An Intercomparison of a Two-Pressure/Two-Temperature Frost Point Generator and Chilled Mirror Condensation Hygrometer

Speaker/Author: Ken Soleyn, Product Manager Metrology
GE Sensing
1100 Technology Park Drive
Billerica, MA 01821 USA
Tel: 978-437-1000
Email: ken.soleyn@ge.com

Abstract
Dew point sensors are used in industry to detect the presence of small levels of water vapor. Critical measurements in compressed air, breathing air, metals processing, battery making, plastics processing, natural gas and petrochemical production require water vapor levels to remain in the 1– 6000 PPMv (parts per million by volume) or equivalent –76 to 0ºC T_d (frost point temperature) range. Two temperature/two pressure generators are used to supply a test gas for calibrating and validating a wide variety of sensors and instruments. The system produces a controlled dew or frost point temperature (T_d) by saturating air or other test gas at a depressed temperature in a pressure controlled vessel. The gas exiting the saturator is then depressurized and warmed to the test conditions. Chilled mirror hygrometers fundamentally measure dew or frost point temperature by controlling the temperature of metal mirror to an equilibrium point by the use of feedback from an infrared emitter and detector pair such that the mass of condensed mass of water (frost) is constant. A design of experiment and review of the expected uncertainty of the system will be presented.

Background
The system will be used by GE Sensing to automate the calibration of chilled mirror hygrometers by comparing a master hygrometer against chilled mirrors under test. Since the chilled mirrors and dew/frost point generator are equipped with a digital interface (RS-232), the calibration system will be automated. National Instruments data acquisition hardware and Labview software to control the generator collect and reduce the data. A similar system is currently in use by GE Sensing for the calibration of trace moisture instruments that utilize aluminum oxide sensors. The commissioning of the automated chilled mirror calibration system was planned for January of 2006 however delays in installing the hardware and the set up of the data acquisition system precluded providing test data for this paper. The system is now planned to be fully functional by September 2006. The material however will be useful be useful for metrologist and technicians responsible for performing calibrations in the +10 to -80°C dew/frost point range.

Equipment
A Thunder Scientific Model 3900 Frost Point Generator will be used. Compressed dry nitrogen is piped to the generator at 90 PSIG (7 Bar) via stainless steel tubing. The nitrogen is dried by "cryogenic knockout" and is said to be at a pressure frost point (T_d) of -90°C. The generator is

illustrated schematically in figure 1. Regulated compressed nitrogen is directed through the saturator, which is a heat exchanger surround by temperature-controlled fluid. While nitrogen is used, the test gas can also be compressed air per ISO-8573-1.1.1. specifications.

The saturator contains several planes of pure ice or water that create intimate contact with the gas that flows through it. As the gas thermally equilibrates, it becomes saturated with water vapor. The saturation temperature (T_s) and saturation pressure (P_s) are measured at the point of final saturation. The saturation pressure is then reduced to test pressure (P_t) and the conditioned gas is admitted to chilled mirror hygrometer. The final pressure (P_t) and temperature, (T_t), of the gas is measured within or just after the chilled mirror. The gas flows through the Chilled Mirror at a regulated flow rate of 1 liter per minute (LPM).

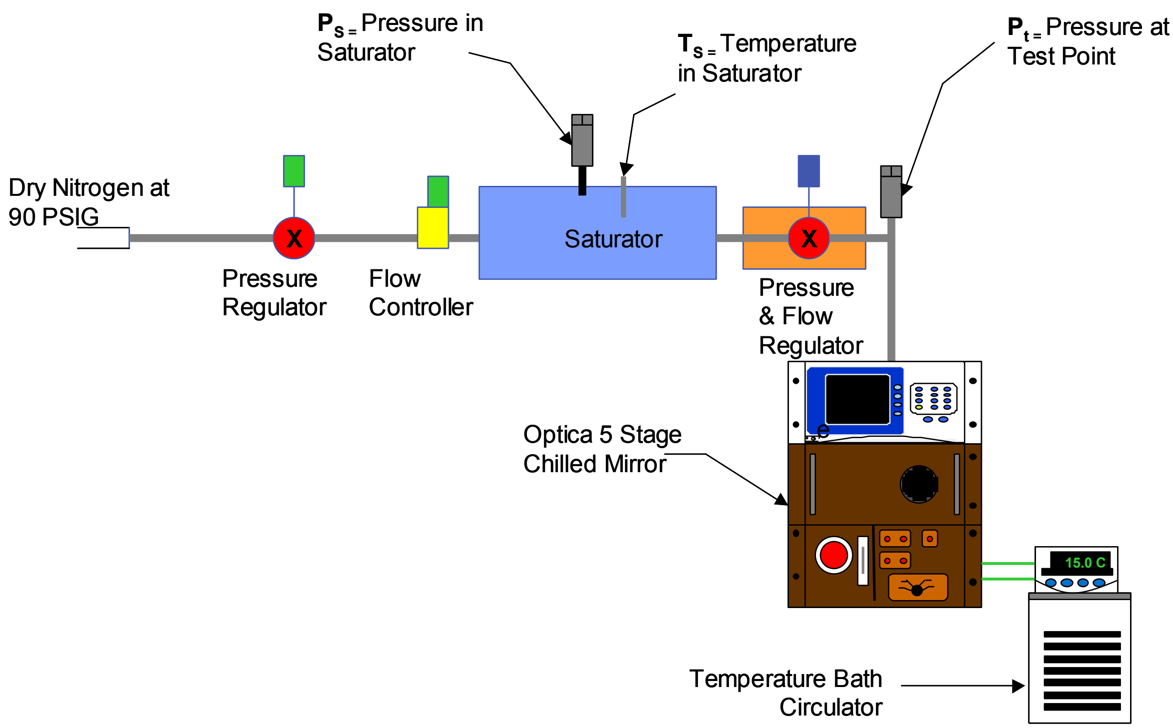

Figure 1. Schematic of dew/frost point generator.

A GE Optica/1311-XR chilled mirror hygrometer with auxiliary water bath/circulator is used to measure the dew/frost point temperature (T_d). The sensor is depicted schematically in figure 2. The chilled mirror fundamentally measures dew/frost temperature by utilizing a 5-stage solid-state thermoelectric heat pump to cool a platinum mirror. A GaAs emitter produces infrared light that is aligned at a 45° angle to the normal. When the mirror is dry, virtually 100% of the reflected signal is received by a photodetector which at a complimentary 45° angle. When the mirror is cooled to or below the dew/frost point, water or ice condenses on the surface which causes the reflected light to scatter, thereby decreasing the signal received by the photodetector.

The signal from the photodetector is used for feedback in a digital control system that regulates the heat flux from the mirror such that the water or ice condensed on the mirror is at a constant mass.

When a mass of the condensate and the surrounding gas are at equilibrium, the temperature of the mirror is by definition equal to the dew or frost point temperature. A precision four-wire platinum resistance temperature detector (PRTD) is imbedded in a copper block thermally bonded the base of the mirror and used to measure the mirror's temperature. Since the PRTD is very stable and hermetically sealed, the chilled mirror sensor is characterized by having negligible long-term drift and producing high repeatability.

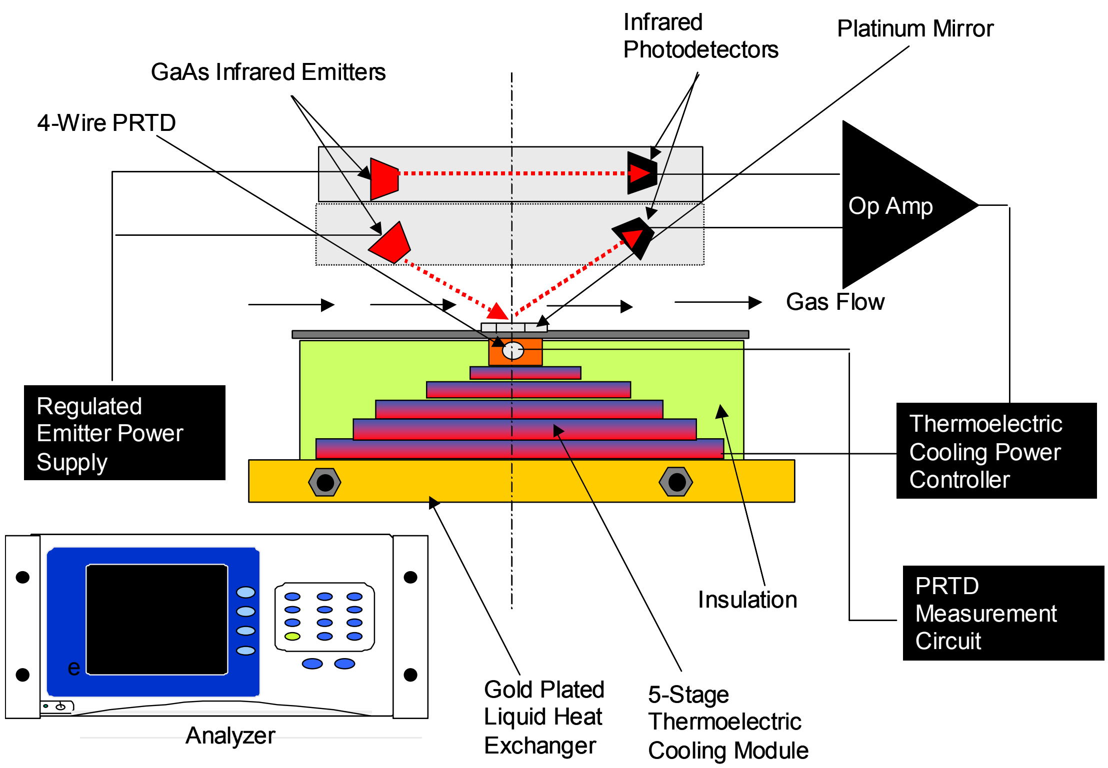

Figure 2. Schematic of chilled mirror hygrometer.

Stainless steel is used for all of the sampling components. Stainless steel is used because of its low moisture adsorption.

Dew/Frost Point Generation

The dew/frost point generator produces a stable water vapor concentration by saturating air or nitrogen at a depressed temperature and known pressure. The gas is then heated to the test requirement (nominally 25°C) and expanded to the test pressure (nominally 1 atmosphere). The saturation water vapor pressure over water can be determined by equation (1) and the saturation water vapor pressure over ice is determined by equation (2).

(1) $$e_s(\text{water}) = 6.1121\exp\left(\frac{17.502t}{240.97 + t}\right)$$

(2) $$e_s(\text{ice}) = 6.1115\exp\left(\frac{22.452t}{272.55 + t}\right)$$

$\mathbf{e_s}$ = Saturation Water Vapor Pressure
t = Temperature in °C
Ref: A.L. Buck. *Equations for Water Vapor Pressure at Saturation*

If the air or gas from the saturator is warmed without the addition or loss of any water vapor and the pressure is held constant, the gas stream will be unsaturated and the water vapor pressure will remain the same. If an ideal test gas is expanded then the change in water vapor pressure will be proportional to the change in pressure by the following relationship (3).

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

$\mathbf{e_t}$ = Water vapor pressure of test gas
$\mathbf{e_s}$ = water vapor pressure of gas in saturator
$\mathbf{P_t}$= Absolute pressure of test gas
$\mathbf{P_s}$ = Absolute pressure of gas in saturator

At higher pressures a binary mixture of air or nitrogen with water vapor deviates from an ideal gas by holding more water vapor than predicted by the saturation water vapor formulas. To compensate, enhancement factors are applied.

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

$\mathbf{K_s}$ = Enhancement Factor based on saturator pressure and state (ice or water)
$\mathbf{K_t}$ = Enhancement Fator based on test pressure and state (ice or water)

(5) $$K_w = 1.0007 + 3.46\text{x}10^{-6}P$$

(6) $$K_i = 1.0003 + 4.18\text{x}10^{-6}P$$

$\mathbf{K_w}$ = Enhancement factor for saturation water vapor pressure over water
$\mathbf{K_i}$ = Enhancement factor for saturation water vapor pressure over ice
P = Absolute Pressure in millibars

The question often arises as to which set of vapor pressure equations should be used for a particular test condition; water vapor pressure over water or ice? Very often the answer is determine by iterations. The water vapor pressures at saturation equations referenced above are the A.L Buck equations. The author recommends a review of the Hardy equations, as these are incorporated into the Thunder model 3900 Generator.

The test dew or frost point temperature (T_d) can be back calculated from the water vapor pressure as follows:

$$(7) \quad T_{dew} = \frac{240.97 \cdot \ln\left(e / 6.1121\right)}{17.502 - \ln\left(e / 6.1121\right)}$$

$$(8) \quad T_{frost} = \frac{272.55 \cdot \ln\left(e / 6.1115\right)}{22.452 - \ln\left(e / 6.1115\right)}$$

The partial pressure of water vapor as delivered by the generator can be expressed as.

$$(9) \quad e_t = \frac{f(P_t)}{f(P_s, T_s)}$$

The ratio of a function of the pressure and temperature in the saturator to the function of the pressure at the test is equal to the vapor pressure. The dew or frost point in turn is a function of the vapor pressure.

Uncertainty Estimation

Under conditions where the saturator pressure is less than 345 KPa and the test pressure is at atmospheric pressure, the uncertainty of the frost point generator is estimated in table 1.

Table 1. Uncertainty estimate of frost point generator.

Model 3900 2T2P			
	U	Unit	°C Td
Saturation Vapor Pressure	0.071	Kpa	0.010
Test Pressure	0.071	KPa	0.010
Saturation Temperature	0.046	°C	0.046
Saturator Efficiency	0.004	°C	0.004
Vapor Pressure (Calc)	0.004	°C	0.004
Enhancement Factor	0.004		0.004
Adsorption/Desorption	0.004	°C Td	0.004
Combined U (RSS)			0.049
Expanded U K = 2			0.098

The uncertainity of the chilled mirror hygrometers is estimated in table 2.

Table 2. Uncertainty estimate of chilled mirror hygrometer.

	Chilled Mirror	
	Td >-35°C	Td<-35°C
NIST Transfer Standard	0.040	0.100
Correlation to NIST Std	0.020	0.020
PRTD	0.020	0.020
Control Stability	0.050	0.050
A/D 16 Bit	0.003	0.003
Combined U (RSS)	0.070	0.115
Expanded U K = 2	0.140	0.231

The chilled mirror calibrated directly against the GE Sensing primary chilled mirror, which in turn is calibrated against the NIST two-pressure system. Two expanded uncertainties for the NIST generator are given: 0.04°C T_d for frost points less than -35°C and 0.1°C T_d for dew/frost points greater than -35°C T_d.

It is therefore estimated that the agreement between the frost point generator and chilled mirror will be 0.27°C T_d with 95% confidence for frost points less than -35°C and 0.25°C T_d for dew/frost points greater than -35°C T_d

Saturate at Low Temperature or High Pressure?

The frost point generator has the ability to saturate the test gas at either a lower temperature and low pressure or a higher temperature and pressure to yield the same dew or frost point. Table 3 provides calculated settings from +10 to –80°C T_d in 10ºC T_d increments at 1, 3 & 7 atmospheres respectively. Two values are given for 0°C T_d as both the water vapor pressure over water and ice are used.

Table 3. Calculated saturator temperature for 1, 3, & 7 atmospheres.

Frost Point (°C)	Dew Point (°C)	Saturation Temperature °C	Saturation WVP (mBar)	Saturation Pressure (mBar)	K Factor for Sat Pressure	Test Pressure (mBar)	K Factor for Test Pressure	Saturation VP at Test (mBar)
	9.98	10.00	12.275981	1013.35	1.004206	1013.35	1.003193	12.263593
	-0.01	0.00	6.112100	1013.35	1.004206	1013.35	1.003193	6.105932
-0.01		0.00	6.111500	1013.35	1.004206	1013.35	1.003193	6.105333
-10.00		-10.00	2.598725	1013.35	1.004536	1013.35	1.004536	2.598725
-20.00		-20.00	1.032670	1013.35	1.004536	1013.35	1.004536	1.032670
-30.00		-30.00	0.380290	1013.35	1.004536	1013.35	1.004536	0.380290
-40.00		-40.00	0.128515	1013.35	1.004536	1013.35	1.004536	0.128515
-50.00		-50.00	0.039396	1013.35	1.004536	1013.35	1.004536	0.039396
-60.00		-60.00	0.010805	1013.35	1.004536	1013.35	1.004536	0.010805
-70.00		-70.00	0.002608	1013.35	1.004536	1013.35	1.004536	0.002608
-80.00		-80.00	0.000543	1013.35	1.004536	1013.35	1.004536	0.000543
	10.00	27.69	37.119598	3039.75	1.011218	1013.35	1.003193	12.276221
	0.00	16.26	18.481508	3039.75	1.011218	1013.35	1.003193	6.112218
0.00		16.26	18.479540	3039.75	1.011218	1013.35	1.003193	6.111567
-10.00		3.09	7.861286	3039.75	1.013006	1013.35	1.004536	2.598774
-20.00		-7.91	3.123885	3039.75	1.013006	1013.35	1.004536	1.032690
-30.00		-18.87	1.150398	3039.75	1.013006	1013.35	1.004536	0.380297
-40.00		-29.79	0.388766	3039.75	1.013006	1013.35	1.004536	0.128518
-50.00		-40.66	0.119176	3039.75	1.013006	1013.35	1.004536	0.039397
-60.00		-51.50	0.032686	3039.75	1.013006	1013.35	1.004536	0.010805
-70.00		-62.30	0.007890	3039.75	1.013006	1013.35	1.004536	0.002608
-80.00		-73.05	0.001643	3039.75	1.013006	1013.35	1.004536	0.000543
	10.00	43.28	87.813474	7092.75	1.025241	1013.35	1.003193	12.276215
	0.00	30.52	43.721376	7092.75	1.025241	1013.35	1.003193	6.112194
0.00		30.52	43.715836	7092.75	1.025241	1013.35	1.003193	6.111420
-10.00		14.25	18.649611	7092.75	1.029948	1013.35	1.004536	2.598752
-20.00		2.36	7.410917	7092.75	1.029948	1013.35	1.004536	1.032683
-30.00		-9.45	2.729107	7092.75	1.029948	1013.35	1.004536	0.380291
-40.00		-21.17	0.922287	7092.75	1.029948	1013.35	1.004536	0.128517
-50.00		-32.82	0.282727	7092.75	1.029948	1013.35	1.004536	0.039397
-60.00		-44.38	0.077543	7092.75	1.029948	1013.35	1.004536	0.010805
-70.00		-55.86	0.018718	7092.75	1.029948	1013.35	1.004536	0.002608
-80.00		-67.27	0.003898	7092.75	1.029948	1013.35	1.004536	0.000543

The most significant source of uncertainity is from the saturator temperature. Figure 3 shows that the uncertainty from saturating at elevated pressure and expanding the test gas to atmospheric pressure. While operating the generator at an elevated saturator pressure does not appear to provide a significant contribution the uncertainity of the dew/frost point generated. The advantage of higher pressure saturation is that the saturator temperature is increased to yield the same dew/frost points and this might result in faster stability time.

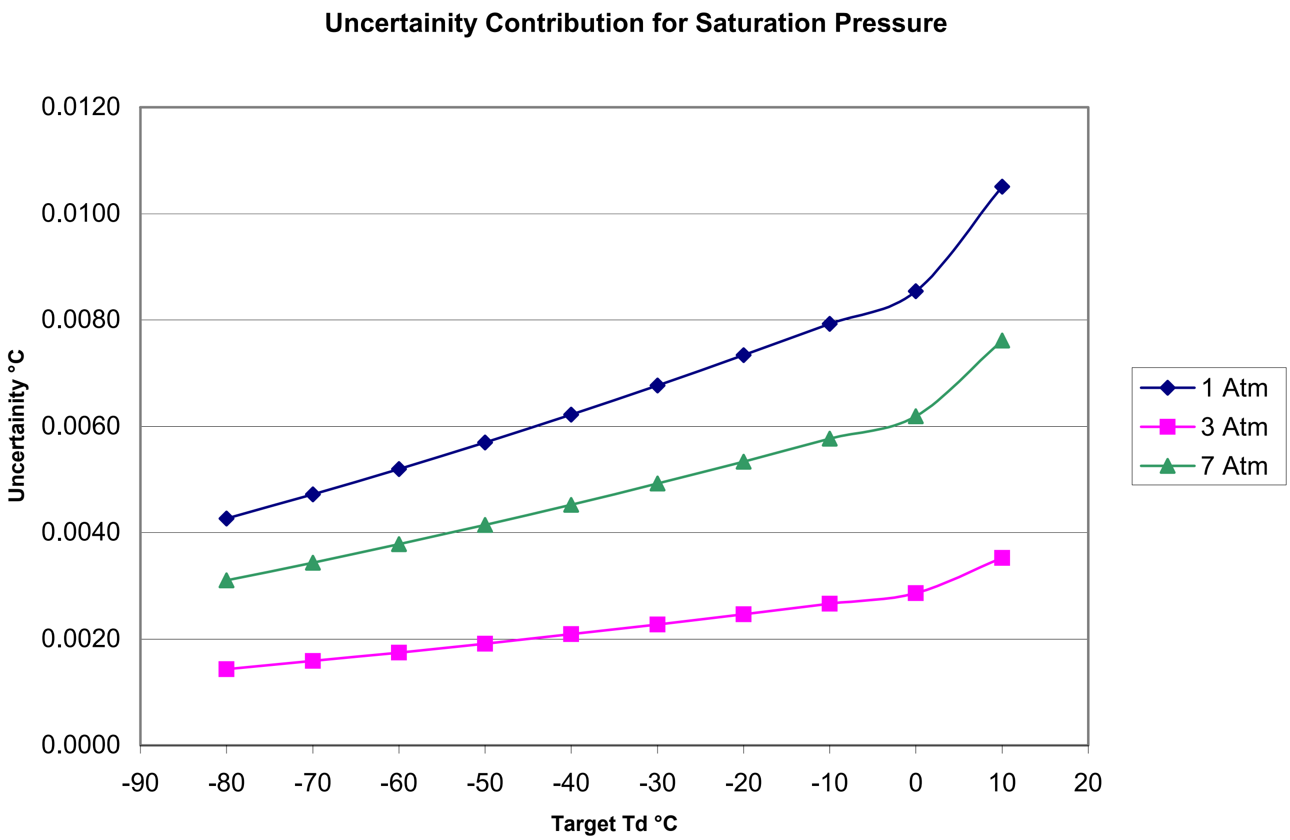

Figure 3. Uncertainty contribution at 1, 3 & 7 atmospheres.

Procedure

Recommended best practices for frost point calibrations is to go to the driest point first and sequentially work upwards. The nature of calibrating intruments trace water vapor concentrations (below -60°C T_d) is that practically all sensors and sampling components (tubing, valves, fittings etc.) have an affinity for water vapor. In general smooth clean surfaces have less affinity for water vapor adsorption than oxidized or rough surfaces. The greater the surface area the more places water molecules adhere to and the more time and energy it will take to desorb the last remaining traces of water. Electropolished stainless steel with VCR fittings is generally recommended for this type of calibration.

The chilled mirrors sensors under test as well as the standard are cleaned by manual methods and the Optica's self-cleaning and electronic optical balancing cycle is also run prior to each calibration run.

When the saturator is controlled to cryogenic temperatures (below –60°C), sufficient time is required for stabilization. Recording the readings and looking for a "flat line" response will determine the actual dwell time at each set point. To measure dew point less than -60º C T_d, it takes approximately 2-6 hours for the condensate on the chilled mirror to achieve a stable mass equilibrium with the test gas. In addition, the mirror must first be cooled approximately 10°C below the frost point to first acquire a frost layer. At the stable equilibrium state, water vapor condensed as ice sublimates to gas and is reformed at a constant rate maintaining a stable mass on the mirror. Past experience with aluminum oxide trace probe calibration has determined the dwell times as shown in table 4.

Table 4. Dwell times for test points.

Target Td °C	Dwell Time (Hours)
-80	24
-70	6
, -60	4
-50	2.5
-40	1
-30	1
-20	1
-10	1
0	1
10	1

Frost Point Seeding

One school of metrologist has employed "frost point seeding" techniques to accelerate formation of the frost layer. This is typically accomplished by setting up a bypass line with with a porous tube typically made of sintered steel or Nafion. The test gas is switched to the bypass line for a few very brief intervals (<1 sec). Frost seeding can improve the response time remarkably, often by magnitudes of up to 5X or better. Another school of metrologist feel artificially seeding the mirror might skew measurements to produce readings that are higher than actual. In test trials between "frost point seeding" and "natural frost formation" at frost points less than -70°C, agreement to 0.2°C T_d after approximately four hours has been observed. After 15-30 minutes however "frost point seeded" method yields a readings that is approximately 0.5 to 1.5°C T_d higher than the readings some 4 hours later. Part of the offset seen in the frost point seeding method may also due to frost point generator and the desorption of the sample tubing and wetted components. Since the data acquisition will be automated, frost point seeding will be employed. The instruments are considered to be stable when the readings do not vary by more than 0.05°C T_d over a 20-minute span.

Conclusions

1. The uncertainty of the chilled mirror is based on an unbroken chain of traceability to the NIST humidity standard. The NIST humidity standard is traceable to mass standards. The NIST humidity standard has international recognition to other National Metrological Institutes (NMIs).

2. The uncertainty of the generator is derived from an unbroken chain of traceability to NIST traceable pressure and temperature standards. The pressure standard in turn is traceable to an unbroken chain of mass and length (area) standards.

3. Experimental data is be required to validate the calculations and estimations.

4. A study should be conducted to compare the uncertainty of chilled mirror readings at various dew point utilizing “frost point” seeding vs. “natural frost formation”.

5. A study should be conducted to compare the uncertainity of chilled mirror readings at various frost/dew points generated at increasing saturator temperature and increasing the saturator pressure.

6. Based on the published and calculated uncertainties of the frost /dew point generator and chilled mirror agreement of 0.25-0.27ºC Td is expected from –80 to +35°C.

7. The A.L Buck equations for saturation vapor pressure were used for simplicity. Hardy’s equations, which are ITS-90 derivations of the Hylan-Wexler equations, are utilized by the generator. The generator is equipped with a computer that provides iterative calculations of the water vapor pressure and dew/frost point in real-time.

References

1. 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.

2. Thunder Scientific. *Dew/Frost Point Uncertainty Analysis of the Model 3900 Two-Temperature, Two-Pressure Low Humidity Generator.* Document number TSC3900. Albuquerque, NM.

3. Hardy, Robert. *ITS-90* Formulations *for Vapor Pressure, Frost Point Temperature, Dew Point Temperature and Enhancement Factors in the Range –100 to +100°C.* Proceedings of the Third International Symposium on Humidity & Moisture, Teddington, London, England, April 1998

4. Hasegawa, S. and Little, J. *The NBS Two–Pressure Humidity Generator, Mark 2, S.* National Bureau of Standards, (U.S.), 81A (1), 81–88 (Jan.–Feb. 1977). Gaithersburg, Maryland 20899

5. Huang, Peter. *NIST Calibration Services for Humidity Measurement*, NISTIR 4677–A (Superseding NISTIR 4677, Oct. 1991). National Institute of Standards and Technology, Gaithersburg, Maryland 20899

6. 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

7. Soleyn, Ken. *The Theory and Operation of Chilled Mirror Hygrometers for Humidity Calibration.* Cal Lab, The International Journal of Metrology. July, August, September 2002. San Deigo, California.

8. Wiederhold Peter, R. *Water Vapor Measurement: Methods and Instrumentation*. ISBN 0-8247-9319-6. 1997. Marcel Dekker, New York, NY.