WHEN CAPABILITY IS CRITICAL

Daniel R. Potter, Gas Market Specialist, AMETEK Process Instruments, explains the process of measuring critical natural gas quality components in pipeline operations.

he measurement and control of contaminants in natural gas pipeline systems are crucial to maintaining safe, reliable transport and consistent quality final product. Contaminants that require continuous analysis include total sulfurs (primarily hydrogen sulfide, or H₂S), water vapour, carbon dioxide (CO₂) and heavier hydrocarbons (as hydrocarbon dew point temperature).

The water connection

DIGITAL DEW POINT

NGINEERING

Natural gas at the wellhead is typically saturated with water under natural conditions. Water, 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. 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 that has an 'ice like' appearance but possesses a different structure to ice. Figure 1 shows a nearly fully obstructed pipeline as a result of hydrate formation.

Excess water vapour content reduces the combustion quality of the gas and may lead to corrosion of components used to transport the natural gas when

Table 1. Typical water dew point/content specifications			
Country/region	Unit	Maximum	РРМ
Europe (EASEE)	Dew point (°C)	- 8 °C (@ 70 bara)	85 ppm (approx)
Canada	mg/Nm³	65 mg/Nm³	85 ppm (approx)
United States	lbs/million ft ³	7 lbs/million ft ³	150 ppm (approx)



Figure 1. Natural gas hydrate, partial pipeline blockage.





combined with any of the acid gases present in the natural gas.

Removal of the water is achieved using a variety of liquid or solid desiccants to strict specifications. Examples of water content (or dew point temperature) specifications are provided in Table 1.

Water and hydrocarbon dew point measurement technologies

For measurement of the water content, water vapour or water dew point in natural gas, two classes of measurement devices are used: the primary measurement devices and those that measure concentrations. The measurement requirement and customer choice generally determine which class of measurement device is chosen.

Measurement devices capable of determining the water dew point temperature of natural gas are generally referred to as primary measurements. Devices based on chilled mirror technology have been used in the pipeline industry for nearly 80 years, and, to this day, are considered a primary method for determining the physical property of water dew point temperature.

Chilled mirror instruments operate by continuously flowing sample gas across a temperature-controlled, polished surface, such as 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, as with the AMETEK Model Chanscope II manual (portable) dew point tester, shown in Figure 2.

Manual chilled mirror dew point testers are very useful as portable, 'spot-checking' devices and offer additional benefits, such as being able to determine both the water and hydrocarbon dew point temperatures in natural gas pipelines. However, their use is limited to portable applications and experienced operators are generally required to produce repeatable results.

Automated chilled mirror devices are commonly used for the detection of hydrocarbon dew point temperatures in natural gas. The formation of hydrocarbon liquids (condensate) due to the presence of heavier hydrocarbons in natural gas can lead to increased pressure drops in the pipeline system, flooding and safety hazards associated with liquids, such as hot spots on compressor turbine blades.

The second class of analysers measure concentration (e.g. ppmv, ppmw, lbs/million ft³, 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 (aluminium oxide or thin-film technology), fibre-optic hygrometry and more recently the development of near-infrared (IR) tunable diode laser absorption



Table 2. Limits of detection of commonly used water measurement technologies		
Technology	Limit of detection	
TDLAS (AMETEK Model 5100 NCM)	5 ppm standard range, 1 ppm low range	
QCM (AMETEK Model 3050-OLV)	0.1 ppm standard range, +/- 0.01 ppm for low range applications	
P205	1 ppm	
Capacitance	+/- 2 °C accuracy for most std capacitance probe devices*	
Fibre-optic sensor (fabry-perot interferometer)	+/- 1 °C precision/resolution*	
*scales provided in dew point, no LOD data provided		

spectrometers (TDLAS). All of these techniques provide an indirect measure of the sample dew-point, which is calculated from compositional information.

Table 2 highlights the analytical capabilities of some of the most commonly used technologies for measuring water vapour in natural gas pipeline applications. While there has been a significant shift in the natural gas industry to use non-contact sensor approaches such as tunable diode laser absorption spectroscopy (TDLAS) devices, traditional means of water vapour analysis offer some significant benefits, which should be considered when choosing the appropriate water vapour analyser technology for the application.

QCM analysers have been used as reliable means to accurately determine the water vapour content of natural gas since the early 1970s. This technology continues to serve as a workhorse in the industry, and recent advances in the technology have provided dramatic performance improvements. At the heart of the technology is a simple quartz-crystal oscillator. To fabricate the sensor, the electrodes on the quartz crystal are coated with a hygroscopic material. When exposed to a sample gas containing water vapour, the hygroscopic layer will absorb 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.

QCM devices have several key benefits over many other water vapour measurement technologies:

- Non-equilibrium based sensor technology (rapid speed of response).
- Low limit of detection.
- Verification/online calibration.
- Resistance to sensor fouling and degradation.

The measurement of water vapour using an optical (or spectroscopic) technique has received a very favourable response from the natural gas process and transmission industry. The use of non-contact spectroscopic methods for determining the water vapour concentration offer several key benefits, chief among



Figure 3. AMETEK Model 241 automated chilled mirror hydrocarbon dew point analyser.



Figures 4 and 5. QCM analyser and analyser cell.



Figure 6. AMETEK Model 5100 TDLAS system.







Figure 8. AMETEK Model 5100 HD analyser with sealed reference cell and built-in sample system.

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 vapour in industrial process applications.

TDLAS devices have extremely high spectral resolution. A laser spectrometer can be used to monitor a single rovibrational transition that is unique to the analyte species, thereby 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.

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 CO_2 , H_2S , and methane (CH_4). Figure 7 shows a TDLAS analyser system capable of detecting water vapour and CO_2 , configured with dual lasers, dual reference cells and single cell design.

Advancements in NIR TDLAS technology have included the use of sealed reference cells. The reference cell consists of a sealed glass ampoule, which contains a known amount of water vapour. The availability of an on-board reference cell with the TDLAS analyser provides two key features. First, it ensures the TDLAS analyser maintains laser 'line-lock' to the laser output wavelength - a key requirement to ensuring a TDLAS provides an accurate output - and second, to provide continuous verification of instrument performance.

The measurement of hydrogen sulfide (H_2S) in natural gas

A critical measurement of natural gas quality is the concentration of hydrogen sulfide (H_2S). Remarkably, the common technique for making this measurement, lead acetate tape, is at least 70 years old. Users of this archaic technology report general dissatisfaction with it due to high maintenance, the cost and shelf life of tape cassettes, the need for reagents, difficulty handling H_2S overload conditions, the sensitivity of the technology to ambient extremes, and, last but not least, used cassette disposal. An alternative approach, using a combination of a high-resolution UV analyser system and proprietary frontal elution chromatographic sample system to separate potentially interfering sulfur compounds has been developed to provide a low-maintenance, reliable, and rugged H_2S analyser system.

This technology offers several key benefits compared to traditional paper tape technology including multicomponent sulfur species analysis, interference-free detection of H₂S, and long-term unattended operation.

Summary

The measurement of critical components in the natural gas processing and transmission industry include water vapour, hydrocarbon dew point, CO_2 and H_2S . These



are important quality control parameters to ensure natural gas meets strict pipeline specifications to reduce hazards and maintain pipeline integrity. Among the many analytical technologies available to determine the various components have found wide acceptance in the industry. Understanding the technologies and their analytical capabilities has allowed for the design of sophisticated, reliable and accurate instruments capable of providing fast responding single, and multicomponent measurement capability. WP

Bibliography

- CARROLL, J.J., 'Natural Gas Hydrates: A Guide for Engineers,' Gulf Professional Publishing (2003).
- HAUER, R., POTTER, D., 'Instruments for Measuring Water and Hydrocarbon Dew Points in Natural Gas,' *Canadian School of Hydrocarbon Measurement* (2004).
- POTTER, D., 'Analytical Devices for the Measurement of Water Vapour in the Natural Gas Process and Transmission Industry,' 6th International Gas Analysis Symposium and Exhibition GAS 2011.
- AMEROV, A., FIORE, R., FULLER, M., 'An Internal Verification Approach for On-Line Moisture Analysis in Hydrocarbon Gas Streams Using Laser Spectroscopy,' Proceedings of the ISA 53rd Annual Analysis Division Symposium (2008).
- POTTER, D., 'Analytical Devices for the Measurement of Water Vapour and Hydrocarbon Dew Point in Natural Gas,' Proceedings of the 3rd Natural Gas Sampling Technology Conference NGSTECH (2011).



Figure 9. AMETEK Model 933 low concentration H₂S analyser.