Moisture Measurement Using Laser Spectroscopy
Class # 5320

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Introduction

Tunable Laser Diode Spectroscopy (TDLAS) is rapidly becoming the measurement technology of choice for continuous online moisture measurement in natural gas. 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 is a tradeoff between profits and the reduction of “gas quality”. Water increases maintenance cost within the gas pipeline infrastructure. Water vapor present in excess amounts in natural gas results in pipeline and component corrosion, can cause ice buildup, methane hydrate formation, lowers the calorific value and increases the energy consumption for compression and transportation.

No technology is without limitations however TDLAS technology offers several advantages over the other types of sensor-based system including fast response and long-term stability. This technology does not rely on a wetted moisture sensing surface. Light energy transmitted through an inert sample cell is the basis of the measurement. The fundamental principle of measurement is based on the Beer-Lambert law which relates the concentration (mole fraction) of a specific gas in gas media to the absorption of light at a specific frequency.

Principle of Operation

The Beer-Lambert law (Eq.1) states that the mole fraction (concentration) of a gas can be measured in a homogenous gas mixture by measuring the intensity of light at a given wavelength entering the medium and comparing the intensity of light exiting the medium. In a similar fashion the ratio of laser light transmitted through background gas with presence of a specific analyte can be compared to laser light transmitted through the same background gas absent of the analyte over equal path lengths. In addition the ratio of the intensity of an absorbing frequency specific to a given analyte can be compared to the frequency of a non-absorbing frequency. “Tunable” lasers have the ability to scan over a narrow band frequency by controlling the injection current and base temperature therefore a single path can be used and the ratio of the baseline (or zero absorption) frequency compared to an absorbing frequency can be used to measure the concentration of the analyte.

\[
A = \ln\left(\frac{I}{I_0}\right) = S \cdot L \cdot N
\]

- \(A\) = Absorption
- \(I\) = The measurement of beam intensity tuned to an absorbing frequency
- \(I_0\) = The reference measurement or beam intensity when tuned away from the moisture absorbing frequency
- \(S\) = The fundamental absorption line strength
- \(L\) = The path length of the beam through the sample.
- \(N\) = The mole fraction of water contained in the beam path passing through the sample

\(\ln\) is the natural log

The fundamental absorption line strength \((S)\) is constant for a given gas composition at a specific pressure and temperature. Since the path length \((L)\) is constant, the mole fraction \((N)\) is inversely proportional to absorption.

The mole fraction by virtue of Dalton’s Law is directly proportional to the partial pressure. Dalton’s Law states (Eq. 2) that in a gas mixture, each component gas exerts a “partial pressure” directly proportional to its mole fraction or volume.
\[ P_T = P_1 + P_2 + \ldots P_n \]

\[ P_T = \text{Total Absolute Pressure} \]
\[ P_1, P_2, \ldots P_n = \text{Component Gases} \]

The concentration may be expressed by dividing the partial pressure of the analyte by the total pressure. The concentration of water in natural gas is commonly expressed as parts per million by volume (ppmv) (Eq. 3)

\[ \text{ppm}_v = \frac{P_{H2O}}{P_T} \cdot 10^6 \]

\[ P_{H2O} = \text{Partial Pressure of Water Vapor} \]
\[ P_T = \text{Total Pressure} \]

The absolute humidity is the mass of water over a specific volume. For water in natural gas, pounds per million standard cubic feet (lbs/mmscf) or milligrams per cubic meter (mg/m^3) are commonly used units. A standard cubic foot referenced one atmosphere at sea level and 60°F/15.6°C. The equation below yields the absolute humidity in grams per cubic meter (Eq 4).

\[ \frac{g}{m^3} = \frac{216 \cdot P_{H2O}}{T + 273.16} \]

\[ P_{H2O} = \text{Partial Pressure of H2O} \]
\[ T = \text{Temperature in °C} \]

Table 1 provides conversion factors between some of the most commonly used concentration and absolute humidity units. The conversion factors are for estimation and are based on standard conditions (1 Atmosphere at sea-level and 60°F/15.6°C).

<table>
<thead>
<tr>
<th>From</th>
<th>To</th>
<th>Multiply By</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/m^3</td>
<td>g/ m^3</td>
<td>1000</td>
</tr>
<tr>
<td>lbs/mmscf</td>
<td>mg/m^3</td>
<td>16.02</td>
</tr>
<tr>
<td>lbs/mmscf</td>
<td>ppm_v</td>
<td>21.07</td>
</tr>
<tr>
<td>mg/m^3</td>
<td>ppm_v</td>
<td>1.32</td>
</tr>
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</table>

The partial pressure of water is also correlated to the dew point temperature (or frost point temperature below 0°C/32°F). The dew point may be defined as the maximum temperature at a given pressure, where the gas remains saturated with water vapour. At the dew or frost point temperature the addition of any addition water vapor to the system or an increase in pressure will result in water condensing as either water or ice. In addition any surface that is below the dew or frost point temperature will acquire dew or frost (ice) layer. A given dew or frost point temperature yields a specific saturation pressure. The equations below yield the saturation water vapour pressure at the prevailing dew or frost point (Eq. 5 & 6).

\[ P_{H2O\,(water)} = K_w \cdot 6.1121 \exp \left( \frac{17.502t}{240.97 + t} \right) \quad K_w = 1.0007 + 3.46 \times 10^{-6}P \]
\[ P_{H2O\,(ice)} = K_i \cdot 6.1115 \exp \left( \frac{22.452t}{272.55 + t} \right) \quad K_i = 1.0003 + 4.18 \times 10^{-6}P \]

\[ P_{H2O\,(water)} = \text{Saturation water vapor pressure over water in mBar} \]
\[ P_{H2O\,(ice)} = \text{Saturation water vapor pressure over ice in mBar} \]
The coefficients ($K_w$ & $K_i$) compensate for the non-ideal behavior of pressurized standard air. The coefficients will be different for various other gases based on the “compressibility”. Since the water vapour pressure increases proportional to the total pressure Equation 7 expressed that relationship.

\[
\text{[Eq. 7]} \quad P_{H2O(2)} = P_{H2O(1)} \cdot \frac{P_2}{P_1} \cdot \frac{K_2}{K_1}
\]

$P_{H2O(1)}$ = Partial Pressure of H2O at System Pressure
$P_{H2O(2)}$ = Partial Pressure of H2O at Sample Pressure
$P_1$ = Absolute System Pressure
$P_2$ = Absolute Sample Pressure
$K_1$ = Coefficient to correct non-ideal gas at $P_1$
$K_2$ = Coefficient to correct non-ideal gas at $P_2$

If the light is “tuned” to a specific wavelength the analyte (in this case water) will absorb a portion of the photonic energy. The light energy is not lost but is converted to other types of energy. Water’s O-H (Oxygen-Hydrogen bond) embodies very unique stretching and vibro-rotational characteristics resulting in absorption at very specific wavelengths of light. Water has particular absorption bands for light in near infrared spectrum (800-2500 nm). The laser is typically held to a constant base temperature by thermal bonding to a thermoelectric heat pump. By ramping the injection current the laser is swept through a narrow frequency band. The current ramp is also modulated at high frequency as illustrated in figure 1. This technique is known as wavelength modulation spectroscopy (WMS).

![Figure 1. Ramp of laser injection](image-url)
Figure 2 shows the direct absorption signal. The signal loss is attributed to water vapor. The second harmonic (second derivative) is used for direct correlation to the partial pressure of water therefore yielding the water concentration by dividing, by the total pressure. The second harmonic is referred to as the 2F signal. Figure 3 shows the 2F signal at moisture concentrations ranging from approximately 10-1000 ppmv. The height of the peaks centered on the frequency index of approximately 75 is attributable to water vapor.

Construction of a TDLAS Analyzer

Figure 4 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 quartz and the mirror that which is made from gold alloy. Those components are selected for their resistance to corrosion and “optical purity”. The path length is related to lower detection limit. A longer path length is needed for measurement to trace moisture levels. For measurement to 5 ppmv, a path length of approximately 1 meter is required. For measurement 100 ppbv (part per billion by volume), a path length of approximately 36 meters is required. One method of increasing the path length is utilization of a finesse or “Herriot” cell. The finesse cell utilizes specially curved mirrors on both ends that enable the light to bounce back and forth enabling the absorption cell to fit into a smaller footprint. A PRTD (Platinum Resistance Temperature Detector) measures 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.

In general all of the wetted surfaces in the system as well as the sample transportation and conditioning system are constructed of non-hygroscopic materials. Stainless steel tubing is primarily used for sample transport. It has been shown that stainless steel has faster desorption rates that most other types of commonly used materials such as copper or plastic tubing. For ultra-low moisture levels the stainless steel tubing may be electro-polished or lined with Silicon and welded (VCR) fittings utilized.

For field installation a sample conditioning system is required. Figure 5 is an illustration of a typical system. The sample conditioning system performs the following functions:

- Pressure reduction: Typically gas line pressures are between 600-1200 PSIG. For TDLAS technology the pressure must be reduced to near atmospheric pressure. When the natural gas pressure is reduced the gas is cooled due to the Joule-Thomson (JT) effect. Natural gas cools approximately 7°F/100 PSI of pressure drop. The pressure reduction may be accomplished in multiple stages or heated pressure regulators utilized to compensate for the JT effect.
- Filtration: Generally three main types of filters are used; Particulate, Coalescing and Membrane. Filter media must not contain absorbent material such as activated carbon or desiccant that will adsorb water nor should the media evaporate water into the sample stream.

Figure 4. Schematic of TDLAS Moisture Analyzer
Particulate filters are typically consists of a sintered steel element with pore size ranging from 50-3 microns. In some cases a coarse filter is used in series with a finer filter. Coalescing filters utilize either a media such as glass fiber or glass spheres to enable aerosols (fine mist) to accumulate in to larger liquid droplets. Centrifugal force and gravity is as well as the flow of the inlet gas is used to sweep the liquid droplets away. Coalescing filters are typically employed when Triethylene-Glycol (TEG) dehydration is used. Membrane filters consist typically of proprietary membranes resulting in media that interdict aerosols and liquids but allow gases to pass through. In many sampling systems filters may be used in series to prevent overloading of the final elements.

- **Temperature Control:** Whenever natural gas is decompressed care must be taken to assure that the Joule-Thompson effect does not cool the gas to or below either the water or hydrocarbon dew point where liquids or ice will condense. The use of a heated pressure regulator and heat-traced tubing may be applied. The enclosure which houses the sample conditioning system and absorption cell may also be heated. When the analyzer is used outdoors or in a cold climate the analyzer and sampling system may be heated to within its operating temperature. To avoid the formation of condensates (liquids) in the sample, API Chapter 14.1 recommends that the sample system and tubing be kept 30°F/17°C above the hydrocarbon dew point and this recommendation also serve well for the water dew point.

- **Flow Control & Speed Loop:** While the optical response of TDLAS technology provides the fastest of all industrial moisture analyzers (typical response of <2 seconds), there is a lag-time associated with purging length of sample tubing and sample system components prior to analyzer. Typical flow-rates for TDLAS analyzers are 1-2 SCFH/0.5-1LPM. The purge can be increased by venting gas though a bypass (commonly called a “speed loop”). The recommended bypass to sample rate is 10:1 however practice has shown that even at 5:1 rate is sufficient. In some designs the bypass flow also functions to sweep liquids out of the coalescing filter.

- **Environmental and Safety:** Since a flow of natural gas runs through the analyzer the use of explosion proof or intrinsically safe system is needed. Most analyzers are certified for use in hazardous areas by a third party recognized agency. The gas that is vented may be released to the outdoor atmosphere if the volume is sufficiently low. Vent gas may also be sent to a flare (burned off) or catalytic converter.
Response Time

One of the benefits of TDLAS technology is the fast response to changes in moisture concentration. Dehydration process upsets are detected in practically real time. Once the process upset is fixed and the system normalized, this technology is useful in indicating when the process is sufficiently dry to meet both operational and contractual specifications. The response time of any moisture analyzer is highly dependent of the sampling system’s materials, length and sampling technique. An experiment in the lab was set up to illustrate the response time. Two dew point generators were configured to flow to a common 3-way ball valve resulting in the ability to switch from one stream to the other instantly. The streams were sampled through 10 feet/3 meters as well as an inline filter. The flow rate was set to 1 SCFH/0.5 LPM. Table 2 shows the moisture concentration related to the dew point and absolute humidity. Figure 6 shows a wet up step from 11 to 5375 ppmv and figure 7 shows the response in the reverse direction. In both cases the full response was acquired in less than 60 seconds.

Table 2.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Dew Point °C</th>
<th>Dew Point °F</th>
<th>ppmv</th>
<th>mg/m³</th>
<th>Lbs/mmscf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stream 1</td>
<td>-59.8</td>
<td>-75.6</td>
<td>11</td>
<td>8.4</td>
<td>0.52</td>
</tr>
<tr>
<td>Stream 2</td>
<td>-1.5</td>
<td>29.4</td>
<td>5375</td>
<td>4087</td>
<td>255</td>
</tr>
</tbody>
</table>

* Dew Point referenced to 1 Atmosphere
Figure 8 is a simulation of a dehydration process upset. A TDLAS unit was set up with natural gas stream with 8 ppm\textsubscript{v} of moisture. The flow rate was adjusted to 1 SCFH/0.5 LPM. The analyzer was allowed to stabilize. Liquid water was injected via a septum into the process stream by the using of a syringe. Within a few seconds the reading spiked greater than 3,000 ppm\textsubscript{v}. The system recovered back to within a few ppm\textsubscript{v} of the original reading in less than 3 minutes and back to the original reading within 7 minutes.
Pressure and Temperature Compensation

Wavelength modulated TDLAS moisture analyzers are generally operated at low pressure 10-30 PSIA/69-207 KPa. When the pressure and to a lesser extent temperature is increased there is more “interaction” between the water molecules as well as interactions between water molecules and the background gases. These interactions result in a decrease of the raw 2F signal. This is called “collision broadening”. Figure 9 shows the response of a gas sample with 100 ppm\(v\) constant moisture concentration. The analyzer is calibrated throughout a matrix of varying pressure and temperature and the data is stored in an electronic table. The electronic data tables are used to by the analyzer compensate for collision broadening effects.

Figure 8. Process upset simulation and recovery.

Figure 9. A graph of the 2F water peak height while varying the pressure and temperature while holding the moisture concentration constant at 100 ppm\(v\).
Gas Composition

As the background gas composition in natural gas changes, the dynamics of the interactions between water and other molecules change, affecting the absorption characteristics. There is also the influence of molecules that co-absorb and overlap the same frequencies of water. These effects can be mitigated by calibration in a mixture that models the process gas. In general, if the analyzer is calibrated in a specific concentration of methane (the most abundant gas in natural gas), the analyzer will be able to maintain a ±2% of reading or ±4 ppmv specification if the methane concentration does not vary within ±10% methane concentration.

Figure 10 shows the error of an analyzer that was calibrated using 98% methane. The moisture concentration was kept constant at 190 ppmv, and the methane concentration was lowered by dilution with nitrogen.

![Figure 10. Graph of deviation from reference standard at various methane concentrations while holding the moisture concentration constant](image)

Calibration

TDLAS analyzers typically require an automated and highly repeatable calibration process to meet their published accuracy specifications (Figure 11). The calibration system should be traceable to National Institute of Standards and Technology (NIST) or another globally recognized metrology institute. A humidity generator such as a two-pressure system or permeation system is utilized to produce gas with constant moisture content. The first step is to characterize the system response to changes in pressure and temperature. The two-pressure system saturates gas at an elevated pressure and low temperature (figure 12). The gas is expanded and warmed as it flows to the equipment under test (EUT). The fundamental measurement of the saturator and test pressures and temperatures yields the dew/frost point temperature and subsequently moisture concentration by calculation. Permeation generators (figure 13) utilize a selective membrane that releases a specific mass flow rate of water vapor into a carrier gas at a specific temperature and pressure. The outlet gas of the permeation device is often diluted in multiple
stages to produce low or trace moisture levels by employing mass flow controllers. The moisture content of the carrier gas is determined by the permeation rate and mass flow rates.

The two-pressure generator utilizes liquid nitrogen (LN2) boil off as the source gas. Typically the LN2 boil off gas has a frost point temperature of less than \(-90^\circ\text{C}/-130^\circ\text{F}\) (equivalent to 90 parts per billion by volume). The gas flows through each of the analyzers under test as well through a chilled mirror standard. A high precision pressure standard is utilized to measure the sample pressure. Data collected from each analyzer under calibration and the reference standard is used to produce a table of the generated partial pressure of water versus the 2F signal at multiple test points (typically six). The analyzers utilize these data tables and linear regression algorithms to convert the fundamental 2F signal to water vapor pressure. The water vapor pressure combined with pressure and temperature measurements are converted to moisture concentration, absolute humidity or dew point temperature.

The analyzers are then calibrated and verified in a gas mixture that represents natural gas. A typical mixture might be 90% methane, 4% Carbon Dioxide and 6% Nitrogen. The mixture may be custom blended to model the application. The carrier gas is dried using desiccant to near zero then moisture is injected into the gas by a permeation device. The gas stream may be further diluted to achieve the desired concentration. A small offset and span adjustment might be applied.

\[\text{Dew Point Generator}\]
\[\text{Pressure Ref}\]
\[\text{EUT \#1}\]
\[\text{EUT \#2}\]
\[\text{Ref Chilled Mirror}\]
\[\text{Data Acquistion \& Control}\]
\[\text{Stainless Steel Tubing}\]
\[\text{Digital Bus}\]

*Figure 11. Schematic of Moisture Calibration System*
Field Verification

TDLAS moisture analyzers have been proven to maintain their accuracy specifications for many years. The analyzers can be verified in the field by direct intercomparison to a portable analyzer such as impedance sensor based analyzer or a “Bureau of Mines” (BOM) type chilled mirror. In many instances the precision of the TDLAS analyzer is better than that of the reference instrument so the verification is
often “sanity check”. With impedance analyzers the best practice is to have a recently calibrated sensor and with BOM chilled mirrors a skilled and experience operator is required. BOM chilled mirrors rely on throttling a coolant thermally coupled to a reflecting mirror. The user has to observe the formation of a dew or frost layer while simultaneously recording the temperature. Since the reference instruments fundamentally measure the dew point temperature intercomparisons must be performed at the same pressure (or the readings adjusted to compensate for pressure differences).

Moisture analyzers are also routinely verified by intercomparison to bottled gas standards. Special care must be employed to avoid using the bottles. For example a cylinder of 100 ppmv water in methane at 2000 PSIG/140 Bar has a dew point temperature of approximately 11°C/52°F (the dew point of the gas will decrease to approximately –42°C/-44°F when the gas is expanded to atmospheric pressure). If the cylinder is exposed to a temperature lower than 11°C/52°F, water vapor will condense inside the cylinder and therefore lower the water vapor concentration of the gas extracted. The suppliers of the gas standards also advise not to use the bottles below a certain threshold level and have also advise that there is a limited shelf life.

References


Sparages, Narge and Soleyn, Ken “The Development of an Automated Calibration System for Tunable Laser Based Moisture Analyzers”. Proceedings from the ISA 55th Analysis Division Symposium New Orleans, LA USA April 2010