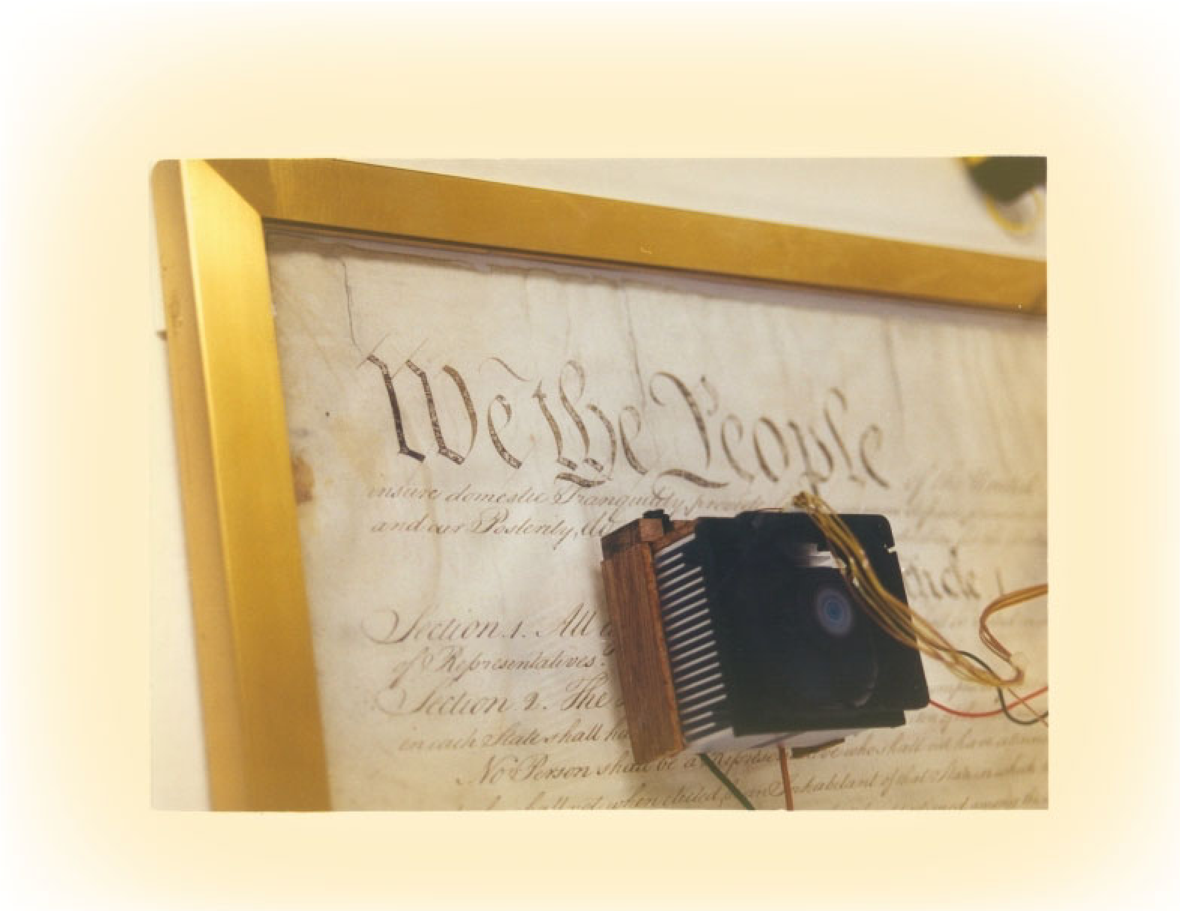
Measuring Humidity in the Charters of Freedom Encasements Using a Moisture Condensation Method



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Introduction

In 1951, the Declaration of Independence, the U.S. Constitution (four pages), the Letter of Transmittal of the Constitution, and the Bill of Rights, collectively called the U. S. "Charters of Freedom," were sealed in new air-tight glass encasements. The National Bureau of Standards, given the responsibility for the preservation of the Charters of Freedom stated its two principal considerations for preservation as (National Bureau of Standards, 1951, page 2) [1]:

First, the selection of a suitable inert gas is necessary because the atmosphere contains components which are destructive—in particular, oxygen.

Second, the presence of either too much or too little moisture contributes to deterioration. It is necessary to determine and establish an atmosphere surrounding the documents that has just the right amount of moisture.

The National Bureau of Standards document expanded on the importance of maintaining the right of amount of water vapor in the sealed encasements (National Bureau of Standards, 1951, page 4) [1]:

The presence of large amounts of moisture leads to deterioration of documents in two ways: There is a loss in strength of the parchment material and there is the danger of attack of the material by micro-organisms that do not require air but do require high-moisture environments. On the other hand, too little moisture leads to brittleness and cracking and eventually to breaking up of the parchment.

Research at the National Bureau of Standards indicates that the appropriate relative humidity of the helium should be between 25 and 35 percent at room temperature.

To preserve and protect the historic parchment documents from the chemical deteriorating effects of air, the air in the encasements was pumped out and replaced with a mixture of helium and water vapor at a relative humidity between 25 and 35 percent at room temperature (National Bureau of Standards, 1951) [1]. Helium, an inert gas is chemically safe for the documents and the water vapor is needed to maintain the stability of the documents. The Charters of Freedom are exhibited and maintained in the visitor's rotunda of the National Archives and Records Administration (NARA) building in Washington, DC. Each year more than 1.2 million visitors view these important and historic documents.

Over the last few years, some experts have questioned the stability of the helium/water vapor atmosphere in the encasements. NARA was very interested in determining whether the seven encasements still contained the original 1951 mixture of helium and water vapor or had the helium/water vapor mixture leaked out of the encasement and was replaced by chemically corrosive air? (Leary, 1999, 2000). On July 28, 1998, Margaret A. T. Kelly [2], of NARA, contacted Dr. Joel S. Levine at NASA Langley Research Center (LaRC) to request assistance in determining the present-day chemical composition of the atmosphere inside the encasements (Kelly, 1998) [2]. Levine established several teams of Langley researchers to address this question, each team employing a different measurement technique, including both non-invasive and invasive measurement approaches. Over the following months, LaRC researchers performed a series of non-invasive and invasive measurements on all seven Charters of Freedom.

In March 2000, samples of the atmosphere in the encasements containing Pages 2 and 3 of the U. S. Constitution were extracted and chemically analyzed at LaRC. The gas samples were analyzed on a gas chromatograph. The water vapor content of the samples were analyzed on a dew point hygrometer that utilized a silicon based (impedance change) water vapor sensor. The results of these analyses were summarized in a report, "The Chemical Composition of the Atmosphere in the Encasements Containing the U.S. Constitution, Pages 2 and 3 (Davis et al., 2000) [3] which was submitted to NARA on April 14, 2000.

Additional measurements were conducted at NARA, College Park Maryland on July 23, 2001 using a non-invasive measurement technique, named the "cooling/condensation" measurement technique. This paper describes the method and results of relative humidity measurements made on encasements containing Pages 1 and 4 of the U.S. Constitution, the Bill of Rights, and the Declaration of Independence using a non-invasive technique moisture condensation technique developed at NASA LaRC.

The four Charter of Freedom encasements (seals intact, no extraction or samples previously taken) were subjected to localized cooling until dew (condensed water droplets) was visually observed on the interior of the glass. The exterior glass surface temperature was measured and noted at the first clear indication of dew formation on the interior. At no time was dew observed on the encasement external glass surface indicating that the internal encasement relative humidity was higher than the ambient room conditions of 40% relative humidity (40%RH).

Measurements of the relative humidity in the sealed encasement atmosphere using the cooling/condensation technique yielded the following values (two measurements were performed on each encasement at two different locations) and all measurements were performed for an ambient temperature of 20.0 C).

<u>U.S. Constitution, Page 1</u>	57.2% RH (Location 1)
	55.0% RH (Location 2)
<u>U.S. Constitution, Page 4</u>	59.2% RH (Location 1)
	61.2% RH (Location 2)
<u>Bill of Rights</u>	55.7% RH (Location 1)
	56.5% RH (Location 2)
<u>Declaration of Independence</u>	57.2% RH (Location 1)
	58.4% RH (Location 2)

For comparison, the measured relative humidity of the atmosphere in the encasements containing the U.S. Constitution, Pages 2 and 3 based on gas extraction and analysis based on a dew point hygrometer yielded the following results at an ambient temperature of 22.0 C (Davis et al., 2000)

U.S. Constitution, Page 2: 63.7% RH

U.S. Constitution, Page 3: 63.9% RH

Approach

A fundamental technique to measure relative humidity is accomplished by chilling a surface, usually a small mirror, until condensation (dew) is detected. Commercial instruments using this technology are referred to as chilled mirror hygrometers and are considered one of the most accurate ways to measure relative humidity. After the hygrometer causes dew formation by chilling, the mirror surface is heated slightly until a thin uniform layer of dew is maintained at a unique constant temperature that allows condensation and evaporation to occur simultaneously. This is accomplished by utilizing a sensitive optical detection circuit that controls the mirror temperature by comparing the light reflected from a clean dry mirror to that of the light received when scattered by dew. Once this stable equilibrium temperature is achieved, the chilled mirror surface temperature is measured using an embedded temperature sensor and can be referred to as the "dew point" temperature or saturation temperature.

The water vapor pressure at the dew point temperature can be identified using well established Smithsonian Meteorological Tables (List, 1984) [4] or formulas that give saturation temperature versus vapor pressure. To relate dew point temperature to relative humidity, the ambient temperature must also be measured. When air (or any gas) is saturated with water, it is unable to absorb any additional water vapor and is at 100% humidity relative to that temperature. If the gas is not saturated, then the relative humidity for that temperature can be determined by chilling the gas as described above to obtain the actual water vapor present. A ratio can then be determined by using the Smithsonian Meteorological Tables [4] to identify what the vapor pressure would be if the gas were saturated at ambient temperature. This ratio of water vapor present to the maximum possible water vapor (at ambient temperature) is the definition of relative humidity when expressed in percent.

For a given temperature: $\% \text{ Relative Humidity} = \frac{\text{actual water vapor pressure}}{\text{saturation water vapor pressure}} \times 100$

The relative humidity inside the sealed encasements was measured in a manner similar to the chilled mirror technique described with two significant differences. First, a temperature controlled mirror could not be used without violating the integrity of the encasement seals. Instead, a thermoelectric based device (same technology as chilled mirror hygrometer) was used to chill the outside of the encasement glass until dew formed on the interior surface. The presence of dew was then detected visually with the aide of a hand held low power magnifying glass (see Photograph 1). The other major difference was the inability to achieve dew point equilibrium because there was not an effective feedback mechanism to accurately control the interior glass temperature at the dew point (equilibrium). It is very important to note that errors caused by this technique will result in data that shows the encasements to have a lower relative humidity (drier) than they actually are.

The first difference occurred because of the angle of view and location underneath the cooling “foot” pad. As a result of this, the dew had already started to form before it was definitively observed. This means it formed at a slightly higher temperature than was noted in the data as "observed dew". Second, because accurate temperature control was not available to control at the dew point temperature, all of the dew point readings were taken with dew still accumulating, not during equilibrium. Again, both of these differences from commercial hygrometer methods will result in driving the interior glass temperature lower than was actually needed to form dew at equilibrium. A lower dew point temperature results in lower relative humidity calculations.

Relative Humidity Measurement

A heat pumping device was constructed using a Melcor model SH 1.4-125-06l thermoelectric module. A small cooling fan and heat sink were thermally bonded to the "hot" side of the thermoelectric module to discharge heat that was removed from the encasement glass. The "cool" side of the module was thermally bonded to an aluminum plate that had a small foot or pad protruding out one end. Seven 30 gage Type" K" thermocouples were used to measure both the internal temperature of the aluminum cooling pad and six locations on the glass surface. The thermocouple temperatures were displayed on four, two-channel Fluke model 52 readouts (Figure 1). Thermal grease was applied to the cooling foot and thermocouples to assure good thermal contact (Photograph 2).

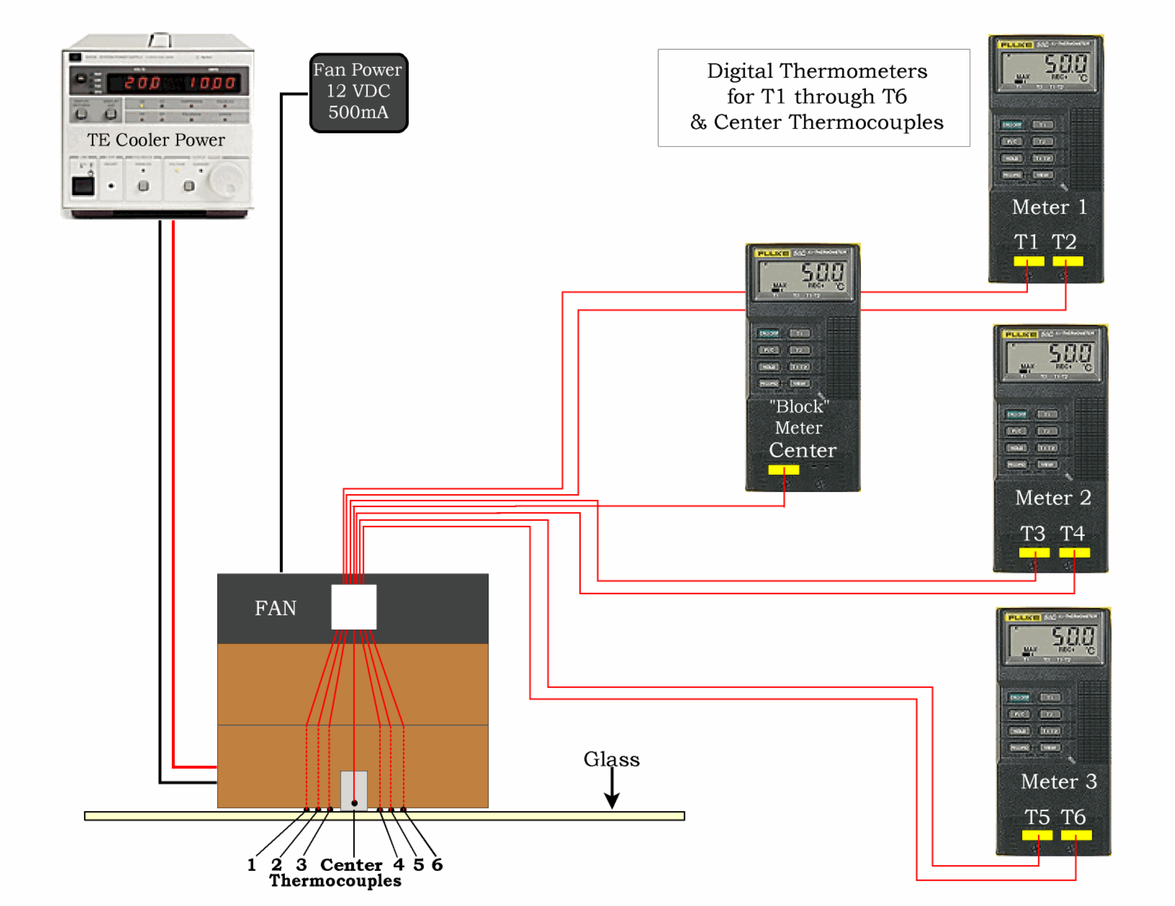


Figure 1: Thermoelectric cooler device set-up as used at NARA

Photograph 1: Observing dew formation

The thermoelectric module was powered by a Hewlett-Packard model 6038A precision power supply with built-in voltage and current readouts. A 12-volt D.C. wall adapter provided the heat-sink fan cooling power. The housing for the device was made of hardwood to avoid scratching the glass and for its insulation properties. See Figures 2 and 3 for details of the construction.

Each measurement was made by placing the thermoelectric cooler directly on the encasement glass surface (see Figure 4 for placement locations). Sufficient power was applied in steps to the thermoelectric module (based on previous lab testing) to cause the encasement glass under the cooling “foot” pad to chill. A small flashlight and low power magnifying glass were used to look for clear indications that dew was condensing on the interior of the encasement glass (none formed on the exterior surface of the encasement glass). Temperature readings were taken during the cool down period and conditions were noted when dew formation was observed.

Temperature measurements were taken on common plate glass at LaRC and on glass from a disassembled encasement (glass from top of U.S. Constitution, Page 2 encasement) at NARA, to provide a correction factor because the thermocouples were measuring external glass surface temperature, not the actual location of the observed dew on the internal glass surface.

Identical test set-ups were used at both LaRC and NARA with the exception of a 0.002" diameter fine wire Type "T" thermocouple which was placed directly under and centered beneath the cooling “foot” pad during the LaRC test. The results of these tests indicate that a difference of +0.4°C through the glass (vertical correction) and +0.5°C (horizontal correction) for the difference between the most representative surface thermocouple and the temperature at the dew location on the interior surface for a total temperature correction of +0.9°C.

Table 1. Dew Point Temperature Measurements, Corrections and % Relative Humidity (RH) for Each Encasement (See text for details)

Charter Encasement	[1]**Observed Dew Point in °C**	[2]**Dew Point Correction in °C**	**Water Vapor Pressure @ Corrected Dew Point in MilliBars**	**Saturation Water Vapor Pressure @ Ambient of 20°C**	**Calculated Encasement % Relative Humidity @ Ambient of 20°C**
Constitution, Page1, Location #1	10.4	0.9	13.383	23.373	57.2
Constitution, Page 1, Location #2	9.8	0.9	12.860	23.373	55.0
Constitution, Page 4, Location #1	10.9	0.9	13.833	23.373	59.2
Constitution, Page 4, Location #2	11.4	0.9	14.297	23.373	61.2
Bill of Rights, Location #1	10.0	0.9	13.032	23.373	55.7
Bill of Rights, Location #2	10.2	0.9	13.207	23.373	56.5
Declaration of Independence, Location #1	10.4	0.9	13.383	23.373	57.2
Declaration of Independence Location #2	10.7	0.9	13.652	23.373	58.4

[1] Indicated by T5 – See lab test results

[2] Corrections:

Thermocouple placement correction (vertical) : 0.4 °C

Thermocouple placement correction (horizontal) : 0.5°C

0.9 °C

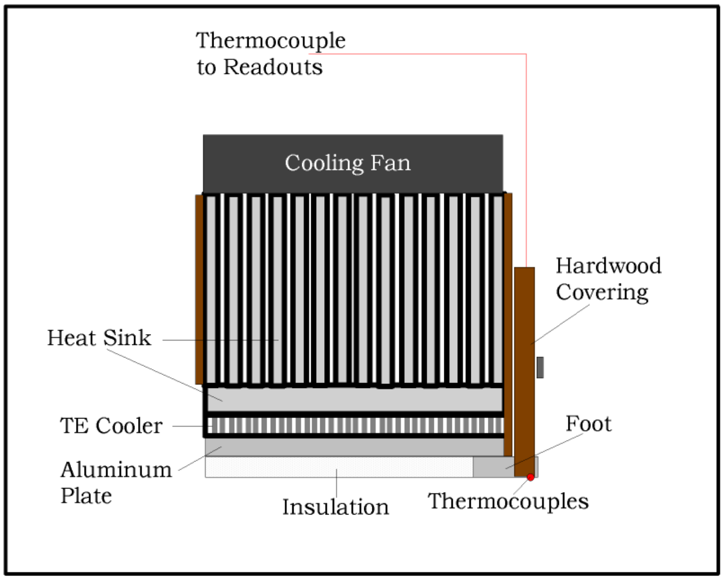


Figure 2: Side view cut-away of thermoelectric cooler device showing construction

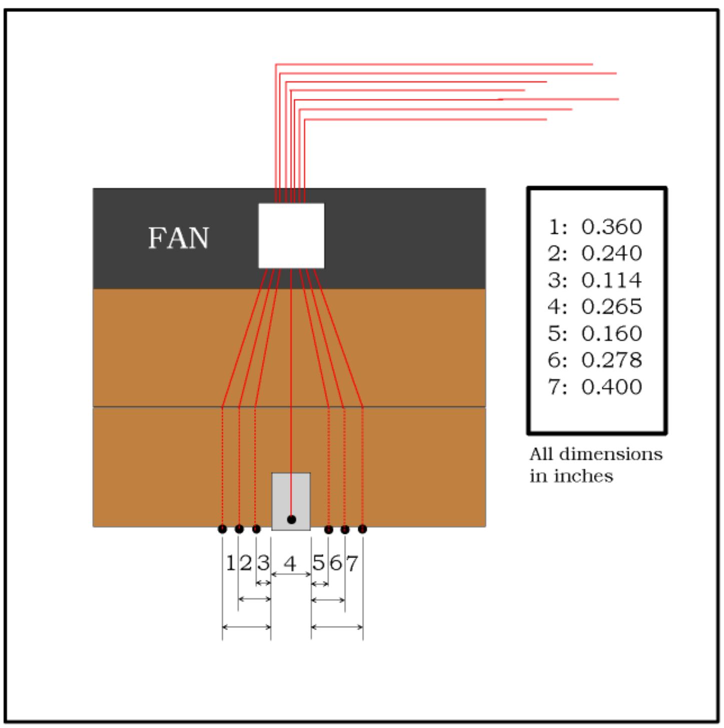


Figure 3: Front view of thermoelectric cooler device showing thermocouple locations.

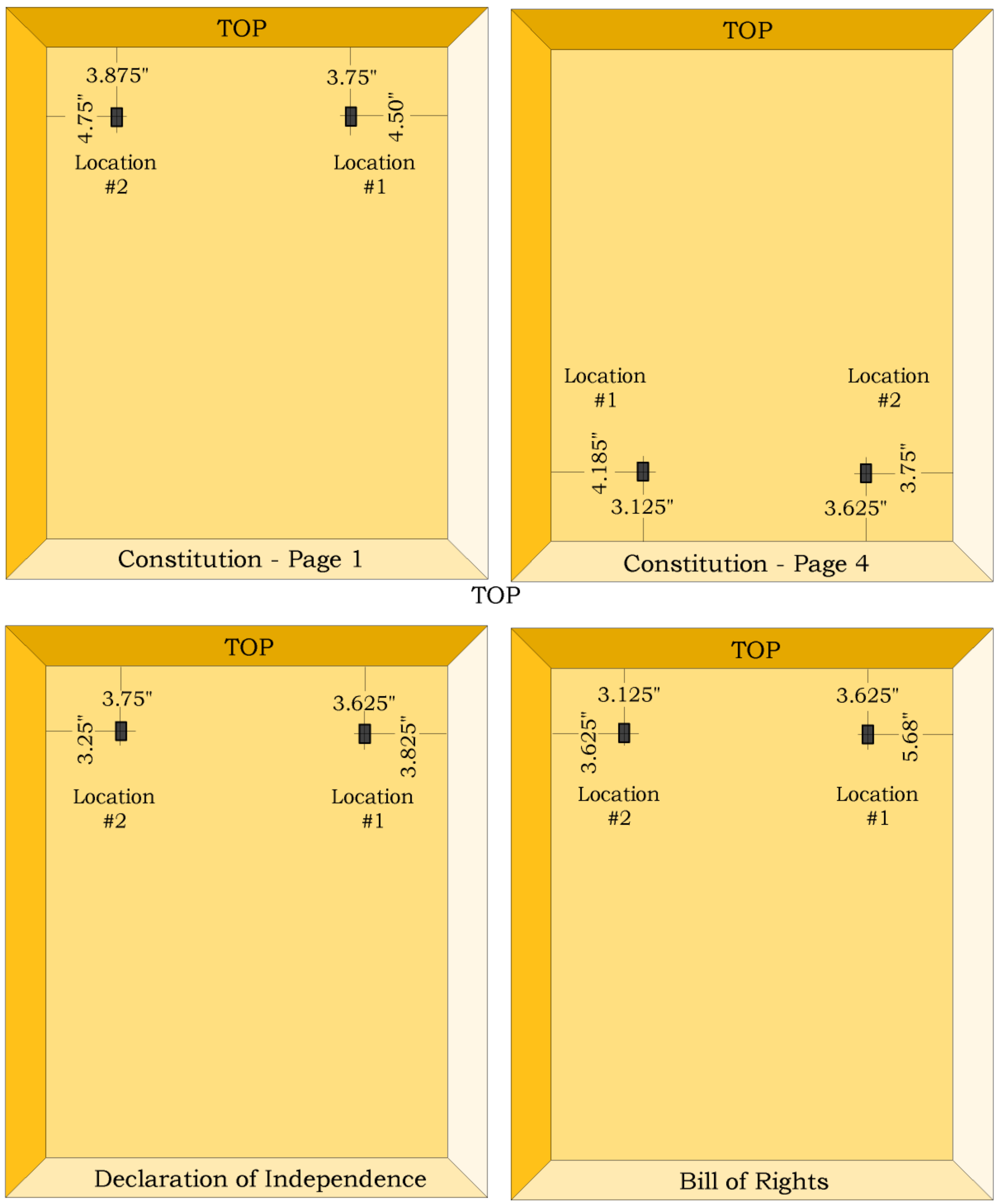
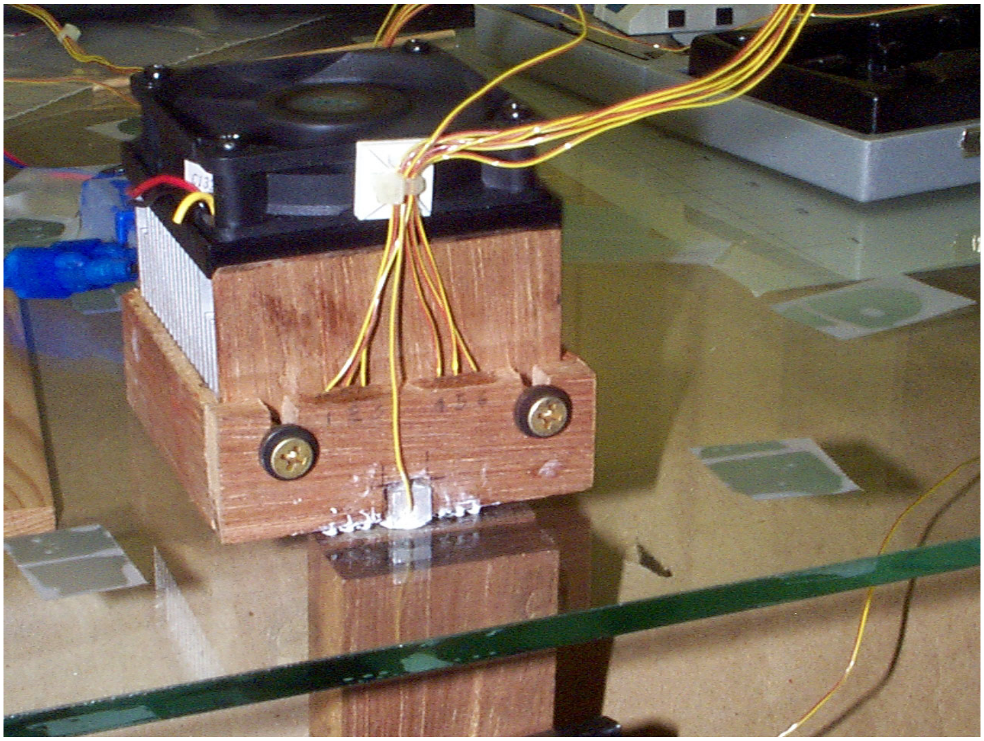
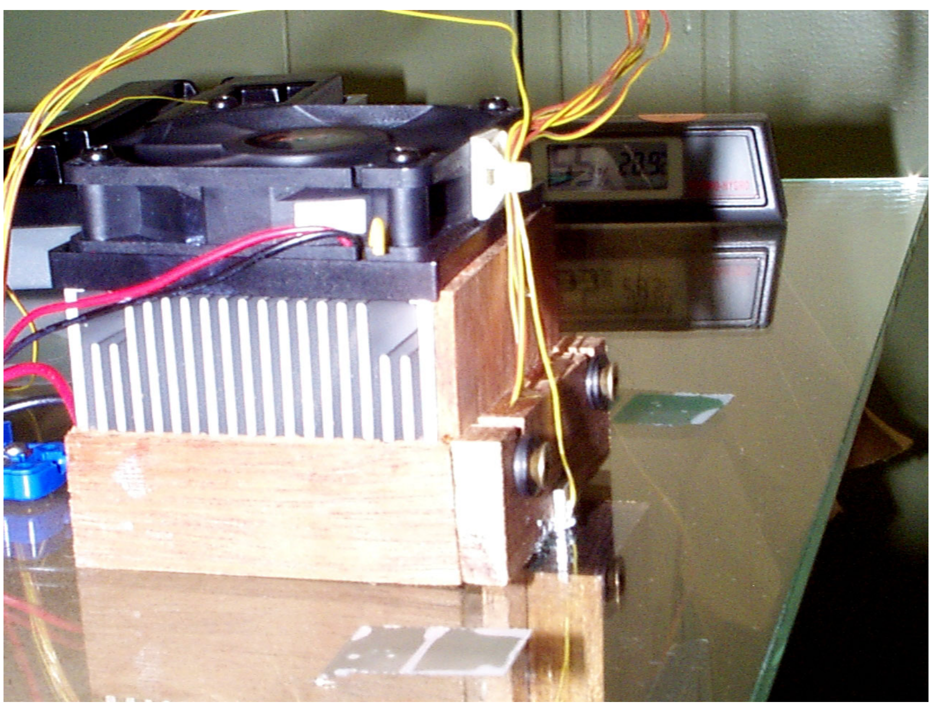


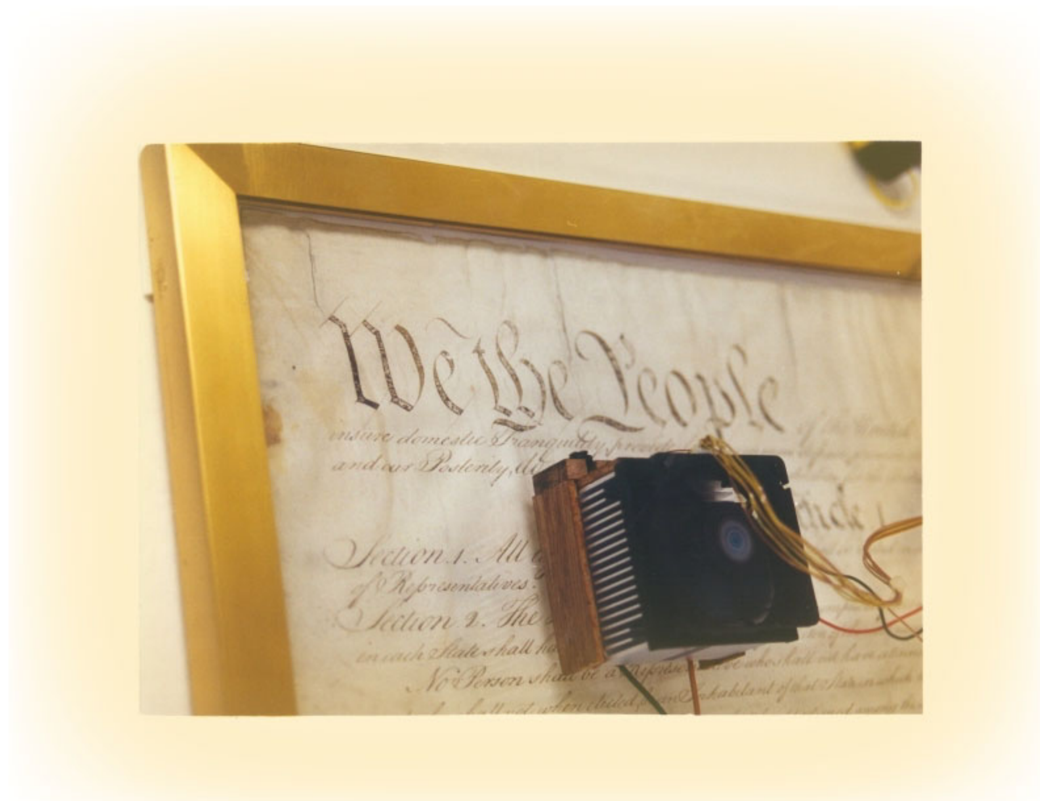
Figure 4: Thermoelectric cooler placement locations for measurements



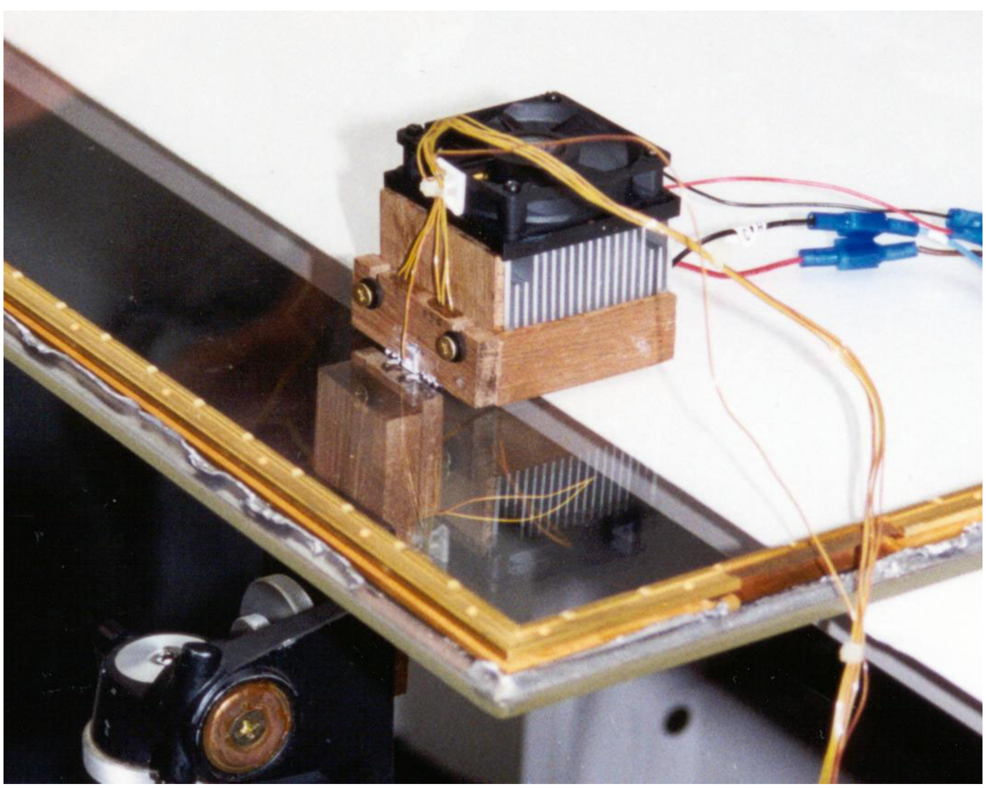
Photograph 2: Front view of thermoelectric cooler device showing heat sink compound under "foot" and thermocouples.



Photograph 3: Side view of thermoelectric cooler device.



Photograph 4 :Thermoelectric cooler device placed on sealed U.S. Constitution encasement



Photograph 5 : Thermoelectric cooler device placed on opened encasement

Measurements to Determine Gradient between Top and Bottom of Glass

Laboratory measurements were performed to provide correction factors for horizontal and vertical thermocouple disparity which were applied to increase the accuracy of the final humidity readings.

To determine the horizontal thermocouple placement correction, through-the-glass measurements were taken to identify which of the thermocouples on the thermoelectric cooler device was most representative of the temperature directly beneath the "foot" on the underside of the glass.

Additional through-the-glass measurements were then taken to determine vertical thermocouple placement correction factors. This was performed to determine the difference in the gradients between the NARA enclosure glass and the glass used at NASA-LaRC because this difference affects the horizontal thermocouple placement correction.

For the test at NARA, the thermoelectric cooler device was placed on the glass that was taken from the disassembled encasement that previously housed the U.S. Constitution, Page 2 - top glass. The thermoelectric cooler device was placed on the former inner surface of the encasement glass, 6 inches from the bottom inside edge, and 2.5" from the right inside edge. The spring-loaded device to measure through-the-glass temperatures was centered directly below the "foot" on the former exterior surface of the encasement glass. Readings were taken at one (1) minute intervals for a duration of 20 minutes, as previous measurements indicated the glass had essentially reached thermal equilibrium in a localized area within that time.

Upon return to NASA LaRC, measurements were repeated several times to measure differences due to thermocouple placement under the glass. An additional 0.002" type "T" thermocouple (unavailable for NARA test) was centered directly underneath the "foot", sandwiched between the "foot" and the top of the plate glass. This thermocouple was used to determine both the vertical and the horizontal thermocouple placement corrections.

Analysis of these data provided corrections that were applied to derive the final values for the encasement measurements taken at NARA. Figure 7 & 8 shows the measurement setup used both at NARA and at NASA LaRC.

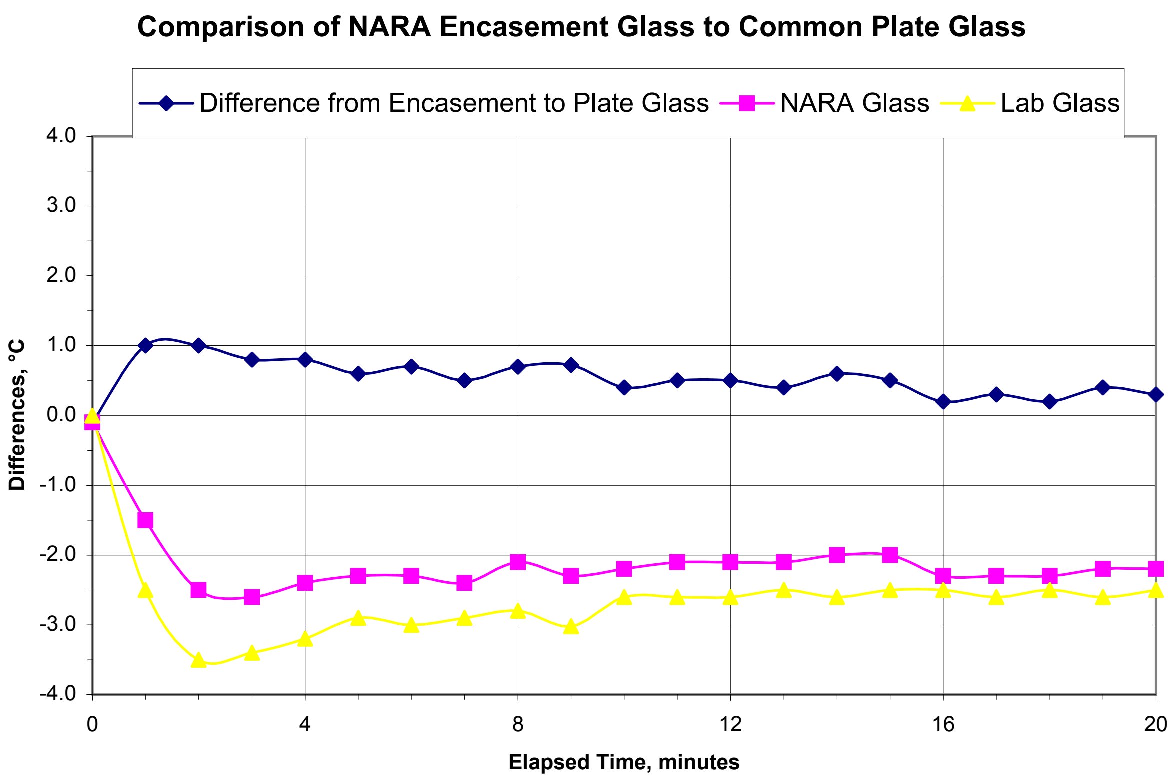
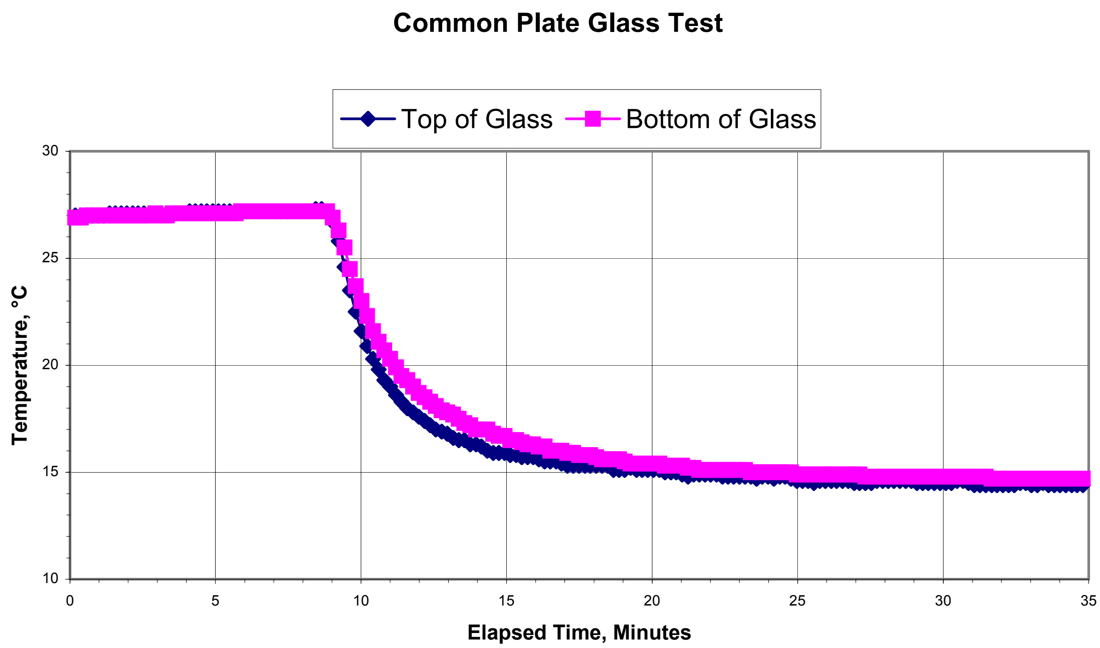


Figure 5 Comparison of NARA Encasement Glass to Common Plate Glass.



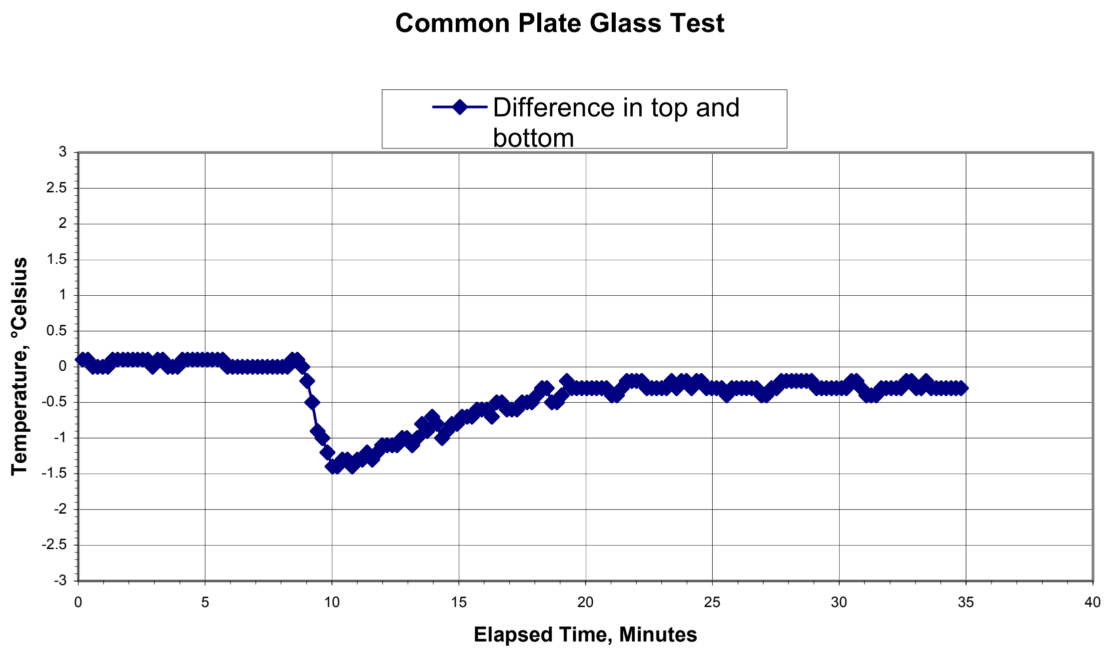


Figure 6. Common Plate Glass Test.

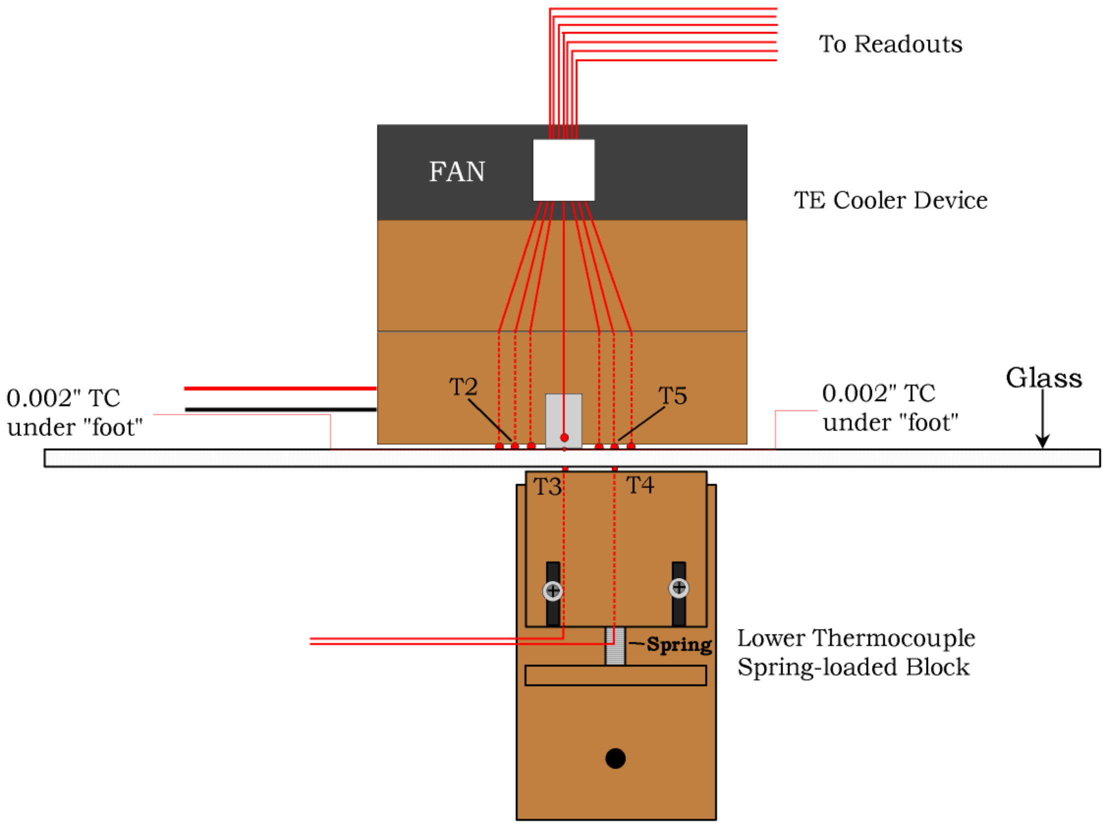


Figure 7: Front view of through-the-glass measurements at NARA and NASA LaRC (0.002" TC used only at NASA LaRC).

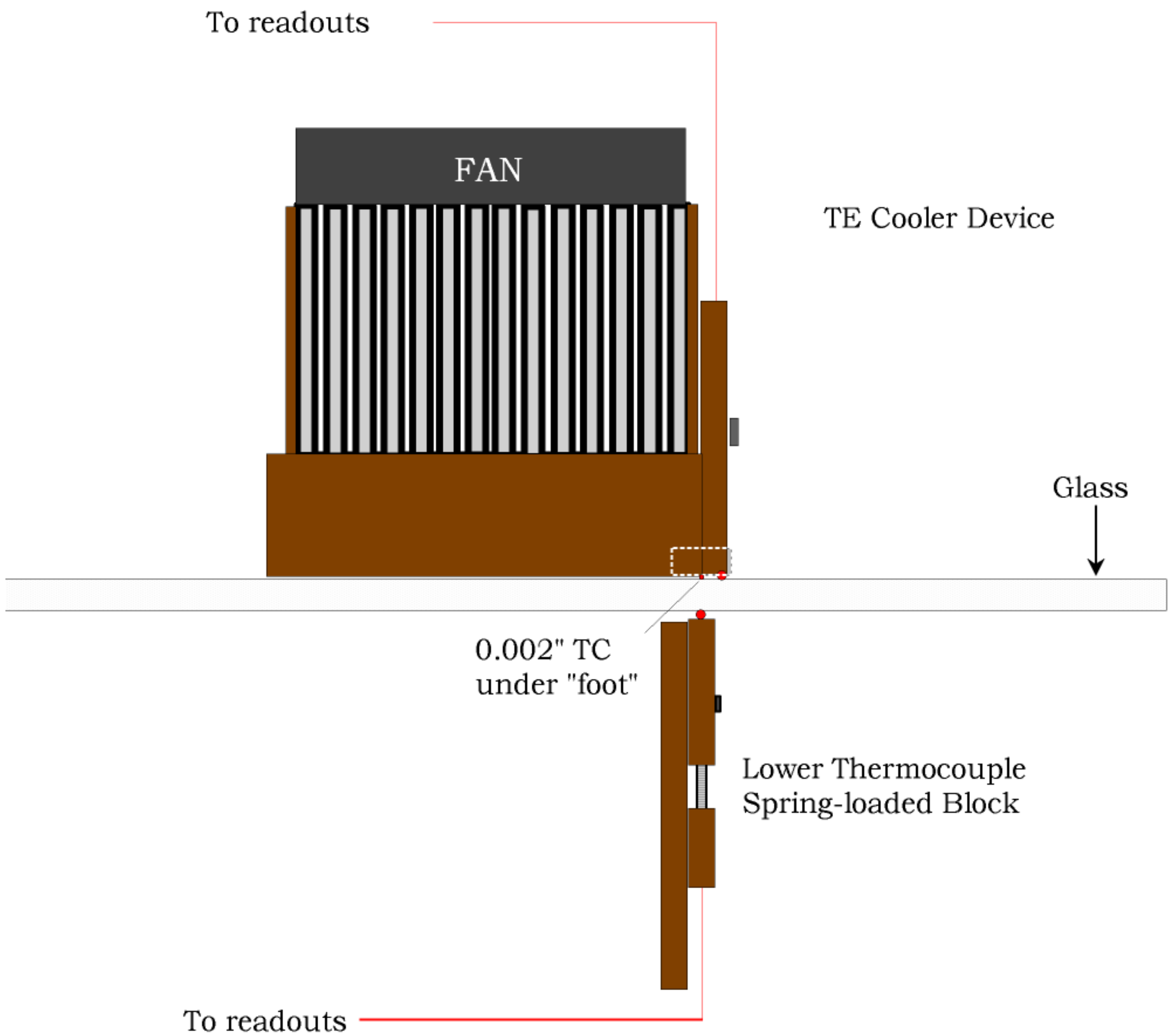


Figure 8: Side view of through-the-glass measurements done at NARA and NASA LaRC (0.002” TC used only at NASA LaRC).

Conclusions

The relative humidity of the atmosphere in the encasements containing the U.S. Constitution Pages 1 and 4, the Declaration of Independence, and the Bill of Rights was measured to be in the range of 55% to 61%. This value is significantly higher than the presumed relative humidity between 25 to 35 % (NBS Circular 505, 1951) [1], but is consistent with the measured samples extracted from Pages 2 and 3 of the U.S. Constitution (Davis et al., 2000) [3]. The cooling/condensation measurement technique used at NARA on July 23, 2001, and described in this paper to measure the water vapor content of the atmosphere in the hermetically sealed encasements containing the U. S. Constitution, the Declaration of Independence, and the Bill of Rights, proved to be a powerful new measurement technique. The cooling/condensation technique developed at NASA LaRC and utilized at NARA has important applications in the non-invasive measurement of relative humidity in the atmospheres of sealed encasements and could become a standard measurement technique in this type of analysis.

We would like to thank Dr. Joel Levine of Langley's Atmospheric Sciences Research Group for including us in this test at NARA.

References

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