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MOISTURE Technical Paper

Analytical Devices for the Measurement of Water Vapor and Hydrocarbon Dew-Point in Natural Gas

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ANALYTICAL DEVICES FOR THE MEASUREMENT OF WATER VAPOR AND HYDROCARBON DEW-POINT IN NATURAL GAS

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Introduction

The determination of water vapor (water dew point) is crucial in the processing, custody transfer and transport of natural gas. High levels of water vapor in a natural gas stream can lead to a number of problems which include the formation of hydrates and the contribution to corrosion of plant and equipment. Furthermore, water vapor present in natural gas streams affects the overall quality of the gas, making the measurement of water vapor in natural gas an important requirement to producers, suppliers and end users in the industry.

Equally important is the need to determine the hydrocarbon dew point temperature in a natural gas sales pipeline network. The formation of hydrocarbon liquids (condensate) due to the presence of heavier hydrocarbons in the natural gas can lead to increase pressure drops in the pipeline system, flooding and safety hazards associated with liquids such as hot spots on compressor turbine blades.

There are a number of ways of determining the water vapor concentration in natural gas, and the various suppliers of the analytical technologies utilized have spent many years developing, improving and optimizing their analyzers to provide accurate, reliable and robust solutions for their customers.

AMETEK Process Instruments has been in the business of moisture analysis and hydrocarbon dew point determination for the natural gas industry for nearly four decades, and has pioneered the development of many on-line devices used for the detection of water vapor in many industrial applications. This paper presents a brief review of the most common methods and technologies used for the determination of water vapor, water and hydrocarbon dew point temperatures in natural gas applications.

Water Concentration vs. Water Dew-Point Measurement

The dew-point of a gas is a physical property; the temperature at which the sample gas becomes saturated and condensation first begins to appear. At this temperature, the gas exists in equilibrium with a condensed phase. Although the term dew-point is used in a generic sense, strictly speaking, the dew-point temperature refers to the equilibrium established over a liquid phase. In the case of water vapor measurements, temperatures below zero degrees Celsius typically refer to equilibrium over a solid phase (i.e., ice), so the term frost-point is used. Because the vapor pressure over a solid phase is lower than that over a liquid phase, the dew- and frost-points of a sample gas are not equivalent. The discrepancy between the two increases as the temperature decreases. Because the dew/frost-points are the result of thermodynamic equilibrium between two phases, they will not only be a function of the component concentration (e.g., hydrocarbon or water), but also the sample pressure and the sample gas composition. Thus, while the concept of a dew-point has a direct physical meaning, correlating this property to the component concentrations is not so straightforward.

There are two classes of measurement devices. Devices capable of determining the physical dew point of either a hydrocarbon or water in natural gas, and those devices which are capable of determining or measuring the concentration of water in a natural gas sample.

Analyzers capable of measuring the dew-point temperature directly are based on chilled mirror technology and are sometimes referred to as ‘first principle’ devices. Expressing water content in terms of dew-point originates from this first principle device tracing its history back to the early dates of the natural gas industry when the U.S. Bureau of Mines developed the manual chilled mirror device.

The other class of measurement devices used for the determination of water vapor in natural gas determine the concentration of water vapor or partial pressure of water in the natural gas sample. Common concentration or content outputs of these devices include mg/Nm^3, lbs/mmscf and parts per million either by weight (ppmw) or

volume (ppmv). Water vapor measurement technologies most commonly used in the natural gas industry include capacitance-based sensors, Quartz-Crystal-Microbalance (QCM), Tunable Diode Laser Absorption Spectroscopy (TDLAS) and electrolytic-based sensors (also referred to as P_2O_5). These technologies will be discussed in more detail in this paper.

The accepted conversion between the measured concentration of water vapor and dew-point temperature is based on empirical data from the original research of the Institute of Gas Technologies (IGT), published in the 1950's in IGT's Bulletin No. 8, and republished in the American Society for Testing and Materials (ASTM) standard ASTM-D1142-95. More recently, a European calculation adopted by the European Gas Research Group (GERG) and published by the International Organization for Standardization Society (ISO) as method ISO 18453:2004 specifies a method to provide users with a reliable mathematical relationship between water content and water dew point in natural gas.

Chilled Mirror Hygrometry

As previously described, chilled mirrors actually measure a physical property. A chilled mirror consists of means to accurately measure the temperature at which water condenses on a temperature-controlled surface, which is in contact with the process gas. Chilled mirror instruments typically operate by continuously flowing sample gas across a temperature-controlled, polished surface (i.e., a mirror). As the temperature of the polished surface is slowly lowered, formation of condensate is identified visually, either by directly observing the surface of the mirror, or by means of a magnified viewer, which superimposes the mirror temperature on a magnified mirror surface (Figures 1A and 1B). Once the condensate has formed and a "dew-point" temperature has been established, the sample pressure and temperature may be recorded.

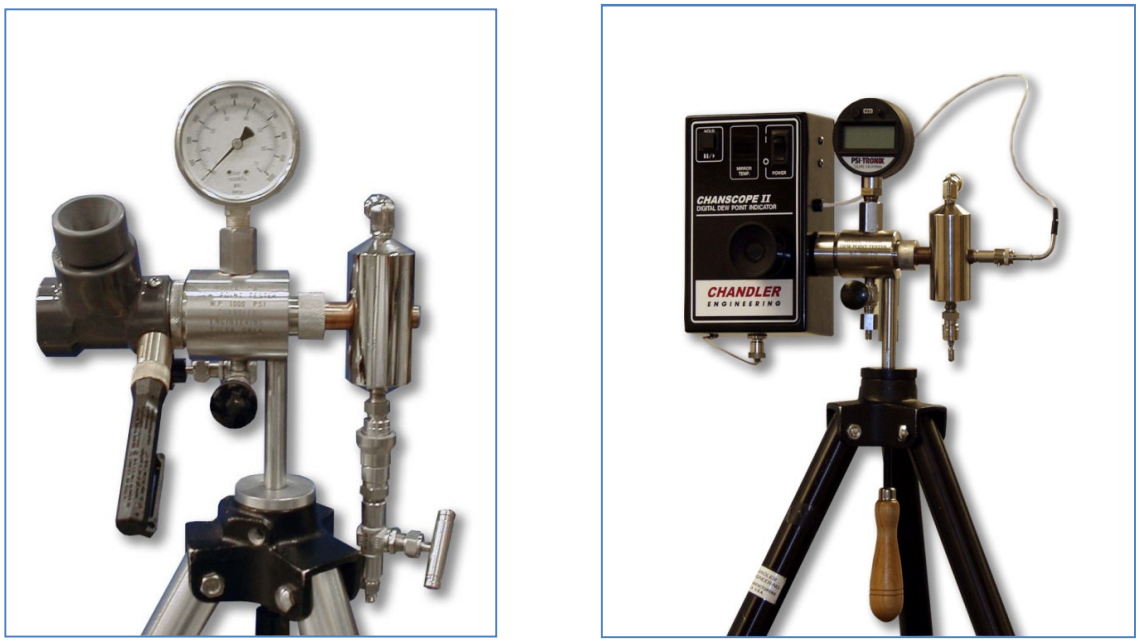


Figure 1A and 1B – Examples of Manually Operated Dew Point Chilled Mirror Devices

Chilled mirrors can be classified into two categories, manually operated or automated, on-line devices. Manual devices are typically available at a fraction of the cost of on-line water vapor measurement devices, but require frequent maintenance and experienced technicians to perform the measurement. Mirror cooling is achieved using an external coolant (refrigerant) to reduce the temperature of the mirror to the desired dew point temperature. Careful control of the cooling is required to ensure that accurate and repeatable dew point detection is achieved.

Advantages of the manually operated chilled mirror device includes the ability to detect both water and hydrocarbon dew-points, provided there is enough separation between the two condensation temperatures, and that one of the dew-points does not obscure or wash off the other. Generally the detection of multiple dew point

temperatures using a manually operated chilled mirror is reserved for experienced technicians trained to distinguish between water, hydrocarbon or other potential condensable in a natural gas stream. Figures 2A and B highlight the differences in appearance of hydrocarbon and water dew point 'stains' on the surface of a manually operated chilled mirror device.

Manually operated chilled mirrors are generally designed to require very little set-up time by the user. Manual chilled mirror instruments generally require no external power, are very light weight, suitable for monitoring water dew point temperatures in sour gas applications (high H_2S applications) and come completely assembled and ready-to-use.

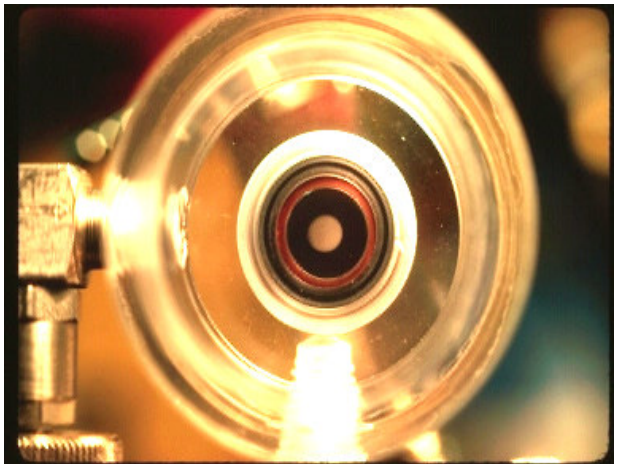


Figure 2A - Water Dew Point with Chilled Mirror

Figure 2B - Hydrocarbon Iridescent Ring (Dew Point)

The major disadvantage of using manually operated chilled mirrors is that manual devices require experienced operators to make reproducible observations of condensate formation. Natural gas streams may also contain components which could condense and cause erroneous dew-point temperatures for the water and hydrocarbon dew-points (e.g., glycol, amines, and methanol). Inexperienced operators of manual devices frequently 'call' water-like condensable substances on the surfaces on the mirror water, when in fact the condensable may be a methanol or a glycol. Manually operated devices are non-continuous and are typically only used to perform spot checks to ensure a pipeline specification is met, or to verify readings and confirm the operation of continuous moisture analyzers installed on natural gas pipelines.

Automated chilled-mirror devices generally follow the same "direct" measurement criteria as do manual devices. The mirror is cooled by either thermo-electrical coolers (Peltier elements) or external coolants such as natural gas or CO_2 (Joule-Thompson cooling). A well-designed electronic cooling system will allow for stable and exact temperature control and is generally preferred. The detection of condensate is achieved using electro-optical detection systems, typically consisting of a combination of light-emitting-diodes as the source, and phototransistors as the detectors.

The construction of the mirror for water dew point detection generally follows the same criteria as for the manually operated devices, a smooth reflective mirror constructed of material which is resistive to corrosion and with good thermal characteristics. The thermo-electric cooler is close-coupled to the mirror assembly, which is in contact with the flowing gas. Highly accurate temperature devices (e.g. PT 1000 RTD) embedded within the mirror measure the temperature of the mirror surface.

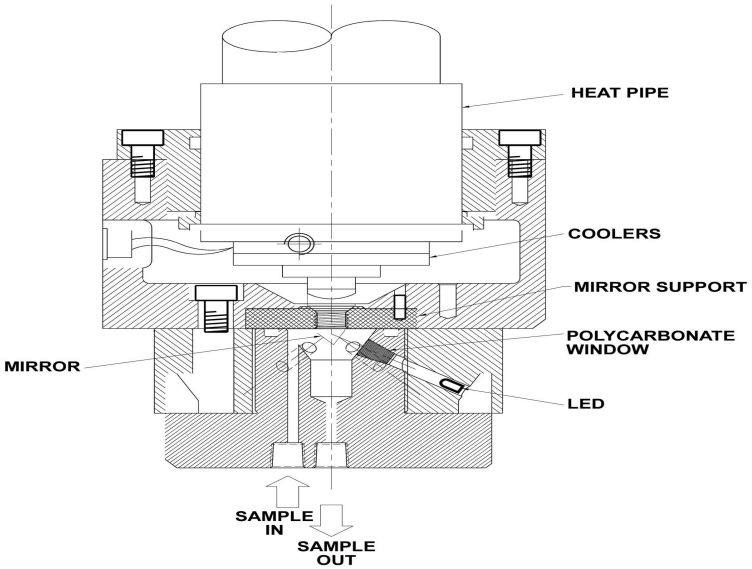


Figure 3 - Automated Chilled Mirror Analyzer

For the measurement of hydrocarbon (HC) dew point, the optical surfaces of the mirrors may be modified to take advantage of the different wetting properties of the hydrocarbon components, as compared to water. Because of the high surface tension of water, condensate will form in droplets on the surface. Hydrocarbon condensate spreads into a thin reflective film due to lower surface tension. To measure the HC dew-point, a rough, semi-matt surface is typically used as the condensation surface. As hydrocarbon condensation occurs on the optical surface, it becomes reflective, and detection of the hydrocarbon dew-point is made.

Automated chilled mirrors provide a number of key features and benefits compared to their manual counterparts. Integrated electro-optical detection systems eliminate any bias associated with the measurements, providing a consistent, accurate determination of dew point temperatures. Thermo-electric cooling systems provide the means to control the cooling rates of the chilled mirrors, enhancing sensitivity and providing more accurate 'first stain' detection. Finally, automated chilled mirrors provide a continuous update of dew point temperatures without requiring continuous supervision or intervention by experienced technicians.

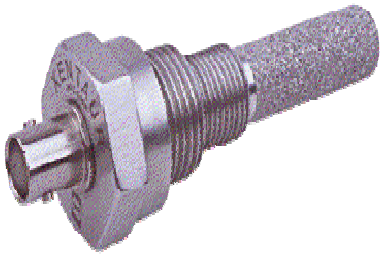
The major drawbacks of the automated chilled mirror devices are initial cost of the systems. Automated chilled mirrors generally require sample systems and some environmental control (installation in enclosures or shelters) to operate properly.

Capacitance Sensors

Capacitance sensor is the general term referring to the use of metal oxide, ceramic, or polymer films as a moisture-sensitive dielectric sandwiched between two electrodes. The most common example in industry is the aluminum oxide type. This sensor consists of an aluminum substrate upon which a thin layer of aluminum oxide is chemically formed. A thin layer of gold is then deposited on top of the aluminum oxide, which acts as the top electrode of the capacitor. The gold layer is thin enough so the water molecules can readily permeate through and enter the aluminum oxide layer below. Water molecules entering the aluminum oxide layer change the dielectric constant of the layer, and thereby change the capacitance of the sensor. The water vapor pressure is then monitored as a function of the capacitance of the sensor.

In practice, the sensor element is shielded with a porous sintered-metal sheath, which forms the tip of a probe assembly. The sensor is connected to remote electronics via signal cable. Although this probe design is suitable for in-situ operation, it is common practice to install them in an extractive sample system. Typically, one or more probes are installed on a manifold so a sample of the natural gas can be conditioned to remove contaminants, and the pressure can be regulated. This design allows for the probes to be removed, or isolated from the process, as required for maintenance.

The primary advantage of capacitive-sensor-based probes is low installed cost. These sensors also have some significant weaknesses. Specifically, any material in the sample gas that can coat, or foul, the sensor element will effectively prevent the sensor from contacting the sample gas (i.e., the readings from the sensor remain constant, independent of the changing moisture concentration in the sample gas). Aluminum-oxide sensors calculate dew point based on the water that has permeated through the metallic electrode and been absorbed by the dielectric material. These sensors can only provide an accurate representation of the process gas after the moisture within the sensor has reached equilibrium with the moisture in the process gas.



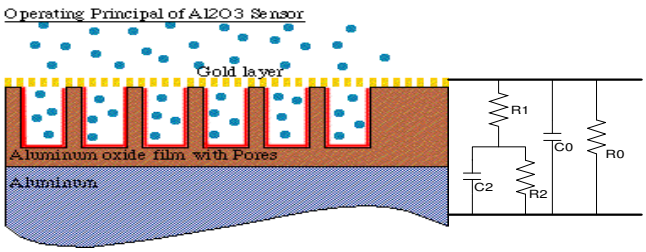


Figure 4A and 4B - Capacitance Probe Assembly and Operation

Quartz-Crystal Microbalance Sensors

The Quartz-Crystal Microbalance (QCM) sensor has been used for water vapor measurements since the early 1970s. There have been numerous advancements made to the technology since then which have provided dramatic performance improvements.

Quartz Crystal moisture analyzers are fairly simple and straightforward operating devices. At the heart of the technology is a simple quartz-crystal oscillator. To fabricate the sensor, a portion of the quartz crystal is coated with a hygroscopic material. Figure 4A illustrates the QCM cell construction and figure 4B and C highlight the basic operation of the QCM system. When exposed to a sample gas containing water vapor, the hygroscopic layer will adsorb water from the gas phase, thereby increasing the mass loading of the quartz crystal. This increase in mass decreases the resonance frequency of the oscillator; the moisture concentration is measured as a function of the frequency change. The QCM sensor technology is incorporated into an extractive sampling system, which is used to alternately expose the sensor element to the sample and a dry reference gas. The moisture concentration is then measured as a function of the difference in oscillator frequency measured for the sample and reference streams.

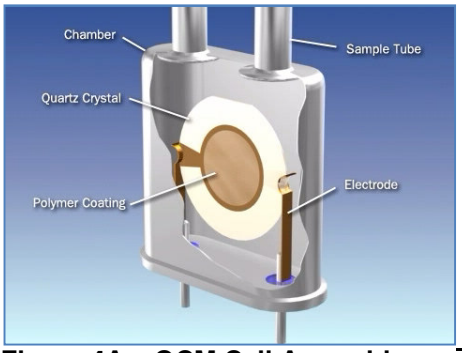
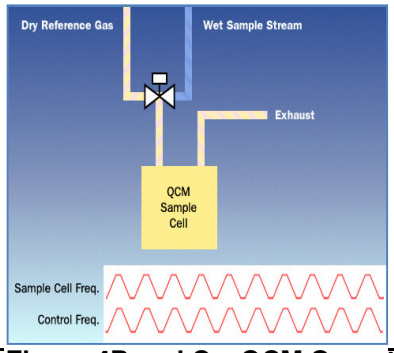


Figure 4A – QCM Cell Assembly



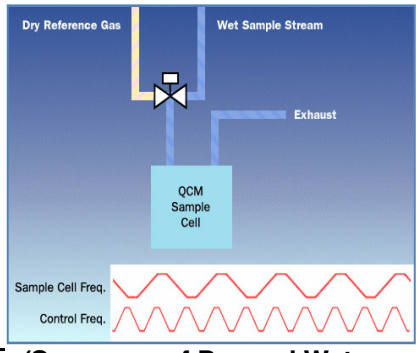


Figure 4B and C – QCM Operation (Sequence of Dry and Wet Measurement Cycles)

The measurement does not require the sensor to come to equilibrium with the moisture in the sample gas, resulting in relatively fast speed of response to both increasing and decreasing moisture concentrations. Materials that stick to, or foul, the sensor will cause a shift in the oscillator frequency, but will not substantially influence the frequency difference recorded between the sample and reference gases, making these sensors more resistant to contaminants found in natural gas streams. In a typical QCM-based analyzer, a means of testing sensor

performance (i.e., a permeation device to produce known moisture challenges) is built into the sample system to eliminate the need for removal and remote testing of the sensor. The moisture measurement is made under controlled operating conditions by keeping the temperature, pressure and flow of the analyzer constant.

The non-equilibrium based approach is a major advantage of QCM technology, when compared against other contact sensor approaches. In an equilibrium-based sensor, the speed of response depends on the magnitude of the change in measurement value. A large step change will result in a big difference in the partial vapor pressure of the water molecules and the sensor will respond relatively fast. If the change is small, the sensor takes much longer to equilibrate because of the small differential in the water vapor pressure. With a non-equilibrium based sensor, such as the QCM, every measurement cycle looks at a big signal even if the change in the measured value is small because a difference between a dry reference gas (a small signal) and wet sample gas (a big signal) is observed. The end result is a fast response to the rate of change in the moisture concentration. Additionally, the exposure of the sample to a cleaner (and in some cases pre-conditioned) 'reference' gas stream minimizes the amount of time the sensor is exposed to 'dirty' gas. Dual mode sensor calibration is provided and users can choose to have the sensor exposed to cleaner reference gas for extended time periods (sensor saver mode).

These devices are widely applicable in the natural gas market, due to the inherent accuracy of the measurement technology. QCM analyzer technology is extremely sensitive and capable of providing measurement accuracies of +/- 10 ppb for low concentration water vapor analysis operation in natural gas processing applications such as cryogenic turbo expansion, LNG processing and other low-level detection applications typically requiring extremely low levels of moisture.

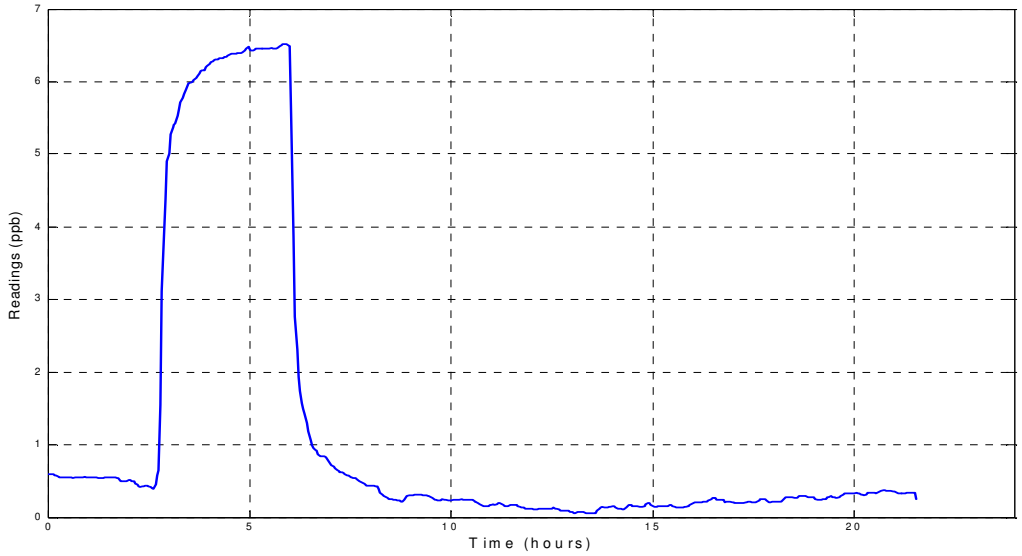


Figure 5 – QCM Performance Capability, Moisture Challenge of 6 ppb(v) and Analyzer Response

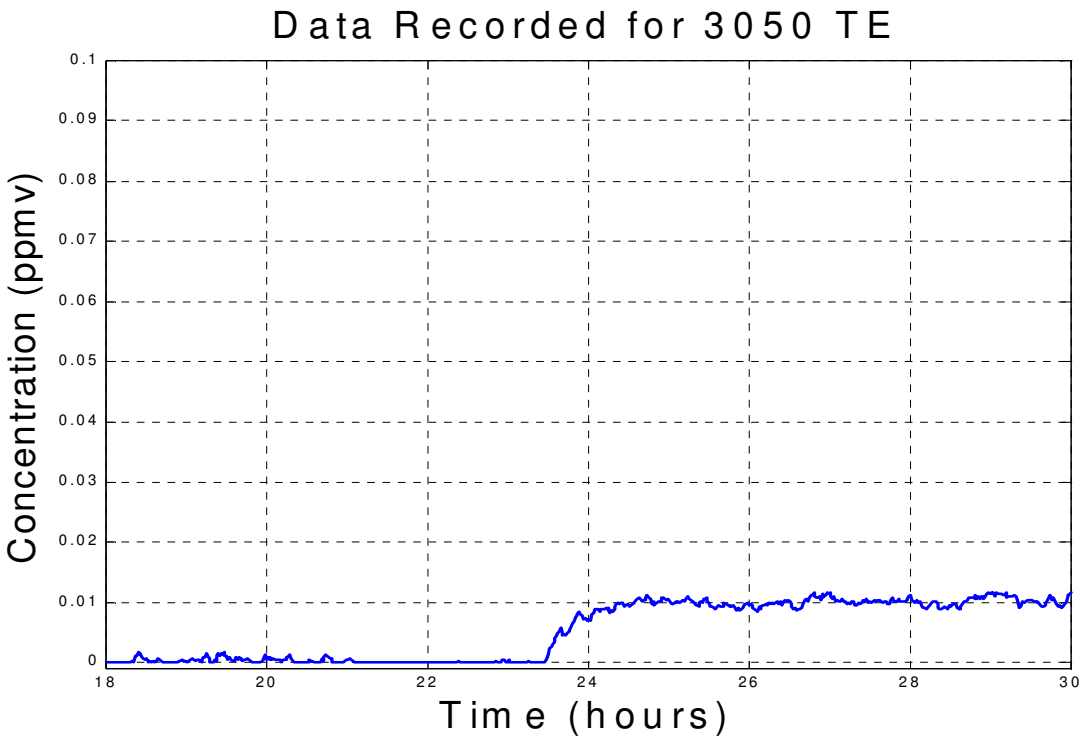


Figure 6 – QCM Analyzer Performance Data for Low Concentration Moisture Measurement at Outlet of Molecular Sieve Dryer (Cryogenic Natural Gas Processing), Response to a 10 ppb(v) Challenge

Electrolytic Sensors

Electrolytic moisture sensors have been in use since the late 1950's and were among the first on-line water vapor analyzers available to industry. They continue to be in service today due primarily to their simplicity and selectivity for detecting water vapor, and the fact that the technology, in theory, is considered to be a 'first principles' device. DuPont Analytical (now AMETEK Process Instruments) was the first company to offer these devices, and the instruments were first developed to measure water vapor concentrations in gases that liquefy at higher temperatures (freons).

The analytical cell of the instrument is constructed from two co-helically wound platinum wires that are embedded on the inside surface of a small-diameter glass tube. The surface of the sensor is coated with phosphoric acid (P_2O_5). With the sensor maintained under a DC potential, the P_2O_5 serves as a hygroscopic substrate for the absorption and electrolysis of water molecules. Figures 7A and B show the basic construction of an electrolytic sample cell. The water molecules entering the cell are converted into hydrogen and oxygen, and the electrolysis current required for the conversion is measured. Because the total flow of sample gas is controlled, the application of Faraday's Law yields the concentration of water vapor in the sample gas.

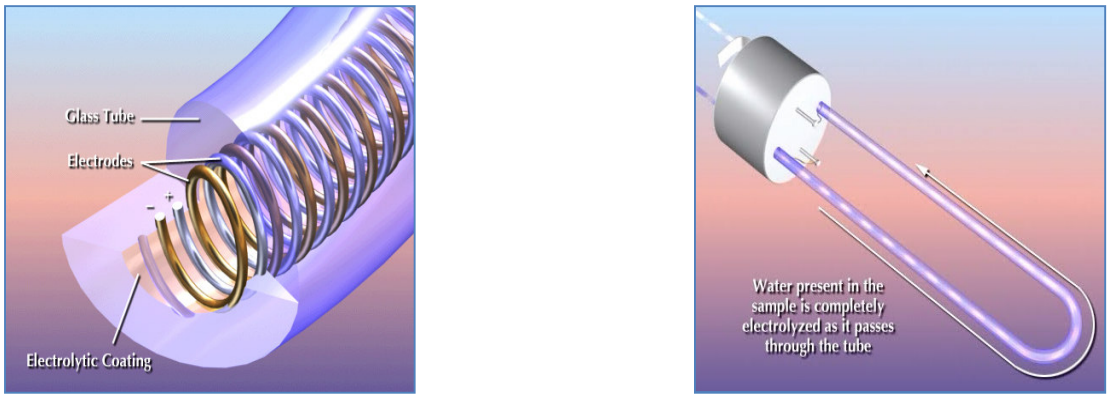


Figure 7A and B – Basic Operation of Electrolytic (P_2O_5) Moisture Analyzer

The advantages of electrolytic sensors are their simplicity and "first principles" performance. Moisture analyzers that use electrolytic sensors are typically small and light enough to be portable, and some commercially available instruments are designed to be battery powered. The primary weakness of the electrolytic sensors is their erroneous performance on sample streams containing hydrogen or oxygen. The presence of high concentrations of these gases in the sample can lead to recombination. Specifically, the hydrogen and oxygen formed in the electrolysis of water entering the sensor can react with the corresponding gas in the sample to form more water. Water molecules formed from recombination are then electrolyzed in the sensor. Because of the recombination effect, it is possible for a water molecule entering the sensor to be "counted" more than once. A second weakness of the electrolytic sensor is that the presence of liquid water in the sample will deteriorate the phosphorous pentoxide coating requiring cell replacement. And finally, the presence of background current in the sensor can add bias to low-level measurements.

Tunable Diode Laser Absorption Spectroscopy (TDLAS)

The measurement of water vapor using this optical (or spectroscopic) technique has received very favorable response from industry for the obvious reasons that these devices employ non-contact sensor technology for the detection of water vapor in natural gas applications. This 'non-contact' approach significantly reduces maintenance requirements of the instruments and reduces the overall costs of maintaining the equipment. While relatively new to the field of natural gas analysis, laser spectroscopy has been around since the 1960s. It was not until the introduction of near infrared tunable diode lasers (TDLs) that it became practical to design a process instrument with the technology. While conventional infrared (IR) and near infrared (NIR) spectrometers have been used to measure water vapor in different sample gases, their limited wavelength resolution has restricted them to simple sample matrices, where there is not much overlap in the spectra of the absorbing species. The key advantage of the laser spectrometer is the extremely high-wavelength resolution; the emission bandwidths are on the order of 30 megahertz. With this high resolution, a laser spectrometer can be used to monitor a single ro-vibrational transition that is unique to the analyte species, thereby reducing (close to eliminating) the background interference encountered by conventional IR-NIR spectrometers. In addition to narrow bandwidths, the TDLs are ideally suited to perform wavelength modulation spectroscopy (WMS), which yields detection limits that are several orders below a conventional absorption measurement.

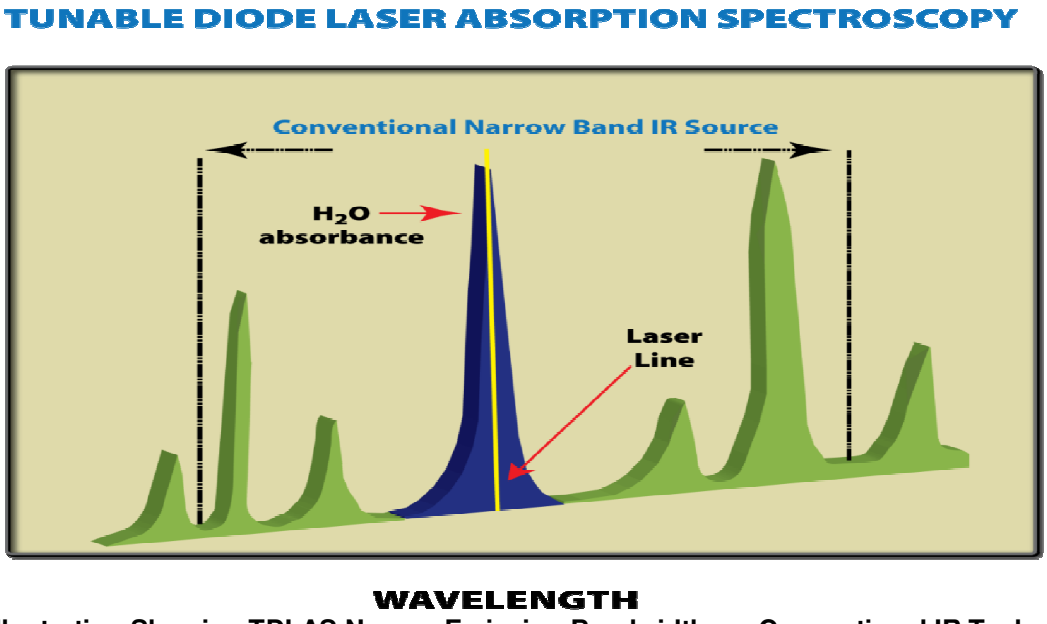


Figure 8 – Illustration Showing TDLAS Narrow Emission Bandwidth vs. Conventional IR Techniques

The key advantage of laser spectroscopy is that it is a non-contact sensing technology. The sample never comes into direct contact with the sensor element. TDL spectrometers are capable of fast response. Additionally, the measurement is not flow dependant, but care must be taken to control the sample temperature and pressure. Changes in sample temperature and pressure affect the line shape of the ro-vibrational transitions and will cause changes in the instrument readings.

A drawback to this technology is the temperature sensitivity of the TDL. The junction temperature of the laser diode is critical to the measurement; any small changes in temperature of the diode will shift the center wavelength of the emission and can result in erroneous measurements or alarm conditions in the analyzer. While most manufacturers use conventional thermo-electric coolers and thermo-couples to maintain a stable temperature of the laser diode, the use of on-board moisture reference cells has been used to provide the TDLAS system with 'line-lock' capability and provide feedback to the temperature control loop of the TDL to increase reliability and confidence in the measurement. Part of the laser beam is passed through the reference cell assembly where the spectra of the analyte sample in the reference cell is monitored and any shift in the observed peak is used as a feedback signal for the temperature control of the tunable laser diode.

A final disadvantage is the range and accuracy capability of the TDLAS device. While it is acceptable to use these instruments in traditional pipeline natural gas applications, their use for low-level detection of water vapor is limited due to the detection capability in a methane-based background. Specialized techniques such as differential spectroscopy add maintenance, cost and potential errors to the measurement systems.

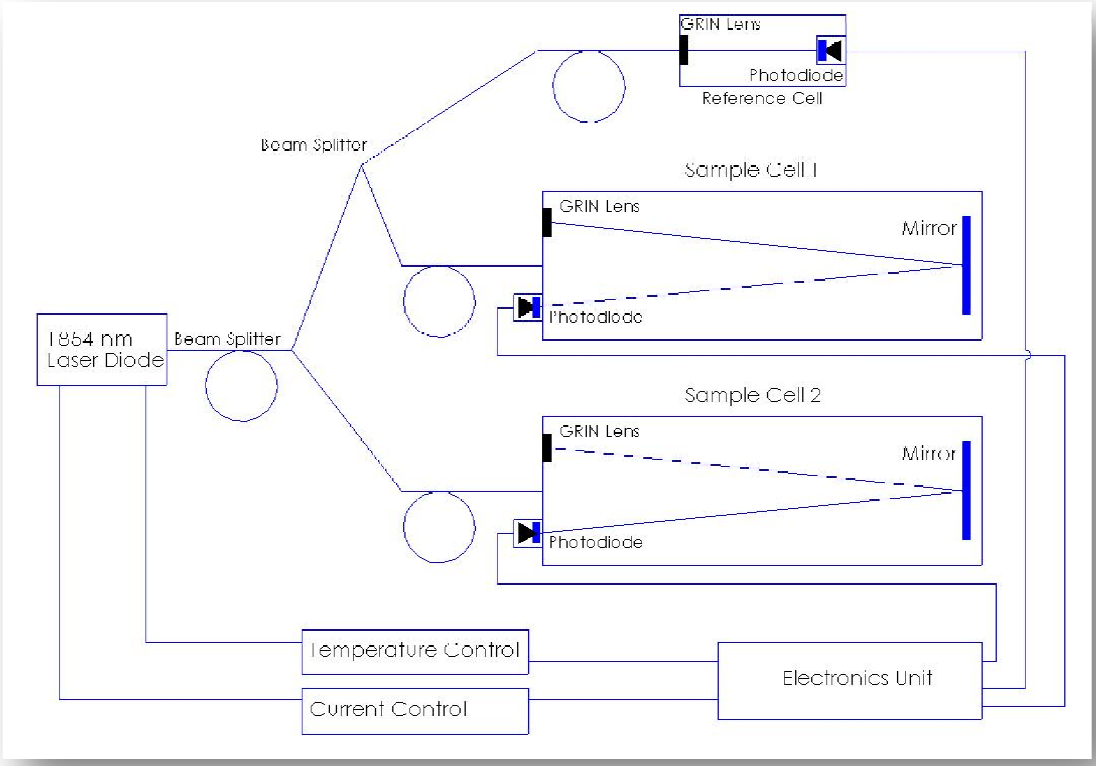


Figure 9 – A Multi-Component TDLAS Analyzer with On-Board Reference Cell for 'Line-Lock'

Sample Conditioning Systems

A great deal has been written on sample-conditioning-system components from probes to pressure regulators, filters and sampling lines. There are a number of key requirements to remember when preparing or transporting a sample to water vapor and dew point analyzers.

The following is a list of critical components and key rules of thumb to maintain when operating chilled mirror devices in natural gas applications:

Water is a small polar molecule that will 'stick' to most surfaces. The adsorption of water onto surfaces in a sample system can cause a substantial decrease in the response speed of a sample system. The lower the water

dew point that is to be measured, the more serious the role of adsorption becomes. When a “wet” challenge is introduced into a dry sample line, water molecules from the gas phase will populate all of the available surfaces. Those water molecules that are lost to the surface of the sample system are not measured by the analyzer. Conversely, when a dry gas is introduced to a wet sample line, the surfaces will desorb water until equilibrium is reached. Thus, surfaces are responsible for substantial lag times in measuring both increases and decreases in the moisture concentration of the sample.

It is therefore always recommended to ensure that the sample transport line is to be kept as short as possible. For installation of manually operated chilled mirrors, it is generally accepted to use flexible, stainless steel braided tubing suitable for use at higher pressures.

For installation of stationary, automated chilled mirror devices or water vapor analyzers, temperature controlled sample lines are preferred as the surface coverage of a sample system is a function of temperature. Higher temperatures result in lower surface coverage. Insulating and heating the line to 60°C or higher is recommended. However, most important is temperature stability. Process piping takes up and releases water with ambient temperature changes. A sample line with a varying temperature, will exhibit the same behavior (i.e., the moisture measurement will serve as a thermometer for the sample line).

Copper, aluminum, and carbon steel tubes are not recommended because the oxide film on the inside wall surface promotes adsorption. Teflon and plastics are not recommended because these materials will absorb (and later desorb) large quantities of water from the sample gas. The highest quality stainless steel sample line should be used. If the application requires monitoring of very low water dew point temperatures, a very different (and very costly) sample system is typically required. The sample line must be 316L, and be electro-polished. Electro-polishing reduces surface roughness (i.e., reduces surface area) and creates a more inert surface.

Filtration to eliminate or reduce the potential for liquids should be considered. It is common practice to use membrane filters incorporated into the sample systems to protect the equipment from liquid slugs and ensure continuous operation of both manually operated as well as automated chilled mirror devices. Filtration may be installed directly upstream of the manual mirror cell assembly, or remotely installed at the pipeline connection (insertion type filters). Insertion membrane filter designs reduce and remove liquids directly at the source and protect the entire sample system of the instruments.

Pressure regulation, when required for monitoring of hydrocarbon dew point temperatures at the cricondentherm, should take Joule Thompson cooling into account and be designed to ensure that on condensation occurs in the sample system.

Conclusion

Chilled mirror instruments for the detection of water and hydrocarbon dew point temperatures have been used in the natural gas industry for nearly 80 years. The determination of water and hydrocarbon dew points using these devices can provide accurate, reliable and repeatable results, provided they are supplied with a representative sample of the process gas, and in the application and operation of manually operated chilled mirrors, are operated by experienced personnel. Automated chilled mirror hydrocarbon dew point analyzers have been designed for rapid, interference free determination of hydrocarbon condensate in natural gas systems and have incorporated sample systems to minimize sample contamination and operation at fixed pressures.

There are a number of chemical-based, contact-sensor approaches available for the determination of water vapor in natural gas samples, each of the presented technologies have advantages and disadvantages which should be considered when making a decision regarding which technology is the most suited for the process or pipeline application. And finally, Tunable Diode Laser-based spectrophotometric techniques have been introduced for fast, low maintenance and reliable determination of water vapor in natural gas transmission (pipeline) applications.

A properly designed sample system reduces or eliminates the presence of contaminants and ensures proper operation of either type of chilled mirror technology.

References:

Bear, R.; and Blakemore C.; "Reducing the Detection Limits for a Process Moisture Analyzer", Proceedings of the 46th Annual ISA Analysis Division Symposium, Volume 34, 2001

Hauer, R.; Potter, D.: "Instruments for Measuring Water Vapor and Hydrocarbon Dew-Point in Natural Gas", Presented at Canadian School of Hydrocarbon Measurement, 2004