The Development of an Automated Calibration System for Tunable Laser Based Moisture Analyzers

Ken Soleyn
GE Sensing
Billerica, MA 01821 USA

Narge Sparages
GE Sensing
Billerica, MA 01821 USA

KEYWORDS

Moisture Measurement, Natural Gas, Tunable Laser Absorption Spectroscopy, Calibration.

ABSTRACT

Natural gas is an important fuel that has global significance as an abundant and clean energy source. Dehydration is required to prevent corrosion and freezing during transportation and to meet contractual BTU requirements. Accurate instruments are required to measure this concentration of moisture. Calibration plays a vital role in the measurement integrity. GE Sensing has developed an automated moisture calibration system applicable to tunable laser hygrometers. The basic measurement technology and the calibration process are reviewed.

INTRODUCTION

Tunable Laser Diode Absorption (TDLAS) hygrometers require an automated and highly repeatable calibration process to provide accurate and continuous measurement of the moisture concentration in natural gas. Ideally the calibration system should be traceable to National Institute of Standards and Technology (NIST).

Nitrogen is used as the carrier gas for the water vapor in the calibration system. The relationship between water vapor and the raw signal of the TDLAS hygrometer is linear. A system capable of recording the raw signal from each EUT (Equipment Under Test), reference data from the moisture generator, pressure, temperature and reference data from a check standard was developed. The system is capable of writing back calibration data to each instrument's on board memory via a digital interface. The data is used in calibration tables to provide direct readings in moisture engineering units including absolute humidity (mass/volume), volume ratio (volume/volume) and dew point temperature. Once the calibration is completed each instrument is verified against the standard in the calibration system. The instruments are then calibrated against a moisture generator that utilizes natural gas as the background gas.

The system produces calibration reports and stores the data on a secured sever for archival purposes, trend analysis and comparisons against future calibrations.

PRINCIPLE OF TDLAS HYGROMETER

The fundamental principle of the TDLAS hygrometer is based on the Beer-Lambert Law (Equation 1) that states that at a given light frequency the analyte (in this case water) absorbs a fraction of photonic energy entering the medium. By comparing the light intensity entering the medium to the light intensity of light leaving the medium, it is possible to determine the water vapor volume ratio.

$$A = \ln\left(\frac{I_0}{I}\right) = SLN \tag{1}$$

A = Absorbance
I_o = Incident light intensity
I = Light intensity transmitted through sample gas
S = Absorption coefficient*
L = Absorption path length
N = Concentration of water vapor (directly related to the ratio of the partial pressure of water and the total pressure)

*The absorption coefficient is a constant for a specific gas composition at a given pressure and temperature.

Dalton's Law states that in a gas mixture, each component gas exerts a "partial pressure" directly proportional to its mole fraction or volume ($P_T = P_1 + P_2 + \ldots + P_n$).

At specific frequencies any water present will absorb light energy while at other frequencies the water is practically transparent. A diode laser is swept through a narrow frequency band in the near infrared spectrum. The laser is also modulated at high frequency. By measuring the laser light intensity with a photodetector it is possible to provide direct measurement of the partial pressure of water by correlation of laser light loss to the incident light. The second harmonic signal, referred to as the 2F signal, reduces the signal to a peak centered on a specific frequency (see Figure 2). The magnitude of the 2F peak height is related to the partial pressure of water. The partial pressure of water divided by the total pressure and multiplied by 10^6 yields ppm_v (parts per million by volume).

The laser light is transmitted through an optical window made of proprietary glass and is reflected off a gold plated mirror then returned through the window where it is measured with a photodetector.

With TDLAS it is possible to measure the light intensity of a non-absorbing frequency with respect to water and utilize that frequency to establish a zero baseline. This eliminates the need for a zero purge gas. Since the light signal at the absorbing frequency is constantly compared to the non-absorbing frequency the system is also very forgiving with respect to the accumulation of contaminants. Preliminary testing indicates that up to 80% of the light signal can be lost and the system will still maintain its range and accuracy specifications.

At a given concentration, the absolute signal for water will differ with changes in pressure due to pressure broadening. As the pressure increases, the interaction between water molecules increases, as does the collision frequency between the molecules, increasing the broadening. Temperature also has a broadening effect but the magnitude is much less than pressure. Variance in the composition of the sample gas will also change the absolute signal due to interactions between the component gas molecules. Thus the absolute signal is a function of state. In this instrument the pressure and temperature of the sample gas is simultaneously measured and these parameters are used in dynamic compensation based on empirical data.

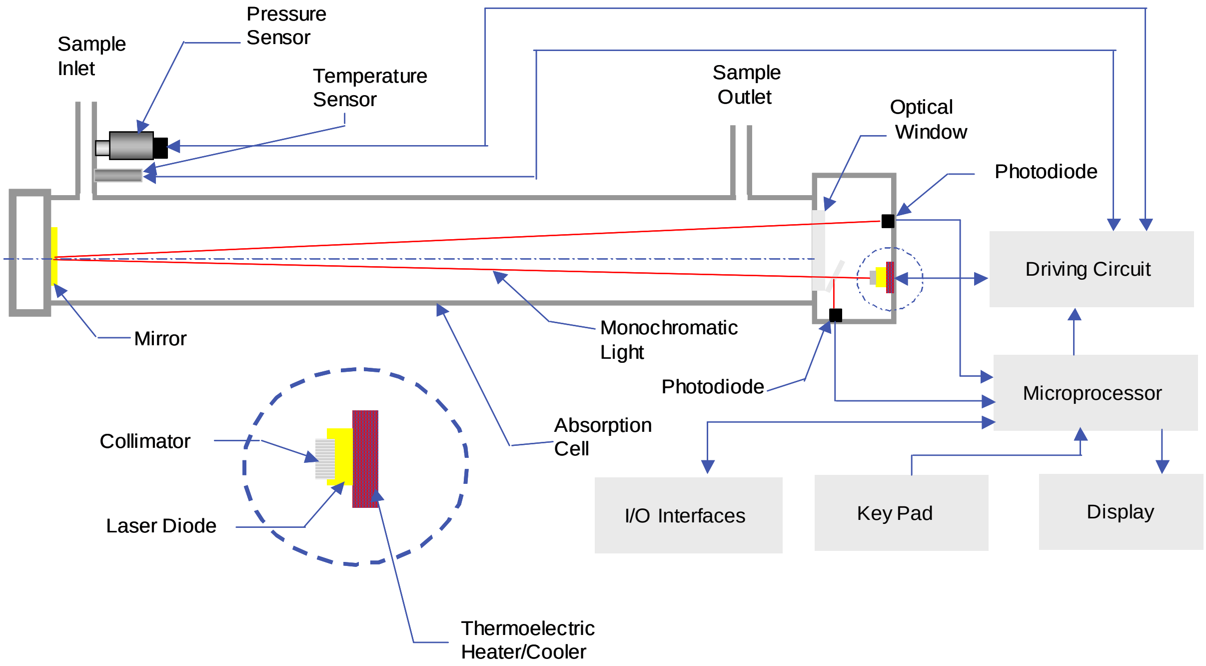

FIGURE 1. SCHEMATIC OF TDLAS HYGROMETER

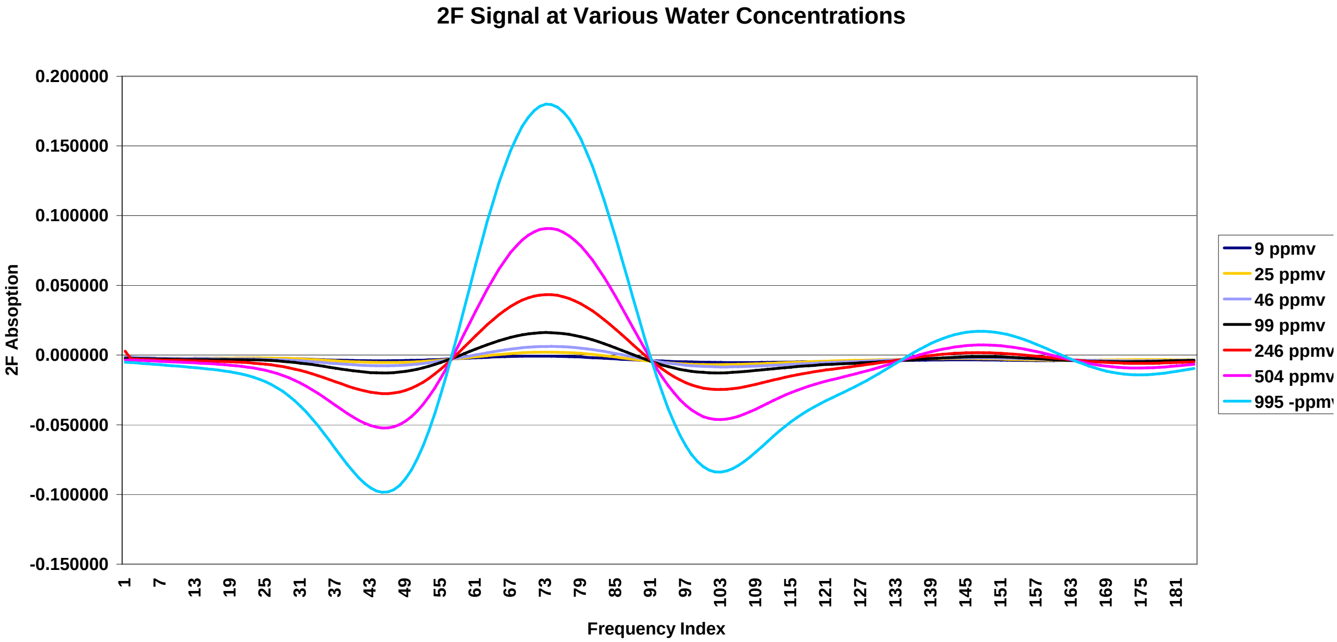

FIGURE 2. 2F ABSORPTION SIGNALS AT VARIOUS MOISTURE CONCENTRATIONS

MOISTURE GENERATOR AND STANDARD

A two-pressure two-temperature moisture generator produces an outflow of gas at a stable dew/frost point temperature. It is based on saturating the carrier gas with water vapor over ice at a controlled temperature and pressure. The gas exiting the saturator has a dew point temperature equal to the saturation temperature. Equation 2 is used to compute the saturation vapor pressure over ice. When the gas is expanded the water vapor pressure decreases proportionally to the decrease in pressure.

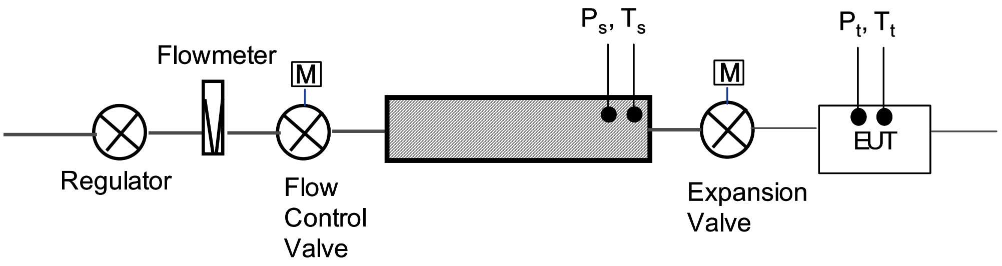

FIGURE 3. SCHEMATIC OF TWO-PRESSURE TWO-TEMPERATURE GENERATOR

$$e_s = (6.1115)(\mathrm{EXP}\frac{22.452T}{272.55 + T}) \quad (2)$$

e_s = Saturation water vapor pressure over ice (mBar)
T =Temperature (°C)

$$e_t = e_s(\frac{P_t K_t}{P_s K_s}) \quad (3)$$

e_t = Water vapor pressure at test point
e_s = Saturation water vapor pressure
P_t = Absolute pressure at test point
P_s = Absolute pressure in saturator
K_s = Enhancement factor*
*Enhancement factors are related to the absolute pressure and used to correct for the non-ideal behavior of water vapor.

$$ppm_v = \frac{e_t}{P_t} \bullet 10^6 \quad (4)$$

ppm_v = Parts per million by volume
e_t = Water vapor pressure at test point
P_t = Pressure at test point

The moisture generator is an intrinsic standard as defined by the National Conference of Standards Laboratories (NCSL), RISP-5 *Two-Pressure, Two-Temperature Humidity Generator* January 2002. The generator has a stated accuracy of ±0.1ºC dew point. A more detailed uncertainty analysis is given on Table I.

TABLE I. UNCERTAININTY OF THE MOISTURE GENERATOR IN DEW POINT

	Uncertainty	Unit	Dew Point °C
Saturation Vapor Pressure	0.071	KPa	0.010
EUT Pressure	0.071	KPa	0.010
Saturation Temperature	0.046	°C	0.046
Saturator Efficiency	0.004	°C	0.004
Vapor Pressure Calculation	0.004	°C	0.004
Enhancement Factor	0.004	°C	0.004
Absorption/Desorption	0.004	°C	0.004
Combined Uncertainty (RSS)			0.049
Expanded Uncertainity (95% Confidence)			0.098

The moisture concentration of the outflow of the generator is also confirmed and constantly monitored by a chilled mirror reference hygrometer. The chilled mirror provides direct NIST traceability. It thermoelectrically controls the heat removed from a metal mirror to provide an equilibrium temperature ensuring that the mass of condensate is constant. The feedback control consists of an infrared emitter and photodetetctor. A Platinum Resistance Thermometer (PRT) measures the temperature of the mirror. When an equilibrium temperature is attained the temperature of the mirror is by definition equal to the dew/frost point temperature. The chilled mirror has a stated accuracy of ±0.15ºC dew point. While the instrument is not used directly in the calibration it is a useful "check standard" and provides assurance that the set point is achieved and maintained at a stable value.

A Druck DPI-142 Barometric Pressure Indicator measures pressure. The pressure reference utilizes a Silicon resonant pressure sensor, which is NIST traceable. The barometer has a stated accuracy of ±0.02% F.S.

CALIBRATION SYSTEM

The system is controlled by a computer system that utilizes National Instruments LabView to control the set point of the generator. The computer system has a digital interface with the dew point generator, equipment under test, reference chilled mirror and pressure meter via their respective serial interface. The data points are continuously monitored and periodically collected by this system.

The system first runs a nitrogen purge, supplied from liquid nitrogen boil off. Although the theoretical frost point of the nitrogen at this point is equivalent to the boiling point of nitrogen (-198°C), due to trace moisture ingress from various sources (transportation from the gas supplier, tank refilling, etc.), its frost point temperature is approximately -85°C at 85 – 95 psig (5.9 to 6.6 bar) pressure. The pressure of the nitrogen is reduced to near atmospheric pressure, which further reduces the frost point to approximately -95°C (<50 parts per billion).

Cold drawn stainless steel tubing and stainless steel fittings are used exclusively throughout the system. Water vapor, even in trace concentrations, takes time to desorb from wetted surfaces. While stainless steel has excellent characteristics, a 12-hour purge is applied to fully dry out the system and EUT.

The set point of the generator is stepped through the profile listed in Table II. At each dwell point the calibration system monitors the stability and will not advance to the next step until stability is achieved. For each step the EUT 2F peak height, the moisture generator's dew point and pressure are recorded. The partial pressure of water is determined from the dew point and pressure per equation 4.

After six calibration points are run, a table of the 2F peak height at the water absorbing frequency vs. water vapor pressure is written into each analyzer's memory. The calibration points are rerun to verify the units.

TABLE II. CALIBRATION STEPS

Step	Description	Dew Point (°C)	Volume Ratio (ppm_v)*
1	Pre-Cal Purge	N/A	N/A
2	EUT Soak @ -65.5	-65.5	5
3	EUT Soak @ -50	-50.0	40
4	EUT Soak @ -35	-35.0	220
5	EUT Soak @ -25	-25.0	624
6	EUT Soak @ -15	-15.0	1631
7	EUT Soak @ -2.3	-2.3	5000
8	Post Cal Purge	N/A	N/A
9	Cal Ver @ -65.5	-65.5	5
10	Cal Ver @ -50	-50.0	40
11	Cal Ver @ -35	-35.0	220
12	Cal Ver @ -25	-25.0	624
13	Cal Ver @ -15	-15.0	1631
14	Cal Ver @ -2.3	-2.3	5000

TABLE III. UNCERTAINITY OF THE MOISTURE GENERATOR

Dew Point °C	ppmv at 1 Std Atm	U1	U2	Uc	SL
-65.5	5	0.08	0.0006	0.08	4.00
-50	39	0.48	0.0044	0.48	4.00
-35	222	2.42	0.0251	2.42	4.44
-25	628	6.30	0.071	6.30	12.56
-15	1639	15.19	0.1853	15.19	32.78
-2.3	5006	42.11	0.5659	42.11	100.12
U1 = Error Due to Dew Point Generator in ppmv					
U2 = Error due to pressure standard in ppmv					
Uc = Combined uncertainity. 95% Confidence					
SL = Specification Limit					

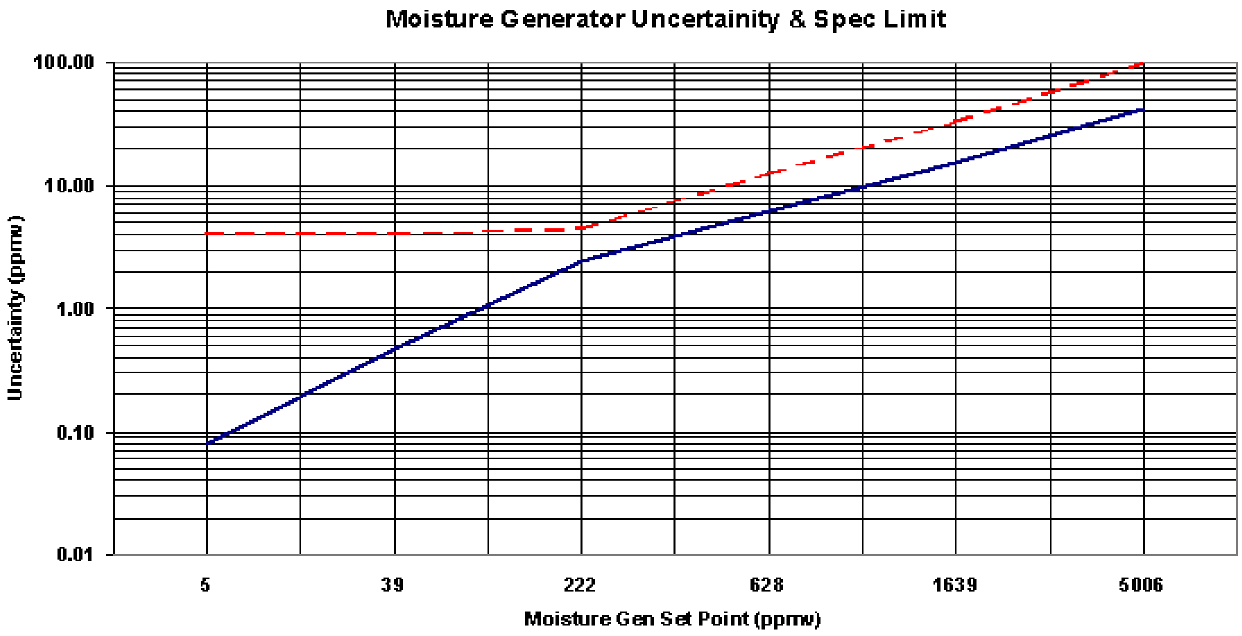

FIGURE 4. UNCERTAINITY OF THE MOISTURE GENERATOR VS. SPECIFICATION LIMIT

TABLE III. UNCERTAINITY OF THE MOISTURE GENERATOR

Dew Point °C	ppmv at 1 Std Atm	U1	U2	Uc	SL
-65.5	5	0.08	0.0006	0.08	4.00
-50	39	0.48	0.0044	0.48	4.00
-35	222	2.42	0.0251	2.42	4.44
-25	628	6.30	0.071	6.30	12.56
-15	1639	15.19	0.1853	15.19	32.78
-2.3	5006	42.11	0.5659	42.11	100.12
U1 = Error Due to Dew Point Generator in ppmv					
U2 = Error due to pressure standard in ppmv					
Uc = Combined uncertainity. 95% Confidence					
SL = Specification Limit					

The units are then run through a two-point calibration using 90% methane (balance nitrogen). The moisture generator for the methane calibration is a custom made unit consisting of ports for gas bottles. Mass flow controllers are used to blend nitrogen flowing through a temperature-controlled saturator with the dry methane to produce the desired moisture concentration. The outflow of the system is monitored by a NIST traceable chilled mirror hygrometer.

The gas matrix influences TDLAS analyzers. This is because the background gas influences absorption characteristics. Various background gases interact with water to vary the absorption characteristics. Calibration in 90% methane insures the instrument will maintain its accuracy specification in natural gas compositions ranging from 70-100%. The instrument can be applied to gas compositions outside this range by calibration in custom blends.

RESULTS

The calibration system was commissioned in September 2009. Below is data from five units. The absolute value of the deviation from the standard at each set point was plotted against the accuracy specification limits.

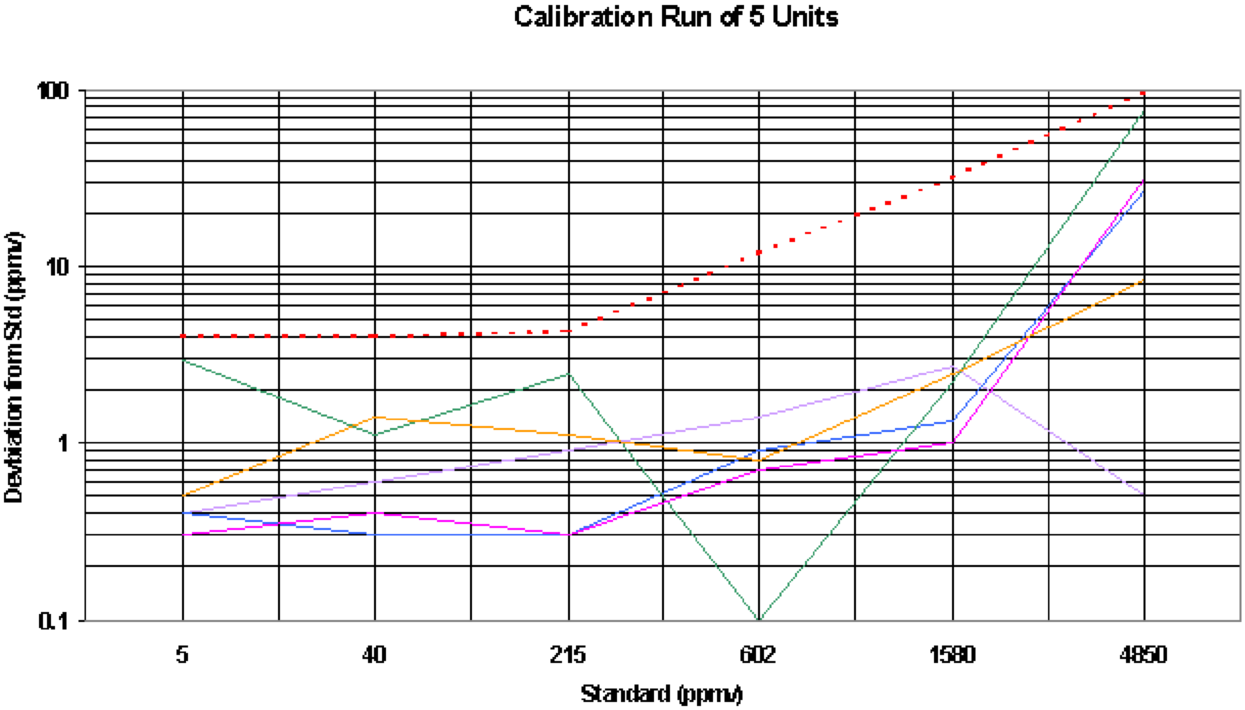

FIGURE 5. CALIBRATION DATA FROM FIVE UNITS

CONCLUSIONS

Moisture calibrations are challenging due to the hygroscopic nature of the water molecule. This calibration system and technique address both this reality and the challenge of calibrating an instrument with a hazardous species, methane, as the background gas.

The technique allows for calibration for moisture in an inert and commonly utilized background gas, nitrogen. The instrument is then characterized for use in natural gas of varying compositions.

The calibration system's high level of automation results in a high level of accuracy and repeatability. The data storage, analysis performed, and the built-in check standards provide historical reference integrity. The system design and firmware are documented and reproducible, enabling replication at global sites as demand arises.

AKNOWLEDGEMENTS

The authors would like to acknowledge John Poole, Sr. Design Engineer and Leslie Peters, Systems Engineer of GE Sensing & Inspection Technologies for their valued input and discussions.

REFERENCES

Mucha, J.A., Barbalas, L.C., *"Infrared Diode Laser Determination of Trace Moisture in Gases"*, Moisture and Humidity 1985 Measurement and Control in Science and Industry. Proceedings of the 1985 International Symposium on Moisture and Humidity, Washington D.C. April 15-18, 1985. Instrument Society of America Research Triangle Park, North Carolina. ISBN 0-87664-865-0

Two-Pressure, Two-Temperature Humidity Generator Working Group of the National Conference of Standards Laboratories International. "*Two-Pressure, Two-Temperature Humidity Generator. Recommended Intrinsic/Derived Standards Practice. RISP-5*". January 2002. ISBN 1-58464-036-7. Boulder, Colorado 80301.

Soleyn, Ken, "*An Intercomparison of a Two-Pressure/Two-Temperature Frost Point Generator and Chilled Mirror Condensation Hygrometer*", Proceedings of the 2006 NCSL International Workshop and Symposium Nashville, TN USA.

Buck, A.L., *"New Equations for Computing Vapor Pressure and Enhancement Factor"*, Journal of Applied Metrology, Vol. 12, Issue 20, 1527-1532, 1981

Huang, Peter. "*Determining Uncertainties of Relative Humidity, Dew/Frost-Point Temperature, and Mixing Ratio in a Humidity Standard, Generator"*. Process Measurements Division. National Institute of Standards and Technology, Gaithersburg, Maryland 20899.