Development of a New Method and Apparatus for the Measurement of Water Vapor Transmission Rates (WVTR) in Packaging Materials

By

Ben Dailey

A senior thesis submitted to the faculty of

Brigham Young University-Idaho

In partial fulfillment of the requirements of the degree of

Bachelor of Science

Department of Physics and Astronomy

Brigham Young University-Idaho

April 2013

BRIGHAM YOUNG UNIVERSITY-IDAHO
DEPARTMENTAL APPROVAL

Of a senior thesis submitted by

Ben Dailey

This thesis has been reviewed by the research advisor, research coordinator, and department chair and has been found to be satisfactory.

Date

David Oliphant, Advisor

Date

Stephen McNeil, Coordinator

Date

Brian Tonks, Committee member
ABSTRACT

Development of a New Method and Apparatus for the measurement of Water Vapor Transmission Rates (WVTR) in Packaging Materials

Ben Dailey
Department of Physics and Astronomy
Bachelor of Science

In response to a need for a more affordable as well as accurate way of making measurements on the permeability of packaging materials in the food science industry, a new method and apparatus for measuring Water Vapor Transmission Rates (WVTR) has been developed. Various potential methods of calculating WVTR were mathematically modeled. Based on these models it was eventually decided to focus efforts on one method that used change in relative humidity. By constructing an apparatus wherein a given packaging material is used as a membrane between a high relative humidity and a low relative humidity, the rate at which water vapor permeates through the membrane can be used to calculate the resistance of the membrane. This process requires the construction of such an apparatus, a calibration process that will allow for determining the capacitance of the apparatus, and a systematic experimental procedure involving the limitations of errors caused by: leakage, equipment, measurement, and the mathematical model upon which the experiments were based. Such an apparatus was constructed, and a method was developed and tested. The apparatus proved able to measure WVTR values with limited accuracy, which could be improved with further research.
Acknowledgements

I would like to acknowledge Dr. Gaylon Campbell, without whom this project would never have been possible. His helpful suggestions, as well as the trust and autonomy he provided were invaluable. I would also like to thank Brady Carter, who provided materials and direction to the procedures of this project. Finally, I would like to thank my advisors, Brian Tonks, David Oliphant, and Stephen McNeil, whose suggestions, corrections, and continued advice were both necessary and deeply appreciated in the process of completing this thesis.
CHAPTER 1. INDUSTRY AND BACKGROUND

1.1 Importance of Permeability of Packaging

The food science industry is based around allowing food producers and venders to maximize their ability to provide their services to the consumer. This means measuring and controlling water activity and moisture content of various products in order to ensure that products do not crystallize, mold, or in other ways spoil; therefore, the shelf life of a food product is based on its water content. Decagon Devices Inc. bases a large percentage of their annual revenue in the food science industry, having carved out a large portion of a niche market for themselves and their highly rated products. Decagon has developed several products that measure water activity in order to determine how long a product can last before being ruined. These measurements however, rely on a water vapor transmission rate (WVTR) value.

1.2 Current Practices for and Problems with Measuring WVTR

Of the various current methods of measuring WVTR, there are two basic methods that are the most common. The first method is based on ASTM E 95-96, which consists of creating a hole of known area in an aluminum cover, which is placed over a Petri dish of water. The material to be tested is sealed over the hole with an epoxy and the dish is placed in a convection oven. The loss of mass in the dish is used to calculate how much water has evaporated through the material, and thus WVTR is calculated.

This procedure, while not invalid or useless, is not as accurate as might be hoped. It is also somewhat impractical when used for testing large amounts of different materials, which makes it ill suited to being mass produced.
The second procedure is based on ASTM F1249, wherein a material is used as a barrier between two chambers, both of which are at ambient atmospheric pressure. One chamber is purged by a donor gas, such as nitrogen. The other undergoes the same process, but with a humidified gas or acceptor gas. Moisture from the acceptor gas permeates through the material and is then carried by a stream of the acceptor gas to be analyzed by Mass Spectrometry (MS) and a moisture sensor based on Near Infrared Diode Laser Spectroscopy.

This method is extremely accurate, and various forms of it exist in the food science industry. However, the advanced technology and need for donor and acceptor gases etc. lead to a much higher cost than other methods.

Thus, the goal of this project was to find a new method and apparatus for testing WVTR that would provide the advantages noted above while avoiding the disadvantages. With this goal in mind, a low cost and mass producible apparatus that would test WVTR to a reasonable level of accuracy was created. The project to achieve this goal is described as follows. Chapter Two describes calculation that were done to determine whether or not already existing tools or Decagon products could be applied to this new method and apparatus. Chapter two also describes the construction of the apparatus finally settled on and the mathematical model upon which it is based. Chapter Three describes the experiments and calibration of the apparatus, the various problems encountered and their various solutions, and the improvements on the mathematical model as well as the on the apparatus itself. Chapter four concludes by establishing the results of the project, explaining what research remains to be done and how such research could be executed.
CHAPTER 2. PREPARATORY CALCULATIONS AND USE OF THE VAPOR SORPTION ANALYZER

2.1 Critical Time

The Vapor Sorption Analyzer (VSA) is an existing product invented by and currently sold by Decagon. It is an advanced tool that allows for the control and measurement of relative humidity as well as temperature for a small sample over time, and provides information in the form of an isotherm for a given material. Initial mathematical models were developed to determine whether or not the controlled environment provided by the VSA could be used to determine WVTR of materials. This could be done by constructing an apparatus that would hold a material, and measurements could be made as to how water vapor transmitted through the membrane. Determination of whether or not such an apparatus could be used to measure given changes under the conditions rendered by the VSA was reached by modeling both possibility and practicality of a given method. In other words, possibility was determined by whether or not WVTR could be measured and/or calculated mathematically, and practicality was measured based on the critical time of a measurement. Critical time is defined in this project as the amount of time necessary for a test to run while providing the minimum measureable desired quantity.

2.1.1 Critical Time for Change in mass based on Water Activity ($A_w$)

First, calculations were executed to find critical time of various packaging materials with a large range of known WVTR values. These calculations were based on a
change in water activity using equations and previous calculations, provided by Brady Carter, a Senior Research Scientist at Decagon Devices Inc. They were used to determine whether or not the VSA could be utilized to do tests in a few days or less and still achieve a measurable change in mass. A test would be considered practical if a measurable change in mass could be caused by the VSA in five days or less. For this to occur, a measurable change in water activity would have to be caused.

This was done using the following equations. Critical time is the amount of time it will take for a sample to go from an initial water activity to a final or critical water activity. This amount of time depends on the change in water activity, as well as relative humidity and the components of the time constant $\tau$ as shown in equation 3.

$$A_w = h_a - (h_a - a_{wo}) \exp \left( -\frac{t}{\tau} \right)$$ (1)

Equation 1, developed by Decagon’s Research Scientists, defines water activity as affected by initial water activity, humidity of air, time elapsed in a given test, and a time constant $\tau$ which is defined in equation 2.

$$\tau = \frac{(\alpha p_a M)}{(e, Ag_v)}$$ (2)

These relationships allow us to define critical time.

$$t_{critical} = -\tau \ln \left( \frac{(h_a - a_{wc})}{(h_a - a_{wo})} \right)$$ (3)

Critical time is the amount of time it will take for a sample to go from an initial water activity to a final or critical water activity. This amount of time depends on the
change in water activity, as well as relative humidity and the components of the time constant \( \tau \) as shown in equation 3. The above mentioned variables as found in equations 1-3 are defined below.

\( \alpha \) = slope of the isotherm,

\( a_{w0} \) = initial water activity

\( a_{wc} \) = critical water activity

\( P_a \) = atmospheric pressure (kPa)

\( M \) = total mass of product inside the package (grams)

\( e_s \) = saturation water vapor pressure at package temperature (kPa)

\( A \) = package surface area (\( m^2 \))

\( g_v \) = package conductance \( \frac{g}{m^2 \cdot s} \)

\( h_a \) = humidity of air

\( t \) = time

The time constant \( \tau \) mentioned above contains mostly known values. \( P_a \) is known, and mass and area can be measured. Tabulated values for \( e_s \), and \( g_v \) can be used. The slope \( \alpha \) can be provided by the isotherm generated by the VSA in testing a given material.

In solving for critical time with specific changes in water activity with these equations and using a relative humidity of 0.9 (which could be provided and controlled
by the VSA), experiments would have taken far too many days to be considered reasonable for low WVTR values, and only high values (in the best cases above 0.45 \(\frac{g}{m^2\text{day}}\)) could have been tested. The critical time in most cases was still more than one week, sometimes significantly more, unless the change in water activity was very small as can be seen below. Tables 1 and 2 use the given slopes \(\alpha\) from previous tests done on milk powder with the VSA. Tables 3-5 uses a selected slope \(\alpha\) from a desiccant isotherm selected by Brady Carter and a more accurate surface area based on the VSA sample cups. These are selected results from many that were recorded to represent several values of \(a_{w0}\) and \(a_{w0}\) which were used to yield potential values of \(t_{critical}\).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Table 2</th>
<th>Table 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aw 0.3-0.4  (\alpha = 0.24)</td>
<td>Aw 0.4-0.5  (\alpha = 0.24)</td>
<td>Aw 0.3-0.4  (\alpha = 0.45)</td>
</tr>
<tr>
<td>WVTR</td>
<td>time (days)</td>
<td>WVTR</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>3</td>
<td>1.44</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>2.16</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>4.31</td>
<td>1</td>
</tr>
<tr>
<td>0.75</td>
<td>5.75</td>
<td>0.75</td>
</tr>
<tr>
<td>0.45</td>
<td>9.58</td>
<td>0.45</td>
</tr>
<tr>
<td>0.23</td>
<td>18.75</td>
<td>0.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aw 0.3-0.5  (\alpha = 0.045)</td>
<td>Aw 0.3-0.35  (\alpha = 0.045)</td>
</tr>
<tr>
<td>WVTR</td>
<td>time (days)</td>
</tr>
<tr>
<td>-------</td>
<td>-------------</td>
</tr>
<tr>
<td>3</td>
<td>5.17</td>
</tr>
<tr>
<td>2</td>
<td>7.75</td>
</tr>
<tr>
<td>1</td>
<td>15.5</td>
</tr>
<tr>
<td>0.75</td>
<td>20.67</td>
</tr>
<tr>
<td>0.45</td>
<td>34.45</td>
</tr>
<tr>
<td>0.23</td>
<td>67.39</td>
</tr>
</tbody>
</table>
2.1.2 Critical Time for Change in mass based on Moisture Content

It was then discovered that another possibility was to calculate critical time using moisture content instead of water activity. This was done under the assumption that using these new sets of calculations it would be proved that doing tests in the VSA would be possible and that the following conditions would be met. First, as water content changed and a change in mass occurred, that such a change would be measurable. Second, the critical time for completing the measurable change in mass would be a few days or less, so that the VSA would not be in constant use, and a large amount of tests could be done in a reasonable amount of time. Third, having already seen problems with low WVTR values in the water activity tests, the test would not be limited to high WVTR values, but that all values could be tested.

Calculations for critical time based on moisture content were done using equation 4,

\[
\text{Critical Time} = \frac{\ln(\Gamma_c)}{\left(\frac{kA_P}{\alpha x M}\right)}
\]

where \( \Gamma_c \) is defined in equation 5

\[
\Gamma_c = \frac{(m_e - m_i)}{(m_e - m_c)}
\]

and
Other variables found in equation 5 are defined below

\[
k = \frac{g_s}{x} \frac{1}{P_a}
\]  

(6)

\[
m_i = \text{initial moisture content}, \quad m_c = \text{critical moisture content}, \quad m_e = \text{equilibrium moisture content}
\]

These equations were provided by Brady Carter, or derived from equations provided by him. Equation 4 demonstrates that critical time still depends on most of the same variables as did critical time when calculated based on water activity. \( \Gamma_c \) consists of a relationship between initial moisture content, critical moisture content, and equilibrium moisture content, which can be calculated from the ambient relative humidity, which in this case will be 0.9.

These equations made it possible to calculate the critical time of a change of one milligram (minimum measurable change in mass using Decagon’s equipment) in a given sample. Again using a relative humidity of 0.9 and using the slope found in the drierite isotherm, the resulting critical time for a given test were higher than the desired values.

The tables below note the initial moisture content, critical moisture content, equilibrium moisture content, as well as initial and critical water activities for various values of WVTR. This information as well as corresponding slopes was used to calculate, as noted above, the change in mass and critical time for these specific changes in moisture content. The WVTR values used were of 0.23, 0.45, and 1, to represent high, medium, and relatively low values. The moisture content changes were between 0.2 and 0.3, and 0.28 and 0.3 for each WVTR to give an idea of critical time for a small and a large change in moisture content.
Table 6 labeled $\alpha=0.089$ uses a slope from a desiccant (drierite) isotherm, but the data is limited to the points of interest, which are from 0.1 to 0.4 water activity. Table 7 labeled $\alpha=0.29$ uses the slope provided by a linear regression analysis of the same isotherm.

Table 6

$\alpha=0.089$

<table>
<thead>
<tr>
<th>WVTR</th>
<th>1</th>
<th>1</th>
<th>0.45</th>
<th>0.23</th>
<th>0.45</th>
<th>0.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aw1</td>
<td>0.2</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.285</td>
<td>0.285</td>
</tr>
<tr>
<td>Awc</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Mi</td>
<td>0.0578</td>
<td>0.06524</td>
<td>0.06524</td>
<td>0.06524</td>
<td>0.06562</td>
<td>0.06562</td>
</tr>
<tr>
<td>Mc</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
</tr>
<tr>
<td>change mg</td>
<td>8.93</td>
<td>1.49</td>
<td>1.49</td>
<td>1.49</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Me</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
</tr>
<tr>
<td>Critical Time (days)</td>
<td>26.6</td>
<td>4.84</td>
<td>10.76</td>
<td>21.1</td>
<td>8.1</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Table 7

$\alpha=0.29$

<table>
<thead>
<tr>
<th>WVTR</th>
<th>1</th>
<th>1</th>
<th>0.45</th>
<th>0.23</th>
<th>0.45</th>
<th>0.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aw1</td>
<td>0.2</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
<td>0.285</td>
<td>0.285</td>
</tr>
<tr>
<td>Awc</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Mi</td>
<td>0.0578</td>
<td>0.06524</td>
<td>0.06524</td>
<td>0.06524</td>
<td>0.06562</td>
<td>0.06562</td>
</tr>
<tr>
<td>Mc</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
<td>0.06673</td>
</tr>
<tr>
<td>change mg</td>
<td>8.93</td>
<td>1.49</td>
<td>1.49</td>
<td>1.49</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Me</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
<td>0.010629</td>
</tr>
<tr>
<td>Critical Time (days)</td>
<td>86.8</td>
<td>15.8</td>
<td>35.1</td>
<td>68.6</td>
<td>26.3</td>
<td>51.4</td>
</tr>
</tbody>
</table>

This data shows a critical time of between 4.8 days (Table 6) and 15.8 days (Table 7) for even a small change in moisture content, for a large WVTR. At higher values the critical time explodes, reaching a possible 86.8 days (Table 7). Based on this
data, it became clear that using water activity and moisture content would not provide the
desired measureable change in mass in a sample.

2.1.3 Critical Time for Change in Mass using Relative Humidity

Based on the above conclusions, a final attempt was made at harnessing the VSA for the use of this experiment. Change in mass per time of a sample is defined below, where all variables are the same as defined previously.

\[
\frac{dM}{dt} = -Ag \cdot \left( \frac{e(T)}{P_a} \right)(h_a - h_s)
\]  

(7)

In equation 7 the difference in relative humidity would be close to 0.9. This value is calculated as the difference between inside a chamber as close to zero as possible and outside the same chamber, which would be maintained at ninety percent. Using these values, critical time for a change of 1 mg was calculated and the following changes in mass per specific changes in time were determined. Using the above equation and solving for dM when dt= 1 day, 3 days, and 5 days, and then solving for dt when dM = 1 mg, the following data was generated.

Table 8.

<table>
<thead>
<tr>
<th>WVTR</th>
<th>Time (days) required for mass change of 1 mg</th>
<th>Change in mass (mg) in 1 day</th>
<th>Change in mass (mg) in 3 days</th>
<th>Change in mass (mg) in 5 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.55</td>
<td>1.83</td>
<td>5.49</td>
<td>9.15</td>
</tr>
<tr>
<td>1</td>
<td>1.64</td>
<td>0.61</td>
<td>1.83</td>
<td>3.05</td>
</tr>
<tr>
<td>0.75</td>
<td>2.19</td>
<td>0.46</td>
<td>1.37</td>
<td>2.29</td>
</tr>
<tr>
<td>0.5</td>
<td>3.28</td>
<td>0.3</td>
<td>0.91</td>
<td>1.52</td>
</tr>
<tr>
<td>0.45</td>
<td>3.64</td>
<td>0.27</td>
<td>0.82</td>
<td>1.37</td>
</tr>
<tr>
<td>0.35</td>
<td>4.69</td>
<td>0.21</td>
<td>0.64</td>
<td>1.07</td>
</tr>
</tbody>
</table>
The correlation between critical time for change in mass based on relative humidity, and WVTR values can be seen in Fig. 2.1 below.

This information yielded the conclusion that measuring a change in mass was not the best way to determine WVTR values, especially using so much valuable time in the VSA. However, use of the VSA equation provided the inspiration to attempt measurements based on change in relative humidity as opposed to change in mass.

2.2 Experiment and Apparatus
Another way to measure WVTR is to design an apparatus in which a sealed chamber can be dried down to close to zero percent humidity and the outside humidity can be controlled. If a material is used to seal the chamber, and humidity inside the chamber is monitored, then the rate at which humidity inside is changing can be used to calculate WVTR. Based on the equations in section 2.3, resistance to water vapor transmissions could be calculated and from resistance the WVTR. Such an apparatus would have a capacitance that is necessary for calculating resistance of a given membrane, and this capacitance would be measured using a calibration plate. This plate, used to seal the chamber instead of a packaging material, would have a hole in the center. Water Vapor could diffuse through this hole, and if the dimensions were correct, a resistance comparable to those that would be seen in the various packaging materials to be used would be measurable. With a known resistance, capacitance of the chamber could be more accurately calculated, and with this value for capacitance, resistance could be calculated for any material. From these resistances WVTR values could be easily calculated.

2.3 Calibration Plate and Resistance Calculations

The resistance calculations are as follows. The following equations were developed based on mathematical models found in An Introduction to Biophysics by Thomas M. Nordlund, and Environmental Biophysics by Dr. Gaylon Campbell.

The WVTR values used in previous calculations were tabulated based on a test done at T=38°C with a relative humidity of 0.9.

WVTR or E is defined below,
Since $\frac{d\rho_{vs}}{dt}$ is the change in saturation vapor density, this change per time can be defined as ambient saturation vapor density minus saturation vapor density divided by resistance of a material through which water vapor is flowing. Equation 8 can be rearranged solving for resistance to become

$$r_v = \frac{\rho_{va} - \rho_{vs}}{E}$$

In equation (9) $\rho_{va}$ will be equal to the saturation vapor density at a given ambient temperature. This value is reached by multiplying a tabulated density value at a given temperature $\rho'_y(T)$ by the ambient relative humidity as shown below in equation 11.

The density value at a given temperature (as mentioned above, 38º C) can be found in An Introduction to Environmental Biophysics, as shown in equation 10.

$$\rho'_y(38) = 46.3 \frac{g}{m^3}$$

The value reached in equation 10 will be multiplied by the relative humidity, which gives a value of

$$\rho_{vs} = h_r \rho'_y = 0.9 \times 46.3 = 41.7 \frac{g}{m^3}$$

Since the inside of the chamber will have a value of humidity of as close to zero as possible, the value of $\rho_{vs}$ will be equal to 0. In this case a WVTR or E value of $1 \frac{g}{m^2 \text{ day}}$ will be used. This can be converted into seconds to give
Solving for resistance using these values gives equation 12.

\[ r_v = \left( \frac{\rho_{wa} - \rho_{va}}{E} \right) = \frac{\left( \frac{41.7 \, \text{g}}{\text{m}^3} \right)}{\left( \frac{1 \, \text{g}}{(\text{m}^2 \times 86400 \, \text{s})} \right)} = 3.6 \times 10^6 \, \frac{s}{m} \]  

Thus, as shown above, with a given WVTR value, we known that a certain resistance more or less along the lines of the result of equation 12 should exist in a material as water vapor passes through as shown below in figure 2.3.1

**Figure 2.3.1**

It is next necessary to then solve for the dimension of a calibration plate and hole apparatus that will produce a similar resistance, as shown below in Figure 2.3.2
This is done using the equations for resistance through a pore of a given diameter $d$ and thickness $l$, including end corrections on both sides.

$$r_v = \left( l + \left( \frac{\pi d}{4} \right) \right) \left( \frac{\pi n d^2}{4 D} \right)$$

(13)

In equation 13, $D$ is diffusion coefficient $2.4 \times 10^{-5} \, \text{m}^2/\text{s}$ and $n$ is the number of pores per surface area. $l$=the thickness of the calibration plate, and $d$ is the diameter of the hole shown above in figure 3.2.3. When looking at only a portion of the denominator of equation 13, equation 14 is found to defines the area of a circle, or the hole in the calibration plate.
Since $n$ in equation 13 and 15 is the number of holes per total area, then

$$\frac{\pi n d^2}{4}$$  \hspace{1cm} (15)

could be restated as

$$\frac{a (\text{area of hole})}{A (\text{area of plate})}$$  \hspace{1cm} (16)

Substituting equation 16 into equation 13 and using values of $l = 1 \text{ mm}$ and $d = 1 \text{ mm}$ the result is equation 17.

$$r_v = \frac{A}{a} = 1.2 \times 10^5 \frac{s}{m}$$  \hspace{1cm} (17)

A higher value would be preferable, to be closer to the calculated resistance of $3.6 \times 10^6 \frac{s}{m}$. This can be done by increasing the thickness of the calibration plate. If a value of 1 cm is used, the resultant resistance comes to $7.2 \times 10^5 \frac{s}{m}$. This is satisfactorily close. The project then, will use the above described calibration plate with a known resistance to solve for capacitance. This value can be used to solve for resistance of a given material when the calibration plate is not in use. The next step is to calculate a change in Relative Humidity (RH) per time to evaluate whether or not this change will be measurable in a relatively short period of time.
The WVTR rate or Evaporation rate is stated in equation 8

\[ E = C \left( \frac{d\rho_{\text{vs}}}{dt} \right) = \frac{(\rho_{\text{vs}} - \rho_{\text{va}})}{r_v} \]  \hspace{1cm} (8)

Where \(\rho\) is defined in equation 18

\[ \rho_{\text{vs}} = \rho'_{v} h_s \quad \text{and} \quad \rho_{\text{va}} = \rho'_{a} h_a \]  \hspace{1cm} (18)

Equation 8 can then be simplified by substituting equation 18 into equation 8 to get

\[ C \left( \frac{d(\rho'_{v} h_s)}{dt} \right) = \frac{\rho'_{v} (h_a - h_s)}{r_v} \]  \hspace{1cm} (19)

The constant \(\rho'_{v}\) can then be factored and divided out. Solving for change in humidity per change in time gives equation 20.

\[ \frac{dh_s}{dt} = \frac{(h_a - h_s)}{(r_v C)} \]  \hspace{1cm} (20)

The value for \(C\), the volume of the chamber over surface area, will give a value for the depth of the chamber in meters. For the first trial, the depth will be estimated to be one centimeter. Once resistance calculations are completed, this value can be more accurately selected and used in future calculations. The difference in humidity will be the difference between inside and outside of the chamber. The relative humidity outside of the chamber will be maintained at about ninety percent. The inside will initially be as close to zero as possible, making the difference in humidity \(h_a - h_s = 0.9\). The value for \(r_v\), as calculated above using a calibration plate thickness of 0.01 m, came to \(7.2 \times 10^5 \frac{s}{m}\).
Thus equation 20 becomes

\[ \frac{dh}{dt} = \frac{0.9}{0.01 \times 7.2 \times 10^5 \frac{s}{m}} = 1.25 \times 10^4 \frac{1}{s} \]  \hspace{1cm} (20)

or converted into hours 0.45/hr. This means that the given conditions will provide a relatively rapid rate of change in humidity, which can be measured with relative ease in a decently short amount of time.
CHAPTER 3. INITIAL EXPERIMENTS AND CALIBRATION

3.1 Apparatus

The initial design for the testing apparatus is as follows. The lower chamber consists of an open cylindrical chamber with a diameter of four centimeters. The rim of the chamber is 2.1 centimeters wide, making the outside to outside diameter of the chamber 8.2 centimeters. There are four threaded rods equally spaced around the outside perimeter of the rim pointing straight up. The inside chamber has three holes drilled through the rim, two on opposite sides of each other, where plastic tubes which can be opened and shut provide air intake and outtake for controlling initial relative humidity inside the chamber. The third hole is for the RH sensor, which is then sealed from the outside once the RH sensor is in place. A groove is located two millimeters from the inside of the rim, wherein an O-ring is placed, providing a seal for the chamber. A ring, measuring 2.1 cm wide and 1.3 cm thick has four equally spaced holes which can be placed over the threaded rods. When the ring is in place, four wing nuts can be applied to the rods, effectively sealing the chamber shut over whatever packaging material is placed between the ring and the chamber. Initially, a calibration plate will be placed over the chamber. This plate is 1 cm thick and has a hole of 1 mm drilled exactly in the center. The plate is 6.2 cm in diameter. The initial seal plate is one mm thick and is also 6.2 cm in diameter. Figure 3.1.1 shows a top view diagram of the apparatus and Figure 3.1.2 shows a side view using the calibration plate. The apparatus itself is shown in Figure 3.1.3 with the Calibration plate.

Figure 3.1.1
3.2 Experimental Procedure

All tests were based on the fact that the chamber would have an initial Relative Humidity of close to 0. This was to be accomplished by using a pump and dry down apparatus. This apparatus consisted of a Rena Air 50 pump, which was connected by a 3/8 inch hose to a desiccant cartridge with barbed fittings. These fittings could be inserted into the air intake of the test apparatus, and after a given period of time, the pump can be disconnected and both valves sealed. This procedure put the initial relative humidity value at close to zero. After running several tests, the results show that the in about two minutes or less the chamber can be lowered to a relative humidity of about 0.1. In fifteen minutes or so the chamber can be lowered to 0.05 RH.

Initial tests were done in ambient Relative Humidity (RH) with a RH at about forty percent. Eventual tests were moved to a glove box where RH could be raised to
about eighty percent. Once the chamber interior was dried down to close to zero, change in internal RH was measured using a data logger hooked up to the RH/temp sensor inside the chamber to monitor the relative humidity inside the chamber for an extended period of time.

3.3 Seal Plate and Calibration Plate tests

3.3.1 Inlet/Outlet Leakage

The purpose of the first test was to verify that the seal on the apparatus was functioning properly. If the seal was functioning, then the relative humidity readings from the data logger was expected to remain unchanged over time. These values should have been comparably different than if the calibration plate was used to seal the chamber instead of the solid plate.

Over the course of three tests executed, as explained above, the data revealed that for some reason, the chamber was not being properly sealed. The results from one of the three tests is shown below in Figure 3.3.1.

![Figure 3.3.1](image-url)
The above graph demonstrates that the relative humidity inside the chamber, which was expected to remain close to zero, climbed as soon as the chamber was sealed. This was interesting, especially compared with the results from sealing the chamber around the calibration plate. One of two initial calibration plate tests is shown below, where column B represents the relative humidity inside the chamber, and column D represents the ambient relative humidity outside the chamber.

Figure 3.3.2

Based on these results a new test was initiated. The chamber was pressurized and then submersed in water, the expected result would be the appearance of air bubbles in the place that the seal or other portion of the apparatus was leaking. Doing so yielded only a small leak in a cracked portion of the seal on the air intake tube. While the leak did not seem large enough to yield the previous results in change in humidity inside the chamber, the leak did need to be fixed. This could be easily done by adding more glue to the seal.

3.3.2 Remodeling the Apparatus
After the water test was completed another oddity was discovered. When the chamber was left open, the RH/temp sensor left inside the chamber read exactly or close to exactly the same as the outside RH/temp sensor. This was to be expected. However, the moment the chamber was sealed, the RH measurement from the sensor within the chamber began to read higher and higher values of humidity. This was tested several times and consistently the reading for the relative humidity would spike almost instantaneously when the chamber was closed. Sealing the chamber or covering the chamber yielded almost identical results. The following graph shows this relationship.

Column B displays the ambient humidity remaining constant. Column D displays the changing humidity within the chamber. The following data was gathered after drying down the chamber to about 0.07 humidity. The chamber was then covered by the seal plate. At around 10:10 a.m. the chamber was dried down again, and this time sealed, beginning at about 10:20. The resulting data is displayed below.

Figure 3.3.3
The data indicated the possibility of water being trapped in the chamber. Per this potential issue, desiccated air was forced into and around the chamber to ensure complete dryness. The intake and outtake tubes were checked and verified to be completely dry. Desiccated air was indeed moving through both tubes. Several rechecks were done on the results shown in Fig. 10 to ensure that they were consistent and after three separate tests the results proved to be the same. The RH sensor was then replaced to ensure that the data was not simply due to equipment malfunction.

After replacing the RH sensor with another without over molding or plastic and resealing the plastic intake and outtake tubes with glue a new test was undertaken wherein the chamber was dried down and sealed. The chamber was then left over an extended period of time and the results showed conclusively that the chamber was still not sealing. While the only evidence of a leak remained in the intake and outtake, the next logical step was to improve the seal of the intake and outtake. If the leak continued, it would be possible to ensure that the leak was occurring through the seal itself.

The hardware selected for the intake and outtake tubes was a brass air cock from McMaster-Carr. It has a 1/8 inch fitting, allowing us to fit it right into our holes, a lever handle for opening and closing the valve, and a barb on the opposite side of the threaded fitting allowing for an easy connection to the 3/8 inch hose used in the drying apparatus.

Once these fittings were applied, with the threads of the fitting sealed, another test was done. Leakage was still occurring. The next step was to try to improve the seal on the sensor cord. This was done by stripping the wires down out of the cable, and using epoxy to seal the hole where they entered the chamber.
Another long test was executed over the course of several days. The chamber was raised to about ninety percent humidity. Over the course of several days, the humidity inside leaked to about seventy percent. This was slow enough to at least show potential for doing tests with some leakage, and using the calibration plate and seal plate results to mathematically calculate the leakage and still get accurate results.

This was tested by putting on the calibration plate and drying down the chamber to zero percent in about two minutes. This in itself was a good sign. As stated above, with the previous seals the chamber could only be dried down to about five percent humidity and this took about twenty minutes. The new chamber was sealed off and left for two and a half hours. The results are as follows

Figure 3.3.4

<table>
<thead>
<tr>
<th>RH in</th>
<th>RH ambient</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3.3.3 Chamber leakage
These results show that there still appeared to be a leak, however, they are inconclusive without retesting the seal plate to verify how much leakage is occurring. The following data shows the results of such a test.

Figure 3.3.5

As shown above, there was faster change in RH through the calibration plate. However, a lot of leakage occurred in the seal plate. Before beginning mathematical corrections for the leakage that was occurring, one more test yielded a host of troubling questions. Silicone grease was applied to the O-ring to determine whether or not there was leakage occurring along the seal. The following results demonstrated that indeed, there was leakage occurring there.

Figure 3.3.6
This test shows a dramatic difference between the change in RH inside the chamber when silicone grease is and is not applied to the O-ring prior to sealing it up. This helped to define where the leak was but upon testing the calibration plate with silicone grease applied to the O-ring, the following puzzling results were produced.

Figure 3.3.7
With so little difference between the calibration plate and the seal plate, any diffusion occurring through the hole in the calibration plate seemed to be lost in the amount of leakage that was occurring, even when using silicone grease.

The next test was to again pressurize the chamber and submerge it in water while sealed in order to verify visually whether there was another leak that needed to be fixed. As predicted by the above results, the only bubbles that were easily located occurred along the O-ring seal, and the leak was not only obvious but fairly extensive. Bubbles were large and developed relatively quickly.

Knowing that the leak was occurring around the O-ring meant that the attempts to stop the leaking could be focused there. The O-ring itself seemed to be in perfect condition. Assuming that the O-ring was in fact doing its job left only the possibility that the surfaces against the O-ring were flawed. A brief test was conducted to verify this idea. The seal plate was set on top of the calibration plate with a small amount of silicone grease in order to force the calibration plate to act as a much thicker seal plate. When this was done, even over a brief twenty minute period, the leakage decreased. Based on this information another seal plate was created, of the exact same dimensions as the calibration plate, but without the hole in the center. Using this new plate, another all night test was run and the results as shown below compare the calibration plate, the old seal plate and the new seal plate.

Figure 3.3.8
3.3.4 Improving the Procedure

While the new seal plate was considerably better than the old one, there is still an extreme steep quick response. Comparing the data in figures 12-16, (those taken after the new fittings were inserted and the chamber could be dried down to 0 RH) shows that the initial spike in RH is nearly identical, regardless of the plate being used, ambient RH, or any other factor. The only thing remaining the same in every test is the chamber itself, meaning that it is causing the initial spike, since that is the same nearly every time. One possibility was that the cause of this problem was leftover moisture caught in the board. One possible solution then was to increase the amount of time that desiccated air was blown through the chamber, hopefully drying out the board and not just the air around it. This was done and the results were as follows. Previously, desiccated air was blown through the chamber for two and a half to three minutes or until the data logger read that relative humidity was down to 0. In this test the dry down process was done for twenty minutes instead of three.
The extended dry down did indeed help the problem, definitely limiting the initial spike in humidity. This demonstrated that some of the initial spike and perhaps some of the creeping increase in humidity inside the chamber could have been a result of an internal leak.

The three most likely explanations for the above results are: the chamber is still leaking, there is moisture stored somewhere inside the chamber that slowly raises the RH value inside and the aluminum is either holding water, or is porous enough to allow water to filter through from outside. The following procedures were setup with the purpose of eliminating the above mentioned possibilities to isolate the actual cause of the unsteady RH values inside the chamber. It should also be noted that the hope continued to be that if the changing values could not be completely eliminated, they could at least be controlled to the point of prediction, or to the point of being able to mathematically remove them and still make our measurements of WVTR.
First the underwater test was undertaken again. This time a plastic tube was attached to one of the open fittings while the other was closed before submersion, allowing a constant stream of air into the chamber to pressurize it, as opposed to previous efforts wherein pressurizing the chamber once before submersion was sufficient to produce air bubbles. While the chamber was submerged and constant pressure was produced, no air bubbles became evident. There appeared to be no leak. If these results were indeed accurate, they yield the conclusion that the chamber itself was not leaking.

The next tests were done to eliminate any kind of interior stored moisture. The extended dry down should have eliminated most of the moisture still sticking to the board or interior of the chamber. In case any moisture was contained in the grease of the valves, the valves were taken apart and cleaned, the interior of the fittings completely wiped out and any grease removed with alcohol. Just enough grease was left on top and bottom of the fitting to allow it to turn, but none of this grease should be exposed to the actual chamber. However, these efforts yielded almost no change in results.

### 3.3.5 Other Considerations

Two more tests are worthy of note. The first was a test of the new seal plate that lasted for twenty hours. The results are shown below

Figure 3.3.10
The above test showed that for the first time, the RH inside the chamber seemed to be leveling out to some extend around twenty-four percent. It remained unknown however whether the chamber was sealing at twenty-four percent, or if the relative humidity inside the chamber was leveling off at a certain percentage of the ambient humidity.

The other interesting test was a calibration plate test that lasted all weekend. The results are as shown below.

Figure 3.3.11
This test provided two extremely important pieces of information. First, water vapor did not appear to be moving quite as quickly as it should have through the calibration plate, because the RH inside the chamber was not changing at the predicted rate and over three days it never actually reached ambient RH, although with a little more time it might have. Second, as the ambient RH changed so apparently did the rate of change inside the chamber. This piece of information supports most clearly the idea that there is indeed a leak in the chamber, or that the aluminum is storing or moving water vapor proportionately to the ambient RH.

According to the submersion test, there does not appear to be any kind of leak occurring anywhere in the chamber or the seal. Thus the most probable cause of the leak is the aluminum. If this is the case, the next question becomes, is this issue something that can be controlled and or calculated to make tests of water vapor transmission rates valid when using this apparatus, or will something else need to be used?

The best way to answer all of these questions was to control ambient humidity and watch the change in RH inside the chamber under a variety of scenarios. Both the seal plate and the calibration plate could then be tested under a variety of specific
ambient RH values. This information would be used to determine whether or not the chamber does indeed seal at a different value, or if the chamber carries moisture at a certain percentage of the ambient RH. If the chamber does seal it can be dried down to that value and tests can be run. If it carries moisture at a certain percentage of ambient humidity, that can be calculated out and tests can be run as well. If neither of these are the case, a new method may need to be employed, or the aluminum may need to be coated with nickel, epoxied, or replaced with stainless steel.

The first test of the seal plate showed an initial climb from zero as had been previously observed, and then a more or less leveling out around eighteen percent humidity as shown below.

![RH vs. Time Graph](image)

The graph above raises several questions. The slope of the ambient RH and the slope of the RH inside the chamber are almost identical. So, after the initial spike, does the RH inside the chamber rise because it is still “leaking” or because the ambient RH is also rising and thus affects the interior of the chamber as well? Hoping to discover some
kind of plateau in the leakage a second test was done with the seal plate, this time starting it at about twenty percent. The results are shown below.

Figure 3.3.11

These tests show that there does not appear to be a point at which the “leakage” stops. This again, suggests a problem with the porosity of the aluminum. However, it also shows that when the Ambient RH rose fairly steeply. The slope of the RH inside the chamber remained relatively unchanged. Another interesting point was that starting at a higher percentage, there was still an initial spike of the RH inside the chamber. The assumption until that point had been that the only spike would occur when the chamber was drastically affected from zero.

3.3.6 Mathematical Model
This knowledge allowed for some improvements in the mathematical model.

Another all night test was performed in the glove box with the calibration plate in place.

The results are shown below.

Figure 3.3.12

The discrepancies at just past three hundred minutes resulted from removing the chamber briefly from the glove box to check the data, and replacing it. Other than this point, a clear curve can be seen. This curve is much steeper than those seen in the Seal Plate tests. However, according to the calculations computed in equation 20,

$$\frac{dh}{dt} = \left(\frac{0.75}{01m \times 7.2 \times 10^5 m}\right) = 1.04 \times 10^{-4} \left(\frac{3600s}{1hr}\right) = \frac{.375}{hr}$$  (20)
This value is far higher than the slope found on the actual line, which is only 0.000713 or .0713 percent per hour, as compared to 37.5 percent per hour. However, equation 20 provides a linear rate of change, whereas what is seen in the calibration tests is logarithmic. Equation 20,

\[
\frac{dh_s}{dt} = \frac{(h_a - h_s)}{(r_v C)}
\]  

(20)

can be algebraically rearranged to find

\[
\frac{dh_s}{h_a - h_s} = \frac{dt}{Cr_v}
\]  

(21)

Then both sides can be integrated to become

\[-\ln(h_a - h_s) = \frac{t}{(Cr_v)}
\]  

(22)

using this logarithmic scale \(h_a\) and \(h_s\) can be plotted as a function of time. The slope which is \(\frac{1}{(Cr_v)}\) can then be used to calculate the resistance that is causing the change in RH to decrease with time.

This was calculated using the calibration plate test and the results showed a resistance of \(8.1 \times 10^4 \frac{s}{m}\). The value calculated for the calibration plate in equation 17 was \(7.2 \times 10^5 \frac{s}{m}\). Obviously this value is off by more than an entire order of magnitude. There are two reasons for this result. One is the capacitance value used in previously calculations. This C value, assumed to be 1 cm (the depth of the chamber), was known to
be somewhat inaccurate. The purpose of the calibration plate was to have a known resistance with which to calculate C for future calculations. The other reason is the unknown issues still present with sealing the chamber, possibly due to porous nature of the aluminum or some kind of trapped moisture inside the chamber. However, if ambient humidity is controlled, it becomes possible to mathematically account for these unknown problems as shown below.

There is a total ability to flow, or conductance represented by the variable $g$ in any given membrane that will be tested. Inversely, there is also a given resistance. It has already been shown that there is some unknown resistance thus we can define the total resistance measured through the above described tests of a given membrane as

$$\frac{1}{r_{\text{total}}} = \frac{1}{r_{\text{membrane}}} + \frac{1}{r_{\text{leak}}}$$

(23)

Where $r_{\text{leak}}$ will encompass the “leakage” occurring because of whatever as of yet undefined problems are causing leakage when the seal plate is on. Because of this definition, $r_{\text{leak}}$ can also represent the amount of leakage occurring when the seal plate is on since supposedly the seal plate is not leaking at all. C is the variable that needs to be solved for so the following equations will be necessary.

As explained above, the slope derived from the graph of equation 22 will be equal to $\frac{1}{(Cr)}$. Consequently, resistance of any material could be solved for if the capacitance of the chamber is known. However, to solve for the resistance of a material, $r_{\text{leak}}$ is needed, as is shown in equation 23. This can be done by using equation 22 to find slopes
for both the calibration plate and the seal plate. When these slopes are accurate and consistent the following calculations can be applied to solve for C.

Using equation 22, \( r_{\text{total}} \) total can be defined as the resistance measured from the calibration plate test. This resistance is known to represent the sum of the actual resistance of the hole drilled in the plate, as well as the unknown leakage, or \( r_{\text{leak}} \). As a result \( r_{\text{leak}} \) will be defined as the resistance of the seal plate when no other resistance is active except the unknown leakage. The actual resistance has been previously calculated. Therefore equation 22 becomes

\[
\frac{1}{r_{\text{cp}}} = \frac{1}{r_v} + \frac{1}{r_{sp}}
\]

or

\[
CM_{cp} = \frac{1}{(7.2 \times 10^5)} + CM_{sp}
\]

Equation 23 can then be rearranged algebraically to solve for C as follows in equation 24

\[
C = \frac{1}{(7.2 \times 10^5(M_{cp} - M_{sp}))}
\]
Thus, to calculate capacitance, all that is needed is the slope from the logarithmic graph produced by equation 22 for both the calibration plate and the seal plate.

The challenge then is to ensure that the graph of equation 22 does indeed produce a straight line. This is only achieved when the difference between RH outside and RH inside the chamber is decreasing. This is not a problem for the RH inside the chamber, however, if the RH outside the chamber increases or even if it decreases (changing the rate at which the difference between the two values changes) the resulting data can be inaccurate. The next sets of tests were dedicated to controlling the outside humidity, even inside the glove box; to within a percent or two in order to ensure that the slopes taken from the resulting lines were accurate and consistently repeatable.

The first several glove box tests did not yield consistent results. However, these tests were done one after another without changing the plate so the seal had not been reset. For glove box tests 11-17, each time a test was completed the chamber was opened, vacuum grease was reapplied and the chamber was dried down. Once this was done, results such as the following were produced.

Figure 3.3.13
Using slopes drawn from tests such as the one above, the Capacitance $C$ of the chamber was calculated to be 0.1. Using this value, resistance of the chamber when sealed with the seal plate was calculated. With resistance of the chamber calculated, the resistance of the actual material could then be calculated. The following spreadsheet was produced allowing for a single test to be run on any given material. The following is based on information gleaned from a test done on a Ziploc bag.
<table>
<thead>
<tr>
<th>time (min)</th>
<th>Ambient RH</th>
<th>Temp C</th>
<th>Long Test RH</th>
<th>Short test RH</th>
<th>-ln((ha-hs))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.71</td>
<td>23.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.341047228</td>
</tr>
<tr>
<td>2</td>
<td>0.71</td>
<td>23.1</td>
<td>0.01</td>
<td>0.01</td>
<td>0.35240578</td>
</tr>
<tr>
<td>3</td>
<td>0.72</td>
<td>23.3</td>
<td>0.01</td>
<td>0.01</td>
<td>0.345743281</td>
</tr>
</tbody>
</table>

1. Paste info from data logger below
2. Take slope from graph at right (first 100 min may have to be eliminated to get straight line)
3. Plug in slope above as slope(m)
CHAPTER 4. DISCUSSION AND FURTHER RESEARCH

4.1 Success and Failure of New Method and Apparatus

The project set out to solve a problem by answering the question: Is it possible to construct a product for Decagon Devices Inc. that would be both affordable and accurate? The project brought to light several interesting ideas and questions with respect to the possible future uses of this method and apparatus. First, measurement of WVTR rates can be measured by change in relative humidity. Tests of different materials using the information calculated and tested as shown above, yielded varying WVTR values as expected. The process is sound and the results are promising. Possible improvements in these results will be discussed further in section 4.2. The apparatus itself is extremely cheap to build. The chamber itself can be machined quickly and easily, the fittings are easy to come by and would be easy to redesign and build in house if so desired. The desiccant cartridge is identical to that already made for the VSA and could be sold as is, or changed to fit specifically to this tool if so desired. Thus, of the two goals, affordability has been reached.
As for the second question of whether or not the product is accurate, that will require further testing. Currently, the apparatus is not much more accurate than the ASTM E 94-95 method. It provides data, and the data is sound, but not extremely precise. In other words, the margin of error is still far outside of the desired goal. This could be changed, but will require further research, and there is a possibility that the kind of machinery and or electronics required to produce such accuracy would increase the expense of the product. However, even considering such increases, it is highly likely that the product itself would still be far cheaper than the donor/acceptor gas method, which costs between $50,000 and $100,000. If the expense of the product can be maintained low enough that the price of the product would be even half the price of its competitors, then both goals will have been achieved, making this product both valuable, and highly competitive.

4.2 Further Research

The inaccuracies of the system could potentially be eliminated if there was no change in ambient RH. The changes in RH of more than about one percent seemed to cause variance in the difference between RH in and RH out. This variance caused the slope of the line to change slightly, sometimes to changing the results of the resistance by more than five, or sometimes even ten percent. This hypothesis could be easily checked by running tests at an exact RH.

These tests could be executed quite simply if an environment were completely controlled. In the food lab this could be done by employing “the bubbler” or alternatively using a smaller chamber in a more controlled environment; where changes in RH were not affected by temperature (a.k.a someone leaving a door open, heat turning on and off
through the night etc.). The downside of this solution is only that a highly controlled environment may cost significantly more in the final product.

Another possibility for improvement of results and continued research is to focus energy on eliminating leakage completely as opposed to simply making it consistent and then mathematically accounting for it. It is possible that eliminating all leakage except through the actual material would limit or even eliminate the accuracy problem. This could be tested by plating the aluminum chamber in nickel. It could also be tested coated entirely in some epoxy, or made of stainless steel instead of aluminum. Other than those changes the rest of the process would remain the same, and the results without leakage would prove interesting, if not successful.