FUNDAMENTALS OF NATURAL GAS WATER VAPOR MEASUREMENT

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INTRODUCTION

This document will introduce the basic approaches to trace moisture measurements for natural gas and provide some advantages and disadvantages of each approach. There are many applications where trace moisture measurements are necessary such as in clean dry air, hydrocarbon processing, heat treatment processes, pure semiconductor gases, bulk pure gases, insulating gases such as those in transformers and power plants, and in natural gas pipelines. Natural gas presents a unique situation where the gas can have extremely high levels of solid and liquid contaminants as well as corrosive gases present in varying concentrations.

CONCENTRATION

Water measurements are made in parts per million, pounds of water per million standard cubic feet of gas, or some unit of the mass of water vapor per unit volume or mass of water vapor per unit mass of dry gas. That is, 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.

DEW POINT

If liquid water has formed in the gas as a result of changes in pressure and temperature during the process of extracting the sample for the analyzer, then the sample being measured will not be "representative" of the gas in the pipeline. Therefore it is essential to understand the phase diagram and to keep the gas in the vapor region of the diagram. See figure 1.

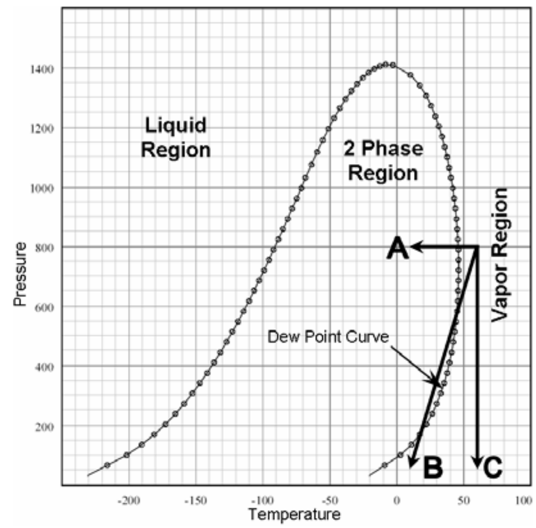

Figure 1 – Typical Phase Diagram for Natural Gas, expressed as a function of multiple condensable gases including water and hydrocarbons.

The dew point curve represents the temperature at a given pressure where liquid begins to form. Arrow A indicates a reduction in temperature starting from the dew point curve and ending inside the 2-phase region (condensation is a result). 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. This is achieved with a probe regulator and the result is that the gas is further from the dew point line than it was in the pipeline. In the latter two cases, heating the extracted gas line would not be necessary (assuming that the final temperature is held throughout the rest of the sampling system). 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.

HUMIDITY MEASUREMENT

Measurement of moisture in natural gas is typically performed with one of the following techniques: 1) Color Indicator Tubes, 2) Chilled

Mirror, 3) Electrolytic, 4) Piezoelectric Sorption, also known as Quartz Crystal Microbalance, 5) Aluminum Oxide or Silicon Oxide, and 6) Spectroscopy. Other moisture measurement techniques exist but are not used in natural gas applications for various reasons. For example, the Gravimetric Hygrometer and the "Two-Pressure" System used by the National Bureau of Standards are precise "lab" techniques but are not practical for use in industrial applications.

STAIN TUBES

The Color Indicator Tube (also referred to as the Drager Tube or 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 as high as 25%. The tubes are used one time and discarded. The color indicator tubes are well suited for infrequent, rough estimations of moisture in natural gas; for example, if the tube indicates 30 pounds of water, there is a high degree of certainty that it is over 10 pounds.

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 the dew is observed. 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 also 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 measurement tends to be high and will have a high standard deviation. Additionally, the condensation of moisture can be confused with condensation of other condensable such as heavy hydrocarbons, alcohol, and glycol. Automated on-line systems are not able to make these distinctions and manual systems must be used only by highly skilled operators.

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 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 frequent basis.

The system has success in some applications. However, in natural gas, interference from glycol, methanol, and damage from hydrogen sulfide result in readings that cannot be relied on. The sensor itself is relatively inexpensive and very precise. The required calibration system is not as precise and adds to the cost and mechanical complexity of the system. The labor for frequent replacement of desiccant dryers, permeation components, and the sensor heads greatly increase the operational costs. Additionally, slugs of water render the system nonfunctional for long periods of time as the sensor head has to “dry-down”.

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.

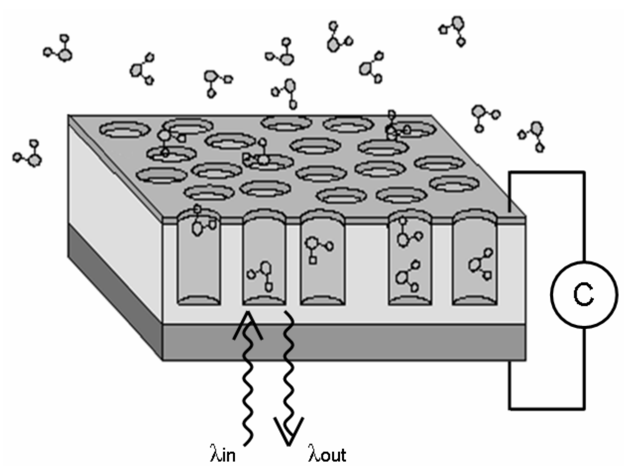

Figure 2 – Cross section of an oxide substrate moisture sensor.

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. Fiber optic connector can be used to separate the sensor head and the electronics.

This type of sensor is not extremely expensive and 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 slug. 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, so the calibration is reliable only at the beginning of the sensor’s life.

SPECTROSCOPY

If 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. Traditional spectroscopic techniques have not been unsuccessful 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 other gas peaks as exemplified in figure 3.

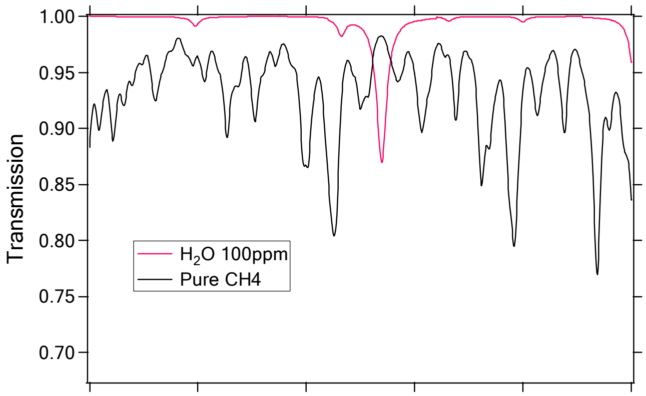

Figure 3 – An absorption spectrum diagram shows the amount of light absorbed by a material through a range of wavelengths. The x-axis indicates wavelength.

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 higher upfront cost compared to the analyzers above. However, the TDLAS technology is the only one that can meet any one of the following: the necessity for an analyzer that will not suffer from interference or damage from corrosive gases, liquids or solids, or an analyzer that will react very quickly to drastic moisture changes, or an analyzer that will remain calibrated for very long periods of time.