

Analytical Devices for the Measurement of Water Vapor in the Natural Gas Process and Transmission Industry

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PRESENTED AT:

GAS2011

ANALYTICAL DEVICES FOR THE MEASUREMENT OF WATER VAPOR IN THE NATURAL GAS PROCESS AND TRANSMISSION INDUSTRY

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ABSTRACT

The determination of water vapor (and 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 freezing and corrosion of plant and equipment. There are a number of ways of determining the water vapor concentration in natural gas, including the use of advanced, near-infrared tuneable diode laser absorption spectrometers (TDLAS)

This paper will discuss AMETEK's experience with water vapor measurements in natural gas applications and highlight the development of their laser-based instruments for the measurement of water vapor in stationary and portable applications in the natural gas and LNG industry.

1 NATURAL GAS AND THE WATER CONNECTION

Natural gas is traditionally recovered from porous or fractured sub surface layers of many various geologic formations on Earth. The recovery process of natural gas generally entails sub surface drilling to extract the gas from these deposits (wells). Although the composition of natural gas varies from well to well, the hydrocarbon content of natural gas consists primarily of light, aliphatic hydrocarbon components comprised of methane, ethane, propane and butanes. The balance includes lower concentrations of heavier hydrocarbons and various gaseous non-hydrocarbons such as nitrogen, carbon dioxide, hydrogen sulfide, helium, elemental sulfur and mercury.

Natural gas at the well head is typically saturated with water under natural conditions, and producers generally remove any condensibles at the wellhead to reduce the likelihood of liquid drop out in the pipeline system responsible for transporting the gas to a processing facility for further treatment.

1.1 The Removal of Impurities in Natural Gas

Natural gas generally requires several processing steps to remove or significantly reduce the non-hydrocarbon constituents present in the gas. Of particular importance to the producers and transporters of natural gas is the removal of the acid gas components, which consist primarily of carbon dioxide (CO₂) and hydrogen sulfide (H₂S). The removal of the acid gas components reduces the corrosivity and toxicity of the gas, which contributes to consistent quality of the final product. While it is not in the scope of this paper to discuss the removal of all potential impurities present in natural gas, the removal of the acid gas components warrants particular mention, as the processes generally employed to remove these impurities can re-

introduce high concentrations of water vapor into the process stream.

1.2. Water Content in Natural Gas

Water, many times in combination with other impurities and the hydrocarbons present in the gas stream, has the potential to severely damage a natural gas processing and delivery system. Since the delivery system in the natural gas industry consists primarily of high pressure pipeline, any potential for damage to the delivery system must be minimized. In addition to reducing the water content in natural gas pipeline transmission systems, cryogenic hydrocarbon processing requires an even further reduction of the water content of natural gas.

A major source of trouble in natural gas pipelines is the formation of a gas hydrate. A hydrate is a physical combination of water and other small molecules to produce a solid which has an 'ice like' appearance but possesses a different structure than ice [1]. Figure 1 shows a nearly fully obstructed pipeline as a result of hydrate formation.

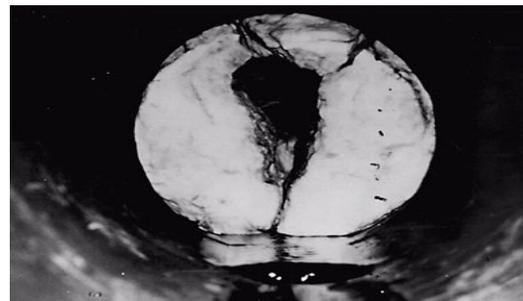


Figure1: A Natural Gas Hydrate

In addition to being a major contributor to the formation of hydrates, water reduces the overall

combustion quality of the gas, further increasing the requirement to remove as much of it as possible. And finally, free water in combination with any of the acid gases present in natural gas contributes to corrosion and cracking of materials typically used in natural gas processing and transmission lines.

2. WATER MEASUREMENT TECHNOLOGIES

For measurement of water content, water vapor or water dew point in natural gas, there are generally two classes of measurement devices: the primary measurement devices and those that measure concentrations. The measurement requirement and customer choice generally determines which class of measurement device is chosen. Table 1 highlights the various water content or dew point specifications found in selected countries.

Country/Region	Unit	Max
Europe (EASEE)	Dew Point (°C)	- 8°C (@ 70bara)
Canada	mg/Nm ³	65 mg/Nm ³
United States	lbs/mmscf	7 lbs/mmscf

Table 1: Typical Water Dew Point/Content Specifications

Analyzers capable of measuring the dew-point temperature directly are based on chilled mirror technology and are sometimes referred to as ‘first principle’ or ‘primary’ 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 instrument. Chilled mirror devices are the only instruments to actually measure the dew-point temperature of a sample [2].

The second class of analyzers measures concentration (e.g., ppmv, ppmw, lbs/mmft³, and mg/Nm³) or partial pressure. For measuring water content the technologies commonly used in the natural gas industry include: quartz-crystal microbalance (QCM), electrolytic cells, capacitance-based sensors (aluminum oxide or thin-film technology), fibre optic hygrometry and more recently the development of near-infrared (IR) spectrometers. All of these techniques provide an indirect measure of the sample dew-point, which is calculated from compositional information.

While it is well beyond the scope of this paper to provide a detailed description of the various technologies capable of determining the water content or dew point temperature in natural gas, it is worth highlighting the general moisture measurement capabilities and accuracy specifications provided by the various technologies.

The performance specifications of the most commonly used techniques is provided in Table 2.

Technology	Limit of Detection	Accuracy
Near-Infrared Tunable Diode Laser (TDL)	4 ppm (AMETEK std Model 5100)	+/- 2% of reading
QCM	0.01 ppm (AMETEK Model 3050-TE)	
	0.1 ppm (AMETEK Model 3050-OLV)	10% of reading
P205	0.1 ppm (AMETEK Model 303B)	5% of reading
Capacitance	Varies	+/- 1°C (for high range) +/- 2° C (for lower ranges)
Fiber optic sensor (Fabry Perot Interferometer)	No data	+/- 1°C dew point temperature (for calibrated scale)
Manual Chilled Mirror	N/A	+/- 0.25°C (based on temperature measurement device)

Table 2: Accuracy Specifications of Various Moisture Measurement Devices

For devices which measure water vapor or concentration, the accepted method of conversion between concentration and dew-point is based on empirical data from the original research of the Institute of Gas Technology (IGT). This work was published in the 1950s in IGT’s Bulletin no. 8. This work is republished in the American Society for Testing and Materials (ASTM) standard D 1142 (latest revision) [2]. While this work is the accepted standard in the natural gas industry in North America and many other regions, it has some significant limitations. Chief among these is the lower-temperature limit of -40°C; use of this method below -40°C is an extrapolation. 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, taking into account the restrictions or limitations of previously published data [3].

A second issue is that these data correspond to dew-point values, and many instrument manufacturers have designed their products to report the frost-point. While this second point is not a problem, it does add to the level of confusion regarding dew/frost-point measurements. For convenience, most electronic instruments include provisions for displaying their readings in both dew/frost-point and concentration. However, it must be remembered that these instruments are converting between the compositional (concentration) and physical (dew/frost-point) information.

3. SPECTROSCOPIC TECHNIQUES FOR THE MEASUREMENT OF WATER VAPOR IN NATURAL GAS

The measurement of water vapor using this optical (or spectroscopic) technique has received very favorable response from the natural gas

process and transmission industry. The use of non-contact spectroscopic methods used for determining the water vapor concentration offer several key benefits, chief among them being that non-contact sensors do not suffer from fouling, depletion or contamination which plagues the chemical sensors traditionally used for the measurement of water vapor in industrial process applications.

3.1 Tunable Diode Laser-Based Technology

The use of near-infrared based Tuneable Diode Laser Absorption Spectroscopy (TDLAS) for the identification and quantification of water vapor in natural gas process and transmission applications has been widely accepted.

TDLAS-based spectrometers offer several important attributes:

- High specificity for the analyte (component) of interest
- High sensitivity
- Fast response speed
- Multi-component capability (e.g. CO₂/CH₄)

To further expand on the above mentioned points, the emission bandwidths of tunable diode lasers are on the order of 10^{-4} to 10^{-5} cm⁻¹, giving the TDLAS technique extremely high spectral resolution, which results in the ability to isolate a single rotational-vibrational line of the analyte species [4]. Figure 2 provides an illustration of the typical bandwidth of a conventional IR source versus the TDLAS. The ability of the TDLAS to produce a near monochromatic light source enables it to provide high specificity and spectral resolution for the component of interest.

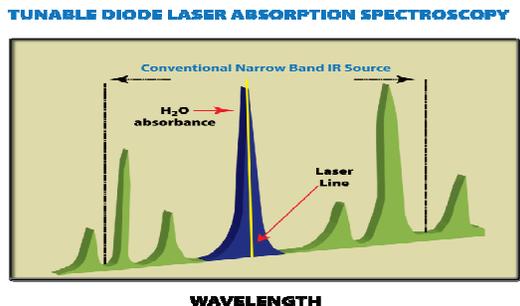


Figure 2: Conventional IR and TDLAS Bandwidth [6]

In addition to providing a fast speed of response, diode lasers operate at room temperature, are very small, operate at very low power (making the devices suitable for operation as stationary and portable instruments) and have a long operational life. Careful selection of additional diode lasers may allow a single TDLAS platform to perform multi-component capability, of specific interest in the natural gas industry are the measurement of CO₂, H₂S, and methane (CH₄). Figure 3 shows a schematic diagram of a dual TDLAS instrument

capable of providing water vapor and carbon dioxide measurements, configured with dual lasers, dual reference cells and single cell design.

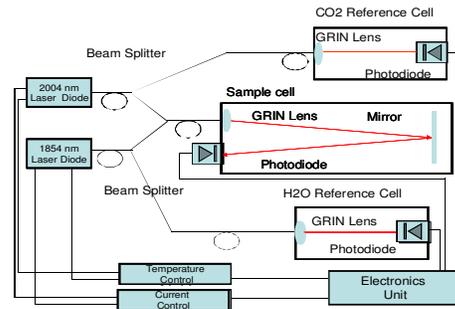


Figure 3: Dual Laser TDLAS Analyzer with Single Cell, Dual Lasers and Dual Reference Cells [9]

3.2 Wavelength Modulation Spectroscopy (WMS)

In addition to providing superior spectral resolution, TDLAS spectrometers typically employ enhanced detection techniques, known as Wavelength Modulation Spectroscopy (WMS). In WMS, the wavelength of the optical source (the diode laser) is modulated at very high frequencies, so that a small region of the absorption spectrum of the analyte (e.g. water molecule), containing a distinct absorption peak, is repetitively scanned. As the wavelength of the source scans through the spectral feature of interest the relative attenuation of the source power is varied. This produces a time-varying signal at the detector, and coupled with phase sensitive detection techniques produces an output signal representing the presence and quantity of the analyte of interest [4].

This type of modulation spectroscopy provides a ‘zero background’ technique and can provide a 10 – 100 times increase in sensitivity over conventional absorption spectroscopy technologies.

3.3. Making Water Vapor Measurement in a Hydrocarbon Background

As described in the previous section, diode lasers have the ability to effectively isolate a single absorption line of the component of interest. However, making relatively low concentration measurements of water vapor in the background of high concentrations of primarily methane in natural gas presents a challenge. Specifically, methane will contribute a small amount of background interference to the measurement which, if uncorrected, will produce a bias in the measurement [4]. Figure 4 shows recorded water vapor spectra in the presence of bulk natural gas components in the background.

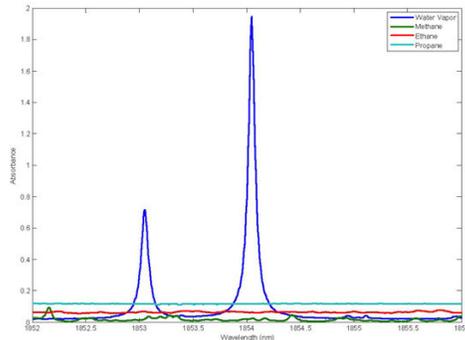


Figure 4: Absorption Spectra of Water Vapor (1%), methane, ethane, propane (100%)

To eliminate or reduce as much (or most) of the potential background interference, wavelengths are chosen which provide the least amount of interference from the background gas.

In addition to the careful selection of the appropriate wavelength, enhanced digital signal processing capability available with the AMETEK Process Instruments advanced line of TDLAS analyzers provide the capability of recording the spectrum around the selected water vapor peak, enabling an accurate measurement and compensation of the methane present in the background gas. This type of design provides distinct performance enhancement over traditional analog implementation of TDLAS technology, as well as providing for the additional measurement of methane with a single laser.

It should also be noted at this point that regardless of the careful selection of wavelength and enhanced detection capability, TDLAS analyzers have minimum full scale range limitations in natural gas backgrounds.

This is of particular importance when dealing with natural gas processing and LNG recovery operations, where the nominal water vapor concentrations typically measured at the outlet of molecular sieve driers are below 1 ppm. Sensor-based technologies, such as Quartz-Crystal-Microbalance (QCM) devices provide superior accuracy and lower limits of detection currently not achievable using traditional near-infrared TDLAS technology.

3.4 TDLAS Performance Issues

While it appears that TDLAS technology is a nearly 'perfect' solution for the measurement of water vapor in natural gas, there are limitations with the technology which should be mentioned.

TDLAS devices operate in the near-infrared region of the electromagnetic spectrum (EMS), in the band from 700 – 2500 nm. In this region, it is the weaker, less sensitive overtone and combination absorption bands which are found, making it inherently more challenging to provide trace level detection of the

analytes of interest. Figure 5 provides the HiTran spectrum of water across the near and mid- IR region of the EMS [5] (the collection of peaks in the far left region on the horizontal axis show the weaker overtone absorption peaks of water found in the near-infrared region, while the larger peaks in the center of the horizontal axis represent primary absorptions found in the mid-IR region of the EMS).

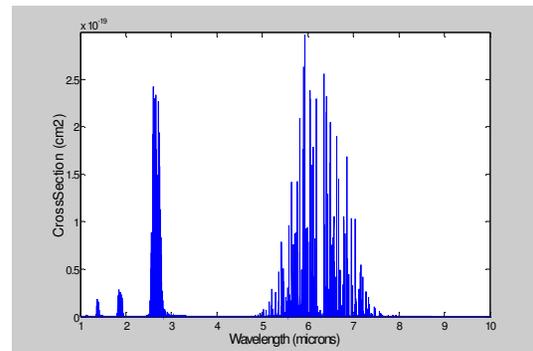


Figure 5: HiTran Spectrum of Water Vapor (1 – 10 micron region)

While it is possible to enhance the sensitivity of TDLAS devices by employing multi-pass cells which effectively lengthen the optical path of the instruments, relatively weak absorption bands coupled with background interference (from methane present in the natural gas) limits the effective full scale range of TDLAS devices used in this service.

Another major (but little discussed) negative aspect of measuring low levels or weakly absorbing compounds with TDLAS is the difficulty of ensuring the TDLAS system is adequately and continuously focused on the very narrow energy band. The junction temperature is critical to the measurement, as even small changes in temperature will shift the center wavelength of the emission and can result in erroneous measurements caused by loss of 'line lock' [9]

Figure 6 shows the spectral 'shift' of the fundamental wavelength as a result of a temperature change.

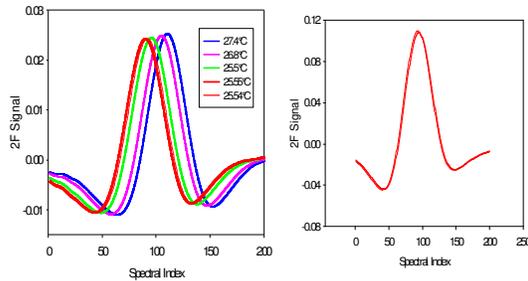


Figure 6: Wavelength Shift with Temperature

To overcome temperature drift issues associated with TDLAS devices, reference cells filled with a known concentration of the required analyte(s), as provided with the AMETEK series 5100 TDLAS analyzers, are scanned repeatedly to ensure the laser knows where to focus and minimize loss of line lock of the instruments.

Figure 7 shows an AMETEK TDLAS analyzer with incorporated sealed reference cell assembly.

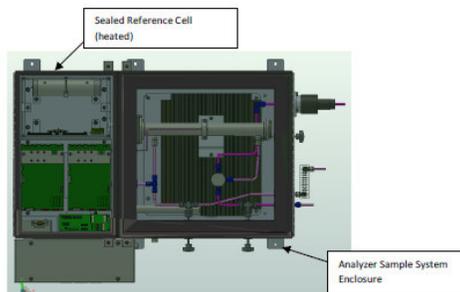


Figure 7: Integrated TDLAS Analyzer with Reference Cell

4. PERFORMANCE VALIDATION AND VERIFICATION

It is an accepted requirement that the performance of an analytical device, fixed or portable, needs to be validated. The measurements produced by the instrument need to be tested against samples that are traceable to recognized standards (e.g., the National Institute of Standards and Technology, or NIST). This can be accomplished by a number of methods: bottled calibration gases, portable permeation calibrators, onboard permeation calibrators, sealed reference

cells with a known concentration of analyte in an inert background gas and factory calibration by returning the device to the manufacturer for certified calibration [2].

AMETEK Process Instruments has successfully used on board permeation devices as moisture calibration sources for nearly four decades. Calibration sources provide the ability to verify and, if required, calibrate contact sensor devices such as the AMETEK quartz crystal microbalance (QCM) line of products. Calibration sources periodically provide the means to verify the operation of the sensor, and make necessary adjustment if drift or sensor degradation has occurred. On board moisture calibration devices are calibrated and traceable to NIST.

In the case of TDLAS based systems, neither the laser source or the detector element come in direct contact with the process and, therefore, there is no change in the system response relative to the sensor contamination issues described above [4].

However, as described in the previous section, it is still possible for the TDLAS analyzers to provide erroneous results. Users of process analyzer systems expect to periodically check or verify system performance to ensure that the analytical systems are performing properly.

The use of sealed reference cells allows the user to periodically check and verify the performance of the analyzer system. Figure 8 shows a TDLAS-based system which provides an on-board sealed reference cell.

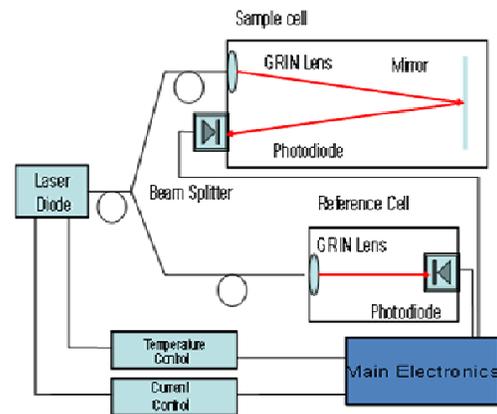


Figure 8: TDLAS Design With Sealed Reference Cell

A small portion of the laser output is split out and passes through the reference cell. Data is essentially collected simultaneously from both the natural gas stream and the water reference sample providing a real-time confirmation that the laser is

locked on the moisture absorption line. The water reference cell is also used to perform a reliability check on the quantitative measurement of the water measured in the sample cell. [4]. Verification of water concentration is achieved by measuring the temperature of the reference cell and using known cell pressure to calculate the water content in the reference cell using well established thermodynamic calculations. The analyzer can be programmed to provide an alarm condition if the measured concentration of the reference cell falls outside of established thresholds of the calculated reference cell concentration.

5. SAMPLE SYSTEM COMPONENTS FOR WATER VAPOR DEVICES

No technical paper on water vapor analysis is complete without a brief discussion on sample system design for water vapor analyzers used in the natural gas processing and transmission industry.

5.1. The Water Molecule And Sample System Surface Interaction

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 moisture concentration 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 [2].

5.2. Sample System Material Selection

ALL wetted components in the sample system (those components which come into direct contact with the sample gas) should be chosen to prevent excessive surface oxidation. Examples of materials which should NOT be used include copper, aluminum and carbon steel. Any material which potentially creates an oxide film and promotes the adsorption and desorption of water molecules is to be avoided. This includes the use of any plastics or teflon.

Acceptable materials of construction include the highest quality of stainless steel (e.g. 316L). Applications which require very low level detection of water vapor (e.g. the outlet of molecular sieve driers in cryogenic hydrocarbon processing) should be designed to incorporate passivated, electro-polished stainless steel as a minimum. The use of electro-polished tubing reduces the surface area and roughness of the sample system.

AMETEK generally recommends a sample system design which follows a 'keep it simple' approach. Any unnecessary tubing lengths, dead legs (including unnecessary gauges) should be avoided. Sample line lengths, certainly required and necessary when using extractive analyzer designs, should be kept to a minimum (and heated).

5.3 Sample System Temperature

The surface coverage (i.e., the total amount of water bound to the surfaces) of a sample system is a function of temperature. Higher temperatures result in lower surface coverage. Insulating and heating sample lines and sample system components upstream of any sensor or sample cell is highly recommended (AMETEK generally recommends a temperature of 60°C or higher). To illustrate this point, a moisture breakthrough calculation program, developed by Air Products and Chemicals Inc., predicts a 100% difference in the breakthrough time for a moisture event when comparing a simulated sample line at 0°C versus the same parameters for 60°C [7].

While a 'warm' sample system is recommended, it is more important to maintain a stable temperature in the sample system, from the process connection to the analyzer sample cell (or analyzer enclosure). Process piping takes up and releases water with ambient temperature changes. A sample line with a varying temperature will exhibit the same behavior. If maintaining a sample temperature of 60°C is not possible, then care should be taken to ensure the temperature is stable, at the very minimum.

5.4 Preventing Contamination

Natural gas can be categorized as a 'dirty' sample. The sample gas generally contains components which have a likelihood of condensing, and most sensor-based and spectroscopic analytical technologies presented in this paper are simply not designed to operate in the presence of liquids. To ensure the sample is kept in the gas phase, temperature control, as mentioned above, will prevent the natural gas (and any impurities present in the gas) from condensing in the sample.

Further sample conditioning, using membrane filters are a must, as the filters prevent liquid slugs from entering the sample system and analyzer during process upsets. Although liquids have different effects on the various analytical technologies, any significant quantities of liquids which break through and reach an analyzer cell or sensor will result in either damage to the instrument, or require disassembly for maintenance, meaning the analyzer will be off line until the system is cleaned or repaired.

Coalescing filters may be required to remove additional impurities such as particulate matter, which may be present in pipeline operations, or dust which may be seen at the outlet of a molecular sieve dryer in natural gas processing.

5.5. Pressure Reduction and Joule-Thomson Cooling

Most analytical technologies designed to monitor the water vapor concentration in natural gas samples require pressure reduction and control. This is of particular importance for laser-based systems, which operate at near atmospheric pressures.

Sample pressure should be kept as low as possible while maintaining the correct flow. Sample pressure should be reduced as close as possible to the source of sample extraction. Volumetric flows (i.e. higher sample flow rates) are desired to keep sweeping through the sample line. Surface effects cannot be eliminated, but by keeping volumetric flow high, their magnitude can be reduced.

Figure 9 provides an example of a typical sample system designed for a natural gas service.

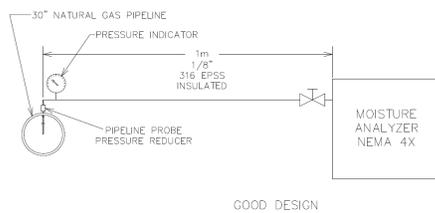


Figure 9: Properly Designed Sample System for Natural Gas Moisture Analyzer

And finally, sample system design should incorporate design to reduce the effect of Joule Thomson cooling in natural gas samples. Regulators surrounded by a soccer ball size ball of ice have often been observed in the field. This ball, although dramatic, is not the problem but is a good indicator. Water molecules stick to cold surfaces better than to hot surfaces. Heated, insulated pressure reduction stages (single or multi-stage, depending upon pressure drop requirements), or alternatively using membrane pressure regulating probes are required when large pressure drops are required to operate water vapor analyzers downstream of the sample system.

6 SUMMARY

The measurement of water vapor in the natural gas processing and transmission industry is an important quality control parameter to ensure natural gas meets strict pipeline specifications to reduce hazards and maintain pipeline integrity. Among the many analytical technologies available to determine the water vapour concentration, near-infrared TDLAS devices have found wide acceptance in the industry. Understanding the technology, its practical limitations and capability has allowed for the design of sophisticated, reliable and accurate instruments capable of providing fast responding single, and multi-component

measurement capability.

7. ACKNOWLEDGEMENTS

The author wishes to acknowledge Dr. Sam Langridge, TDLAS Product Manager, AMETEK Process Instruments for his invaluable contribution and assistance in writing of his paper.

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