of water from natural gas is of considerable costs to the supplier and consumer. Reducing dehydration costs however is a tradeoff between the reduction of "gas quality" and increased maintenance. Water in excess amounts results in pipeline and component corrosion, can cause ice buildup, methane hydrate formation, lowers the calorific value of the gas and increases the energy consumption for compression and transportation.   The embodiment of this method is a process analyzer and sampling system designed to continuously measure the water concentration in natural gas. The system offers advances in speed of response and long-term stability. The TDLAS analyzer is based on the Beer-Lambert principle that fundamentally relates the concentration (mole fraction) of an analyte in a gas matrix to the absorption of tunable diode laser radiation by the sample gas. The system is attractive for monitoring moisture in natural gas because the wetted parts are inert and intrinsically safe thereby assuring long-term operation with infrequent maintenance. Test data that compares a TDLAS hygrometer to humidity standard is presented.

The Requirement to Measure Moisture in Natural Gas
Natural gas is a mixture primarily of methane (CH_4) and other hydrocarbon gases plus; Carbon Dioxide (CO_2), Nitrogen (N_2), Hydrogen Sulfide (H_2S) and water (H_2O).   Natural gas is very important as a source of fuel that can be converted to heat and electrical energy cleanly and efficiently. Natural gas is a fossil fuel that through complete combustion produces heat, CO_2 , H_2O. It is primarily transported and distributed across vast geographical areas through a network of carbon steel pipelines.   The global consumption of natural gas is expected to increase at a rate of 2.5% per year. According to the Energy Information Admistration (EIA) of the United Sates of America, an estimated 2.97 trillion cubic meters (tm^3) was consumed in 2005 and consumption is expected to increase to 4.7 tm^3 in 2030.   Water is present in natural gas and must be removed to acceptable levels. Excess levels of water vapor in natural gas cause a number of issues. Some of the significant issues are summarized below:

- Condenses as liquid. Water leads to corrosion of pipelines and pipeline components. Water combines with gases in natural gas such as Carbon Dioxide and Hydrogen Sulfide to create acids that accelerate corrosion.
- Condenses as solid. Ice formation in pipelines can lead to reduced flow or even blockages. Under high-pressure water also forms a lattice structure around methane to form methane hydrates (a solid ice like substance).
- Increased compression and transportation costs. Water in natural gas increases the cost of transportation by adding mass.
- Water lowers the calorific value of natural gas.

In order to lower the water content natural gas is dehydrated. Dehydration processes include Triethylene Glycol (TEG) contactors, desiccant dryers, membrane dryers and refrigeration/removal of condensate. Each of these methods requires the consumption of considerable amounts of energy.

Industrial users of natural gas have specifications pertaining to natural gas quality inclusive of the water concentration. For example, combined cycle gas turbines preheat the natural fuel feed to a minimum of 28°C above the dew point temperature to insure that liquids will not form. For gas turbines, high-pressure natural gas goes through a series of pressure-reduction stations before it enters the combustion zone. At each pressure reduction the gas will experience cooling due to the "Joule-Thompson" effect. The temperature of the gas will drop approximately 5.6°C per every 1000 KPa (Kilopascals) of pressure reduction. By measuring the dew point temperature of the gas stream sufficient heat can be applied to the fuel to prevent the formation liquids or ice. The gas is typically preheated by water or steam heat exchanger. An online monitor is required to assure that water does not leak due to corrosion within the heat exchange medium.

In the United States the standard for the maximum absolute humidity in interstate pipeline natural gas is 7lbs/MSCF (pounds per million standard cubic feet) or 112mg/m^3 (milligrams per cubic meter). Suppliers who exceed this standard or "tariff" run the risk of being shut out of the pipeline transportation and distribution network.

Moisture/Humidity Measurement Terminology
The terminology used in measuring water vapor in natural gas can be quite confusing. Water can exist as a gas (water vapor), liquid and solid (ice) in natural gas. Much of the global nomenclature refers to water in the gas phase in natural gas as the "moisture content". In other industries water in the gas phase (water vapor) in a gas matrix is referred to as "humidity" while water in the liquid or gas phase in liquid or solid matrix is referred to as "moisture".

At a constant pressure and temperature, the amount of water in the gas phase (water vapor) that a carrier gas can hold is finite. When the gas is holding the maximum amount of water vapor, it is said to be "saturated". When a gas is saturated any additional water vapor added to the system will condense as either liquid or solid depending on the temperature. By virtue of Dalton's Law, the water vapor in the saturated gas will also exert a partial pressure that is proportional to the mole fraction and may be express in terms of the "saturation water vapor pressure"

The saturation water vapor pressure is related to the temperature as follows:

(1) $\quad e_{s(water)} = K_w \bullet 6.1121 exp\left(\dfrac{17.502t}{240.97 + t}\right)$

(2) $\quad e_{s(ice)} = K_i \bullet 6.1115\, exp\left(\dfrac{22.452t}{272.55 + t}\right)$

(3) $\quad K_w = 1.0007 + 3.46 x 10^{-6} P$

(4) $\quad K_i = 1.0003 + 4.18 x 10^{-6} P$

$e_{s\,(water)}$ = Saturation water vapor pressure over water in mBar
$e_{s(ice)}$ = Saturation water vapor pressure over ice in mBar
t = Temperature in °C
K_w = Coefficient to correct for deviation from an ideal gas for liquid water in standard air
K_i = Coefficient to correct for deviation from an ideal gas for ice in standard air
P = Absolute pressure in mBar

Note: The coefficients above compensate for the non-ideal behavior of pressurized standard air. Coefficients will be different for various other gases.

Dew/Frost Point Temperature: The dew or frost point temperature is the maximum temperature that a gas can be cooled to, at a constant pressure, to make it saturated with water vapor. Cooling the gas below the dew or frost point will result in water condensing out as water or ice. An increase in pressure will also increase the dew point. In addition, any plane surface that are below the dew or frost point temperature will acquire a dew or frost layer. The dew or frost point temperature at atmospheric pressure at sea level can be calculated by the following equations.

$$(5) \quad T_{frost} = \frac{272.55 \cdot \ln\left(\dfrac{e}{6.1115}\right)}{22.452 - \ln\left(\dfrac{e}{6.1115}\right)}$$

$$(6) \quad T_{dew} = \frac{240.97 \cdot \ln\left(\dfrac{e}{6.1121}\right)}{17.502 - \ln\left(\dfrac{e}{6.1121}\right)}$$

T_{frost} = Frost point temperature in °C
T_{dew} = Dew point temperature in °C

Absolute Humidity: The absolute humidity is the mass of water vapor per unit of volume of the carrier gas.

$$(7) \quad \frac{g}{m^3} = \frac{216.7e}{t + 273.16}$$

g/m^3 = grams per cubic meter. To convert to pounds per million cubic feet (lbs/MSCF) multiply by 62.43

Mole Ratio or Volume Ratio (V_s): The mole or volume ratio is the ratio of the volume of water vapor to the volume of the carrier gas. Since the partial pressure is directly proportional to the volume the ratio partial pressure of the water vapor to the pressure of the carrier gas is the same as the volume ratio.

$$(8) \quad V_s = \frac{e}{P}$$

For lower values it convenient to express the volume ratio in parts per million (ppm_v):

$$(9) \quad ppm_v = Vs \bullet 10^6$$

For higher values it convenient to express the volume ratio in % by volume

$$(10) \quad \%_v = Vs \bullet 100$$

Note: % volume should not be confused with % relative humidity (%RH). %RH is the ratio if the partial pressure of water to the saturation water vapor pressure.

Mass Ratio (W_s): The mass ratio is ratio of the mass of water vapor to the mass of the carrier gas.

$$(11) \quad W_s = V_s \bullet \frac{18}{MW_{cg}}$$

W_s = Mass Ratio
18 = Molecular weight of water (H_2O)
MW_{cg} = Molecular weight of the carrier gas (Example for Methane CH_4 = 16)

For natural gas contractual specifications for the maximum amount of moisture is normally expressed in absolute humidity or volume ratio. The dew point temperature is also important because it predicts the temperature at which water will condense from the gas phase. Since the dew point temperature is dependent on partial pressure of water and the partial pressure is proportional to changes in the absolute pressure, the dew point temperature is referenced to either the process pressure or standard conditions.

$$(12) \quad e_2 = e_1 \bullet \frac{P_2}{P_1} \bullet \frac{K_2}{K_1}$$

P_1 & P_2 are the respective absolute pressures
e_1 = Partial pressure of water vapor associated with P_1
e_2 = Partial pressure of water vapor associated with P_1
K_1 & K_2 are coefficients that correct the gas to an ideal gas.

For natural gas the coefficients can be derived from formula and tables referenced in the Institute of Gas Technology, Research Bulletin 8 "Equilibrium Moisture Content of Natural Gases", November 1955 or DIN/ISO-18453:2004 "Correlation Between Water Content and Water Dew Point".

Beer-Lambert Law
The mole fraction of a given gas can be determined by measuring the intensities of light entering and exiting a certain path length of a homogenous gas medium.

$$(13) \quad A(\upsilon) = ln \frac{I_0(\nu)}{I(\nu)} = ln \frac{1}{\tau}$$
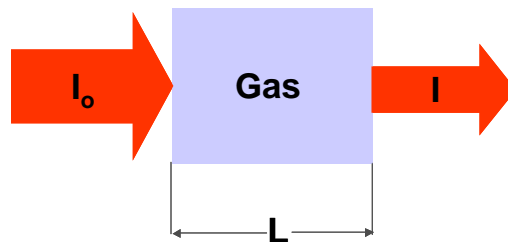
$$(14) \quad \tau(\nu) = \frac{I(\nu)}{I_0(\nu)}$$

$$(15) \quad X = \frac{PS(T)L\Phi(\upsilon)}{A(\upsilon)}$$

A(ν)= Absorbance at frequency ν
$I_0(ν)$ = Intensity of monochromatic light at frequency ν entering the sample
I(ν) = Intensity of monochromatic light at frequency ν exiting the sample
τ(ν) = Transmission coefficient
X = Mole fraction (concentration) of the analyte
P = absolute pressure
S(T) = Spectral line intensity which is temperature dependent
L = Absorption path length
Φ (ν) = Coefficient for normalizing absorption peak shape.

It is possible to change the frequency of a diode laser by changing the temperature or the "injection current". The monochromatic frequency can also be modulated. Representative infrared absorption lines for various gases are given in table 1. Water has several absorption frequencies that can be used. When selecting a given line, consideration must be paid the fundamental line strength as well as whether the line might overlap with the absorption lines of other gases that might be present in the sample. In the case of water when wavelength modulated TDLAS is applied, the second harmonic (refered to as "2F") peak height provides direct correlation to the concentration of the analyte.

Table 1

Gas	Formula	Absorption Wavelength (nm)
Water	H_2O	1392
Ammonia	NH_3	1512
Carbon Monoxide	CO	1560
Carbon Monoxide	CO	1579
Hydrogen Sulfide	H_2S	1579
Methane	CH_4	1654
Methane	CH_4	1684
Hydrochloric Acid	HCl	1730
Nitric Oxide	NO	1790
Water	H_2O	1800
Water	H_2O	1854
Water	H_2O	1877
Water	H_2O	1826
Nitrous Oxide	N_2O	1960
Carbon Dioxide	CO_2	2003
Carbon Dioxide	CO_2	2012
Water	H_2O	2750

The absolute signal for water at the same volume ratio at two different pressures will be different due to pressure "broadening". Broadening is due to the increased interaction and changes in collision frequency between the molecules as the pressure increases. Temperature also has a broadening effect but the magnitude is much less than pressure. Variance in the composition of the sample gas will also change the absolute signal due to the interactions between the component gas molecules. Thus the absolute signal is a "function of state". Empirical data for various gases, pressures and temperatures can be used to reduce the absolute signal to a direct correlation of the water vapor volume ratio.

Construction of the TDLAS Hygrometer

Figure 1 is a schematic that illustrates the components of a TDLAS hygrometer. For use in natural gas the wetted components are constructed of stainless steel with the exception of the optical window that consists of proprietary glass and the mirror that consists of proprietary polished metal alloy. Those components are selected for their resistance to corrosion and "optical purity". The path length is related to lower detection limit. The path length was optimized for a volume ratio of approximately 5 to 5000 ppm_v. The photodiode and reference photodiode are housed in a hermetically sealed and dry enclosure. A PRTD (Platinum Resistance Temperature Detector) measures the gas temperature and a silicon micro-machined strain gauge pressure sensor measures the sample pressure. The temperature sensor is encased in a 316 stainless steel sheath and the pressure sensor is also constructed of 316 stainless steel with a hastelloy-wetted diaphragm.

For field installation a pipeline-insertion membrane filter and pressure regulator will separate liquids (hydrocarbons, liquid water and glycol carry over from the dehydration process) and drop them back into the pipeline and also reduce the pressure. A coalescing filter will remove any additional liquids, aerosols and particulate not interdicted by the membrane filter. A second pressure regulator will decrease the pressure close to atmospheric. The flow rate through the absorption cell will be controlled with a needle valve and a rotameter will monitor the flow rate. The sampling system and absorption cell are installed in a stainless steel enclosure that is heated by a thermostatically controlled electrical resistance heater. The application of heat will also aid in keeping the sample in the gas phase.

The optical bench, flow cell and housing for the microprocessor and driving circuitry are designed to meet NEC Class 1, Division 1, Groups C & D, ATEX Zone 0 and the CSA equivalent. This is commonly referred to as explosion-proof (XP). The hygrometer is equipped with three programmable digital displays, three programmable analog (4-20mA signals) and a RS-232/485 digital serial interface with MODBUS protocol. The keypad of the analyzer utilizes magnetic induction therefore the user may program the unit in the hazardous area without the need for a "hot permit".
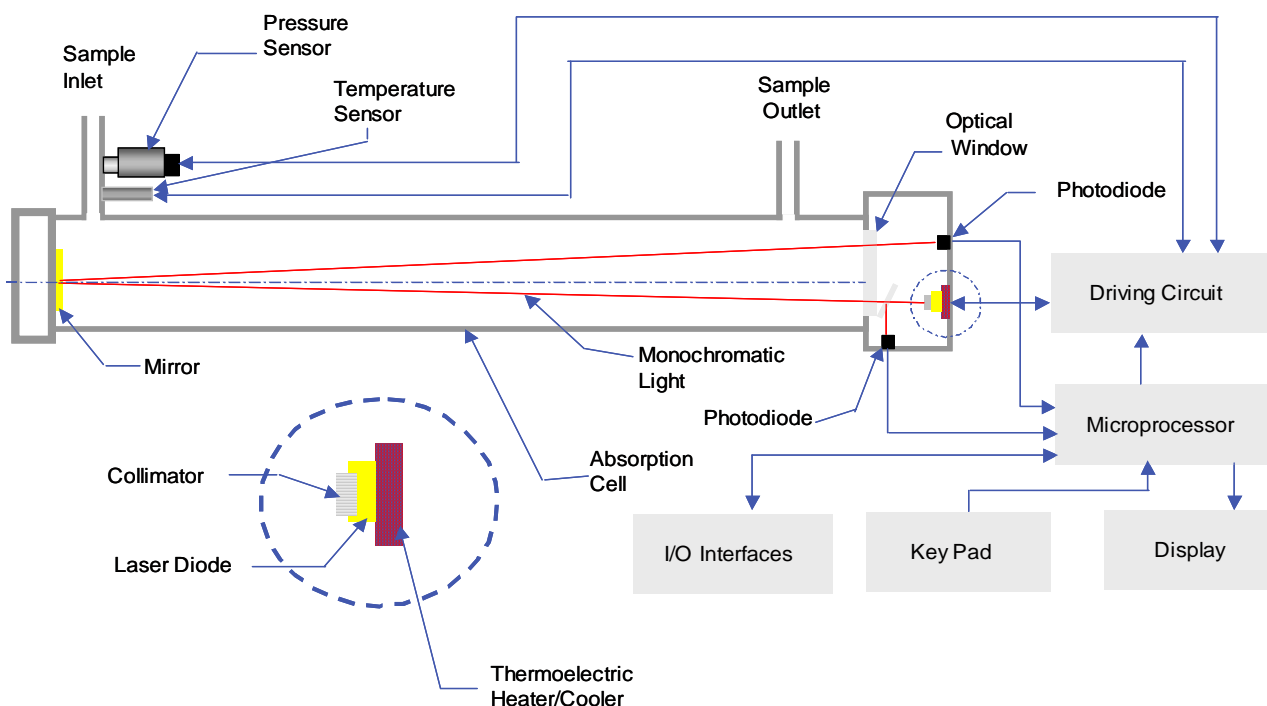

Figure 1

Intercomparison to Reference Standard

The laser wavelength swept through a certain spectral line by holding the diode temperature constant and the ramping the injection current. The injection current and thus the laser wavelength were modulated at a higher frequency to facilitate the measurement of the second harmonic (2F) peak height at various water vapor partial pressures. Figure 2 shows the direct absorption and Figure 3 shows the second harmonic (2F) signal.
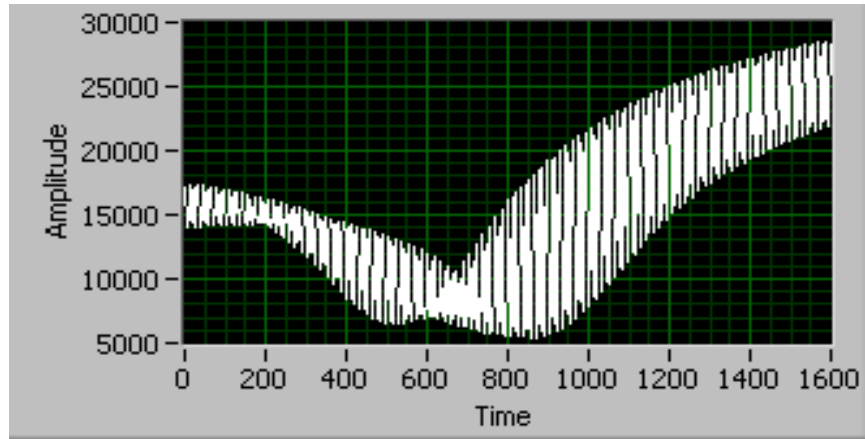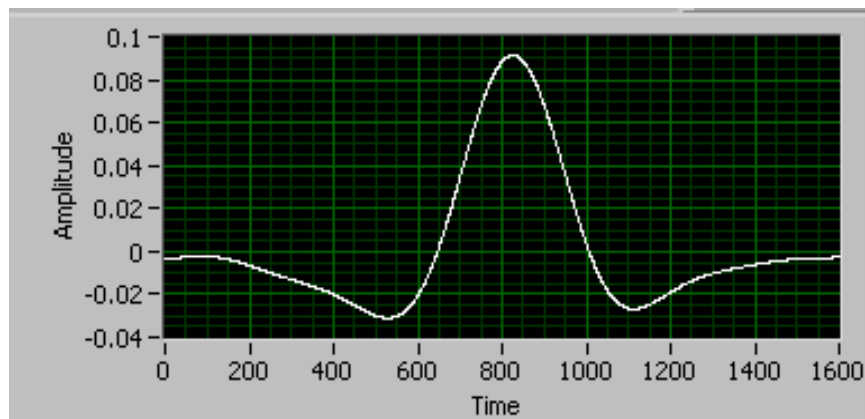

Figure 2

Figure 3

Nitrogen was used as the carrier gas. The water vapor generator consists of a saturator through which a controlled volume of nitrogen flows. The dew point temperature of the nitrogen is close to the headspace temperature above the water. Liquid nitrogen is evaporated, depressurized and mixed with the moisturized nitrogen in controlled proportions by using precise rotameters. The source of dry nitrogen has a water vapor concentration of less than 500 ppb_v (parts per billion by volume). A reference-chilled mirror samples the same gas. The pressure of the sample gas flowing through the TDLAS hygrometer and chilled mirror sample was measured and the flow rates were controlled to approximately one liter per minute. The digital output (RS-485/232) of the TDLAS and chilled mirror hygrometers were recorded by computer.

The chilled mirror fundamentally measures the dew or frost point temperature by using optical feedback from infrared light reflected off a Rhodium plated copper mirror to control the heat flux removed from or applied to it such that the condensed mass on the surface of the mirror is constant.   The chilled mirror is cooled with an integral five stage thermoelectric cooling module (TEC) that is coupled to a gold plated copper water jacket. Chilled water is circulated through the jacket.   When the mass of water or ice condensed on the mirror is constant as indicated by the reflected light, the temperature of the mirror is by definition equal to the dew or frost point temperature. The mirror temperature is measured with a precise Platinum resistance temperature detector (PRTD).   By measuring the sample pressure, the partial pressure of the water is back calculated with high certainty. The accuracy of the chilled mirror reference standard is given in table 2. in terms of the fundamental frost point measurement and the derived volume ratio and absolute humidity referenced to atmospheric pressure.

Table 2

Td C	Accuracy Td °C	ppm_v	Accuracy ppmv	mg/m^3	Accuracy mg/m^3
-60.48	±0.15	10	±0.21	7.36	±0.15
-53.52	±0.15	25	±0.48	18.41	±0.36
-49.77	±0.15	40	±0.75	29.45	±0.55
-47.95	±0.15	50	±0.92	36.81	±0.68
-45.14	±0.15	70	±1.25	51.54	±0.92
-35.91	±0.15	200	±3.30	147.25	±2.43
-30.67	±0.15	350	±5.53	255.68	±4.07

2F Peak Height vs. Water Vapor Pressure

$y = 14.741x + 0.0009$
$R^2 = 0.9992$

H2O Vapor Pressure (mbar) vs. 2F Peak
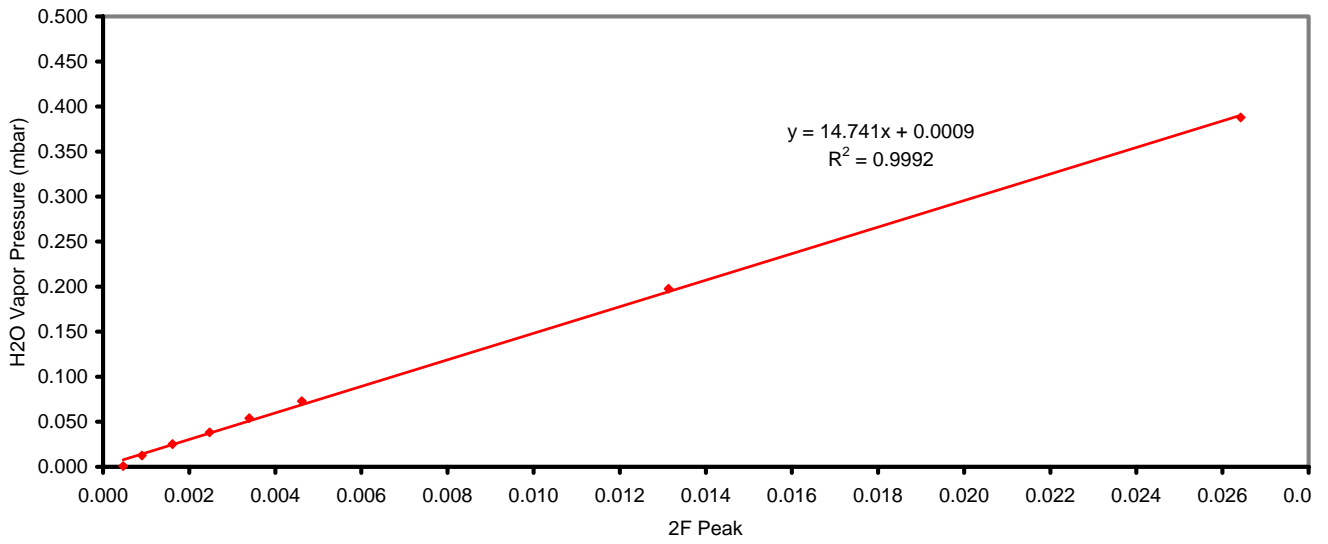
Figure 4

Intercomparison of TDLAS Hygometer with Chilled Mirror

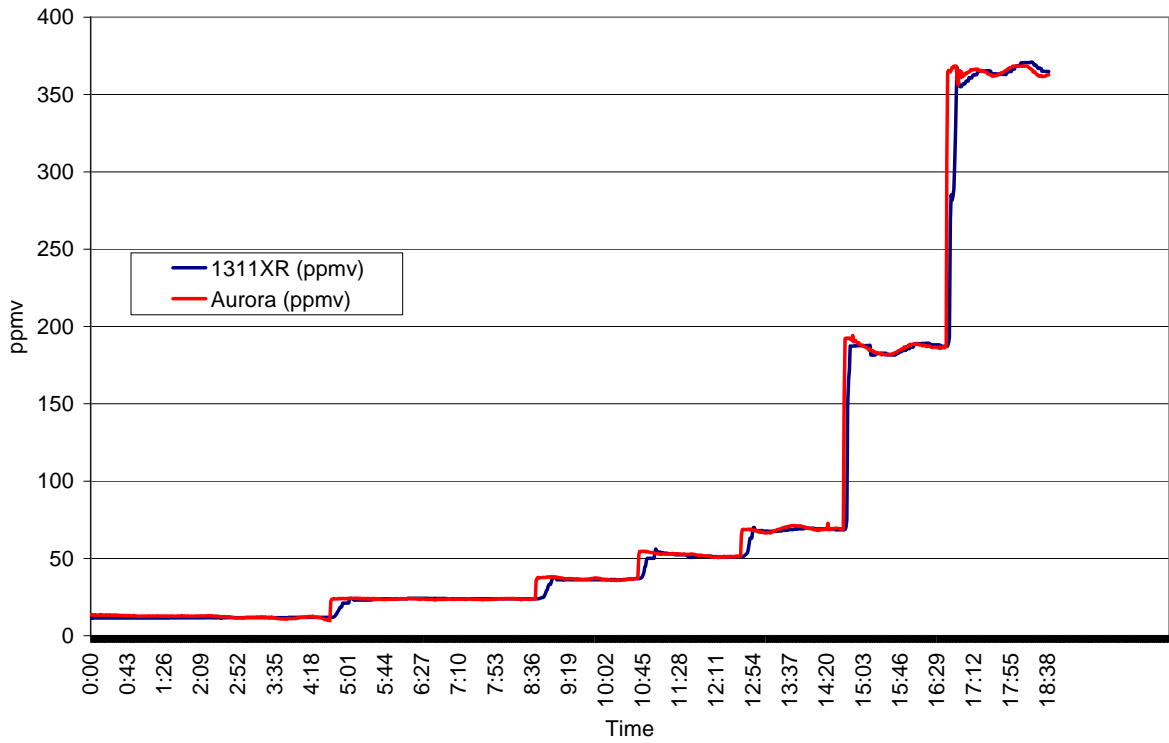
Legend:
— 1311XR (ppmv)
— Aurora (ppmv)

ppmv vs. Time

Figure 5
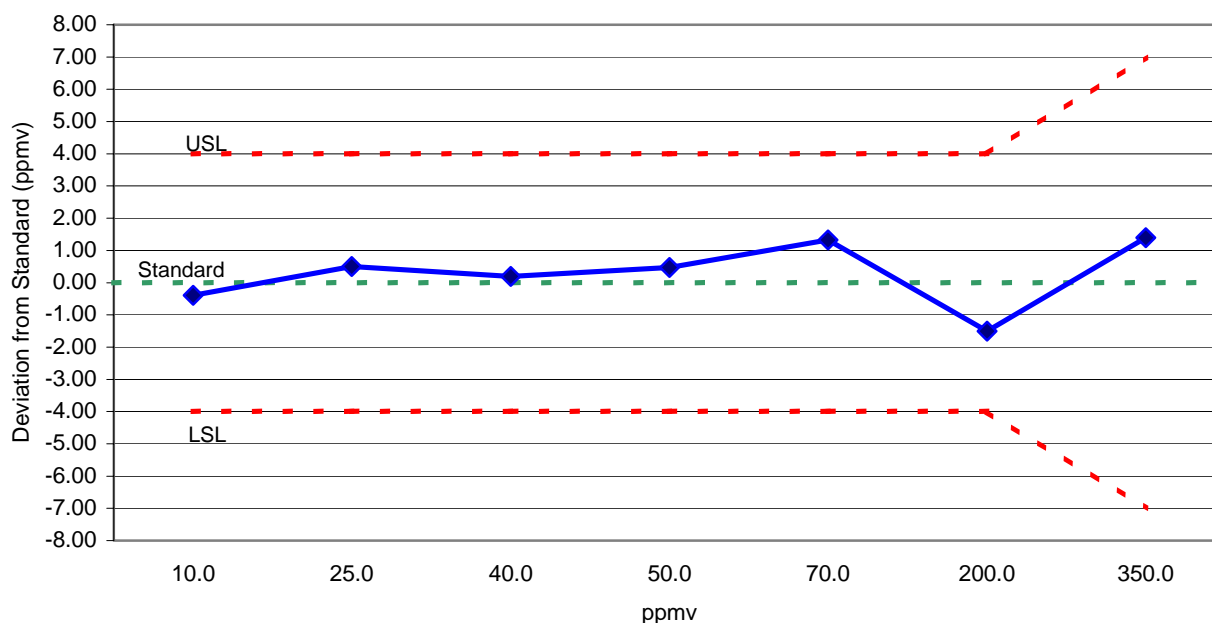
Intercomparison of TDLAS to Chilled Mirror

Figure 5

Conclusions

1. The TDLAS hygrometer has excellent response time. It is considerably faster than the reference chilled mirror as well as impedance based dew point sensors. While there is a lag-time to purge the absorption cell, once purged, the system responds in approximately 2 seconds.

2. The 2F peak height is linear with respect to the partial pressure of water in the sample gas.

3. The TDLAS hygrometer has very good correlation to the reference standard. The hygrometer exceeds the goal of ±4 ppm_v < 200 and ±2% of reading > 200 ppm_v.

4. The calibration system is traceable to NIST (National Institute of Standards and Technology) by virtue of the chilled mirror hygrometer.

5. The moisture generator exhibited small changes in the moisture output tests due to variation in the saturator temperature caused by variation in the room temperature. The TDLAS hygrometer has the sensitivity to record these changes.

6. A two-pressure/two-temperature generator with precise temperature controlled saturator and pressure measurements will be used for future calibrations. The system has an estimated accuracy ±0.1°C frost point. The two-pressure/two-temperature generator is an intrinsic standard that is referenced to: NCSL-RISP-5, National Conference of Standards Laboratories, Recommended Intrinsic Standards Practice, *Two-Pressure, Two-Temperature Humidity Generator. July 2002.* That system will also use a redundant chilled mirror reference hygrometer.

7. The instrument will be calibrated in nitrogen as the carrier gas. Empirical data relating the absolute signal to the moisture concentration in various component gases of natural gas including methane, ethane, propane, carbon dioxide, nitrogen etc. The empirical data matrix will enable the analyzer to be applied to moisture measurement in natural gas in various assays. This process will be the subject of a follow up paper.

8. If pipeline natural gas is sampled and conditioned such that the sample flows through the TDLAS absorption cell at low pressure (<207 KPa) and the pressure and temperature are simultaneously measured, this design will provide to provide long-term, drift-free and accurate moisture monitoring in natural gas.

9. GE Sensing and Inspection Technologies have applied two patents on the specific design.
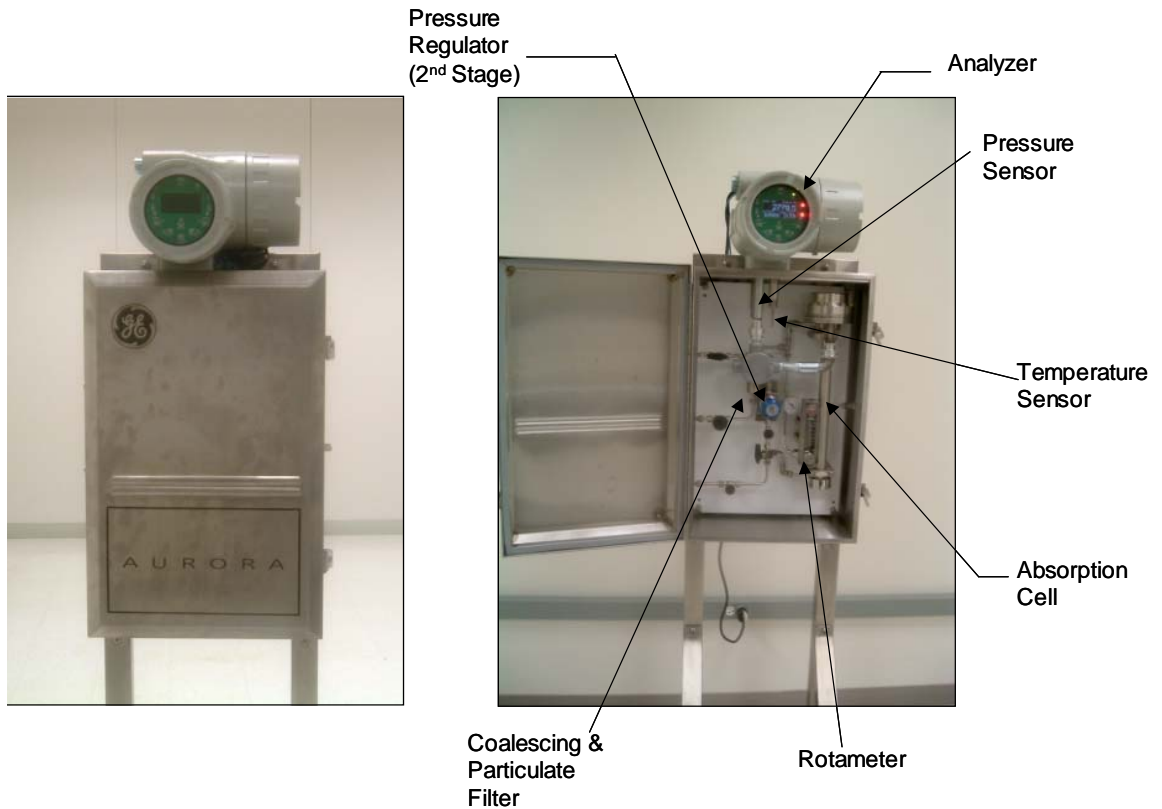
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Appendix

1.   Test Setup

Optica Chilled Mirror Analyzer

1311-XR: 5-Stage Chilled Mirror Sensor

MG-101 Frost Point Generator

Absorption Cell

TDLAS Analyzer

Temperature Controlled Chamber

2.   TDLAS Hygrometer

Pressure Regulator (2nd Stage)

Analyzer

Pressure Sensor

Temperature Sensor

Absorption Cell

Coalescing & Particulate Filter
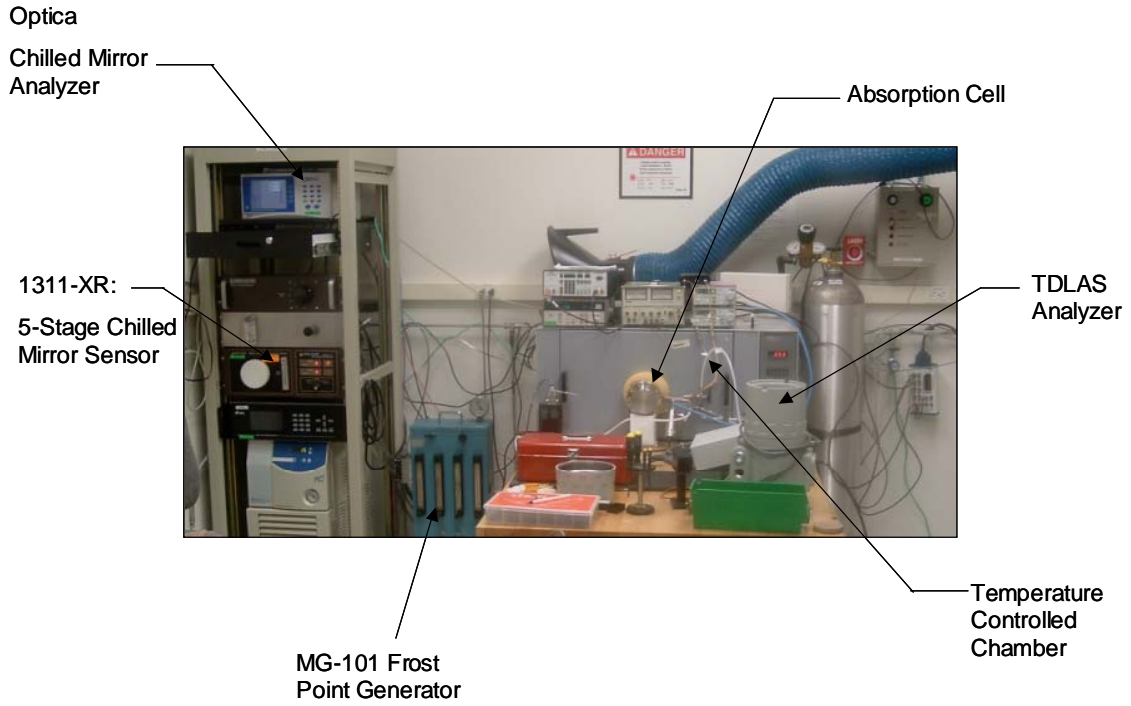
Rotameter

3.   Calibration System for Production

Reference Barometer

Reference Chilled Mirror

Unit under Test

Up to 6 units may be tested

2P2T Frost Point Generator