

# Mission Critical Moisture Measurement

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## ABSTRACT

Measuring the amount of water vapor in a gas presents a variety of challenges; especially challenging are measurements in contaminated hydrocarbons such as Natural Gas. A multitude of methods are available for performing these types of measurements, each with their own limitations, and with varying costs of ownership. This paper illustrates a solution that allows one of the lowest cost approaches to become one of the best performers.

## INTRODUCTION

Measuring water vapor in gases is difficult even in pure gases, which is the best of circumstances. Technologies such as automatic or manually cooled (chilled) mirrors, Karl Fisher titration, oscillating crystals, infrared absorption, metal oxide or polymer capacitive film, electrolytic, and others are used to perform water vapor content measurement. The prices range from many tens of thousands of dollars to under a thousand dollars. The feasibility of each technology for an application depends on many factors; measuring range, response time, accuracy, long term stability, temperature coefficient, susceptibility to contaminants, approvals for use in Hazardous Areas, minimum detection limits, cost of ownership. Various manufacturers have addressed the above-mentioned factors by methods best suited for their specific technologies, however susceptibility to contaminants (including interferences from the gas under measurement) still presents a significant problem for these instruments.

The aim of this paper is to present an approach, borrowed from other measurement technologies, to accurately and reliably measure the water vapor content in a potentially contaminated gas using a hyper thin film (HTF) aluminum oxide sensor. It is desirable for the measurement to have National Institute of Standards and Technology (NIST) traceability. Specific examples will be presented for measuring in Natural Gas after a

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glycol drying station. Natural Gas was chosen as the example because it presents challenges to all of the technologies mentioned above.

The hygroscopic nature of glycol provides an effective method for drying Natural Gas, but it also provides a significant interference with the water vapor equilibrium when utilizing the capacitive and electrolytic technologies. Other contaminants in Natural Gas can also interfere or (in the case of corrosives) even damage most of the sensing technologies. The infrared absorption of water vapor occurs at many wavelengths, however methane's absorption is always nearby and thus causes interferences. The presence of hydrocarbons, which may coalesce at higher temperatures than water, interferes with an automatic chilled mirror's ability to perform accurate measurements, as do particulate contaminants. Oscillating crystals are also very sensitive to contamination, and are best suited for in-lab use. Karl Fisher titration will perform accurate measurements, but is best suited for laboratory, or single sample use; it is not practical as an online continuous duty measurement.

## CALIBRATION STRATEGY

The strategy used to provide a cost effective and traceable quality water vapor measurement is borrowed from other process instrumentation. A valve is included in the sample system, such that under the instrument's control, the sensor can be switched from the process gas to a NIST traceable Nitrogen/Water blend bottle. Refer to figure 1. The known water content of the bottle is pre-entered in the instrument's memory together with a time schedule of verification / recalibration. The unattended instrument follows the schedule and performs the pre-programmed task of recalibrating. Thus the measurement near the water content of the bottle is essentially with NIST traceable accuracy even if the contaminants in the process gas have caused the sensing element to drift. As the measurements get further and further from the calibration point, the accuracy diminishes slightly but with the appropriate sensor technology can be easily kept within the specified tolerance of the instrument. This method is particularly attractive for uses where there is an accepted alarm point, e.g. for Natural Gas – seven (7) pounds of water per million standard cubic feet (lbsH<sub>2</sub>O/mmscf), the calibration bottle can be ordered to contain 143 parts per million by volume (ppmV) of water which corresponds to 7 lbsH<sub>2</sub>O/mmscf. When an alarm is generated one can have an extremely high confidence in the measurement near that point, suspicions can quickly be settled with a verification/recalibration against the traceable bottled standard. There are 5 challenges in constructing the system described above. Each one was analyzed and existing solutions were sought, and if not available special equipment was developed.

1. *Challenge:* Provide a consistent Nitrogen/Water blend throughout the pressure life of the bottled standard. The higher the water content the more difficult it becomes to release a constant concentration.  
*Solution:* A manufacturer was located who produces specially lined high-pressure bottles that will release a constant water concentration from ~1800psi to ~200psi for up to 145 ppmV Nitrogen/Water blend. Two such bottles were tested with a NIST traceable chilled mirror, and were verified to provide a consistent blend

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throughout the specified bottle pressure, for ambient temperatures as low as 60°F. For colder ambient temperatures a bottle warmer was added and the bottle continued to release a constant concentration.

2. *Challenge:* Use an extremely low leakage electrically actuated 3-way valve, which is approved for use in Class1 Div 2 areas. Solenoid valves are not sufficiently tight, thus the gas that is being shut-off can corrupt the measurement or calibration. Air actuated valves may not be practical for areas that do not have available instrument air. Many Natural Gas measurements are performed in Hazardous Classified areas, while commercially available motorized 3-way valves do not have approvals for use in these areas.  
*Solution:* A motorized actuator was specially developed to operate a Swagelok SS-43XS4 3-way ball valve. This valve is essentially leak-free for these measurements. This actuator utilizes a 24VDC stepper motor thus eliminating the ignition source of motor commutator brushes, and facilitating Hazardous Area use approval.
3. *Challenge:* Assure that the contaminants do not damage the sensor or so-degrade it, such that even the recalibration is not sufficient in providing an accurate measurement. Conventional aluminum oxide capacitive sensors are highly affected by glycol's hygroscopic properties, they are easily damaged by contaminants, and they are prone to drift due to metal migration.  
*Solution:* Utilizing a hyper thin film (HTF) aluminum oxide sensor, afforded several orders of magnitude greater sensitivity (refer to figure 2) compared to conventional aluminum oxide sensors. The greater sensitivity prolongs the time it takes for the sensor to be damaged to a point where it is not any more recalibrateable. The greater sensitivity also reduces the effects of the glycol contamination. Testing showed that several years of high performance could be expected with these sensors in typical Natural Gas measuring environments.
4. *Challenge:* Assure that drift is minimized between recalibrations, such as temperature sensitivity. Conventional aluminum oxide sensors can have significant drift with temperature, thus the periodic recalibrations will not assure that the instrument is consistently reporting the correct measurement as the temperature changes from daytime to nighttime. Refer to figure 3.  
*Solution:* It was found that the HTF sensors have negligible temperature drift and thus are ideally suited for these kinds of harsh environment applications.
5. *Challenge:* Assure a low maintenance requirement, and ease of use. Measurements in Natural Gas typically require significant maintenance at short intervals. For example conventional aluminum oxide sensors may have to be replaced on a monthly basis, or in some cases more often to maintain a good degree of accuracy. Other technologies have inherent drifts that also require monthly service and recalibration by well-trained personnel.  
*Solution:* During testing it was discovered that recalibrating once every two weeks is sufficient to maintain the specified accuracy; at 7 lbsH<sub>2</sub>O/mmscf this translates to +/- 1 lbsH<sub>2</sub>O/mmscf. The calibration gas bottle chosen, discussed in a previous paragraph, can provide in excess of 50 calibrations worth of gas. However the manufacturer guarantees it for only a period of 1 year. Thus the bottle has to be

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replaced once per year, and calibrations can be performed as often as once per week.

By this time it is obvious to the reader that the technique utilized is common in many process instruments. The success of this approach in moisture measurement is centered on the high sensitivity HTF sensor. Therefore a quick overview of the sensor technology follows.

## SENSOR TECHNOLOGY

The Mission-Critical Self-Calibrating Natural Gas Sample System takes advantage of the uniquely large and quasi-linear response to moisture of Xentaur HTF sensors. The large response to moisture of HTF sensors is an absolute requirement for adjusted moisture computations based on a single point calibration.

HTF and all other aluminum oxide sensors share the same basic operating principle: the capacitance measured between the sensor's aluminum core and a gold film deposited on top of the oxide layer varies with the water vapor content in the pores of the oxide layer. Three fundamental structural improvements in the oxide layer give HTF sensors much increased sensitivity and stability: HTF sensors have much thinner oxide layer, a better defined barrier layer between the aluminum and the aluminum oxide and a unique pore geometry enhancing the entrapment of water molecules.

*Hyper-Thin Layer:* With HTF technology, sensors can be produced with hyper-thin oxide layers without compromising insulation strength. The thinner oxide layer of HTF sensors results in much higher capacitance changes because capacitance is inversely proportional to the distance of the capacitor's plates from each other. The thinner layer also means that water molecules will travel faster in and out of the pores. HTF aluminum oxide sensors therefore respond several times faster than conventional sensors.

*Barrier Layer:* In HTF sensors, the transition between the aluminum oxide and the aluminum is sharp and clearly defined. This thinner barrier layer produces a capacitor with its electrodes very close together, which in turn causes the sensor's wet to dry capacitance ratio to be high. The benefit of high wet to dry capacitance ratio is that drift in capacitance due to undesirable factors is less significant. This is clearly a benefit as can be seen in HTF vs. conventional sensor comparisons of temperature sensitivity and aging drift. The sharp transition from aluminum to aluminum oxide also reduces metal migration, one of the major causes of aging drift in conventional sensors.

*Pore Geometry:* The most significant difference between HTF sensors and conventional sensors is, however, their pore geometry. While conventional sensors rely on hygroscopic aluminum oxide structures to attract water, HTF sensors rely on a pore geometry that slows the Brownian motion of the water molecules when entering the pores. The freed energy is absorbed by the mass of the sensor and the decreased entropy of the water molecules is equalized by an increase in their total number. This results in more dielectric in the pores and consequently a higher capacitance. The HTF pore geometry does not significantly change over time, while conventional hygroscopic aluminum oxide structures are not stable and collapse slowly into non-hygroscopic structures. Therefore,

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conventional sensors are subject to drift and need to be re-calibrated frequently, while HTF sensors need no re-calibration when used in clean, non-corrosive gasses.

## FIELD TEST RESULTS

The Mission-Critical Sample system was field tested (at DOW Sep- 27- 99 to Jan- 6- 00) to work in challenging applications. Figure 4 shows 90 days of dewpoint monitoring data with calibration adjustment in an application where glycol carry-overs have prevented conventional systems from producing reliable results. After a settling period of two weeks, the system has reliably provided accurate results. This settling period is due to the initial buildup of Glycol on the sensor and the resultant water vapor pressure equilibrium shift, as discussed in the introduction. The settling period can be shortened and or eliminated by setting up the instrument to perform calibrations once every 3 days for the first two weeks.

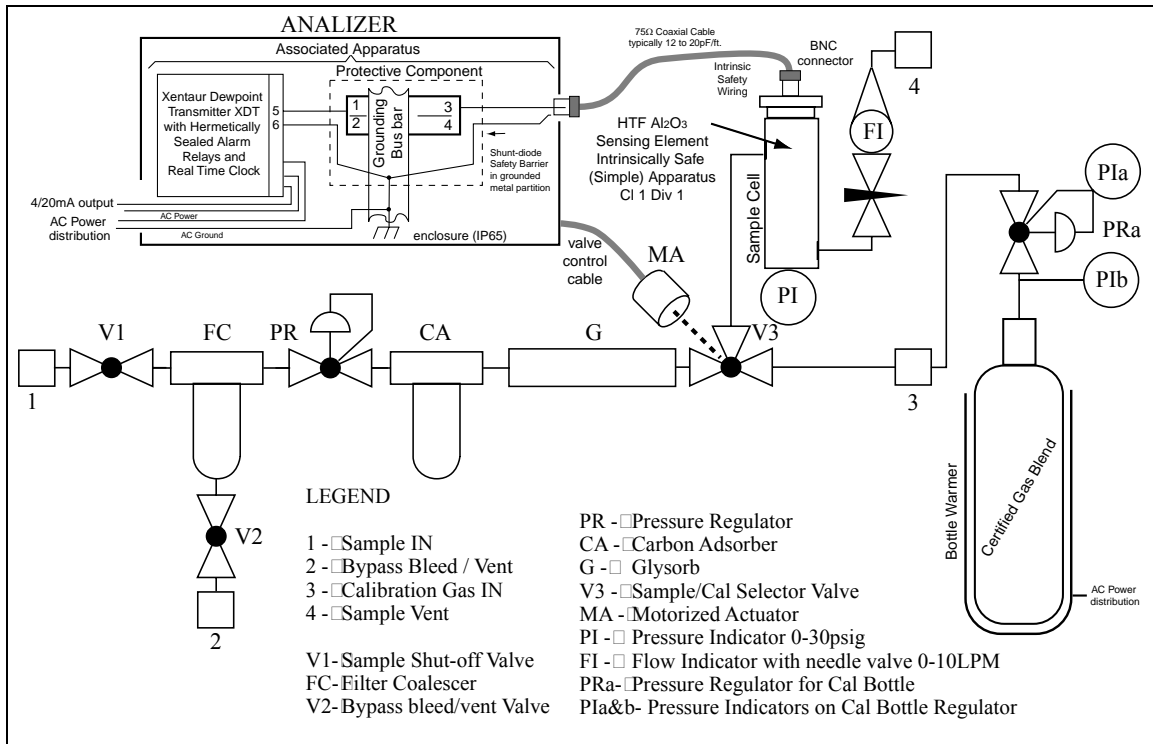
Figure 5 depicts a typical field installation; the calibrated bottle regulator and pressure gauges are barely visible at the bottom right corner.

## CONCLUSION

It should be made clear that no technology solves all problems, or is perfect for all applications. However, for moisture content measurements in harsh environments that have to be cost effective and require high degree of accuracy near a single point with a good accuracy thorough out a wide range, it is believed that automatic traceable recalibrations provide the best solution. Our experience has shown that recalibration alone cannot compensate for all sensor weaknesses, but seems to perform within acceptable parameters using HTF aluminum oxide sensors as described in this paper.

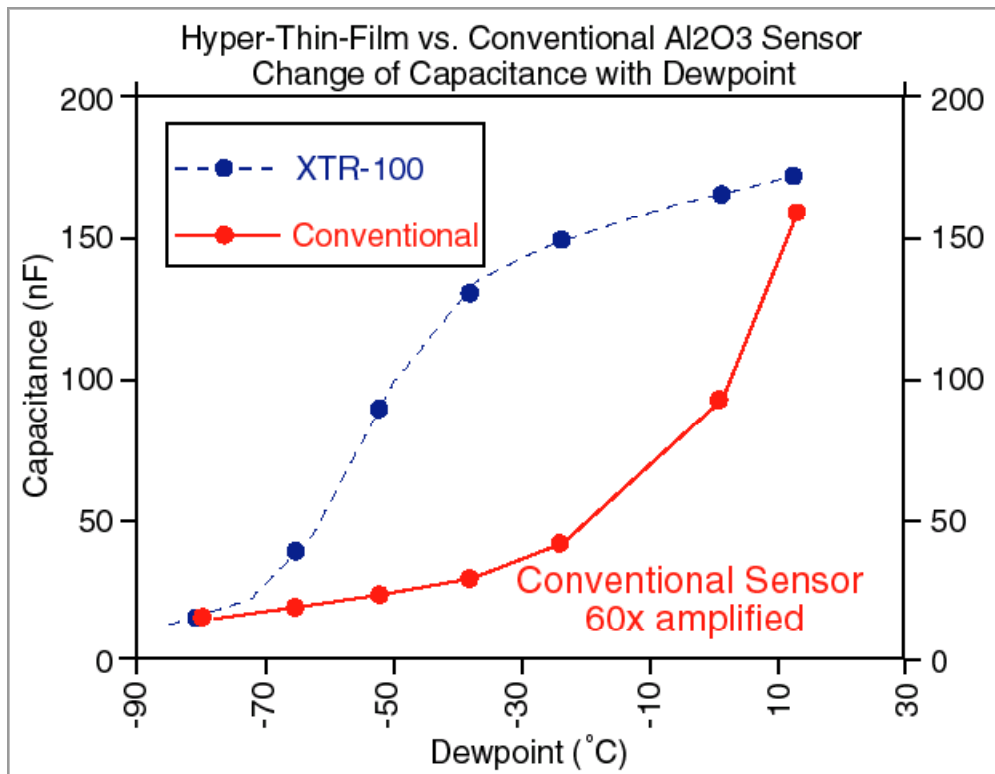
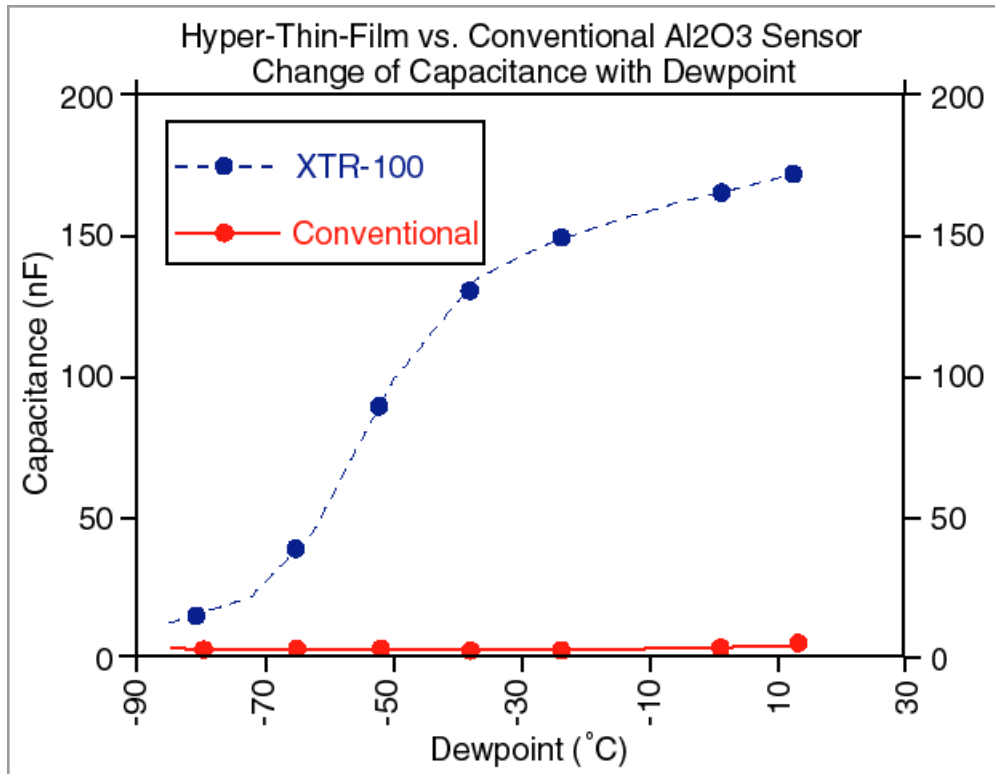
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## Figures



**FIG 1 – SAMPLE SYSTEM CONFIGURATION**

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**FIG 2 – Comparison of Capacitance vs. Dewpoint for HTF and Conventional Al<sub>2</sub>O<sub>3</sub> sensors**

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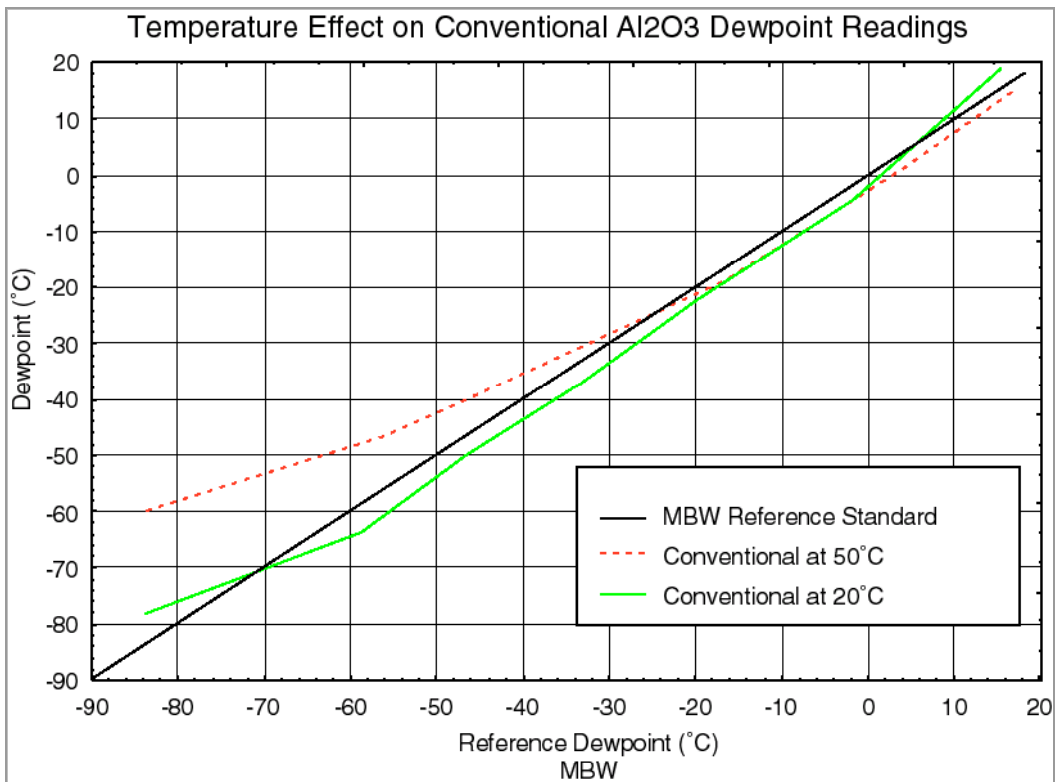
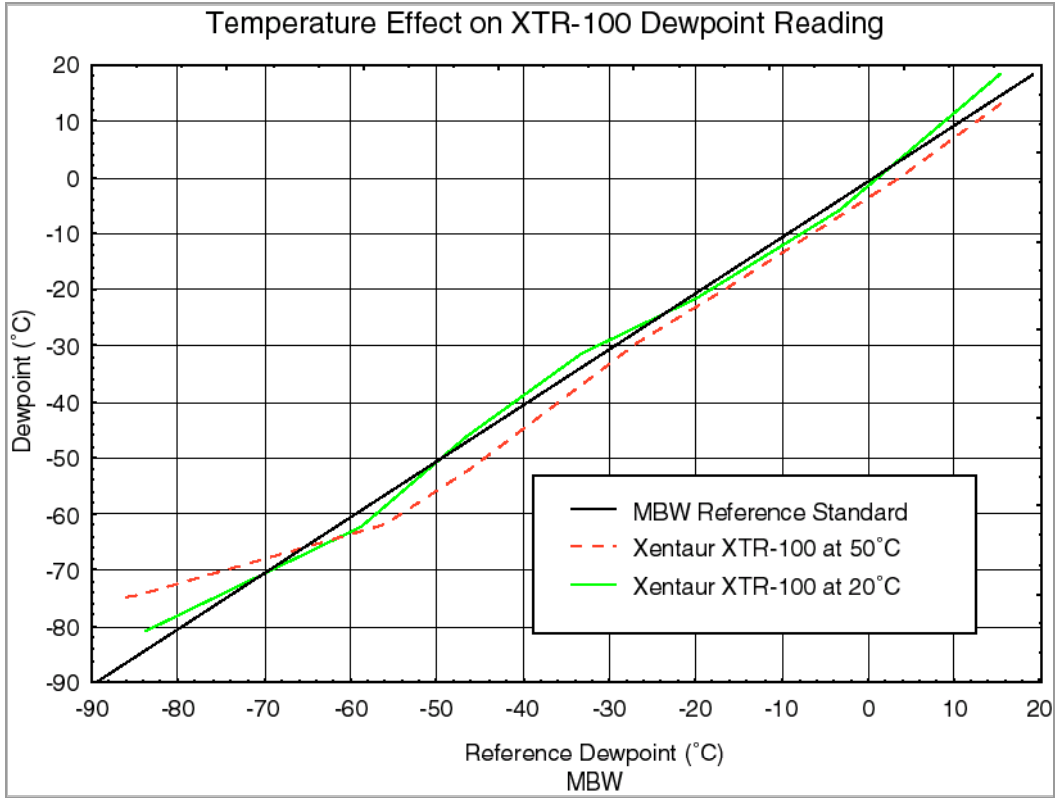
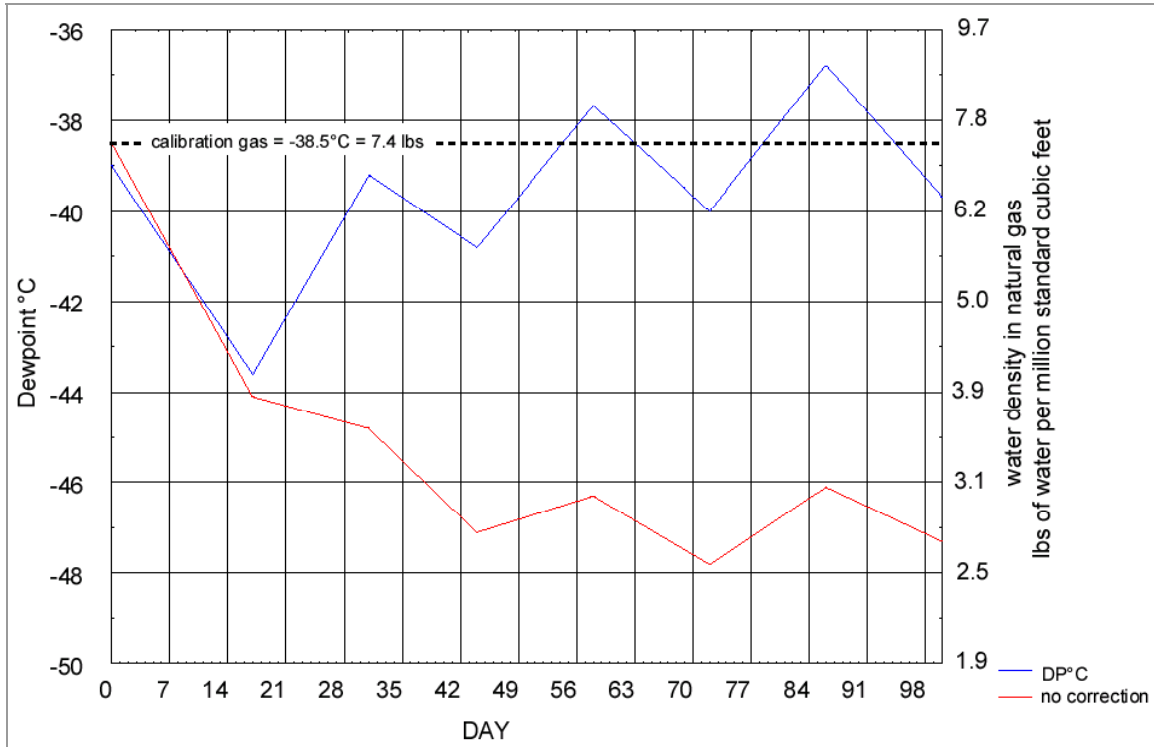


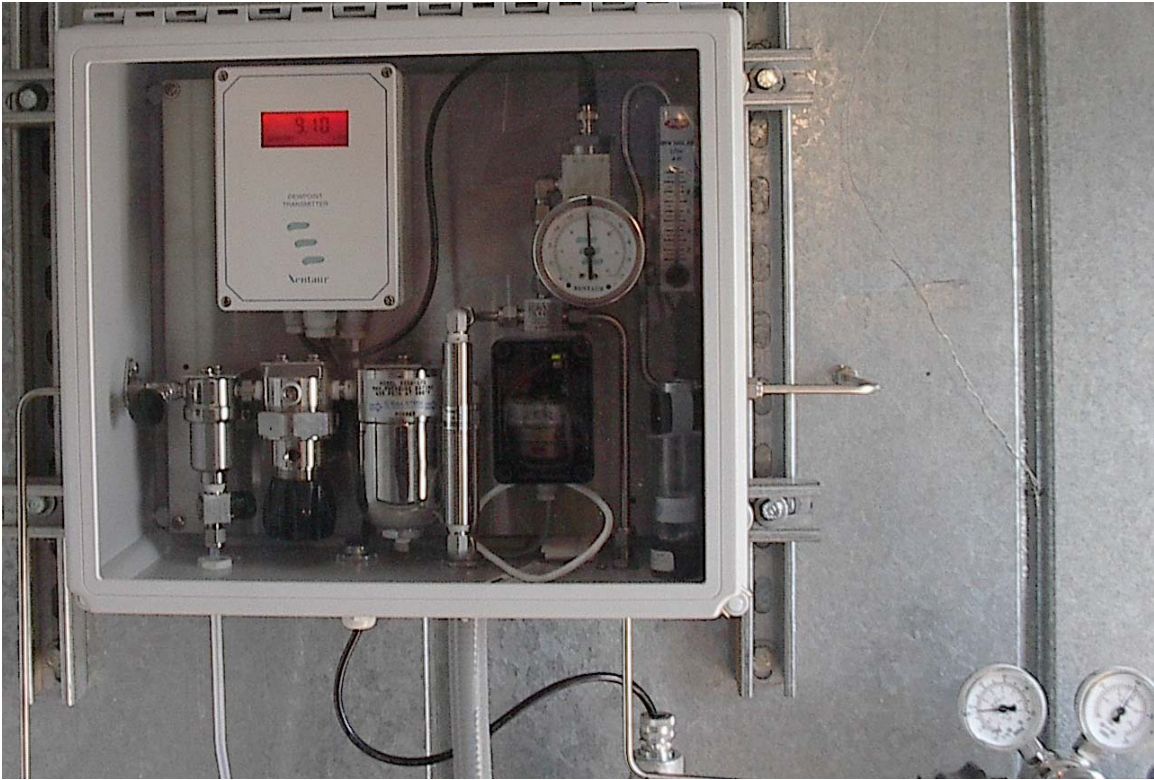
FIG 3 – Temperature effect on HTF and Conventional Al<sub>2</sub>O<sub>3</sub> sensors

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**FIG 4 – FIELD TEST RESULTS**  
showing reported measurements (blue) and what would be reported (red) without recalibrations

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**FIG 5 – Field Installation**