A Reference Standard for Measuring Humidity of Air Using a Re-entrant Radio Frequency Resonator

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Abstract: We developed a stable reference hygrometer suitable for operation at temperatures above ambient that has a robust design, inherent stability, and a well-understood theory of measurement. This hygrometer uses a reentrant, radio-frequency, cavity resonator operating near 370 MHz to convert the known humidity-dependence of the dielectric constant of H_2O/air mixture into easily-measured frequency changes. In this paper, we discuss the achievable repeatability of this device. We expect this hygrometer will be especially valuable for validation of humidity standard generators at mixing ratios in moist gases higher than 20000 parts per million by mass.

Key words: dielectric constant, radio-frequency resonator, gas mixture, humidity standard, high temperature.

1. INTRODUCTION

Humidity measurement and control are crucial for efficient and consistent operations of many industrial processes, including food processing, chemical, paper, polymer, cement, semiconductor, and textile industries. Food processing and new fuel-cell applications, in particular, require humidity measurement and control at high temperatures and high relative humidity. For example, the humidity measurement/control system for a proton-exchange membrane fuel cell (PEMFC) has been recognized as one of the most critical component in automotive fuel cell operation. At the anode of the PEMFC, Mawardi et al. [1] demonstrated that optimal operating conditions are a temperature of 100 °C and a relative humidity as close as possible to 100 % without incurring condensation. Other PEMFC systems will require accurate humidity measurements at temperatures up to 200 °C in both moist air and moist hydrogen. To provide standards for these high-temperature, high humidity applications, we are developing a compact primary hygrometer that can conveniently be operated at high temperatures and elevated pressures.

In this work, standardized mixtures of {CO_2-free air + water vapor} were generated at ambient pressure and then flowed through a reentrant, radio-frequency (RF), cavity resonator operating at frequencies near 370 MHz (see Fig. 1). As the generator increased the mole fraction of water vapor x_w in the mixture, the dielectric constant (relative electric permittivity) ε_r of the gas in the cavity increased and the resonance frequency decreased. For example, the resonance frequency decreased 0.2 % as the relative humidity increased from 0 % to 100 % at 90 °C. The repeatability of the frequency measurements was, fractionally, 4×10^{-7}, or better. This repeatability corresponds to humidity changes of 0.04 % at 90 °C. Because the resonator is robust, mechanically simple, moderately-sized (7 cm outside diameter, 7 cm high), and constructed from corrosion-resistant materials (Inconel [2] with gold and ceramic seals), it is a promising candidate to become a reference standard for humidity measurements up to the highest temperatures and pressures proposed for fuel cell operation. Similar resonators have been used at the National Institute of Standards and Technology (NIST) to accurately measure the dielectric constant of gases and of liquid water and also to determine the dipole moments of gases. [3,4,5].

2. THEORY OF MEASUREMENT

For design purposes, we consider CO_2-free air and water vapor to be a mixture of non-interacting species. For such a mixture, an approximate expression [6] for the dielectric constant is:

$$\frac{\varepsilon'-1}{\varepsilon'+2} \approx \sum_i \rho_i A_i + \rho_w \left(A_w + \frac{B_w}{T} \right) \quad . \tag{1}$$

In Eq. (1), ε' is the real part of the complex dielectric constant $\varepsilon = \varepsilon' - i\varepsilon''$; ρ_i and A_i are the molar density and the molar polarizability of the ith species in air ($i = N_2, O_2, Ar$); ρ_w is the molar density of water vapor, and T is the absolute temperature. Reference [7] tabulates values of the Debye constants [A_w and B_w in Eq. (1)] from seven sources. These sources predict values of ($A_w + B_w/T$) ranging from 60.31 to 61.39 $cm^3 \cdot mol^{-1}$ at 90 °C. In Eq. (1), we used the mean value, 60.91 $cm^3 \cdot mol^{-1}$. For air, the A_i are nearly independent of the temperature and have a very small density dependence. At 90 °C and 100 kPa, A_{N2} = 4.3882 $cm^3 \cdot mol^{-1}$ and A_{air} = 4.1561 $cm^3 \cdot mol^{-1}$, where “air” is CO_2-free and dry. [8] In contrast, the values of (A_w + B_w/T) are density dependent. In Eq. (1), we substitute products of (mole fractions) × (partial pressures) for the densities and we account for real gas effects with the second virial coefficient for the mixture $B_{mix}(T)$ [9] to obtain:

$$\frac{\varepsilon'-1}{\varepsilon'+2} = \frac{P}{RT(1+B_{mix}P/(RT))}\left[\sum_i x_i A_i + x_w \left(A_w + B_w/T\right)\right] \tag{2}$$

Here, R is the universal gas constant and P is the total pressure. We used Eq. (2) to determine values of x_w(resonator) from the measurements of ε', P and T; we obtained B_{mix}, $(A_w + B_w/T)$, and A_i from the literature. In Table 1, the values of x_w(resonator) are compared with the values x_w(generator) deduced from the dew-point temperature in the humidity generator, the saturated vapor pressure of water, and the enhancement factor $f_{mix}(P,T)$.

3. The Measurement of Dielectric Constant

In this study, we used one of the two resonators described in detail by Goodwin *et al.* [3] Using a network analyzer, we measured the transmission $\boldsymbol{S_{21}}$ through the resonator as a function of the frequency f near 370 MHz. We deduced the complex resonance frequency $\boldsymbol{F} = f_\alpha + \mathrm{i}g_\alpha$ by fitting the values of $\boldsymbol{S_{21}}$ using the resonance function:

$$\boldsymbol{S_{12}}(f) = \frac{\boldsymbol{A} f}{f^2 - \boldsymbol{F}^2} + \boldsymbol{B} + \boldsymbol{C}(f - f^*) + \boldsymbol{D}(f - f^*)^2 \quad . \tag{3}$$

Here f^* is any fixed frequency near f_α and the fitting parameters $\boldsymbol{A}$, $\boldsymbol{B}$, $\boldsymbol{C}$, and $\boldsymbol{D}$ are complex numbers. Thus, eight parameters were used in the fit. In dry gas, repeated determinations of f_α had a fractional standard deviation $\sigma < 10^{-7}$; for the moist gases, $\sigma < 4\times10^{-7}$. Hamelin et al. [4] give a complete equation relating the complex resonance frequency $\boldsymbol{F} = f_\alpha + ig_\alpha$ to the dielectric constant of the gas-filled resonator. (We call f_α the "resonance frequency" and g_α the "resonance half-width".) Corrections must be applied for the electrical resistivity of the resonator's wall and for the coupling of external circuitry to the resonator. We determined these corrections from measurements of the resonance frequency when the resonator was filled with dry nitrogen and from the frequency dependence of the half-width as the water concentration was varied. If $\boldsymbol{F_0} = f_0 + \mathrm{i}g_0$ is the complex resonance frequency of the evacuated resonator, and g_{0s} and $g_{\alpha s}$ are the components of g_0 and g_α due solely to the resistive losses, the dielectric constant may be obtained from:

$$\varepsilon' = \left(\frac{f_0 + g_{0s}}{f_\alpha + g_{\alpha s}}\right)^2 \quad . \tag{4}$$

For precise work, Eq. (4) must be corrected for the resonator's deformation with pressure. [4]

4. Preliminary Results

To test the performance of the resonator-hygrometer, we connected the resonator to the output of the NIST Hybrid Humidity Generator and measured the dielectric constant for water vapor-air mixtures of varying water concentration. The generator produced a gas stream of CO_2-free atmospheric air saturated with water vapor at carefully-defined dew-point temperatures, all of which were below the temperature of the thermostatted bath containing the resonator. The design of the saturation section of the Hybrid Humidity Generator [10] follows the general principles of past NIST humidity generators [11]. Air containing mole fractions of water vapor from 0.081 to 0.567 was introduced into the inlet of the resonator at a flow rate of 360 $\mathrm{cm^3 \cdot min^{-1}}$. When the temperature, pressure and flow of the sample air reached stable conditions, resonance frequency and half-width were measured. The dielectric constant was calculated using Eq. (4) and reference values [f_α and $g_{\alpha s}$ in Eq. (4)] that had been measured while dry nitrogen flowed through

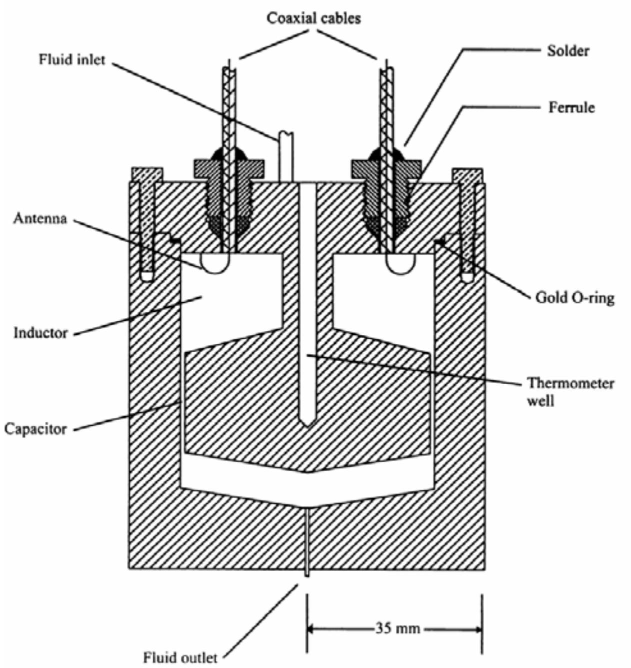

Figure 1- Cross section of re-entrant resonator

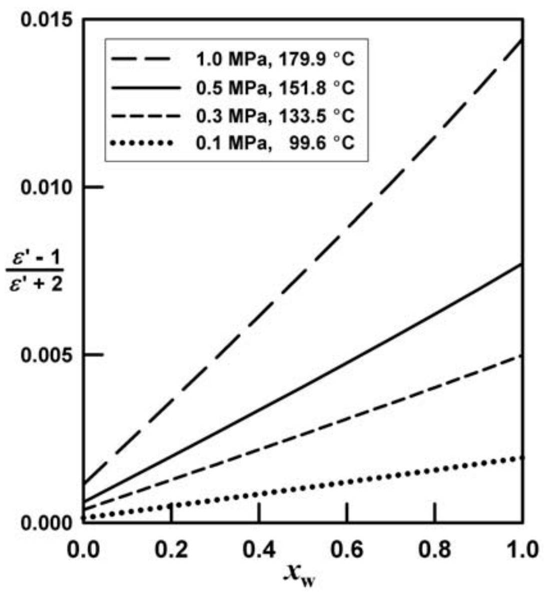

Figure 2- Mole fraction of water vapor as a function of (ε' - 1)/(ε' + 2) calculated from Eq. (2) for total pressures from 0.MPa to 1.0 MPa

The mole fraction of water x_w(resonator) was calculated from Eq. (2) using literature values of $B_{mix}(T)$, the polarizability of nitrogen, water, and CO_2-free air. The last column of Table 1 is the difference $\Delta x_w \equiv x_w(\text{generator}) -$

x_w(resonator). We deduced x_w(generator) from the dew-point temperature in the humidity generator, the saturated vapor pressure of water, and the values of the enhancement factor. [9,12] Remarkably, $|\Delta x_w| \leq 0.0022$. The uncertainty of x_w(resonator) is dominated by the uncertainty of the molar polarization of water molecules, ($A_w + B_w/T$). Of the seven data sets available for these parameters [7], the two sets with the lowest claimed uncertainty are from the same research group, and these two results deviate significantly from the remaining sets. Thus, it is likely that there are unidentified systematic biases in the available data, and we take the standard uncertainty of the polarization to be the standard deviation of the polarization obtained with the seven sets of parameters. At 90 °C, the relative standard uncertainty of the polarization is 0.8 %. We hope to redetermine A_w and B_w at improved uncertainty in the future. However, we are currently repeating the experiment in an effort to establish the repeatability standard deviation of Δx_w for at least four repeated measurements. This standard deviation along with the standard deviation of x_w(generator) will be used to determine the standard deviation of x_w(resonator).

Table 1- Properties of the generated gas stream (total pressure P, water vapor mole fraction x_w,, dew-point temperature t_{dp}); properties measured with the resonator (temperature t, frequency, half-width); dielectric constant computed from f and g, and the inconsistency of x_w. Row 1 is for N_2.

generated gas stream			measured from resonator				comparison
P (Pa)	x_w generator	t_{dp} (°C)	t (°C)	f (MHz)	g (MHz)	ε'	x_w(generator) – x_w(resonator)
100626	0.000	n.a.	90.193	367.76888	0.79917	1.000437	−0.0002
100656	0.081	41.78	90.195	367.68659	0.79908	1.000883	0.0022
100597	0.199	59.93	90.180	367.56509	0.79898	1.001547	0.0014
100471	0.461	79.26	90.192	367.29190	0.79872	1.003035	−0.0001
100393	0.567	84.41	90.203	367.18247	0.79861	1.003632	−0.0019

6. CONCLUSIONS

We are currently repeating the experiment in an effort to establish the repeatability standard deviation of Δx_w for at least four repeated measurements. From these measurements, the Type A Bayesian standard uncertainty can be determined which will be used with the standard deviation of x_w(generator) to determine the standard deviation of x_w(resonator).

One potential error in this hygrometer is the adsorption of water on the inner surface of the resonator, which will give an apparent value of dielectric constant that is too high. Since the thickness of the adsorbed layer grows rapidly as the temperature of the resonator is reduced to the dew point of the gas stream, we plan to measure the apparent variation in x_w(resonator) with resonator temperature, with x_w(generator) maintained at a constant value. We will thereby determine the minimum temperature difference between the resonator temperature and the gas stream dew point to attain acceptable uncertainties.

The excellent agreement of the resonator-hygrometer with the generator over a broad range of water vapor concentrations demonstrates that the hygrometer can serve as a reliable reference standard, at water vapor concentrations well in excess of the upper limits of the NIST Hybrid Humidity Generators. With its robust design, inherent stability, and well-understood theory of operation, we expect that the RF-resonator hygrometer will enable traceable measurements of water vapor mole fraction over the full range of temperatures and pressures necessary for fuel cell applications.

Acknowledgments

We thank Wyatt Miller and Christopher Meyer for their valuable and timely contributions to the NIST Hybrid Humidity Generator. We thank Allan Harvey for suggesting improvements to our draft manuscript.

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