DETERMINING UNCERTAINTIES OF RELATIVE HUMIDITY, DEW/FROST-POINT TEMPERATURE, AND MIXING RATIO IN A HUMIDITY STANDARD GENERATOR

*Peter H. Huang**

* National Institute of Standards and Technology, Gaithersburg, Maryland, USA

Abstract: This paper presents an extension of the author's previous work on determining the uncertainty of dew/frost-point temperature to cover uncertainties of both relative humidity and mixing ratio in a two-pressure and/or two-temperature type precision humidity generators which are used by most of national standards laboratories in the world. Three analytical equations, based on the thermodynamic relations governing such generators are derived to express the expanded uncertainties of the relative humidity, dew/frost-point temperature, and mixing ratio, respectively.

Examples are given using the data obtained with the National Institute of Standards and Technology (NIST) Two-Pressure Humidity Generator. The maximum expanded uncertainties for the relative humidity range of approximately 12 % to 100 % are 0,3 % for the temperature range 0 °C to 25 °C; 0,8 % for the range -20 °C to 0 °C; 2,0% for the range -40 °C to -20 °C, and 2,6 % for the range -55 °C to -40 °C. These percentage uncertainties, in units of dew/frost-point temperature, correspond to a maximum expanded uncertainty of 0,05 °C for the temperature range -20 °C to 25 °C, 0,07°C for the range -40 °C to -20 °C, and 0,14 °C for the range -65 °C to -40 °C. These uncertainties when expressed in units of µmol/mol by volume, correspond to a maximum expanded uncertainty of 2,0 % of the value for mixing ratios 4 µmol/mol to 25 µmol/mol; 1,4% of the value for the range 25 µmol/mol to 200 µmol/mol; 0,7 % of the value for the range 200 µmol/mol to 1 200 µmol/mol, and 0,4 % of the value for the range 1 200 µmol/mol to 33 000 µmol/mol.

Keywords: uncertainty, humidity, standard

1 INTRODUCTION

The National Institute of Standards and Technology (NIST) has the responsibility to provide humidity calibration services for accurate and uniform humidity measurements throughout the U.S. and overseas. In order to provide and improve the services, NIST has established national primary standards, developed precision humidity generators, provided equations for the saturation water vapor pressures as a function of temperature, developed secondary standards, and provided data for saturated salt solution fixed points. These activities form the core of the U.S. national humidity measurement system and have been reported by Wexler [1], summarized by Hasegawa [2], and revised by Huang [3,4]. This paper presents an extension of the author's previous work on determining uncertainty of dew/frost-point temperature [5] to cover uncertainties of both relative humidity and mixing ratio.

Humidity standards maintained by national laboratories are generally two-pressure and/or two-temperature type precision humidity generators which are used to generate gas streams of known relative humidities, dew/frost-point temperatures, and mixing ratios for testing various hygrometers, including relative humidity sensors, optical dew/frost-point meters, and electrolytic analyzers [6]. An estimate of the uncertainty in gas streams produced by precision generators is required for the validation of humidity calibration standards and for humidity measurements [5,7].

Three analytical equations, based on the thermodynamic relations governing such generators are derived to determine standard uncertainties (estimated standard deviations) in gas stream relative humidity, dew/frost-point temperature, and mixing ratio produced. A combined standard uncertainty in a relative humidity or a mixing ratio can be expressed in terms of the saturation water vapor pressure and relative standard uncertainties of saturation water vapor pressure e_w; ambient pressure P_c; saturator total pressure P_s and enhancement factor of water vapor-air mixture. The first derivative of saturation water vapor pressure with respect to a generated dew-point temperature is required in addition to obtain a combined standard uncertainty in a dew/frost-point temperature. In accordance with the guidelines for evaluating and expressing the uncertainty of NIST measurement results [8], a coverage factor of 2 is used for the expanded uncertainties derived here. Results of uncertainty analysis are given using the NIST two-pressure humidity generator for the relative humidity range of 12 % to 100 % in the temperature range of -55 °C to 25 °C, for the dew-point range of 25 °C to -65 °C, and for the mixing ratio range of 4 μmol/mol to $3{,}3 \times 10^4$ μmol/mol.

2 RELATIVE HUMIDITY

The relative humidity RH of a water vapor-air mixture produced by a two-pressure and/or two-temperature humidity generator is defined as the ratio of the mole fraction of water vapor in the saturator at pressure P_s and temperature T_s with respect to the mole fraction of water vapor in test chamber, if saturated, at pressure P_c and temperature T_c. By substituting appropriate expressions for the mole fractions, the relative humidity in the test chamber of the generator can be expressed in terms of percent (%) by

$$RH = \frac{f(P_s,T_s)}{f(P_c,T_c)} \times \frac{e_w(T_s)}{e_w(T_c)} \times \frac{P_c}{P_s} \times 100\ \% \tag{1}$$

where $f(P_s,T_s)$ is the enhancement factor, i.e., the correction of non-ideal behavior of water vapor-air mixture at saturator pressure P_s and temperature T_s;
$f(P_c,T_c)$ is the enhancement factor, i.e., the correction of non-ideal behavior of water vapor-air mixture at test chamber pressure P_c and temperature T_c;
and $e_w(T_s)$ and $e_w(T_c)$ are the saturation water vapor pressure over a plane surface of the pure phase of liquid water or solid ice at the saturator temperature T_s and test chamber temperature T_c, respectively.

The temperature and pressure have units of kelvin and pascal, respectively. Wherever °C appears, the relation t/°C = T/K – 273.15 was used. It has been the practice at NIST to use the Wexler [9,10] vapor pressure formulation and the Greenspan [11] enhancement factor equation for all work in humidity standards since the late 1970's. After 1990, Huang [12] modified their equations to account for changes on the temperature scale to ITS-90.

2.1 Analytical expression of uncertainty determination

Based on guidelines for reporting uncertainty [8], the standard uncertainty u, the relative standard uncertainty u_r, and the combined standard uncertainty u_c, associated with Eq. (1) can be derived in terms of components that contribute to the uncertainty. The combined standard uncertainty $u_c(RH)$ of the relative humidity RH is the positive square root of the combined variance $u_c^2(RH)$, which is obtained as a sum of an estimated relative variance of each component in Eq. (1) with $RH \neq 0$. This is the case where all the input components are treated uncorrelated [8]. Although enhancement factors are expressed as a function of pressure and temperature, they are independently measured and are not correlated.

$$[u_c(RH)\ 'RH]^2 = u_r^2[f(P_s\,,T_s)] + u_r^2[f(P_c\,,T_c)] + u_r^2[e_w(T_s)] + u_r^2[e_w(T_c)] + u_r^2(P_s) + u_r^2(P_c) \qquad (2)$$

where $u_r^2[f(P_s\,,T_s)] = \{u[f(P_s\,,T_s)]\ '\ f(P_s\,,T_s)\}^2$; $u_r^2[f(P_c\,,T_c)] = \{u[f(P_c\,,T_c)]\ '\ f(P_c\,,T_c)\}^2$;
$u_r^2[e_w(T_s)] = \{u[e_w(T_s)]\ '\ e_w(T_s)\}^2$; $u_r^2[e_w(T_c)] = \{u[e_w(T_c)]\ '\ e_w(T_c)\}^2$;
and $u_r^2[f(P_s)] = \{u[f(P_s)]\ '\ f(P_s)\}^2$; $u_r^2[f(P_c)] = \{u[f(P_c)]\ '\ f(P_c)\}^2$

The combined standard uncertainty, then , is given by

$$u_c(RH)=RH \times \{ u_r^2[f(P_s\,,T_s)] + u_r^2[f(P_c\,,T_c)] + u_r^2[e_w(T_s)] + u_r^2[e_w(T_c)] + u_r^2(P_s) + u_r^2(P_c)\}^{1/2} \qquad (3)$$

If T_c is equal to $T_{s,}$ as is in the case of a two-pressure system, then Eq.(3) reduces to

$$u_c(RH)=RH\times\{u_r^2[f(P_s\,,T_s)] + u_r^2[f(P_c\,,T_s)] + 2u_r^2[e_w(T_s)] + u_r^2(P_s) + u_r^2(P_c)\}^{1/2} \qquad (4)$$

When the measurement of uncertainty is the expanded uncertainty U, then a coverage factor of two yields

$$U = 2u_c(RH) \qquad (5)$$

where $u_c(RH)$ is the combined standard uncertainty of a relative humidity at a temperature.

3 THERMODYNAMIC DEW- OR FROST-POINT TEMPERATURE

The thermodynamic dew/frost-point temperature T_d, of a water vapor-air mixture produced by a two-pressure and/or two-temperature humidity generator is defined as that temperature at which the mixture is saturated with respect to a plane surface of liquid water or ice. The dew/frost-point of the mixture at a pressure P_c , is obtained from the solution of the following equation which is based on the fundamental principle of conservation of mass, namely, the mole fraction of water vapor in the saturator X_{ws} , is equal to that in the test chamber X_{wc}. Thus

$$X_{ws} = X_{wc} \qquad (6)$$

where $X_{ws}=f(P_s\,,T_s)e_w(T_s)\ 'P_s$ (7)
$X_{wc} = f(P_c\,,T_d)e_w(T_d)\ 'P_c$ (8)
and $f(P_s\,,T_s)$ is the enhancement factor, i.e., the correction of non-ideal behavior of water vapor-air mixture at saturator pressure P_s and saturator temperature T_s ;
$e_w(T_s)$ and $e_w(T_d)$ are the saturation water vapor pressure over a plane surface of the pure phase of liquid water or solid ice at the saturator temperature T_s and dew-point temperature T_d , respectively;
$f(P_c\,,T_d)$ is the enhancement factor of the mixture at dew/frost-point temperature T_d and pressure P_c in the test chamber of the humidity generator or in the mirror chamber of a dew-point hygrometer.

3.1 Analytical expression of uncertainty determination

The combination of Eqs. (6), (7), and (8) leads to the following equation:

$$e_w(T_d)f(P_c\,,T_d) = e_w(T_s)f(P_s\,,T_s)(P_c\ '\,P_s) \tag{9}$$

The following relationship is the relative standard uncertainty (estimated standard deviation) of saturation water vapor pressure at the dew-point temperature T_d [5]

$$u[e_w(T_d)]\ '\ e_w(T_d) = [(1\ '\,e_w)(\ Me_w\ \ 'MT)]\Big|_{T_d}\ u(T_d) \tag{10}$$

By following the same procedures to derive Eq. (4), the combined standard uncertainty $u_c(T_d)$ is derived from Eqs. (9) and (10). Thus

$$u_c(T_d) = \{u_r^2(P_c) + u_r^2[e_w(T_s)] + u_r^2[f(P_s\,,T_s)] + u_r^2(P_s) + u_r^2[f(P_c\,,T_d)]\}^{1\,'\,2}\ '\ [(1\ '\ e_w)(Me_w/MT)\Big|_{T_d} \tag{11}$$

The combined standard uncertainty of a dew-point temperature is the ratio of two functions. The function in the numerator is the positive root of a linear sum of terms representing the variation in the estimate T_d due to the relative standard uncertainty in the observable parameters, saturation water vapor pressure at the saturator temperature, and the enhancement factor at both saturation and dew-point temperature conditions. The function in the denominator of Eq. (11), defined by Eq. (10), is the first derivative of saturation water vapor pressure evaluated at the dew/frost-point temperature.

If P_c is equal to $P_{s,}$ as is in the case of a re-circulated two-temperature system, then Eq. (11) reduces to

$$u_c(T_d) = \{u_r^2[e_w(T_s)] + u_r^2[f(P_s\,,T_s)] + 2u_r^2(P_s) + u_r^2[f(P_c\,,T_d)]\}^{1\,'\,2}\ '\ [(1\ '\ e_w)(Me_w/MT)]\Big|_{T_d} \tag{12}$$

The expanded uncertainty U, with a coverage factor of two [7] yields

$$U = 2u_c(T_d) \tag{13}$$

4 MIXING RATIO BY VOLUME

The mixing ratio by volume of the moist gas produced by a two-pressure and/or two-temperature generator can be expressed in terms of the mole fraction of water vapor in a given saturated sample of moist air characterized by the pressure P_s and temperature $T_{s.}$ Using the definition of mole fraction given in Eq. (7), the mixing ratio is given by

$$R_v = \frac{X_{ws}}{1 - X_{ws}} \tag{14}$$

Mixing ratio by volume can also be given by

$$R_v = \frac{f(P_s, T_s)e_w(T_s)}{P_s - f(P_s, T_s)e_w(T_s)} \tag{15}$$

Equation (15) can be expressed in terms of mass ratio by simply multiplying it by the ratio of molar mass of water to that of dry air, 0,6220 [4].

4.1 Analytical expression of uncertainty determination

Following the same procedures used to derive Eq. (2) and performing the necessary mathematical manipulations, it can be shown that the relative combined standard uncertainty of a mixing ratio by volume can be expressed as:

$$u_c(R_v)\ '\ R_v = \frac{P_s}{P_s - f(P_s, T_s)e_w(T_s)} \{u_r^2[f(P_s, T_s)] + u_r^2[e_w(T_s)] + u_r^2(P_s)\}^{1/2} \tag{16}$$

provided $R_v \neq 0$.

The relative expanded uncertainty U, with a coverage factor of two yields

$$U_r = 2\ u_c(R_v)\ '\ R_v \tag{17}$$

where $u_c(R_v)$ is the combined standard uncertainty of a mixing ratio by volume R_v. A mixing ratio by mass, instead by volume, has the same uncertainty as obtained from Eq.(17).

5 EXPERIMENTAL RESULTS

In this section, Eqs. (4), (12), and (16) are applied to assess the uncertainties of relative humidity, dew/frost-point temperature, and mixing ratio delivered by the NIST Two-Pressure Humidity Generator. This serves as an example of the use of the mathematical approach outlined here for evaluating standard uncertainties of working standards.

The NIST Two-Pressure Humidity Generator is used to calibrate various instruments (e.g., relative humidity sensors, dew-point hygrometers, electrolytic analyzers etc.) used as hygrometers. Type A standard uncertainty components consist of the random uncertainties of the measured temperatures and pressures (averaged over a period of at least twenty minutes or longer) in the final bath that contains the saturator and the test chamber. Type B standard uncertainty components consist of the systematic uncertainties in the temperature and pressure measurements attributed to the uncertainties in the pressure gage and the thermometer (determined from the calibrations) as well as the temperature gradient in the final bath. The standard uncertainty in the measurement of enhancement factor is included as the Type B standard uncertainty components of the generator. The maximum estimated uncertainties in saturation water vapor pressure and enhancement factor assigned to previous measurement data [9,10,13] are used to derive the relative standard uncertainties of saturation water vapor pressure and enhancement factor. This analysis method includes the uncertainties in temperature and pressure measurements and vapor pressure values from the equations.

Table 1 lists the values of standard uncertainty components using the NIST Two-Pressure Humidity Generator. At each operating condition, temperature and pressure were observed continually. Averages and standard uncertainties were calculated at selected time intervals. The Type A standard uncertainties of Table 1 are averages of these averages.

Table 1: The standard uncertainty components

Saturator		Type A standard uncertainty		Type B standard uncertainty		
Temperature (°C)	Pressure (Pa)	Temperature (°C)	Pressure (Pa))	Temperature (°C)	Pressure (Pa)	Enhancement factor
25	1 x 10^5	0,00011	7,6	0,016	69,0	0,00017
25	2 x 10^5	0,00014	6,2	0,016	69,0	0,00038
25	5 x 10^5	0,00004	8,3	0,016	69,0	0,00089
0	1 x 10^5	0,00003	5,5	0,016	69,0	0,00036
0	2 x 10^5	0,00003	3,0	0,016	69,0	0,00063
0	5 x 10^5	0,00004	11,0	0,016	69,0	0,00158
- 20	1 x 10^5	0,00016	15,9	0,030	69,0	0,00046
- 20	2 x 10^5	0,00014	13,8	0,030	69,0	0,00088
- 20	5 x 10^5	0,00011	8,3	0,030	69,0	0,00219
- 40	1 x 10^5	0,00032	13,1	0,061	69,0	0,00054
- 40	2 x 10^5	0,00025	11,1	0,061	69,0	0,00115
- 40	5 x 10^5	0,00021	9,3	0,061	69,0	0,00288
- 55	1 x 10^5	0,00085	13,6	0,072	69,0	0,00060
- 55	2 x 10^5	0,00080	11,5	0,072	69,0	0,00139
- 55	5 x 10^5	0,00068	18,6	0,072	69,0	0,00345

5.1 Experimental uncertainties in relative humidity standard

Using the type A and type B standard uncertainties listed in Table 1, relative standard uncertainties in the measurement of saturation water vapor pressure, saturator pressure, test chamber pressure, enhancement factor at the saturator pressure and temperature, and enhancement factor at the test chamber pressure and temperature were calculated as described in reference [5]. By operating the humidity generator over range of saturator temperature and pressure conditions and using Eq. (1), a range of relative humidities from 25 °C to -55 °C was calculated from the measurement data for the test chamber pressure of 0,1 MPa (see first two columns of Table 2). Below 0 °C, the relative humidity is expressed with respect to liquid water or with respect to solid ice [3], as listed in the first two columns of Table 2. In the next five columns, Table 2 lists the relative standard uncertainties for the components of Eq. (3) or Eq. (4). The last two columns of the table list the expanded uncertainties for each relative humidity and temperature with respect to liquid water and with respect to ice at the same temperature.

Table 2: Experimental uncertainties in relative humidity standard

RH (water) (%)	RH (ice) (%)	$u_r[e_w(T_s)]$ or $u_r[e_w(T_c)]$	$u_r(P_s)$	$u_r(P_c)$	$u_r[f(P_s, T_s)]$	$u_r[f(P_c, T_c)]$	$U = 2u_c(RH)$ (water) (%)	(ice) (%)
100		0,0006	0,0007	0,0007	0,0002	0,0002	0,27	
50,14		0,0006	0,0003	0,0007	0,0004	0,0002	0,12	
20,23		0,0006	0,0001	0,0007	0,0009	0,0002	0,06	
100		0,0008	0,0007	0,0007	0,0004	0,0004	0,32	
50,17		0,0008	0,0003	0,0007	0,0006	0,0004	0,16	
20,28		0,0008	0,0001	0,0007	0,0016	0,0004	0,09	
82,26	100	0,0025	0,0007	0,0007	0,0005	0,0005	0,62	0,75
41,34	50,21	0,0025	0,0003	0,0007	0,0009	0,0005	0,31	0,38
16,74	20,34	0,0025	0,0001	0,0007	0,0021	0,0005	0,14	0,17
67,56	100	0,0065	0,0007	0,0007	0,0005	0,0005	1,25	1,86
33,96	50,26	0,0065	0,0003	0,0007	0,0011	0,0005	0,63	0,94
13,80	20,42	0,0065	0,0001	0,0007	0,0028	0,0005	0,27	0,27
58,36	100	0,0090	0,0007	0,0007	0,0006	0,0006	1,49	2,56
29,36	50,31	0,0090	0,0003	0,0007	0,0014	0,0006	0,75	1,29
11,96	20,50	0,0090	0,0001	0,0007	0,0034	0,0006	0,32	0,54

Table 2 and Eq. (4) together show that the largest components of the expanded uncertainty are the uncertainties in saturation water vapor pressure and enhancement factor. For a saturator total pressure above 0,1 Mpa , the effect of relative standard uncertainty in the enhancement factor can be as significant as that in the value of saturation water vapor pressure. For example, at a saturator pressure of 0,5 MPa and saturator temperatures of 25 °C and 0 °C, the relative standard uncertainties in enhancement factor are approximately 1,5 and 2 times greater, respectively, than those in saturation water vapor pressure. At a saturator pressure of 0,5 MPa and saturator temperature of -55 °C, the relative standard uncertainty in the enhancement factor is approximately one-third of that in saturation water vapor pressure. The uncertainty values are, however, approximately equal for a saturator temperature at -20 °C, as indicated in Table 2. The results in Table 2 also show that the differences between the expanded uncertainty of the relative humidity with respect to super-cooled water and that with respect to ice (at the same saturator and test chamber conditions) increases as the test chamber temperature decreases. For example, consider the case of 58,36 % relative humidity (for equilibrium with respect to super-cooled water) and 100 % relative humidity (for equilibrium with respect to ice) at -55 °C. Here, the respective expanded uncertainties of 1,49 % and 2,56% are significantly different. However, for this case, the ratio of the expanded uncertainty to the relative humidity value is constant. Thus, the relatively larger uncertainty is due to the fact that at a given temperature the effective saturation water vapor pressure of ice is lower than that of super-cooled water.

5.2 Experimental uncertainties in dew/frost-point standard

By operating the humidity generator over range of saturator temperature and pressure conditions and using Eq. (9), a range of dew/frost-point temperatures, from 25 °C to approximately -65 °C was calculated from the measurement data for the test chamber pressure of 0,1 MPa. Table 3 lists the corresponding relative standard uncertainties based on the standard uncertainty components given in Table 1. The last two columns of the table list the calculated expanded uncertainty for each dew/frost-point temperature and its corresponding frost-point temperature at atmospheric pressure of 0,1 MPa.

Table 3: Experimental uncertainties in dew/frost-point standard

Dew-point t_d (°C)	Frost-point t_d (°C)	$u_r[e_w(T_s)]$	$u_r(P_s)$	$u_r(P_c)$	$u_r[f(P_s, T_s)]$	$u_r[f(P_c, T_d)]$	$U = 2u_c(t_d)$ Dew-point (°C)	$U = 2u_c(t_d)$ Frost-point (°C)
25,00		0,0006	0,0007	0,0007	0,0002	0,0002	0,040	
13,91		0,0006	0,0003	0,0007	0,0004	0,0003	0,034	
0,66		0,0006	0,0001	0,0007	0,0009	0,0004	0,037	
0,00		0,0008	0,0007	0,0007	0,0004	0,0004	0,038	
- 9,14	- 8,13	0,0008	0,0003	0,0007	0,0006	0,0004	0,034	0,030
- 20,15	- 18,09	0,0008	0,0001	0,0007	0,0016	0,0005	0,046	0,042
- 22,24	- 20,00	0,0025	0,0007	0,0007	0,0005	0,0005	0,063	0,058
- 29,83	- 26,98	0,0025	0,0003	0,0007	0,0009	0,0005	0,060	0,055
- 39,04	- 35,58	0,0025	0,0001	0,0007	0,0021	0,0005	0,066	0,062
- 43,73	- 40,00	0,0065	0,0007	0,0007	0,0005	0,0005	0,124	0,117
- 49,97	- 45,93	0,0065	0,0003	0,0007	0,0011	0,0006	0,117	0,112
	- 53,25	0,0065	0,0001	0,0007	0,0028	0,0006		0,112
	- 55,00	0,0090	0,0007	0,0007	0,0006	0,0006		0,141
	- 60,19	0,0090	0,0003	0,0007	0,0014	0,0006		0,135
	- 66,63	0,0090	0,0001	0,0007	0,0034	0,0006		0,134

As discussed above, with regard to the uncertainty in the relative humidity delivered by the two-pressure humidity generator considered here, the largest components of the expanded uncertainty in dew/frost-point temperature are attributable to the relative standard uncertainties in saturation water vapor pressure and enhancement factor. The results in Table3 also show that the difference in expanded uncertainty for a dew-point temperature and its corresponding frost-point temperature, in the range 0 °C to - 45 °C, is less than 0,01 °C.

5.3 Experimental uncertainties in mixing ratio standard

By operating the humidity generator over range of saturator temperature and pressure conditions listed in Table 1 and using Eq. (15), a range of mixing ratio by volume of the gas-water vapor mixture was calculated from the data. Table 4 lists the corresponding relative standard uncertainties based on the standard uncertainty components given in Table 1. The last two column of the table lists the calculated expanded relative uncertainty from Eq. (17) for each value of mixing ratio by volume.

As with the determination of the relative humidity and dew/frost-point standards described above, the largest components of the expanded uncertainty in mixing ratio are attributed to the relative standard uncertainties in saturation water vapor pressure and enhancement factor. However, unlike the relative humidity and dew/frost-point temperature quantities, the mixing ratio of the water vapor-gas mixture produced by a two-pressure type of humidity generator is independent of the temperature and the pressure of the test chamber. The results in Table 4 also show that the expanded uncertainty for the mixing ratio increases with increasing saturator pressure and temperature. For example, the expanded uncertainty reaches approximately 2 % of the nominal mixing ratio of 4,3 μmol/mol obtained from the standard generator operating at a saturator pressure of 0,5 MPa and temperature of -55 °C.

Table 4. Experimental uncertainties in mixing ratio standard

Mixing ratio R_v (μmol/mol)	$u_r[e_w(T_s)]$	$u_r(P_s)$	$u_r[f(P_s, T_s)]$	$U_r = 2\ u_c(R_v)\ 'R_v$ (%)
32 874	0,0006	0,0007	0,0002	0,19
16 218	0,0006	0,0003	0,0004	0,16
6 480	0,0006	0,0001	0,0009	0,22
6 173	0,0008	0,0007	0,0004	0,23
3 088	0,0008	0,0003	0,0006	0,21
1 246	0,0008	0,0001	0,0016	0,36
1 038	0,0025	0,0007	0,0005	0,53
520,8	0,0025	0,0003	0,0009	0,54
211,0	0,0025	0,0001	0,0021	0,65
129,0	0,0065	0,0007	0,0005	1,31
64,85	0,0065	0,0003	0,0011	1,32
26,35	0,0065	0,0001	0,0028	1,42
21,05	0,0090	0,0007	0,0006	1,81
10,59	0,0090	0,0003	0,0014	1,82
4,31	0,0090	0,0001	0,0034	1,92

6 CONCLUSION

A method of determining uncertainties in humidity units of relative humidity, dew/frost-point temperature and mixing ratio produced by a two-pressure and/or two-temperature humidity generator is described. In this paper, three analytical equations for the expanded uncertainties of these humidity units were derived based on thermodynamic principles.

Sample calculations based on the measurements of the NIST Two-Pressure Humidity Generator indicate that the respective expanded uncertainties in relative humidity, dew/frost-point temperature and mixing ratio are all dominated by relative standard uncertainty in the saturation vapor pressure of water or ice and in the enhancement factor of water vapor-air mixture. The maximum expanded uncertainties for the relative humidity range of approximately 12 % to 100 % are relative humidity values of 0,3 % for temperatures for the range 0 °C to 25 °C; 0,8 % (with respect to ice) or 0,6 % (with respect to water) for the range -20 °C to 0 °C; 1,9 % (with respect to ice) or 1,3 % (with respect to water) for the range -40°C to -20 °C, and 2,6 % (with respect to ice) or 1,5 % (with respect to water) for the range -55 °C to -40 °C. These uncertainties, in units of dew/frost-point temperature, correspond to 0,05 °C for dew/frost-point temperatures for the range -20 °C to 25 °C, 0,07 °C for the range –40 °C to - 20 °C, and 0,14 °C for the range -65 to -40 °C. These uncertainties, when expressed in units of μmol/mol by volume, correspond to 2,0 % of the value for mixing ratios of 4 μmol/mol to 25 μmol/mol, 1,4 % of the value for the range 25 μmol/mol to 200 μmol/mol, 0,7 % of the value for the range 200 μmol/mol to 1 200 μmol/mol, and 0,4 % of the value for the range 1 200 μmol/mol to 33 000 μmol/mol.

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Contact point: Peter H. Huang, Process Measurements Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA.
Tel. 1 301-9752621, Fax: 1 301-5480206, Email: peter. huang@nist.gov