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AUTOMATED CONTINUOUS-FLOW GRAVIMETRIC HYGROMETER AS A PRIMARY HUMIDITY STANDARD

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Abstract: A new primary gravimetric hygrometer has been completed at the National Institute of Standards and This apparatus determines the Technology (NIST). humidity in a steadily flowing gas stream by first separating the water from the carrier gas using desiccants and afterwards independently measuring the water mass and carrier gas mass. These combined measurements yield the mixing ratio r (the ratio of the measured water mass to the measured dry-gas mass) averaged over the collection time interval. The new gravimetric hygrometer design employs an automated, continuous-flow gas-collection and watercollection system for determination of the mixing ratio. The gas-collection system monitors the rate of gas flow by interferometrically measuring the displacement of pistons in two, precision-bore glass tubes. The mass of the water is determined by weighing the system's water-collection tubes before and after passage of the total amount of gas through the hygrometer. System automation enables gas collection at flow rates up to 3 L min⁻¹ for time periods limited only by the patience of the operator, thus enabling the measurement of lower humidity levels than the previous NIST gravimetric hygrometer. The total expanded relative uncertainty (k=2) of the new gravimetric hygrometer is approximately 0.1 % for atmospheric-pressure dew or frost-point temperatures higher than $-35 \,^{\circ}\text{C}$ ($r = 250 \,\mu\text{g/g}$). Below this frost-point temperature the total expanded relative uncertainty gradually increases to approximately 1 % at -55 °C (r = 13 µg/g). The hygrometer has measured the humidity of air and N_2 samples produced by the NIST Two-Pressure Generator and the NIST Low Frost-Point Generator, respectively. Based on measured parameters, the humidity of the generator output streams can be predicted from the thermodynamic properties of water and ice. Differences between the predicted humidity and the humidity measured by the gravimetric hygrometer were less than the combined uncertainties of the respective generator and hygrometer for almost all measurements.

Key words: humidity, hygrometer, gravimetric, primary standard, mixing ratio

1. INTRODUCTION

At the National Institute of Standards and Technology (NIST), humidity calibrations are performed using thermodynamic generators as humidity sources. One source is the Two-Pressure Generator [1], which produces dew/frost points of -64 °C to 24 °C at atmospheric pressures. A second source is the Low Frost Point Generator [2], which produces dew/frost points of -100 °C to -5 °C. In addition to these two sources, a newly-constructed Hybrid Generator (which combines a new Two-Pressure Generator with a wet-gas/dry-gas dilution system) has been constructed and is expected to become operational in 2007 [3].

Although these generators have well-characterized uncertainties [4-5], NIST considers it important to use a primary gravimetric hygrometer [6-7] for validating the performance of these generators. Such a hygrometer measures humidity by way of a mixing ratio r defined by

$$r = m_w / m_o \tag{1}$$

where m_w is the mass of the water in the gas and m_g is the mass of the dry gas. The gravimetric hygrometer separates the water from the gas, enabling mass measurement of each.

The technique of gravimetric hygrometry has been known for over a century [6-7], but because of its cumbersome nature it is generally used only in national standards laboratories [8-9]. The first gravimetric hygrometer at NIST was developed in 1948 by Wexler [10]. In 1963 Wexler and Hyland [11] built a more sophisticated gravimetric hygrometer to be used as the standard hygrometer for NIST, and it was used until 1988. In this paper we give a brief description of the design and construction of a new gravimetric hygrometer which utilizes an automated continuous-flow gas-collection system. The convenience of this system allows for considerably longer gas-collection times, thereby enabling measurement of much lower humidity values.

2. HYGROMETER DESIGN

The gravimetric hygrometer is designed so that the water in the gas passing through is trapped in desiccant-filled watercollection tubes. After passing through these tubes the gas enters the gas-collection system. The mass of the water is determined from the increase in mass of the water-collection tubes after the humid gas passes through the tubes. The mass of the dry gas that has filled a gas-collection tube is determined by measuring the volume and density of the gas.

2.1. The Water Collection System

The water-collection system consists of three desiccantfilled tubes connected in series. A diagram of one of these tubes is shown in Fig. 1. The tube has custom-designed flanges soldered to its ends, allowing them to be connected to the hygrometer manifold and sealed with fluoroelastomer o-rings. The flange design also allows caps to be placed on the top and bottom of the tube. The tubes and caps are made of aluminum plated with electroless nickel for corrosion resistance. The caps are sealed through fluoroelastomer o-ring compression using a custom-made sealing tool which can turn and lift/lower a stainless-steel horizontal rod attached to the cap. Sealing/removal of the caps can be accomplished while the tube is either connected or disconnected to the manifold.

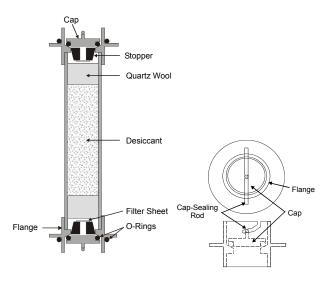


Figure 1 – Diagram of water-collection tubes, including detail of cap-sealing rod and flange slot.

Filter sheet of pore size 4 μ m is used to keep the desiccant from escaping the water collection tubes as gas passes through them. This sheet is attached to rubber stoppers with holes drilled through their axes. Two of these stoppers rest snugly inside the tube, one near each end. As additional protection, a small wad of quartz wool is placed between the desiccant and filter.

The first tube that the gas passes through contains anhydrous $Mg(ClO_4)_2$, and the second and third tubes contain anhydrous P_2O_5 . The first tube is intended to collect the vast majority of the water and the second and third tubes are intended to collect the remaining amount. The unfilled water collection tubes (including rubber stopper and quartz wool) weigh approximately 149 g. The packing of the tubes with desiccant is loose to ensure uniform gas flow through them and to prevent excessive flow impedance. The $Mg(ClO_4)_2$ has an approximate mass of 30 g and the P_2O_5 in each tube has an approximate mass of 8 g.

An important assumption made by the gravimetric hygrometer is that all the water in the gas passing through the water-collection tubes is trapped by the desiccant. This

assumption was tested in an experiment where moist N₂ with a dew point of approximately 18 °C was passed through the collection tubes. The residual humidity in the gas was then measured with a commercial chilled-mirror hygrometer. The flow rates used ranged from 0.5 L min⁻¹ to 3 L min⁻¹. The resulting atmospheric-pressure dew point varied from -100 °C to -86 °C and was found to be independent of flow rate over the range used. From these control tests, we estimate the upper limit for moisture escaping the water collection tubes to be -86 °C (a mixing ratio of 0.13 µg/g). Based on this upper limit we currently estimate the gravimetric hygrometer's standard uncertainty component from moisture escape to be 7.5×10^{-2} µg/g, though this estimate may decrease after further studies are made.

2.2. Water Mass Measurement

Before the mass measurements, the flange o-rings are removed from the tubes. At the beginning of a collection of measurements, the ambient pressure is measured with an aneroid barometer in the room, the ambient temperature is measured by an industrial platinum resistance thermometer, and the relative humidity is measured by a commercial polymer-film capacitance hygrometer; these quantities are used for calculating the buoyancy correction for the mass measurements.

The tubes are weighed using a commercial electronic balance. The closed chamber of the balance has been modified to accommodate the size of the tubes. The mass of each tube is determined using the single substitution method [12]. For each measurement cycle in this method, the tube is first weighed on the balance. Afterwards, a standard mass of approximately the same mass is weighed. Finally, a combination of the standard mass and a 2-g second standard mass (called the sensitivity mass) is weighed. When calculating the tube mass, the latter two measurements provide offset and linear-sensitivity corrections to the value indicated on the balance display. With the currently used balance and weighing method, the repeatability of a mass measurement for one tube is typically 60 μ g.

Because a water-collection tube contains gas as well as solid materials, changes in gas mass must be accounted for when calculating the collected mass of water from the measured change in collection-tube mass. The mass of the water collected is then

$$m_{\rm w} = m_{\rm t}^{\rm f} - m_{\rm t}^{\rm i} - \Delta m_{\rm g} = m_{\rm t}^{\rm f} - m_{\rm t}^{\rm i} - (V_{\rm g}^{\rm f} \rho_{\rm g}^{\rm f} - V_{\rm g}^{\rm i} \rho_{\rm g}^{\rm i}) \qquad (2)$$

where m_t^i and m_t^f are the initial and final masses of the tube as determined by the balance measurements, respectively, and Δm_g is the change of the gas mass in the tube. The values V_g^i and V_g^f are the initial and final volumes of gas in the tube, respectively and ρ_g^i and ρ_g^f are the initial and final gas densities in the tube, respectively.

The gas volume in each collection tube, V_g , is obtained using the known value of the original gas volume inside that tube (before any water has been collected), V_g° . For the first tube, a correction is made to this volume to account for the decrease in gas volume due to the increase in desiccant volume resulting from water absorption. [11] The value of V_g° for each collection tube was measured once and it is assumed to be the same value each time the tube is refilled. The value of V_g° for tube 1 was measured to be $V_g^{\circ} = (55 \pm 2) \text{ cm}^3$, and that for tubes 2 and 3 was measured to be $(61 \pm 2) \text{ cm}^3$.

To obtain ρ_{g}^{i} , temperature and pressure measurements are made of the gas in the collection tubes before their initial weighing. The tubes are first placed in the manifold and flushed with the operating gas. The measurements are made using the gas collection system described in section 2.3. Similarly, ρ_{g}^{f} is determined from temperature and pressure measurements made at the end of the gas collection process.

It is important to determine the maximum amount of water that can be trapped in the first water collection tube before significant amounts of water escape it. This was determined by measuring the ratio of water collected in the second collection tube Δm_2 to that in the first tube Δm_1 as a function of Δm_1 . Humid gas was passed through the gravimetric hygrometer for short periods of time, after which the collection tubes were removed from the manifold, weighed, and replaced on the manifold. The process was then repeated a number of times. The results of these measurements showed that the ratio $\Delta m_2 / \Delta m_1$ is below 0.01 for $\Delta m_1 \leq 8$ g. It is now an operational protocol that the first desiccant tube is emptied and replaced with fresh dry desiccant once the tube has accumulated 8 g of water.

2.3. The Dry Gas Collection System

The centerpiece of the dry-gas collection system is a pair of precision-bore glass vertical cylinders (prover tubes) of length 0.927 m and diameter 0.1437 m. Pistons made of acetal are located inside them, as shown in Fig. 2. The bottom of the prover tubes is closed by an acetal cap. The cap contains a groove in which a fluoroelastomer o-ring is seated, providing an airtight seal. The areas of these prover tubes were measured by the NIST machine shop using a coordinate measuring machine and determined to be uniform over their length to within 4×10^{-6} m². The diameters of the pistons are 2×10^{-5} m smaller than that of the prover tubes. Mercury "o-rings" of diameter 4 mm provide an airtight seal between the pistons and cylinders, yet still allow the pistons to move vertically. The o-rings hold together by the surface tension of the mercury. As each piston moves along its cylinder, the mercury rotates about its axis to maintain the seal.

For each prover tube, a computer-automated laser interferometry system measures the position of the piston relative to its starting position with an uncertainty of 1.6×10^{-7} m. As a prover tube collects gas, the piston rises from its initial position until it reaches a final position about

60 cm higher, at which point the volume of gas collected between the initial position and final position (approximately 9.44×10^{-3} m³) is calculated. Pressure and temperature measurements are then performed to determine the density of gas, which along with the volume yields the mass of the gas collected by the prover tube. Subsequently the gas is purged from the prover tubes by opening a pneumatic valve to the room and allowing the piston to fall to its initial position, allowing another collection of gas at a later time.

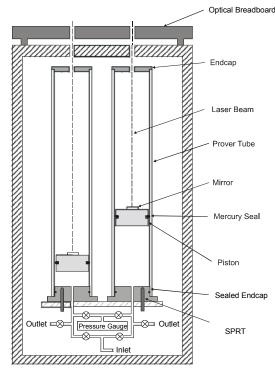


Figure 2-The dry-gas collection system

The manifold connects the incoming gas to the water collection tubes and dry-gas collection system. The tubes of the manifold are made of electro-polished stainless steel to insure cleanliness and minimal water adsorption on the tube walls. During normal gas/water collection the gas is directed sequentially through the water collection tubes and then through the dry-gas collection system. The manifold has been specially constructed to allow convenient insertion and removal of the water-collection tubes.

There are two dead space volumes in the gas collection system, one for each prover tube. These are the volumes between the bottom of each prover piston at its lowest position and the value separating the manifold from the prover tubes. The values of the dead space volumes have been determined for proper accounting of the gas mass collected. The dead space volumes are relevant for the dry gas collection because of possible pressure changes from the beginning of the gas collection cycle (piston at bottom of prover tube) to the end (piston at top). These pressure changes lead to changes in the mass of the gas in the prover tube's dead space. These changes are accounted for when

calculating the mass of gas collected during one piston cycle.

By controlling a set of pneumatic valves, the computer coordinates the gas collection of both prover tubes so that gas is collected by the system at a steady rate. It accomplishes this by opening up the gas flow to one prover tube once the other tube has reached a position close to its final position. After a brief period while both tubes collect gas, the valve to the filled prover tube is closed and all gas collection is performed by the other tube. As the pressure measurements are made in the filled tube and the gas is purged, the collection continues in the other tube. This data collection technique allows a maximum rate of 4 L min⁻¹ for gas flow through the gravimetric hygrometer.

The gas collection system employs a commercial laser interferometer, based on a frequency-stabilized He-Ne laser, to determine the prover piston displacement. The laser uses the Zeeman effect (by way of a magnet surrounding the laser tube) so that the laser beam has two orthogonal polarizations that have slightly different frequencies f_1 and f_2 . The laser is mounted on an optical breadboard positioned over the two prover tubes. A beam-splitter separates the laser light into two beams, one for each tube. A mirror situated immediately above each prover tube directs a beam vertically down along the axis of the prover tube. An optically separating beamsplitter beneath the top mirror reflects the part of the beam with frequency f_2 coming from the top mirror to a side retroreflector; this retroreflector mirror reflects the f_2 beam back to the beamsplitter. The part of the beam with frequency f_1 is transmitted through the beamsplitter to a retroreflector mirror on top of the piston in the prover tube. When the piston moves, the Doppler Effect shifts the frequency of the f_1 beam to give it frequency $f_1 + \Delta f_1$, where the sign of Δf_1 depends on the direction of the piston movement. The f_1 beam is then recombined with the f_2 beam, producing a photodetector signal with a modulation frequency of $f_2 - (f_1 + \Delta f_1)$. This signal is then compared with a reference signal coming from the laser with frequency $f_2 - f_1$. A pulse converter then uses these signals to obtain Δf_1 and provides a pulse for every piston displacement equivalent to $\lambda/4$. Counting these pulses determines the total displacement of the piston with a standard uncertainty of 4.7×10^{-3} cm as it collects dry gas, which includes uncertainties due to piston instability.

The volume of gas collected in the prover tube by the displaced piston, $V_{\rm p}$, is then

$$V_{\rm p} = \int_{z_1}^{z_2} A(z) dz \tag{3}$$

Here, z_1 and z_2 are the vertical positions of the piston at the beginning (bottom) and end (top) of the gas collection cycle, and A(z) is the cross-sectional area of the prover tube at vertical position z.

The pressure underneath the piston inside both prover tubes is measured by a single commercial quartz Bourdon gauge, with an estimated standard uncertainty of 13 Pa. Stainless steel tubes connect the Bourdon gauge to both prover tubes at a connection point at their bottom. Two pneumatic valves select which tube is connected to the gauge. During a collection cycle the pressure is measured before gas collection begins and after gas collection ends.

The temperature underneath the pistons in the prover tubes is measured by two capsule-type standard platinum resistance thermometers (SPRTs). The SPRTs are mounted in the caps at the bottom of the tubes so that their tops protrude into the gas in the tubes. The SPRTs measure temperature with an estimated standard uncertainty of 1×10^{-3} °C.

The gas density is calculated using the pressure and temperature measurements described above along with the virial equation of state. The virial coefficients for air have been obtained from Hyland and Wexler [13] and those for nitrogen have been obtained from Dymond and Smith [14]. The total mass of gas collected for one cycle is

$$m_{\rm g} = \boldsymbol{\rho}_{\rm f} V_{\rm p} + (\boldsymbol{\rho}_{\rm f} - \boldsymbol{\rho}_{\rm i}) V_{\rm d}, \qquad (4)$$

where ρ_i is the density measured at the beginning of the collection cycle (piston at bottom of the prover tube), ρ_f is the density measured at the end of the collection cycle (piston at top of the prover tube), and V_d is the dead space volume mentioned earlier.

3. HYGROMETER OPERATION

For operating the gravimetric hygrometer, the watercollection tubes are first refilled with dry desiccant if necessary. The refilling is done in a dry box to ensure minimal water absorption by the desiccants during the process. A mechanical balance is used for measuring the mass of each collection tube as it is being filled. The first tube is filled until it weighs 179 g and the second and third tubes are filled until they weigh 157 g.

Once the water-collection tubes are ready for use, they are mounted in the manifold of the gravimetric hygrometer. To prepare the tubes for initial weighing, a minimum of 20 L of dry gas of the type of the test gas is flushed through the hygrometer. The valve to the gas source is then closed and the pressure and temperature of the gas underneath the pistons in the active prover tube are measured. The pressure and temperature inside the water-collection tubes are assumed to be equal to those in the active prover tube. The caps to the water-collection tubes are closed and the tubes removed from the manifold. All tube masses are then determined using the procedure described in Section 2.2.

After the tubes have been weighed, they are remounted in the hygrometer manifold and dry gas is once again flushed through it. The valve to the dry gas is closed and that to the moist gas is opened. The collection process is then started, automated through a computer program. Valves in the manifold are subsequently adjusted until a flow rate of 2 to 3 L min⁻¹ is obtained. Calculations are made to determine the amount of gas to collect in order to collect 2 g of water. For the lowest values of humidity, less water may be collected

due to time constraints. Once the desired amount of gas has been collected, the collection is ended by closing the upstream cap of the first collection tube. The pressure and temperature inside the water-collection tubes are measured, the remaining caps are closed, and the computer program is stopped. The total mass of gas collected, $m_{\rm g}$, is then obtained by adding all the gas masses collected for the individual cycles as determined using Eq. 4.

When the collection is over, the tubes are once again removed from the manifold and placed in the chamber of the electronic balance for reweighing. The mass change for all the water-collection tubes is calculated and the total mass of water collected, m_w , is determined using Eq. 2. The mixing ratio is then calculated using Eq. 1.

4. UNCERTAINTY BUDGET

The uncertainty analysis here complies with the ISO Guide to the Expression of Uncertainty in Measurement [15]. It assumes the measurement protocol described in the previous section. Standard uncertainty components are listed in Table 1 and a plot of the total expanded (k = 2) uncertainty of the measured mixing ratio U(r) as a function of r is shown in Fig. 3. The analysis yields $U(r)/r \approx 0.1$ % for mixing ratios greater than 250 µg/g (atmospheric-pressure dew point greater than -30 °C).

Table 1 – Standard uncertainties u for the gravimetric hygrometer, in measurement units and in relative units. The first five items involve the water mass measurement and the last five items involve the gas mass measurement. For the 5th item, r is the mixing ratio. It is assumed that 2 g of water is collected and the temperature and pressure of the gas in the prover tubes are 293 °C and 101325 Pa, respectively.

Quantity	u	$u(r)/r \times 10^{6}$
Balance Repeatability	$1.5 \times 10^{-4} \text{ g}$	75
Sensitivity mass	$1.2 \times 10^{-4} \text{ g}$	60
Buoyancy Correction	$1.2 \times 10^{-4} \text{ g}$	60
Gas in H ₂ O Collect. Tube	$0.5 \times 10^{-4} \text{ g}$	25
H ₂ O Escaping Collection	$0.075 \ \mu g/g \cdot m_g$	0.075/r
Gas Temperature	0.1 °C	340
Gas Pressure	13 Pa	130
Piston Displacement	$4.7 \times 10^{-3} \text{ cm}$	78
Prover Tube Area	$9.0 \times 10^{-3} \text{ cm}^2$	55
Dead Space Volume	$2.8\times10^{-3}~\text{cm}^{3}$	2

The uncertainty of the mixing ratio is dominated by temperature measurement uncertainties during the gas collection. These are not due to temperature measurement uncertainties of the SPRTs, which are 10^{-3} °C, but rather from temperature gradients inside the prover tubes. These gradients are estimated to be 0.1 °C or 0.034 % and are based upon actual measurements which were made using differential thermocouples placed on the exterior of the prover tubes. The next most significant uncertainty is from the gas pressure measurement, which has an uncertainty of 13 Pa (0.013 %), where the dominant uncertainty components are pressure gauge stability and calibration.

Based on the control tests mentioned in Section 2.2, the estimated standard uncertainty due to the possibility of water escaping the water-collection tubes is $7.5 \times 10^{-2} \,\mu\text{g/g} \cdot m_{\text{g}}$ and is independent of the mixing ratio. Its contribution to the total uncertainty is small or negligible for mixing ratios above 250 μ g/g (atmospheric-pressure dew points above -30 °C), but below this the contribution progressively dominates (see Fig. 3).

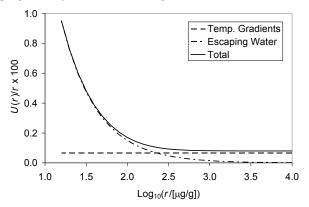


Figure 3 – Total expanded (k=2) uncertainty for the mixing ratio U(r) measurement by the Gravimetric Hygrometer, as a function of mixing ratio r. The uncertainty components for prover-tube temperature gradients and for H₂O escaping collection are also shown. The uncertainty exceeds 0.2 % for atmospheric-pressure frost points less than -40 °C.

5. COMPARISONS WITH NIST HUMIDITY GENERATORS

Initial comparisons have been made with the NIST Two-Pressure Generator [1,4] currently used by NIST to perform calibrations for many customer hygrometers. These comparisons were performed in June, 2004, and consisted of five measurements over the mixing-ratio range 3900 µg/g to 8100 µg/g (corresponding to a one-atmosphere dew-point range of 0 °C to 11 °C). Three of the comparisons were at similar mixing ratios (5400 μ g/g to 5600 μ g/g) in order to test for measurement repeatability. The range and number of comparisons is limited for this first set of measurements, but more comparisons over a wider range are planned for the near future. The Two-Pressure Generator uses air as its working gas, so air properties were used for working-gas density calculations. The results of these comparisons are shown in Table 2a. In four out of the five comparisons the agreement was within the combined expanded uncertainty using a coverage factor of k=2, and in all five comparisons the agreement was within the uncertainty with k=3.

Comparisons have also been made with the NIST Low Frost Point Generator [2,5], which is used to perform calibrations for customer hygrometers in the low-moisture range. These comparisons were performed between December, 2005 and January, 2006. The comparisons consisted of five measurements over the mixing-ratio range 143 μ g/g to 645 μ g/g (corresponding to a one-atmosphere dew-point range of -35 °C to -20 °C). Four of the comparisons were at similar mixing ratios (645 μ g/g) in order to test for measurement repeatability. The Low Frost Point Generator uses nitrogen as its working gas, so N₂ properties were used

for working-gas density calculations. The results of these comparisons are shown in Table 2b. In all of the five comparisons the agreement was within the combined expanded uncertainty using a coverage factor of k=2.

Table 2 – Relative difference between the mixing ratio measured by the Gravimetric Hygrometer, $r_{\rm GH}$, and that generated by a) the NIST Two-Pressure Generator, $r_{\rm 2P}$ and b) the NIST Low Frost Point Generator, $r_{\rm LFPG}$. The atmospheric-pressure dew point (D.P.) is also provided. The combined relative uncertainty $U_{\rm Tot}$ is for a coverage factor of k=2. For these mixing ratios, the expanded uncertainty of the Two Pressure Generator is approximately 0.21 % [4] and that of the Low Frost-point Generator is approximately 0.21 % or less [5].

(a)

Date	D.P. [°C] at 101325 Pa	<i>r</i> _{GH} [µg/g]	r _{GH} - r _{2P} [%]	U _{Tot} [%]
6/21/2004	5.38	5573	0.08	0.24
6/22/2004	5.37	5556	-0.16	0.24
6/23/2004	10.83	8095	-0.04	0.23
6/24/2004	5.08	5442	-0.21	0.24
6/29/2004	0.41	3907	-0.32	0.23

(b)	
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Date	D.P. [°C] at 101325 Pa	<i>r</i> _{GH} [µg/g]	$r_{\rm GH} - r_{\rm LFPG}$ [%]	U _{Tot} [%]
12/21/2005	-34.98	142.6	0.11	0.27
1/06/2006	-20.22	645.1	0.15	0.21
1/09/2006	-20.22	645.1	0.15	0.21
1/10/2006	-20.23	644.1	-0.01	0.21
1/11/2006	-20.22	645.1	0.16	0.21

6. CONCLUSION

A new gravimetric hygrometer has been constructed as a primary humidity standard at NIST. This hygrometer employs a computer-automated continuous-flow gas collection system, which makes use of the hygrometer much more convenient and also makes it possible to measure considerably lower humidity values. The design and operation of the hygrometer have been described in this paper. The expanded relative uncertainty (k = 2) of the hygrometer is less than 0.2 % for mixing ratios of $r \ge 100 \ \mu\text{g/g}$ and approximately 0.1 % for $r \ge 250 \ \mu\text{g/g}$. The hygrometer is now operational, and comparisons have been made with the two NIST humidity generators currently in use For nine out of the ten comparisons made, determinations of the mixing ratios generated agreed with the gravimetric hygrometer measurements to within the combined measurement uncertainties. More comparisons will be performed in the near future.

Future work is planned for lowering the gravimetric hygrometer uncertainties by minimizing the temperature gradients in the prover tubes. We also plan to perform more control tests to better determine the amount of water escaping collection in the desiccant tubes; this may lower the uncertainties for the gravimetric hygrometer for $r < 100 \ \mu g/g$.

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REFERENCES

- S. Hasegawa, J.W. Little, "The NBS Two-pressure Humidity Generator, Mark-2", *Jour. Res. NBS*, vol. 81A, pp. 81-88, 1977.
- [2] G.E. Scace et al., "Performance of a Precision Low Frost-point Humidity Generator", *Papers and Abstracts from the Third International Symposium on Humidity and Moisture*, pp. 180-190, National Physical Laboratory, UK, 1998.
- [3] G.E. Scace, C.W. Meyer, W.W. Miller, J.T. Hodges "An Overview of the NIST Hybrid Humidity Generator", *Proceedings of the 5th International Symposium on Humidity and Moisture*, not published.
- [4] P.H. Huang, "Determining Uncertainties of Relative Humidity, Dew/Frost-point Temperature and Mixing Ratio in a Humidity Standard Generator", *Papers and Abstracts from the Third International Symposium on Humidity and Moisture*, pp. 149-158, National Physical Laboratory, UK, 1998.
- [5] G.E. Scace, J.T. Hodges, "Uncertainty of the NIST Low Frost-point Humidity Generator", *Proceedings of Tempmeko 2001*, pp. 597-602, Berlin, 2002.
- [6] W.N. Shaw, "Report on Hygrometric Methods", Trans. Roy. Soc. Lond. A, vol. 179, p.73-, 1888.
- [7] M.V. Regnault, "Etudes Air l'Hygrometrie", Ann Chim. Phys. vol 3, no. 15, p. 129, 1945.
- [8] G. Scholz, A Standard Calibrator for Air Hygrometers", Bulletin OIML, vol. 97, pp. 18-27, 1984.
- [9] S.A. Bell, "Validation of the NPL Primary Gravimetric Hygrometer", Papers and Abstracts from the Third International Symposium on Humidity and Moisture, pp. 20-27, National Physical Laboratory, UK, 1998.
- [10] A. Wexler, "Divided Flow, Low-Temperature Humidity Test Apparatus", J. Res. NBS, vol. 40, 479-486, 1948.
- [11] A. Wexler, R.W. Hyland., *The NBS Standard Hygrometer*, NBS Monograph 73, 1963.
- [12] M. Kochisiek, M. Gläser, Comprehensive Mass Metrology, p. 42, New York, Wiley-VCH, 2000.
- [13] A. Wexler, R.W. Hyland, Formulations for the Thermodynamic Properties of Dry Air from 173.15 K to 473.15 K, and of Saturated Moist Air from 173.15 K to 372.15 K, at Pressures to 5 MPa, *ASHRAE Trans.*, vol. 89, Part IIa, 520-535, 1983.
- [14] J.H. Dymond, E.B. Smith, *The Virial Coefficients of Pure Gases and Mixtures: a Critical Compilation*, Oxford University Press, New York, 1980.
- [15] ISO, Guide to the Expression of Uncertainty in Measurement, Geneva, International Organization for Standardization, 1993.

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