Moisture measurement technologies for natural gas

By Gerard McKeogh. Global Product & Sales Manager, Panametrics

Panametrics
a Baker Hughes business

The measurement of moisture in natural gas is an important parameter for the processing, storage and transportation of natural gas globally. Natural gas is dehydrated prior to introduction into the pipeline and distribution network. However, attempts to reduce dehydration result in a reduction in "gas quality" and an increase in maintenance costs and transportation as well as potential safety issues. Consequently, to strike the right balance, it is important that the water component of natural gas is measured precisely and reliably. Moreover, in custody transfer of natural gas between existing and future owners maximum allowable levels are set by tariff, normally expressed in terms of absolute humidity (mg/m^3 or lbs/mmscfh) or dew point temperature. Several technologies exist for the online measurement and for spot sampling of moisture content. This paper reviews the most commonly used moisture measuring instruments and provides a comparison of those technologies.

Introduction

Prior to transportation, water is separated from raw natural gas. However some water still remains present in the gaseous state as water vapor. If the gas cools or comes in contact with any surface that is colder that the prevailing dew point temperature of the gas, water will condense in the form of liquid or ice. Under pressure, water also has the unique property of being able to form a lattice structure around hydrocarbons such as methane to form solid hydrates. Ice or solid hydrates can cause blockage in pipelines. In addition, water combines with gases such as Hydrogen Sulfide (H_2S) and Carbon Dioxide (CO_2) to form corrosive acids. Water in natural gas also increases the cost of transportation in pipelines by adding mass and as water vapor has no calorific or heating value it also adds to the expense of compression and transportation.

When natural gas is sold, there are contractual requirements to limit the concentration of water vapor. In the United States the limit or tariff is expressed in absolute humidity in units of pounds per million standard cubic feet (lbs/mmscf). The maximum absolute humidity for interstate transfer is set at 7lbs/mmscf. In Europe, bodies such as EASEE-gas make recommendations on the maximum permissible amount of water vapor in the gas. EASEE-gas has approved a limit of -8°C Dew Point, referenced to a gas pressure of 70 Bar(a). This recommended limit is generally being adhered to in the gas industry across Europe.

Instrument technologies for measuring water vapor in natural gas

Various viable technologies exist for measuring the amount of water vapor in natural gas. These tend to rely on sample conditioning systems, where a gas sample is extracted, filtered, the pressures regulated and the flow controlled. it is not advisable to install a sensor directly in a natural gas pipeline as it can contain both physical contaminants (rust, scale, etc.), additives (such as odorizers, antifreeze agents such as methanol) and liquid hydrocarbons. Another benefit of a sampling system is that it can be isolated from the main pipeline. However, the sample system must not alter the moisture concentration of the sample via leaks or desorption/adsorption from the wetted components.

Currently the most widely used measurement technologies are chilled mirror, impedance sensors, quartz microbalance, Fabry-Perot inferometer and tuneable diode lasers. Each technology has its advantages and disadvantages.

Chilled mirrors

There are two basic categories of chilled mirror hygrometers: manually operated and automated. Automated chilled mirrors are further categorized into cycling chilled mirrors and equilibrium chilled mirrors. Chilled mirrors measure the dew/frost point temperature directly by using a coolant or thermoelectric heat pump to cool a plane surface until condensation forms. When the mass of condensate on the mirror is in equilibrium with the surrounding gas sample, the temperature of the mirror is by definition equal to dew or frost point temperature.

Chilled mirrors can also be used to determine the hydrocarbon dew point. In gas mixtures containing heavier hydrocarbons the partial pressure of hydrocarbons are sufficiently high enough that cooling the gas will result in a phase change from gas to liquid. In a similar principle, the temperature at which hydrocarbon condensate is in equilibrium with the sample gas is the "hydrocarbon dew point".

Manual chilled mirrors typically use the expansion high-pressure gas as the coolant. The manual chilled mirror apparatus (also referred to as the Bureau of Mines type), is described in ASTM-1142. When high-pressure gases such as methane or CO2 are decompressed, cooling occurs due to the Joule-Thomson effect. The user observes the onset of condensation via a view port while the mirror surface is cooling. The rate of cooling is important. If the cooling rate is too rapid condensation occurs prior to thermal stability. ASTM-1142 provides a procedure consisting of repeating the test several times and successively slowing the cooling rate at the observed onset of condensation. The user also has to learn to identify the difference between water and hydrocarbon condensate. Water appears either as fine droplets/fog (water) or opaque crystals (ice) while hydrocarbon liquids appear as shiny film. In some designs a matt black or ablated surface is used for hydrocarbons while a polished metal surface is used for water. The dew/frost reading is subjective, as each operator must decide in both instances when condensation occurs and then identify the condensate. Manual chilled mirrors are typically used for spot-checks and do not lend themselves to providing on-line continuous readings or telemetry.

Automatic chilled mirrors utilize a thermoelectric cooling module coupled to a mirror. The cooling module consists of a multistage stack of arrays of P-N junctions arranged in a back-to-back orientation. When direct current is applied to the P/N junctions electrons flow from the "P" junctions leaving holes. The energy holes are filled with heat energy that flows from the mirror. The P-N junctions are additionally thermally coupled to a metal heat sink. If the polarity of the current is reversed the mirror is heated. Visible or infrared light is emitted and aligned to reflect off the mirror. The reflected light is received by a photodetector. When the mirror is cooled sufficiently, water vapor condenses on the mirror and the light received by the photodetector decreases due to both absorption and scattering of the incident light. The signal from the photodector is then utilized in a feedback control loop to maintain a constant mass. A precision PRTD (Platinum Resistance Temperature Detector) measures the temperature of the mirror. The heat pump can also be augmented by refrigeration (evaporator core) or a liquid coolant block.

The overall measurement capability of typical chilled mirror is –80 to +85°C. The number of thermoelectric cooling stages, auxiliary, governs the full range. This system offers excellent precision and is widely used to provide laboratory reference standards for calibration and metrology applications. However, the footprint and design of most chilled mirror systems means that they have been and are restricted to laboratory applications Some units on the market, such as Panametrics Optica and OptiSonde, can be used for applications in non hazardous areas, thereby offering the precision and repeatability previously found only in laboratory standard instruments. As a result, these instruments could be used both to calibrate existing impedance type sensors on-site and as high accuracy, highly stable humidity sensors in their own right.

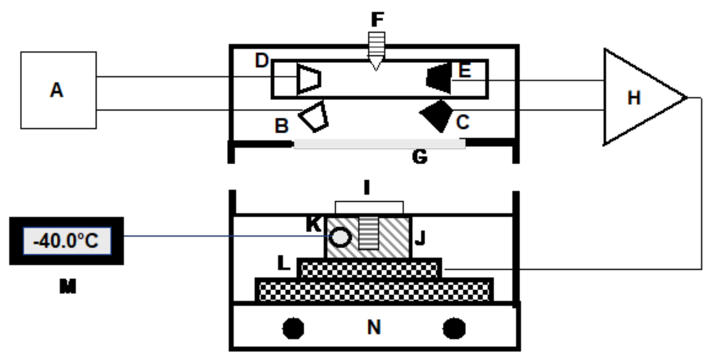

Figure 1. Automatic chilled mirror

A	IR Emitter Regulator
B	IR Emitter
C	IR Detector
D	IR Emitter Reference
E	IR Detector Reference
F	Iris Adjustment
G	Optical Window
H	Operational Amplifier
I	Mirror
J	Mirror Block
K	PRT (Temperature Sensor)
L	Multistage Thermoelectric Cooler
M	Temperature Indicator
N	Heat Sink/Heat Exchanger (Liquid Cooled)

Table 1. Pros and cons of chilled mirror hygrometers

Pros	Cons
Precise: typical accuracy of ±0.1 to ±0.5°C Td	Limited by cooling capacity Not a compact system
Direct fundamental measurement of dew/frost point	Requires containment or installation in a purged enclosure for hazardous area use
Inert wetted components. Longterm stability. 5-20 years of service without any drift	Not specific to water. Other gases may condense prior to water such as heavy hydrocarbons
Some models can measure at process pressure	Loses the ability to measure low frost points as the temperature and pressure increases
	Manual chilled mirror is subjective and requires operator expertise

Impedance Sensors

Figure 2. Natural gas compressor dehydration station – (Transport natural gas moisture analysis)

The most widely used impedance based moisture sensor technology for natural gas is the metaloxide sensor and, specifically, the aluminium oxide sensor. While there are variations on design, the most widely used sensors consist of an aluminium base that has a thin layer of aluminum oxide deposited or grown on the surface by means of an anodization process. A thin layer of porous gold is deposited over the oxide. On a microscopic level the aluminium oxide appears as matrix with many parallel pores. When exposed to even small amounts of water vapour the superstructure enables water molecules to permeate into the matrix where micro-condensation occurs. Since the dielectric constant of dry gases are significantly lower than gases containing moisture (about an 80:1 ratio for nitrogen or standard air) each pore acts as a micro-capacitor. As the micro capacitors are in a parallel arrangement the total capacitance is additive. In essence the sensor acts as a water molecule counter.

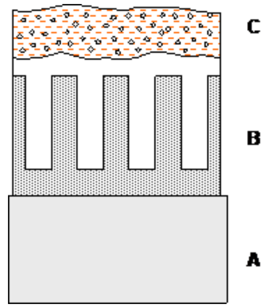

Figure 3. Aluminum oxide sensor

A	Aluminum Base
B	Aluminium Oxide
C	Porous Gold

The sensor is excited with a low voltage alternating current at a fixed frequency. The impedance of the sensor relates to the water vapour pressure by the following relationship

$\mathbf{Z^{-1} = Ae^{BP_w} + C}$

Z = Impedance

$\mathbf{P_w}$ = Partial pressure of water

A, **B**, and **C** are constants

Each sensor is calibrated at multiple dew/frost points, the partial pressure of water being a function of the dew/frost point temperature. The impedance at each dew/frost point is recorded and entered into a digital look-up table either embedded in the memory of the sensor module or programmed into an analyzer. The analyzer utilizes a polynomial expansion equation to convert the measured impedance by reference to the look-up table to produce direct readout in dew/frost point temperature. Typical accuracy is ±2°C Td from +60 to -65°C Td and ±3°C Td from –66 to -110°C Td.

In general impedance sensors provide excellent response to moisture changes in the dry-to-wet direction. They however have significant response times in the wet-to-dry direction.

Aluminium Oxide sensors are subject to drift over time. The typical drift is around 2°C per year and this can be managed by a regime of recalibration. Since Aluminium Oxide sensors are economical, very often users maintain additional sensors that are rotated in and out of service, thus always maintaining the in-service sensors within their recommended recalibration interval (typically one year).

Aluminium Oxide sensors have the capability to be installed at high pressure (up to 5000psig) and their footprint is quite compact. The sensors however are seldom installed directly in the pipeline. Instead, an extraction type sampling system is utilized, allowing the gas to be filtered, the pressure to be regulated and the flow rate to be controlled.

Table 2. Pros and cons of impedance sensors

Pros	Cons
Available with hazardous area certification (XP and IS)	Sensors have significant wet to dry response time particularly after process upsets
The sensor has a small footprint and may be installed long distances from the analyzer	Other polar gases such as alcohols or amines also change the sensor impedance
Sensor may be installed at line pressure. No adjustment required for variation in natural gas composition.	Yearly recalibration is required
Large dynamic measurement range (-110°C to +60°C)	May be attacked by some Sulphur compounds
Sensors are economically priced	Manual chilled mirror is subjective and requires operator expertise
Sensors are easy to replace in the field	

Quartz microbalance hygrometers

Quartz microbalance hygrometers consist of a quartz substrate that is coated with a hygroscopic polymer film. When a voltage is applied, the quartz oscillates at a resonant frequency. When the sensor is exposed to gas with water vapour, water is adsorbed by the hygroscopic coating and the resonant frequency changes in accordance with the increased mass of the sensor. The adsorption of water into the sensor's substrate is proportional to the partial pressure of the surrounding water vapor.

Quartz microbalance sensors have a certain degree of hysteresis and must be "re-zeroed" periodically. The measurement system therefore requires a "zero gas". While no gas supply can have an absolute value of zero, the zero gas may be defined as a gas that is closer to zero than any significant amount of water. Typically accuracy is ±10% of reading from 1-2,500 ppm_v (parts per million by volume).

Some measurement modes employ a non-equilibrium technique where the sensor alternates from being exposed to the zero gas and the process gas. The offline time spent on the zero gas should be factored into response time requirements.

The sensing surface is also susceptible to contamination and must remain clean. A suitable sampling system must be employed. Quartz Microbalance analyzers are characterized by having relatively fast response times.

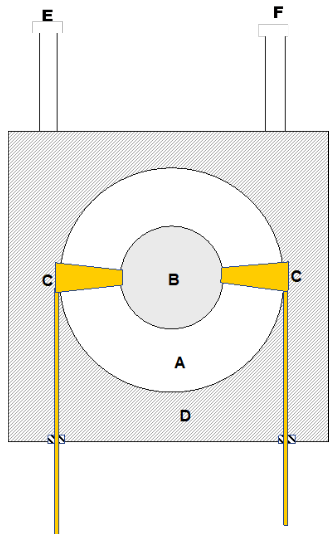

Figure 4. Quartz microbalance sensor

A	Quartz Substrate (Oscillator)
B	Hygroscopic Coating
C	Electrodes
E	Gas Inlet
F	Gas Outlet
G	Stainless Steel Flow Cell

Table 3. Pros and cons of quartz microbalance

Pros	Cons
Wide range ability to measure to sub 1 ppm_v levels	Relatively expensive
Moderately fast response time	Supply of zero and span gases needed
	Readings are step changes above zero baseline not absolute values
	Flow rate, temperature and pressure must be precisely controlled

Fabry-Perot hygrometers

The sensor head in Fabry-Perot type hygrometers consists of a multi-layered structure comprising materials with high and low refractive indices. Typical materials used are SiO_2 and ZrO2. The sensor head is coated with a glass substrate with a maximum surface pore size no bigger than 0.4 nm, making the structure specific to water molecules (pore size 0.28 nm). A light beam is transmitted through the sensor via fibre optic cable. The light source is generally a light-emitting diode (LED). As water molecules penetrate the sensor surface, they change the refractive index of the light beam (refractive index of Air 1: Water 1.33) causing a change in wavelength. The wavelength change is proportional to the amount of water molecules equilibrated on the sensor. The refracted light is detected by a Polychromator and the reading is calibrated in terms of dew point temperature vs. wavelength shift.

The sensor itself is mounted on the end of a stainless steel probe and connected via fiber optic cable to the control unit. The unit requires temperature compensation and pressure compensation if a ppm_v readout is required.

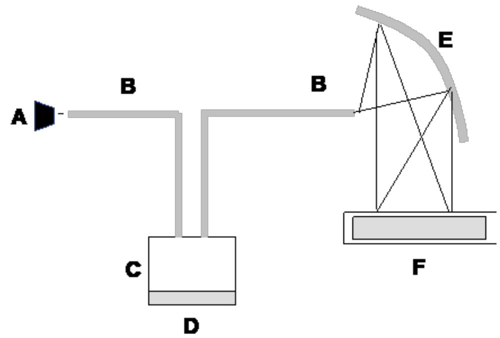

Figure 5. Fabry-Perot hygrometer schematic

A	IR Emitter
B	Fibre Optic Beam Waveguide
C	Glass Carrier (Quartz)
D	Multi-Layered Structure (SiO_2 ZrO_2)
E	Diffraction Grid
F	CCD Array

Table 4. Pros and cons of Fabry-Perot hygrometer

Pros	Cons
Intrinsically safe – light signal	Expensive fiber optic cable needed to connect probe to analyzer
Sensor may be installed at line pressure	Slow response
	Hygroscopic coating may degrade after prolonged exposure to natural gas

TDLAS hygrometers

Tunable Diode Laser Absorption Spectrometers (TDLAS) offer a fully non-contact method of continuous moisture measurement in natural gas. The measuring principle is based on the Beer-Lambert Law.

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

A = Absorption

I = The measurement of beam intensity when tuned to the absorbing wavelength of moisture

I_o = The reference measurement or beam intensity when tuned away from the moisture absorbing wavelength

S is the fundamental absorption line strength and is a fixed constant

L = the path length of the beam through the sample and is a fixed constant

N = the number of water molecules contained in the beam path passing through the sample

ln is the natural log

The Beer-Lambert principle states that when light energy at certain wavelengths travel through gas a certain amount of the energy is absorbed by the water within the path. The amount of light energy lost is related to the concentration of water.

A diode laser is very similar to an LED in that when a current is injected into a p-n junction, holes and electrons recombine and release photons.

A diode laser stimulates the release of these photons and incorporates an optical cavity to create laser oscillation and the release of a beam of coherent light at a single wavelength or frequency.

It is possible to change the frequency of the emitted light by changing the temperature of the "injection current". The monochromatic frequency can also be modulated. Consequently by passing light at the water absorption frequency through a sample chamber containing natural gas of a certain moisture content, it is possible to precisely establish the water content by measuring the amount of loss in the absorption spectrum.

In practice, a TDL system measures the water concentration in natural gas by sweeping a narrow band laser diode and changing its wavelength by ramping the injection current while holding the temperature constant by use of a thermoelectric (Peltier) heat pump array. The laser is also modulated at high frequency. At the center frequency the second harmonic (known as 2F) peak height is measured. The 2F peak height is directly proportional to the partial pressure of water in the absorption cell. By simultaneously measuring the cell total pressure the concentration in ppm_v is determined. Boyle's law, which relates the pressure of a gas to the volume, is then applied. The simultaneous measurement of the gas temperature and process pressure enable other humidity parameters such as absolute humidity, dew point and process dew point to be determined with a high degree of precision.

Figure 6. TDLAS hygrometer

The typical accuracy of a TDLAS hygrometer for natural gas is 2% of reading in terms of the mole fraction or ppm_v. By simultaneously measuring the temperature and pressure, the absolute humidity and dew/frost point temperature is measured with high precision by the use of psychometric equations. Measurement of the process line pressure also enables these units to calculate the pressure dew point.

TDLAS hygrometers are characterized by having very fast response times. The optical response is in <2 seconds. However it takes time to purge the absorption cell and sampling systems. Typical system response times are less than 5 minutes for a 90% step change.

Table 5. Pros and cons of TDLAS hygrometers

Pros	Cons
Very fast response in both directions. Dry to wet and wet to dry Non-contact.	Relatively expensive
No sensing surface to degrade due to exposure	Must be calibrated using a test gas with the same basic major components of the process gas
High long-term stability	Measurement is made a close to atmospheric pressure.
No zero or span gases needed	
Based on fundamental measurement	
Immune to glycol, H2S, methanol and other contaminants found in natural gas.	

Conclusions

The technology with the widest measurement range is typically the impedance type sensor, which can measure from -110°C to +60°C. The narrowest measurement range is confined to the automatic chilled mirror, which is constrained by the number of stages (cooling capacity) of the sensor installed with the device. Fabry-Perot type analyzers have range capability similar to impedance type sensors. The TDLAS technology range of measurement is determined by the type of measurement cell used in the device. A standard measurement cell has a typical lower detectable limit of 5 ppm_v, while the latest instruments extend this to sub 100 ppb_v. Upper ranges can be from 2000 to 5000ppm. Quartz microbalance ranges down to 0.1/1ppm with upper ranges of 1000 to 2000 ppm_v.

In terms of accuracy, the automatic chilled mirror technology is the most precise offering a typical accuracy of 0.1°C to 0.5°C dew point. The TDLAS unit is the next most precise instrument with a typical accuracy of +/-2% of reading (accuracy will vary in terms of dew point due to the non-linear relationship).

The most stable or drift free technologies can be considered to be TDLAS and Chilled Mirror.

Lasers, by their nature are inherently stable and the remaining components in the device can essentially be considered drift free. The non-contact nature of the measurement ensures that there is no process related degradation of the measurement circuitry, laser light source or detectors. At the other extreme, the measurement layer in impedance type sensors is in a continual state of drift, which needs to be continually corrected by regular calibrations.

In terms of response time, TDLAS comes out on top. The technologies that require equilibrium of moisture in the gas sample with a sensing surface/layer suffer in this category due to the polar nature of the water molecule and its tendency to stick to surfaces. A significant contact time with the gas to be measured is required, more specifically in going from a wet sample gas to a dry sample gas.

Maintenance is an important consideration when evaluating the lifetime costs of the different measurement technologies. As more customers outsource the maintenance function, they continually look to install low maintenance equipment. Contact based sensors will always require more in terms of maintenance than non-contact based measurements as their successful operation is much more dependent on a clean sample gas reaching the sensor. Corrosive components in the natural gas stream, like Sulphur compounds will also add to the maintenance requirements for contact based sensors. Maintenance requirements range from periodic inspection/replacement of sample system filters to annual or bi-annual recalibration of the sensors themselves. The TDLAS technology does not have an annual recalibration requirement and is typically sold as a maintenance-free technology, with the exception of any associated sample system filter maintenance. A planned factory calibration check every three to five years is typical with TDLAS technology.

All technologies require a clean gaseous phase sample to reach the sensor, hence a sample handling system is always recommended, although some vendors promote direct inline measurement as an advantage. Mixed phase sample, condensate or liquid glycol carryover, can coat contact based sensors, causing them to become unresponsive or read erroneously, or in extreme cases, can require sensor replacement. Liquid contaminant can also deposit in the TDLAS measuring cell, causing dispersal of the light signal, resulting in an erroneous measurement. The TDLAS technology has the capability to alert the user if contamination occurs, by comparing the measuring photo-detector tuned to a non-absorbing wavelength with a reference photo-detector, to determine if a shift has occurred (within some specified limits).

Contact based sensors may be partially contaminated and continue reading, although experienced users may be able to determine contamination has taken place by observing sensor behavior in terms of response to step changes in moisture or an actual step change in process readings after the contamination event. In most cases, if sensors become contaminated they can be cleaned, purged with a dry gas, and returned to service.

Table 6. Scorecard of moisture measurement technologies for natural gas

	A	B	C	D	E
Range	1	5	3	4	3
Precision	5	2	3	3	4
Stability	5	2	4	4	5
Speed of response	3	2	3	2	5
Maintenance	3	3	2	3	5
Price	1	5	1	2	1
TOTAL	**18**	**19**	**16**	**18**	**23**

5 = Most Desirable, **1** = Least Desirable

A = Chilled Mirror

B = Impedance

C = Quartz Microbalance

D = Fabry=Perot

E = Tuneable Diode Laser

Baker Hughes

BHCS38638 (11/2020)

panametrics.com