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DETERMINATION OF WATER VAPOR CONTENT IN NATURAL GAS

Class # 5100.1

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Introduction

This is an overview of the main approaches to trace moisture measurements for natural gas. Natural gas presents a situation where the stream may have high levels of solid and liquid contaminants as well as corrosive gases present in varying concentrations. Additionally, the stream composition may change gradually or rapidly over time. This unique situation is a challenge for the measurement of moisture.

Concentration

Water measurements are made in parts per million by volume (ppmv), pounds of water per million standard cubic feet of gas (lb/mmscf), milligrams per standard cubic meter (mg/sm^3). The humidity is the amount of "vapor-phase" water in a gas. If there are liquids present in the gas, they are often filtered out before reaching a gas analyzer to protect the analyzer from damage.

Moisture Dew Point

Moisture may be represented as a "dew point" which is the temperature at a given pressure in which the water changes phase from vapor to liquid. Some analytical techniques, such as a chilled mirror inherently measure dew point temperature in degrees Fahrenheit or Celsius. Other techniques inherently report concentration. One can convert from dew point to concentration and vice versa using special equations, but the calculations will add uncertainty to the outcome. Therefore it is best if possible to use the inherent output of the instrument.

Hydrocarbon Dew Point

The hydrocarbon dew point of the gas is an important consideration when making water measurements. Liquid hydrocarbons may form as a result of changes in pressure and temperature during the process of extracting the sample. Therefore it is essential to understand the phase diagram and to keep the gas in the vapor region of the diagram when supplying the analyzer with a sample. See figure 1.

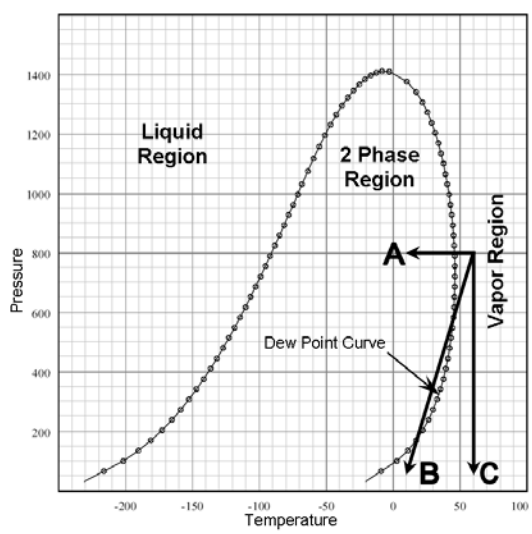

Figure 1 – Typical Phase Diagram for Natural Gas, expressed as a function of multiple condensable gases including water and hydrocarbons.

The dew point curve represents the temperature at a given pressure where hydrocarbon liquid begins to form. Arrow A indicates a reduction in temperature at a constant pressure of 800 psi. Starting at 60 degrees F and ending at 10 degrees F inside the 2-phase region (hydrocarbon liquids have dropped out). Arrow B indicates a reduction in pressure and a corresponding reduction in temperature due to the Joule-Thomson effect. Although the line passes through the 2-phase region, it ends in the vapor region. Arrow C indicates a reduction in pressure without a reduction in temperature. Heating the extracted gas may be necessary in many cases to avoid condensation during the pressure drops needed for the moisture analyzer. Standards[1] state that the gas sample must be maintained at least 18 degrees F (10 degrees C) greater than the dew point at all times. It is necessary to perform a check similar to the one above for every part of the sample handling system where changes in pressure or temperature may occur.

Stain Tubes
The Color Indicator Tube (also referred to as the Stain Tube) is a device used by many natural gas pipeline companies as a very fast and rough measurement of moisture. The process is simple; the tube is manually exposed to the gas for a given period of time, the chemical in the tube reacts to the moisture, and the color changes. The tubes are calibrated by the manufacturer but since the measurement is directly related to the exposure time, the flow rate and the extractive technique, it is susceptible to error. In practice, the error can be greater than ±25%. The tubes are used one time and discarded. The color indicator tubes are well suited for rough estimations of moisture in natural gas; for example, if the tube indicates 20 pounds of water, there is a high degree of certainty that it is greater than 15 pounds if the procedures were correctly performed.

Chilled Mirrors
When gas flows over a chilled surface (the mirror) the moisture will condense on it – the exact temperature at which this condensation begins is the dew point. The temperature of the mirror is reduced from high to low (so that it passes through the dew point temperature), and the temperature is read exactly when dew is observed on the mirror. By obtaining the dew point temperature, one can calculate the moisture content in the gas. The mirror temperature is controlled by the flow of a refrigerant over the mirror or by using a thermoelectric cooler. The detection of condensation on the mirror can be done by eye or by optical means. For example, a light source can be reflected off the mirror into a detector and condensation detected by changes in light reflected from the mirror. The observation can be done by eye; however the exact point at which condensation begins is not visible to the eye. Since the temperature is passing through the dew point rather than stopping exactly at the dew point, the manual measurement tends to be biased and will have a high standard deviation. Additionally, the condensation of moisture can be confused with condensation of other components such as heavy hydrocarbons, alcohol, and glycol. Most automated on-line systems are not able to make these distinctions and manual systems must be used only by highly skilled operators. The proper procedures[2] must be strictly followed.

Electrolytic
The Electrolytic sensor uses two closely spaced, parallel windings coated with a thin film of Phosphorous Pentoxide (P_2O_5). As this coating absorbs incoming water vapor, an electrical potential is applied to the windings that electrolyzes the water to hydrogen and oxygen. The current consumed by the electrolysis determines the mass of water vapor entering the sensor. The flow rate and pressure of the incoming sample must be controlled precisely to maintain a standard sample mass flow rate into the sensor.

The method is fairly inexpensive and can be used effectively in pure gas streams where response rates are not critical. Contamination from oils, liquids or glycols on the windings will cause drift in the readings and damage to the sensor. The sensor cannot react to sudden changes in moisture, i.e. the reaction on the windings' surfaces takes some time to equalize. Large amounts of water in the pipeline (called slugs) will wet the surface and requires tens of minutes or hours to "dry-down". Effective sample conditioning and removal of liquids is essential when using this sensor.

Piezoelectric Sorption
This instrument compares the changes in frequency of hydroscopically coated quartz oscillators. As the mass of the crystal changes due to adsorption of water vapor, the oscillation frequency changes. The sensor is a relative measurement so an integrated calibration system with desiccant dryers, permeations tubes and sample line switching is used to correlate the system on a regular basis.

The system has success in many applications. However, in natural gas, interference from glycol, methanol, and damage from hydrogen sulfide are important considerations. The internal sensor itself is relatively inexpensive and very precise. The on-board calibration system adds to the cost and mechanical complexity of the system but is a necessary part of the measurement accuracy. The replacement of desiccant dryers, permeation components, and the sensor heads should be factored into the operation over the life of the analyzer. Slugs of water can render the system nonfunctional for long periods of time as the sensor head has to “dry-down”. For this method, good sample filtration and an understanding of the potential interferences from common contaminants in natural gas is critical.

Aluminum Oxide and Silicon Oxide

The oxide sensor is made up of an inert substrate material and two dielectric layers, one of which is sensitive to humidity. See figure 2. The moisture molecules pass thru the pores on the surface and cause a change to a physical property of the layer beneath it.

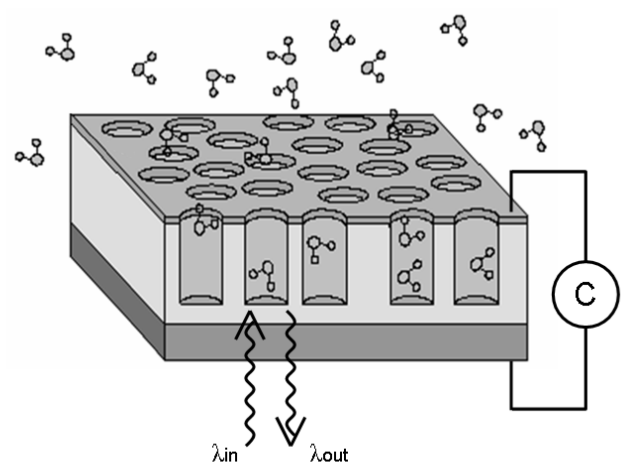

Figure 2 – Cross section of an oxide substrate moisture sensor.

An aluminum oxide sensor has two metal layers that form the electrodes of a capacitor. The number of water molecules adsorbed will cause a change in the dielectric constant of the sensor. The sensor impedance is correlated to the water concentration. A silicon oxide sensor is an optical device that changes it refractive index as water is absorbed into the sensitive layer. When light is reflected through the substrate, a wavelength shift can be detected on the output which can be precisely correlated to the moisture concentration. A fiber optic connector can be used to separate the sensor head and the electronics.

This type of sensor can be installed at pipeline pressure (in-situ). Water molecules do take time to enter and exit the pores so some wet-up and dry down delays will be observed, especially after a large “spike” of water. Contaminants and corrosives may damage and clog the pores causing a “drift” in the calibration, but the sensor heads can be refurbished or replaced and will perform better in very clean gas streams. As with the piezoelectric and electrolytic sensors, the sensor is susceptible to interference from glycol and methanol, the calibration will drift as the sensor’s surface becomes inactive due to damage or blockage. It is important to frequently monitor the calibration.

Spectroscopy

When a water molecule collides with a photon that has a specific amount of energy (the photon’s energy is related to its wavelength), the molecule will absorb the photon. Absorption Spectroscopy is a relatively simple method of passing light through a gas sample and measuring the amount of light absorbed at the specific wavelength. Broadband spectroscopic techniques have not been successful at doing this in natural gas because methane absorbs light in the same wavelength regions as water. However, these regions are actually made up of groups of narrow peaks (see figure 3). If you use a very high resolution spectrometer, you can find some water peaks that are not overlapped by methane peaks as exemplified in figure 3.

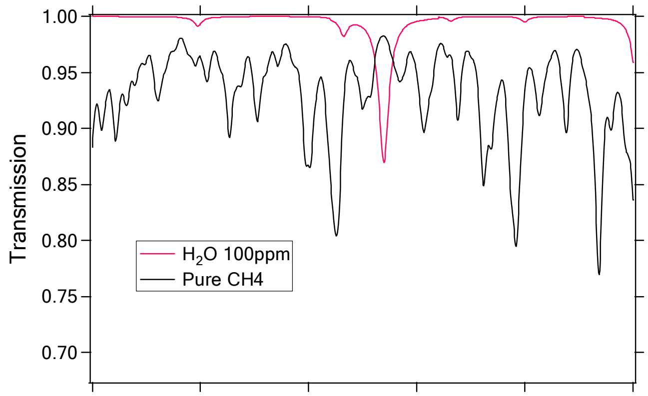

Figure 3 – An absorption spectrum diagram shows the amount of light absorbed by a material through a range of wavelengths. The x-axis indicates wavelength.

The tunable laser provides a narrow, tunable wavelength light source that can be used to analyze these small spectral features. According to Beer's Law, the amount of light absorbed by the gas is proportional to amount of the gas present in the light's path; therefore this technique is a direct measurement of moisture. In order to achieve a long enough path length of light, a mirror is used in the instrument. The mirror may become partially blocked by liquid and solid contaminations, but since the measurement is a ratio of absorbed light over the total light detected, the calibration is unaffected by the partially blocked mirror (if the mirror is totally blocked, it must be cleaned).

The Tunable Diode Laser Absorption Spectroscopy (TDLAS) analyzer has a high upfront cost compared to other analyzers. However, the TDLAS technology is not susceptible to interference or damage from corrosive gases, liquids or solids, the analyzer will react very quickly to drastic moisture changes, and will remain calibrated for very long periods of time.

References:

1. ASTM D5503 - 94(2008) Standard Practice for Natural Gas Sample Handling and Conditioning Systems for Pipeline Instrumentation
2. ASTM D1142 - 95(2012) Standard Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature
3. ASTM D5454 - 11e1 Standard Test Method for Water Vapor Content of Gaseous Fuels Using Electronic Moisture Analyzers