A FIELD DEPLOYABLE METHOD TO VALIDATE ONLINE MOISTURE ANALYZERS

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ABSTRACT

The accuracy of all measuring devices such as analyzers can degrade over time. This is often a result of normal wear and tear, degradation of components or contamination. Changes in the analytical response can also be caused by electric or mechanical shock, changes in sample system performance, or variations in other sensors such as pressure, temperature, or flow measurement devices. To demonstrate the continued reliability of a process or laboratory analyzer, it is recommended that the device be validated against some form of reference or standard.

For many analyzers, the validation is performed by running a calibration standard in which the concentration or property of interest has been independently determined. However, for many of our trace moisture analyzers calibration standards are not readily available, or such standards are not reliable over long periods of time, and as a result many of these analyzers are put into service and never validated against any kind of a standard.

A novel method for field validation of trace moisture analyzers has been developed. The device uses simple and well understood physical phenomena to produce a known concentration of water vapor, and the output concentration is variable over a sufficient range to both validate the performance of an analyzer and demonstrate its linearity. The validation device ensures that three important characteristics are achieved:

- It produces a known and repeatable concentration of water vapor,
- The water vapor concentration can be varied from 0 ppm to full scale of the device, and
- The device responds rapidly across its designed range.

The principles of operation are presented along with the test data demonstrating typical performance of the device.

INTRODUCTION

The quest to quantify and control moisture levels in various environments and substances is a challenge that has persistently engaged scientists, engineers, and practitioners throughout history. From the ancient Egyptians, who needed to predict the flooding of the Nile for agriculture, to the modern semiconductor manufacturers, where the presence of even infinitesimal amounts of moisture can compromise product integrity, the measurement of moisture has always been a cornerstone of progress and productivity.

In "Meteorologica", Aristotle explores the nature of the elements and their transformations, the causes of weather phenomena, and the relationships between different meteorological events. One of the key topics Aristotle discusses is the concept of humidity. Aristotle observed that the amount of moisture in the air can vary, leading to different weather conditions. He notes that humidity plays a crucial role in the formation of clouds, rain, and other meteorological phenomena. Aristotle also considered the concept of condensation and how the cooling of air can lead to the condensation of moisture. Mankind’s interest in humidity and dewpoint dates to some of the great thinkers of ancient and modern history. An incomplete list of some of the historical means to measure humidity [1] and moisture is presented in Table 1.

TABLE I. AN INCOMPLETE HISTRY OF THE DEVELOPMENT OF HYGROMETRY

Year	Inventor	Technology
1450	Nicolaus de Cusa	Describes a hygrometer based on changes in mass of cotton
1481	Leonardo da Vinci	Builds a hygrometer based on idea of de Cusa
1650	Ferdinand II de Medici	Condensation hygrometer
1664	Francesco Folli	First practical hygrometer based on a paper ribbon
1783	Horace de Saussure	Invents the hair hygrometer (used until 1960’s!)
1799	John Leslie	Wet and dry bulb hygrometer (first psychrometer)
1820	John Frederic Daniell	Invents the first dewpoint hygrometer

Trace moisture measurement, the ability to detect and quantify moisture at extremely low levels, is more than a technical necessity; it is a thread that runs through the fabric of human innovation, intertwining with our advancements and setbacks, guiding decisions, and designs. In the annals of history, the ability to understand and control moisture has been a determinant of survival, prosperity, and advancement. From preserving food to producing hydrocarbons and petrochemicals, from crafting precise scientific instruments to enabling the cutting-edge fabrication processes of today's electronics that drive powerful artificial intelligence, the control and measurement of moisture have been indispensable.

The calibration of instruments for measuring trace moisture has, therefore, evolved not merely as a technical challenge but as a critical facet of technological progression. Calibration ensures that the measurements are accurate, reliable, and consistent across time and space, forming the foundation upon which industries can standardize their processes and products. In this context, the calibration of trace moisture measurement devices emerges as a paramount concern that

transcends its apparent simplicity, embodying the intricate relationship between humanity's technological endeavors and the natural world's fundamental properties.

While many laboratories, research facilities and analyzer vendors have developed sophisticated methods to generate known concentrations of water for calibration and validation of equipment in the laboratory, a reliable means to perform field validation of analytical equipment has been lacking. This paper describes a new and patent pending device to enable end users to easily verify the performance of moisture analyzers in industrial environments.

WATER VAPOR CALIBRATION

Water is ubiquitous in all aspects of our lives, including its presence in industrial processes. Water vapor presence in many industrial processes is problematic and as a result it is important that the water content of gases be measured accurately. In natural gas or CO_2 pipelines, the presence of water vapor can contribute to corrosion or natural gas hydrate (clathrate) formation. In semiconductor fabrication, even minute levels of moisture can form a native oxide layer on silicon surfaces, affecting the electrical properties of the semiconductor devices and negatively impacting photolithography processes. In the petrochemical industry, water can interfere with chemical reactions and product purity. For example, water vapor can lead to the formation of unwanted byproducts in ethylene oxide production. Water can also poison catalysts, reducing their lifetime and activity. For example, in olefin polymerization, even parts per million (ppm) water vapor can deactivate Ziegler-Natta catalysts. This results in the measurement of moisture being one of the most common industrial gas measurements in industry.

Numerous methods have been developed to generate reliable calibration gas standards. An early review article by Barret [2] identified the main methods used to generate standards and the relative merits of each. ISO 6145 [3] is a series of standards concerning gas analysis, specifically focusing on the preparation of calibration gas mixtures using dynamic methods. These standards are critical for ensuring accuracy and consistency in gas analysis across various applications, including environmental monitoring, industrial processes, and research. Researchers working on blending gas mixtures are also reminded of the safety implications and referred to “The Safe Preparation of Gas Mixtures” [4].

More recently, significant reviews of methods to produce reliable gas standards have been published [5,6]. Many of these methods have been used by various companies to generate moisture standards in the laboratory. Arguably the most common method has been to use an evaporation method where a gas is allowed to flow over water or ice at a very well controlled temperature and the product gas from this is diluted using flow meters. Other dynamic methods used in laboratory applications are permeation devices and controlled diffusion devices. A good summary of dynamic methods of generating gas phase calibration standards from liquids has been presented by Li et al [7].

In the permeation method the calibration component (liquid water) is contained in a sealed tube or container, which consists of either wholly or partly of a polymer through which the component can permeate. The rate of permeation is dependent on temperature. The mean rate of

permeation may be periodically determined by measuring the change in weight of the permeation tube over time.

In the diffusion method, the vapour of the pure component (water) migrates by diffusion through a long piece of tubing into a flow of complimentary gas. The rate of diffusion should remain constant provided that the system is kept at constant temperature and pressure. The diffusion rate is measured periodically by weighing the cell which contains the water.

None of the above methods have been successfully deployed as a standalone field validation device for low level moisture applications. Devices employing these methods are often bulky, are not suitable for hazardous electrical classifications, and complex to operate. Permeation tubes and validation cycles have been integrated into some analyzers, but the long-term stability is questionable, and they are not capable of providing high concentrations or flow rates. While integration into the analyzer is beneficial, it does not allow the validation source to be used to test the whole sample system response.

Most field validations of trace moisture devices have been performed using calibration cylinders or standards where a small quantity of water vapor is contained in a gas cylinder pressurized with an inert gas. Several reliability and accuracy issues can arise with trace moisture calibration gas standards. The stability of trace moisture calibration gas standards over time is a significant concern. Moisture can adsorb onto the surfaces of the container walls, leading to changes in the delivered moisture concentration. This phenomenon can result in less accurate calibrations.In addition, the calibration gases often do not represent the bulk constituents of the process gas, and thus their use may not account for bias or cross-interference from other components [8].

As well, the accuracy of moisture measurement can be significantly affected by changes in temperature and pressure. If the calibration gas standards are not used under the same conditions as they were prepared or if the instruments are not properly compensated for these variations, the calibration can be inaccurate.

The issues associated with field validation have plagued industry for years and were thoroughly addressed by Sparages and Gerritse[9,10]. In their work, they defined the properties of the ideal moisture generator as:

> *“The ideal moisture generator could use any background gas as the carrier, one would dial in the moisture content they would want to generate, and within minutes the generator would be able to provide the gas at the desired temperature and pressure. The accuracy would match the accuracy requirements of the analyzer in question.”*

DESIGN

The moisture generator block was developed to address issues an end user was having in validating the performance of their online analyzers in a natural gas pipeline application. The goal was to develop a simple, field transportable device which could be included in a service kit

and could reliably demonstrate and validate the performance of an online moisture analyzer regardless of the analyzer type. The moisture generator block presented in Figure 1 integrates components as per the flow schematic in Figure 2. It allows for simple and rapid validation of online or laboratory moisture analyzers. The generator is designed to take a high-pressure gas inlet, typically at several hundred psi. The pressure of the inlet gas is controlled by an adjustable inlet pressure regulator before flowing to the integrated saturator and desiccant dryer. The block operates at ambient temperature and is constructed of nickel-plated aluminum which provides similar adsorption characteristics as electropolished stainless steel.

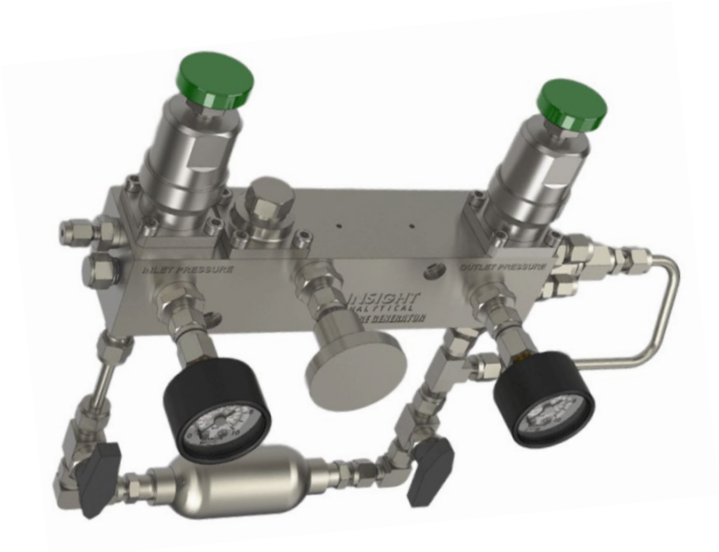

FIGURE 1. MOISTURE GENERATOR BLOCK PHYSICAL LAYOUT

Water content in the vapor space of the saturator, which is a bore machined on the inside of the block, may be predicted using a suitable vapor pressure equation. For example, the Arden Buck equations are a group of empirical correlations that relate the saturation vapor pressure of water to temperature [11,12]. One example is shown in Equation 1.

$$P_{sat}(T) = 0.61121 \times \left[\left(18.678 - \frac{T}{234.5}\right) \times \left(\frac{T}{257.14+T}\right)\right] \quad (1)$$

Where:

T is the temperature (°C)

P_{sat} is the saturation vapor pressure of water at that temperature (kPa)

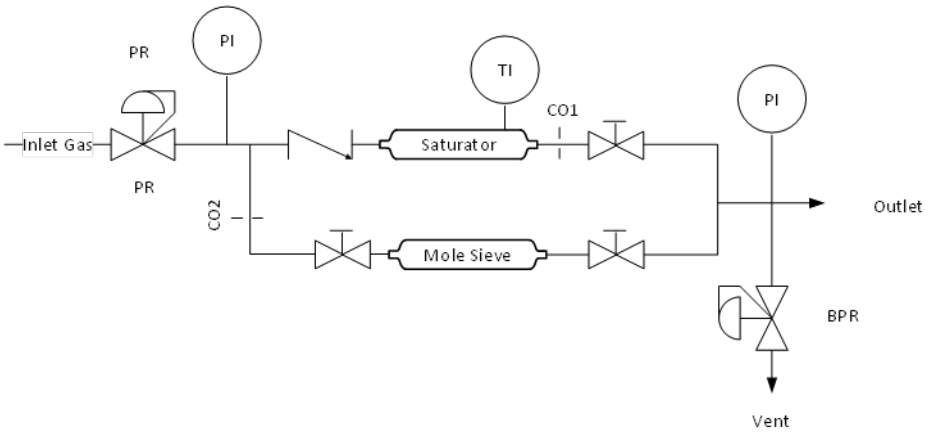

FIGURE 2. MOISTURE GENERATOR BLOCK SCHEMATIC

The Arden Buck equation is optimized for accuracy in the temperature range from -80°C to +50°C which fits well with the predicted operating ranges for the moisture validation device (5°C to 40°C).

The flow through each leg of the generator ("dry" and "wet") is controlled using a different size critical orifice. The ratio of the open orifice size in each critical orifice determines the dilution ratio which is independent of gas composition. The block thus employs a combination of the methods for generating a dynamic calibration standard, specifically the evaporation method to generate a given water content, a pressure-based dilution method to reduce the water content and a further flow dilution method to produce the final output.

It is useful to work through an example. Assume the inlet pressure regulator is set to 3000 kPa (about 420 psig) and the temperature is 20°C. At 20°C the vapor pressure of water is 2.3 kPa. We assume that the gas exiting the saturator is fully saturated and thus the outlet concentration of the saturate is 2.3/3000 or 0.077% H2O or 770 ppm. Assume the orifices have been chosen such that the ratio of the flow rates is 15:1 with most of the flow on the dry side of the flow path. Then the outlet concentration will be 770 ppm / 16 = 48 ppm. Note that the dilution ratio can be estimated by knowing the cross-sectional area of each critical orifice. The backpressure regulator vents any excess gas not needed by an analyzer and controls the pressure at the analyzer inlet.

This simple mechanical configuration can be used to generate a range of moisture concentrations simply by changing the inlet pressure regulator setting or by operating the block at differing temperatures. However, it does not require any elaborate temperature or pressure control; a simple set of calculations which can be performed in an Excel™ spreadsheet, a PLC or even a cell phone application can be used to predict the generated water content provided that the temperature and pressure gauges are read accurately. Surprisingly, this simple configuration meets all or most of the requirements spelled out by Sparages and Gerritse regarding the performance of an ideal moisture generator.

The block can also be used to generate a zero reference for the analyzer, even when wet process gas is at the inlet, by closing the valve from the saturator stage and only allowing flow through the mole sieve dryer.

RESULTS AND DISCUSSION

In evaluating the performance of the moisture generator, it is useful to consider the idealized characteristics of a moisture field validation device listed in the paper by Sparages and Gerritse:

- Can use any background gas,
- Dial in or programmable moisture content,
- Fast response time, and
- Sufficient accuracy to satisfy end-user needs for validation.

CAN USE ANY BACKGROUND GAS

The first desired property for a moisture generator based on the paper was that it "could use any background gas as the carrier". This feature is well addressed in this design, in that any high-pressure gas, be it from compressed gas cylinders to process gas, can be used as the inlet feed gas. The only requirements are that the inlet feed gas:

- Has a pressure preferably over 100 psig (critical orifice operation),
- Has a pressure less than the maximum inlet pressure of the regulator,
- Be below its dewpoint (non-condensing),
- Be compatible with the materials of construction of the block.

In general, the moisture validation block is compatible with any inlet or background gas, including natural gas, carbon dioxide and hydrogen and other common high pressure process gases.

DIAL IN MOISTURE CONTENT

A second desired property for a field moisture validation device is that "one would dial in the moisture content they would want to generate". This capability is present in the design presented, with an effective turndown range spanning at least one order of magnitude. One of the standard configurations for the moisture validation block is to produce moisture content up to about 200 ppm, which works well for natural gas applications where the specifications is often for a maximum content of 84 ppm (4 lbs/mmscf) or 147 ppm (7 lbs/mmscf). This standard configuration uses a dilution ratio of approximately 15, although the actual ratio varies from block to block and must be determined at the factory. Typical output concentrations as a function of operating temperature and pressure are shown in Figure 3. From the predicted performance curves, one sees that operation at 30°C would result in a moisture content of about 25 ppm at 1000 psig, and of about 180 ppm at 200 psig.

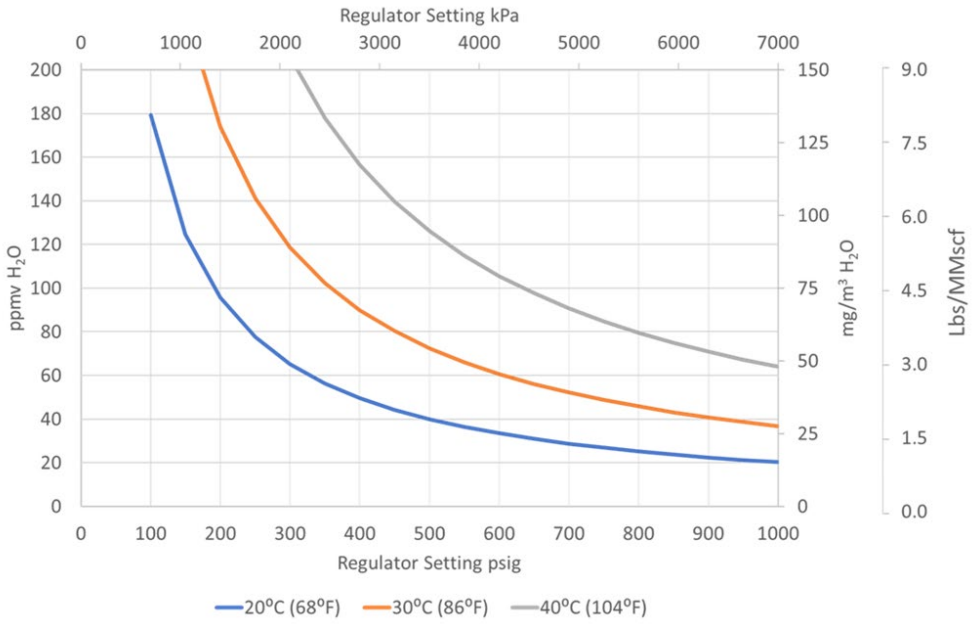

FIGURE 3. MOISTURE VALIDATION BLOCK OUTPUT.

In a second configuration, a higher dilution ratio of approximately 65 is used to generate concentrations in the 0 to 50 ppm range (at ~ 25°C). Using the ideal gas law, the output concentration from the moisture validation block varies as predicted in Equation 2:

$$ppm(T) = 10^6 \times \frac{P_{sat}(T)}{P} \times Dil \tag{2}$$

Where:

T is the temperature (°C).
P_{sat} is the saturation vapor pressure of water at that temperature (kPa) (see EQN 1),
P is the pressure setting of the inlet regulator (kPa),
Dil is the dilution ratio for the specific block $Dil = \frac{Flow_{wet}}{Flow_{wet}+Flow_{dry}}$, and
ppm(T) is the predicted output concentration in parts per million by volume.

In this regard, the method is somewhat like that proposed in ASTM-D4178 [13]. In ASTM D4178, a gas stream is dried with a mole sieve dryer and the flow is split into two streams. The method uses another molecular sieve as a saturating agent, with its temperature controlled at the ice point. Two rotameters are used to vary the dilution ratio between the two streams.

One of the difficulties in testing a moisture generation device is that the concentration in the output is commonly measured by a laboratory or online analyzer. This is problematic in that it inherently assumes that the analyzer is calibrated against some known standard or standards. Anecdotal evidence that moisture calibration standards based on compressed gas cylinders abound in the industry, and are also mentioned in the literature [8,9,10]. However, one method to demonstrate the validity of EQN 2 is to compare the output of the moisture generator as a function of pressure. A moisture generator suitable for a 0 to 50 ppm range was used in the lab at

a temperature ranging from 22 to 23.5°C, while the input pressure was varied from 100 to 800 psi. A plot of measured output concentration versus the inverse of pressure is shown in Figure 4, showing excellent agreement with the predicted behavior. There results clearly indicate the desired performance, "one would dial in the moisture content they would want to generate", has been achieved over a range of concentrations spanning about 1 decade.

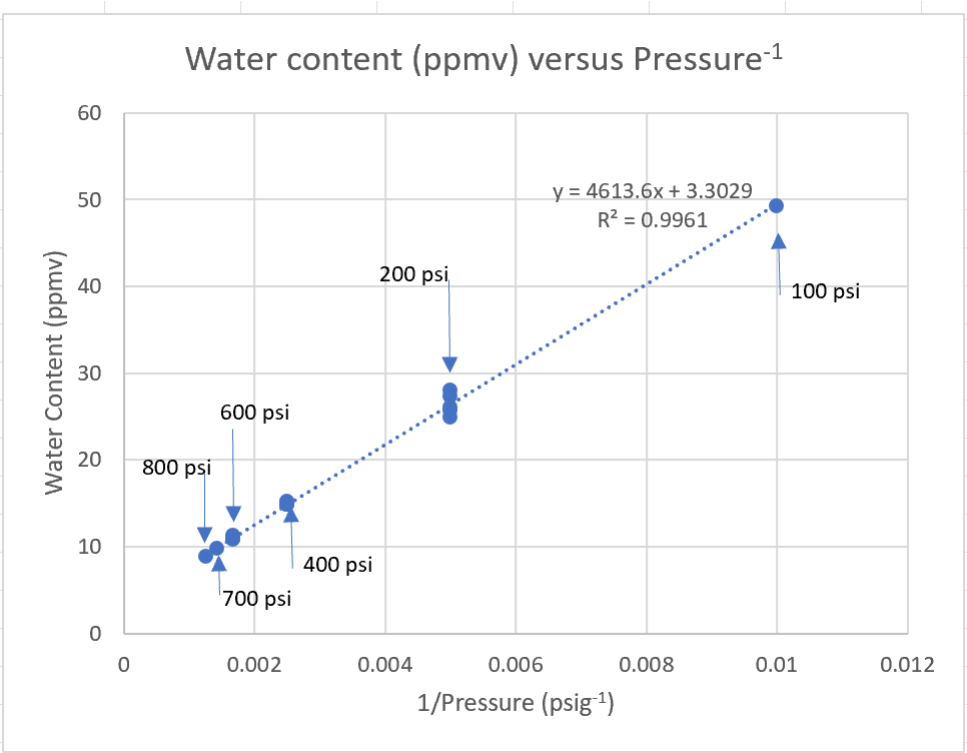

FIGURE 4. MEASURED RESPONSE VERSUS 1/PRESSURE

FAST RESPONSE TIME

An additional desired property of a field moisture validation device is that "and within minutes the generator would be able to provide the gas at the desired temperature and pressure". This requirement is also met with the present design. A set of tests were performed using the Process Insights Tiger Optics Spark™ moisture analyzer and a moisture generator block. These cavity ringdown spectrometers have very fast response time and detection limits in the ppb range. As well, they come factory calibrated.

A gas run was performed where the pressure was varied, and the system response measured over time. The data clearly indicated that the system responded quickly with changes in pressure, with the data points shown in Figure 5 being one minute apart. The system can show a T90 response time on the order of two minutes, with full stabilization in less than five minutes. The figure below does perhaps indicate some small amounts of hysteresis which are under further investigation.

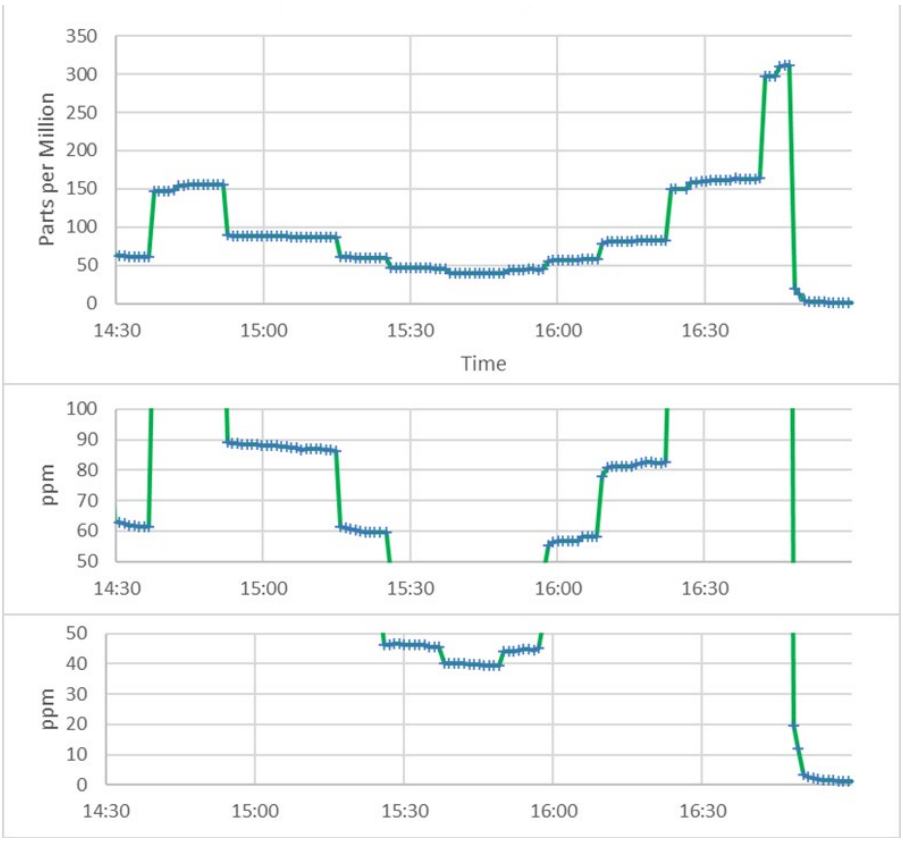

FIGURE 5. MOISTURE VALIDATION BLOCK RESPONSE TIME

The data in Figure 5 was obtained while operating the block at room temperature (21+/- 0.5°C) in the lab. The accuracy during the gas run was typically within+/- 5 ppm versus the factory calibrated analyzer is shown in Figure 6.

ACCURACY OF THE MOISTURE VALIDATION BLOCK

A final desired characteristic is that the accuracy of the validation standard would match the accuracy requirements of the application. It remains questionable whether this requirement is fully achieved with the moisture validation block. In an ideal world, the calibration standard would be of higher accuracy and precision than the analyzer in question. In this regard we separate calibration from verification or validation. The US EPA [14] defines calibration as:

> *"The comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustment".*

Verification, on the other hand, may encompass a set of tests to determine if the instrument is operating within specification or if a calibration is recommended. As per reference [14]:

"When the term "calibration" is used …, it is assumed that a multi-point verification is initially performed and the operator has concluded that calibration (i.e., adjustment) is necessary".

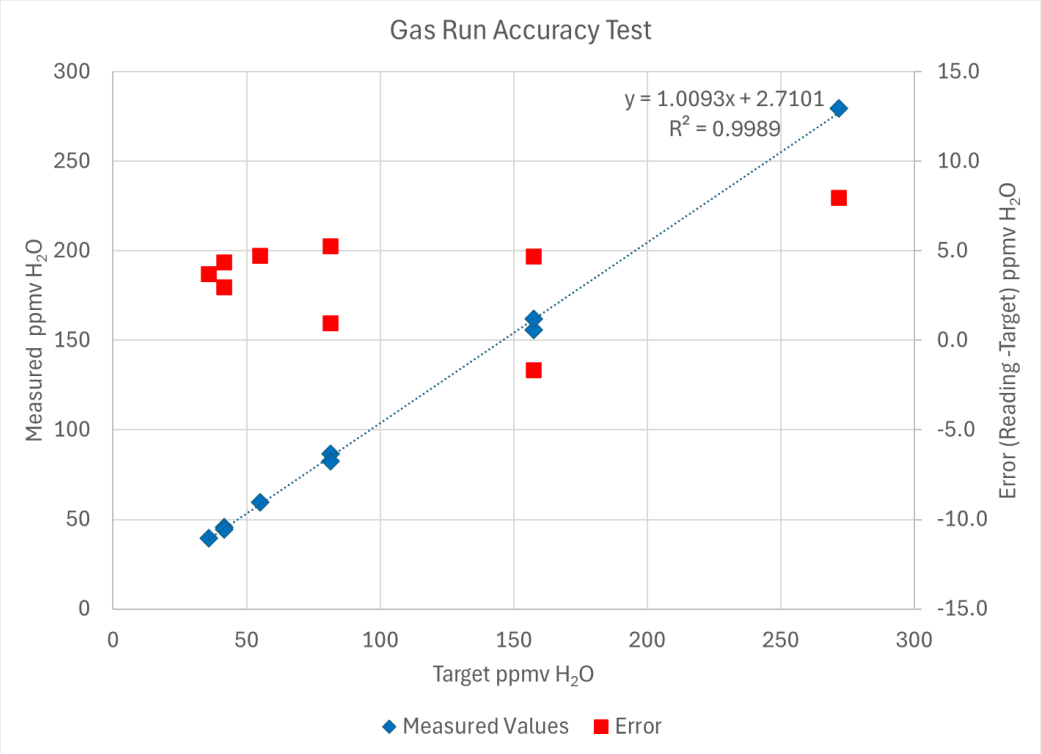

FIGURE 6. ACCURACY DURING RESPONSE TIME TEST

Ideally performance verification or validation will include a multipoint verification which tests the linear range of the device in question. With trace moisture analyzers, this has proven very difficult to do in the field since often at best only a single calibration cylinder is available. EPA QC documents state:

"Multi-point verifications generally consist of a zero and 4 upscale points. Traditionally, the upscale points encompassed the full-scale operating range of the instrument".

The EPA further goes on to state when validation checks and possible recalibration should be considered, and these include:

- upon initial installation,
- following physical relocation,
- after any significant repairs or service that might affect its calibration,
- following an interruption in operation (e.g., power failure) of more than a few days,
- upon any indication of analyzer malfunction or calibration drift, and
- at some prescribed routine interval (e.g., annually).

Data review, verification and validation are techniques used to accept, reject, or qualify data in an objective and consistent manner. Verification can be defined as confirmation, through

provision of objective evidence, that specified requirements have been fulfilled. Validation can be defined as confirmation, through provision of objective evidence, that the requirements for a specific intended use are fulfilled.

The absolute accuracy of the moisture generator block is probably not sufficient to provide field calibration of a high precision device. The accuracy of the moisture content produced is dependant on several factors including:

- The applicability of the ideal gas law at the operating pressures and temperatures,
- The accuracy of the temperature and pressure measurements,
- The accuracy of the dilution ratio, and
- The applicability of the Arden Buck equation at the operating conditions, including differing gases.

To highlight this, a typical error analysis is shown for a 0 to 200 ppm moisture generator in Figure 7. In this figure, it is assumed the pressure can be read to within +/- 10 psi, the temperature to within 0.25°C, and that the dilution ratio is known to be 17 +/- 0.01. Under such conditions the predicted water content will likely be quite accurate when operated at high pressures (< 5% error for pressures > 400 psig). The error increases asymptotically as the pressure gets low since it is assumed that there is +/- 10 psi error in the measurement, so at 50 psig there is 20% error in the pressure measurement. If higher accuracy is necessary, it would be advisable to replace the mechanical gauges with pressure and temperature transducers.

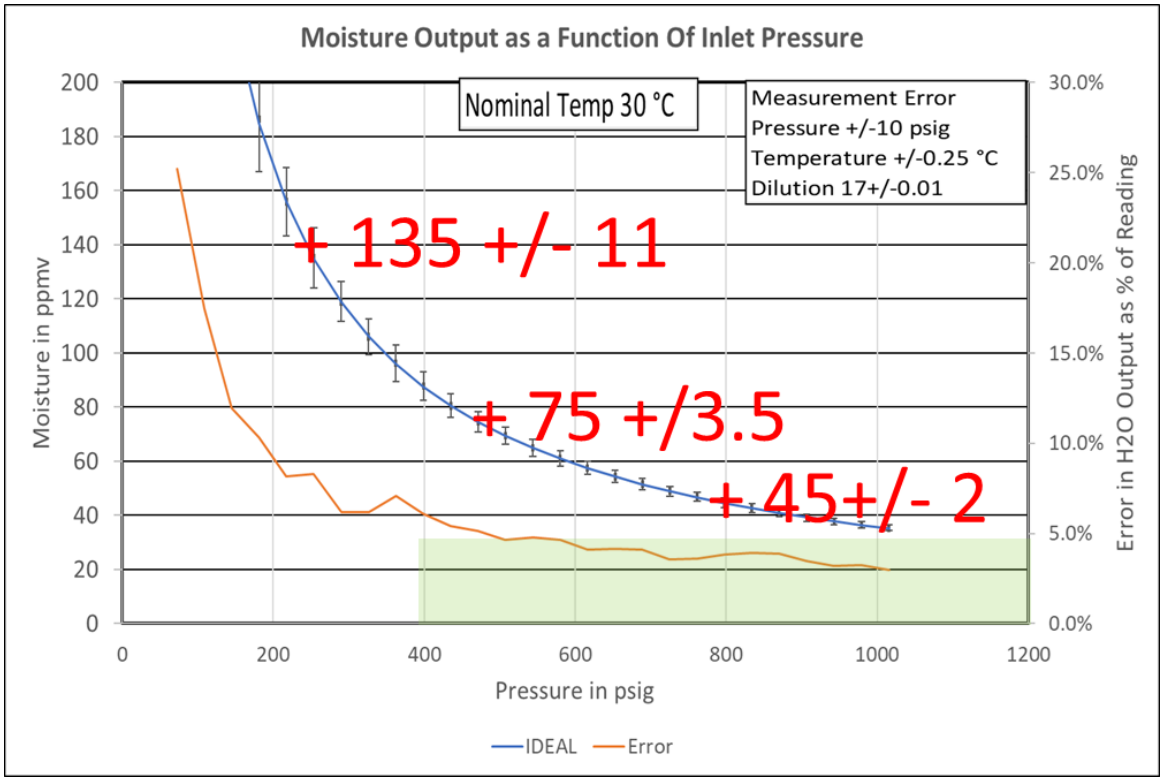

FIGURE 7. PREDICTED ACCURACY OF MOISTURE GENERATOR BLOCK

Whether this accuracy is sufficient for field recalibration of a moisture analyzer is really a decision to be made by the end users. However, given the repeatability of the moisture generator, the fact that the output concentration can be predicted based on simple measurements and first principal assumptions about vapor pressure, and that it enables a multipoint validation in the field, there is little doubt that this tool will prove valuable in validating the performance, linearity, and repeatability of moisture analyzers in the field.

A low range moisture generator block was tested using an AMETEK 3050 quartz crystal microbalance, and the predicted values based on Equations 1 and 2 compared to measured results (see Figure 8). The analyzer has an internal moisture calibration based on a permeation tube device and the calibration was done at 40 parts per million. The response time was somewhat slower than might be expected, which is perhaps a result of the flow having to go through the flame arrestors which may have caused ore adsorption/desorption effects. Despite the relatively high calibration range, the agreement between the predicted results and the measured results is quite good with typical error in the range of 5-10% of reading.

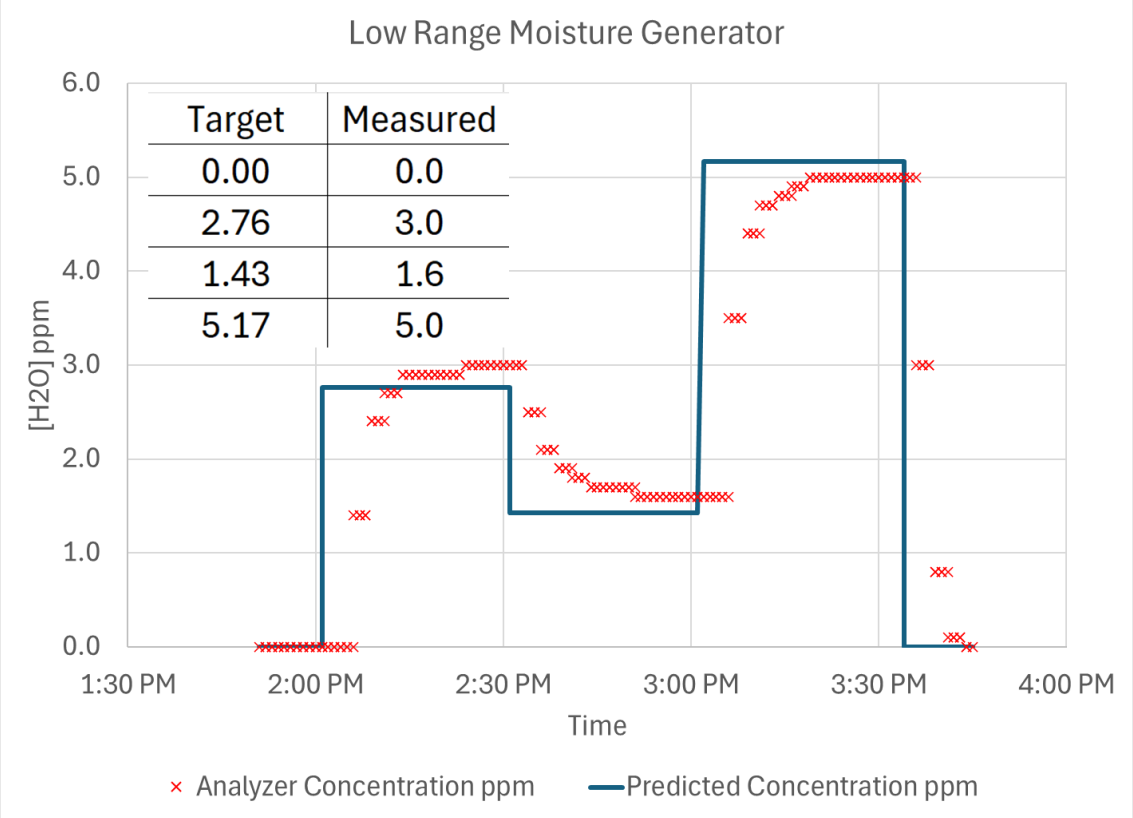

FIGURE 8. EXPERIMENTAL TESTING OF LOW RANGE MOISTURE GENERATOR

CONCLUSIONS

Historically, it has proven very difficult to verify, validate and/or calibrate moisture analyzers in the field. This issue was described in detail in the work of Sparages and Gerritse, where they outlined what the key requirements for an ideal field validation standard would be. An all-mechanical moisture generator has been developed with the intent of meeting those requirements and allowing for reliable testing of moisture analyzers in industrial environments without having to send them back to the factory and without depending on unreliable calibration standards or secondary analyzers. Work to date indicates this is a very viable means for moisture verification in natural gas pipelines, petrochemical facilities, and other industrial applications.

These systems have been installed in the field in the natural gas transmission industry and are proving a valuable means to validated moisture analyzers in real world applications. They have been employed both as transportable spot validation devices and have been integrated into full measurement systems and buildings. A low range (0 to 10 ppm) version of the generator has been launched as a new product.

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