

DEVICES FOR FIELD DETERMINATION OF H₂O IN NATURAL GAS

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INTRODUCTION

H₂O vapor is an undesirable component of natural gas. It takes up space in the pipeline and provides no fuel value. In higher concentrations it can condense into liquid water in the pipeline and cause corrosion, especially in the presence of carbon dioxide or H₂S. Liquid water can also cause damage to turbines. Because of this, most gas transfer tariffs include a limit on the acceptable concentration of H₂O in the gas stream. This paper reviews the devices that can be used in the field to determine the amount of water vapor present in a natural gas stream.

DEW POINT

For any particular concentration of water vapor in a natural gas pipeline there is temperature where the water vapor will start to condense into a liquid phase. This temperature, known as the dew point, depends on the pipeline pressure. The Institute of Gas Technology extensively studied the relationship between the pressure, water vapor concentration, and dew point temperature about fifty years ago. The results of this study have been summarized in a series of charts covering dewpoint temperatures in the range of -40F to 250F, and pressures from 14.7 psia to 5000 psia. These charts are available as Institute of Gas Technology Research Bulletin No. 8 and ASTM Method D-1142. If the dew point and pressure of a natural gas are known, the charts allow the water vapor concentration to be determined. ISO-18453 (International Standards Organization) is based on work more recent work. These charts and calculations are also useful when concentration is known and the dewpoint is desired.

The dewpoint temperature of the gas is most commonly measured using a chilled mirror technique developed by the Bureau of Mines. Figure 1 shows such a chilled mirror device known as a Dew Scope. This instrument consists of a chamber that can be pressurized with the pipeline gas. One end of the chamber has a copper rod inserted into it. The end of the rod inside the chamber has a mirror on it. The opposite side of the chamber has a window through which that mirror can be observed. The gauge on top of the chamber measures the pressure.

Expanding a gas such as CO₂ into the expansion chamber on the right side of the copper rod can lower the temperature of the rod. The more gas expanded into the chamber, the faster the temperature will drop. The thermometer inserted into the rod measures the

temperature of the rod. As the temperature of the rod is lowered, water vapor will eventually condense onto the mirror on the end of the copper rod. The temperature where liquid water just starts to condense on the mirror is defined as the dew point temperature. If the temperature where condensation starts is below freezing, frost will form on the mirror and this is called the frost point.

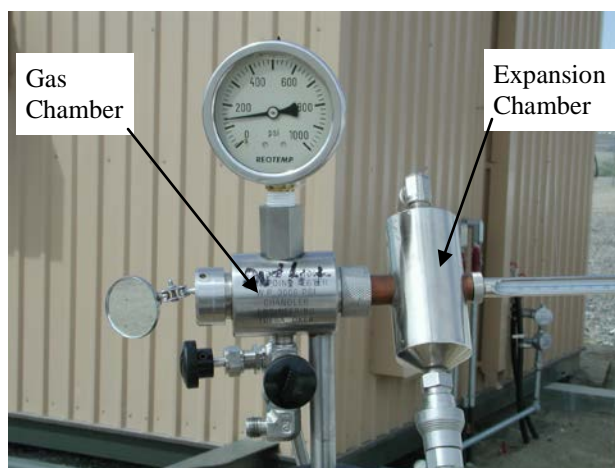


Fig. 1 – Bureau of Mine type chilled mirror device known as a Dew Scope.

The Dew Scope has the advantages of measuring at pipeline pressure and having very simple construction. Unfortunately, it takes considerable skill and experience to see accurately when the condensation first occurs. In addition, there is always some delay between observing the formation of dew and reading the thermometer. An improved configuration of the Dew Scope, places the temperature readout in the gas chamber so that the chilled mirror and the temperature readout can be viewed simultaneously. When the dew point temperature is measured, the water vapor concentration can be determined from the calculation methods mentioned before. Variations among several operators can result in differences in water vapor concentrations as much as 1 lb/mmscf. IGT Bulletin 8 also points out that the gas composition will affect the reading, especially if hydrocarbons condense on the mirror first. In spite of the difficulties in using the Dew Scope, it is generally recognized as a valid method for measuring water vapor in natural gas.

COLOR INDICATOR TUBES

The Color Indicator Tube (also referred to as the Draeger 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; a specific volume of gas is pulled through the tube with a piston, the chemical in the tube reacts with the moisture as gas flows through it, and the color changes. The more moisture that is present, the further down the tube the moisture will travel before it is all reacted. The length of the color change from the reaction (“length of stain”) is proportional to the moisture concentration. The manufacturer calibrates the tubes 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 $\pm 25\%$. The tubes are used one time and discarded. The color indicator tubes are well suited for infrequent, rough estimations of moisture in natural gas. They require an operator and the measurement uncertainty must be taken into consideration.



Figure 2 – Color indicator Tube

ELECTRONIC MOISTURE ANALYZERS

Because of the difficulties in using the Dew Scope the natural gas industry has looked for alternative measurement methods. It is also desirable to have continuous measurement readout without operator intervention. ASTM D-5454 recognizes several types of electronic moisture analyzer. Each of those will be discussed below.

CAPACITANCE CELL

This sensor is made up of a porous dielectric layer (typically Al_2O_3) between two conductive layers. See figure 3. The conductive layers form the electrodes of a capacitor. One of the conductive layers has holes in it so that water molecules can diffuse into the dielectric layer. Because the capacitance changes with the amount of moisture in the dielectric, the moisture concentration in the gas can be determined from the capacitance. Very low levels of moisture can be measured with this type of sensors.

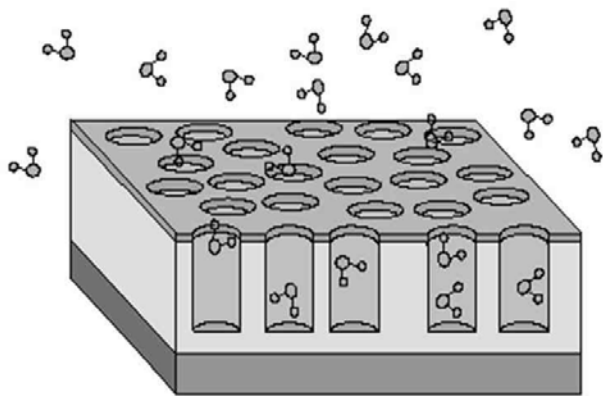


Figure 3 – Cross section of a capacitance moisture sensor.

Although these sensors are not very expensive, the calibration may drift over time and they are susceptible to contaminants commonly found in natural gas. Sample conditioning is essential to prevent contamination. Probe replacement and recalibration costs should be considered in the cost of ownership analysis.

ELECTROLYTIC CELL

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. Errors in mass flow translate directly into concentration errors. Other gas components that can electrolyze (for example, methanol) will create a current similar to water vapor and effect the reading.

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 CELL

This instrument, also known as a quartz crystal microbalance, measures the change in frequency of a hydroscopically coated quartz crystal oscillator as the mass of the crystal changes due to adsorption of water vapor. Because the sensor gives a relative measurement, an integrated calibration must be used to calibrate the system on a regular basis. The calibration cycle starts by putting the natural gas through a drier to remove all water vapor. As this dry gas is passed over the sensor, moisture is released from the surface of the crystal and its oscillation frequency increases. When the crystal has dried, a known standard concentration of moisture is added to the dry gas stream using a permeation cell. This known concentration results in some measured rate of change in the crystal’s frequency. Finally, gas with an unknown moisture concentration is flowed through the cell and the rate of change of the crystal’s frequency is measured again. The unknown concentration can now be determined by comparing the later rate of frequency change with the rate of change from the standard.

The system has success in many applications. However, in natural gas, interference from glycol, methanol, and damage from hydrogen sulfide may damage the cell.

The quartz crystal itself is relatively inexpensive and very precise. However, the required calibration system adds significantly to the cost and complexity of the system. The parts and labor for replacement of the desiccant drier and permeation cell should be considered in the cost-of-ownership analysis.

LASER CELL

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 that specific wavelength. Although the absorption by water and methane occur in the same general wavelength regions, these regions are actually made up of groups of narrow peaks. If you use a very high-resolution spectrometer, you can find some water peaks that are not overlapped by other gas peaks as illustrated in figure 4.

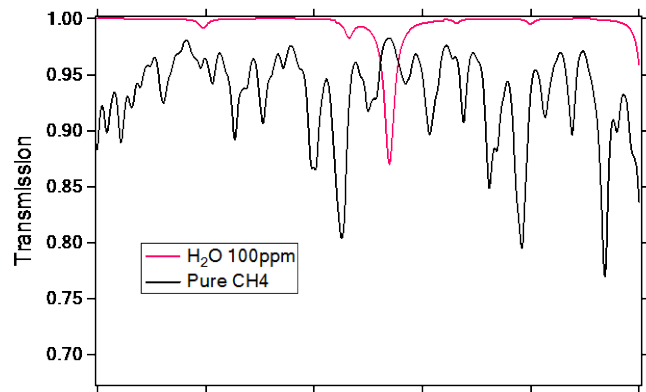


Figure 4 – An absorption spectrum diagram shows the amount of light absorbed by a material through a range of wavelengths. The x-axis indicates wavelength.

When a tunable diode laser is used to measure these small spectral features it is referred to as Tunable Diode Laser Absorption Spectroscopy (TDLAS). 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 contaminants, 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 can be easily cleaned in the field). Because a light beam in the volume of the gas is measuring the moisture, the instrument can respond as quickly as the moisture concentration in the beam path changes.

Because the spectrum contains absorption features from both water vapor and methane in the natural gas, it is easy to verify the proper operation of the analyzer by

comparing the relative size of the water and methane peaks. Having confidence that the reading is correct is important when deciding whether or not to let gas flow into a pipeline.

The TDLAS analyzer has a higher upfront cost compared to the other analyzers above. However, the TDLAS technology is the only one that provides high speed of response, freedom from interference by vapor phase contaminants, easy field cleaning in case of liquid phase contaminants, and stable calibration for years.

SAMPLE CONDITIONING

No discussion of natural gas water vapor analyzers is complete without mention of sample conditioning. Regardless of what type of analyzer is used bad sample conditioning can give bad readings.

To get an accurate measurement of the water vapor content in a natural gas pipeline it is essential that the gas in the analyzer sample cell be representative of the gas in the pipeline. The gas in the pipeline must be pressure reduced and transported to the analyzer without changing its composition. We will examine each step of this process and suggest the best approach.

1) Extract a representative sample of gas from the pipeline. A probe should be used to sample gas from near the center of the pipeline. Sampling from a valve on the wall of the pipeline is a bad technique because contaminants that reside on the walls can be pushed through the valve and into the sampling system. The American Petroleum Institute recommends sampling from the center 1/3 of the pipe diameter (or at least 10" from the wall on large diameter pipelines). Turbulence in the gas flow caused by elbows, valves, diameter changes, etc, can stir up liquids and particles from the pipeline walls into the center of the pipe. For this reason the probe should be located in a straight section of pipe at least 5 pipe diameters upstream and downstream of pipe discontinuities. If liquids are potentially present in the pipeline for any reason, a liquid separating membrane tipped probe should be used to reject liquids. The reason for this is that liquids cannot be reliably sampled from the pipe so the industry practice is to sample only the gas portion of the stream.

2) Reduce pressure without condensing liquids. When gas pressure is reduced without the introduction of heat the temperature of the gas will drop, typically about 7°F per 100 psi. This temperature drop could cause hydrocarbon or moisture condensation to occur in the regulator. To prevent condensation, it may be necessary to add heat. This can be done with a regulator that has its pressure-reducing orifice in the gas stream where it is warmed by the flowing gas, or with an external regulator that is heated with electricity or steam. A phase diagram can be calculated for any particular gas composition to determine if heating may be required. In extremely cold

environments it may be necessary to heat trace the tubing between the pressure regulator and the analyzer. Generally, it is good practice to heat trace the sample transport line to stabilize its temperature and prevent adsorption and desorption to and from the tubing walls. This occurs as the ambient temperature changes throughout the day and night. Heat-traced lines stabilize the tubing temperature and prevent this problem.

3) Maintain the integrity of the gas sample. Moisture can permeate through plastic tubing. Always use stainless steel tubing from the pipeline to the analyzer. The tubing and all components in the line must be dry and free of contamination. Liquid water in the tubing can take a long time to evaporate, especially at low ambient temperatures. Needless to say, the tubing connections must all be leak

free because the moisture concentration in the air is typically a hundred times higher than in the pipeline.

4) Prevent contaminants from entering the analyzer. Use a membrane separator close to the analyzer to prevent liquids and particles from getting into the measurement cell. These separators must be checked on a regular basis to make sure they do not become plugged. It is also necessary to be sure that the maximum flow rate limitations of the separator are observed. Membrane separators will increase the sensor life or cleaning interval on any type of moisture analyzer.

Paying close attention to the sample extraction and conditioning will result in analyzer readings that are representative of the actual gas composition.