TECHNICAL REPORT   AD_____
NATICK/TR-98/025

MEASUREMENT OF WATER VAPOR DIFFUSION THROUGH LAMINATED FABRICS AND MEMBRANES USING A DIODE LASER SPECTROSCOPE

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July 1998

Final Report
November 1997 - February 1998

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SCIENCE AND TECHNOLOGY DIRECTORATE

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REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	July 1998	Final November 1997 / February 1998

4. TITLE AND SUBTITLE

Measurement of Water Vapor Diffusion Through Laminated Fabrics and Membranes Using a Diode Laser Spectroscope

6. AUTHOR(S)

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5. FUNDING NUMBERS

PE: 611101, 622384
Cost Codes:
801A9B
866A10

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Soldier Systems Command
Natick Research, Development and Engineering Center
Science & Technology Directorate
SSCNC-YM
Natick, MA 01760-5020

8. PERFORMING ORGANIZATION REPORT NUMBER

NATICK/TR-98/025

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

*General Physics Institute, Moscow, Russia

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A spectroscopic system based on vapor phase absorption of infrared radiation produced by a diode laser is shown to be useful for measuring water vapor diffusion rates through materials in sheet form. Measurements of water vapor diffusion through four polymer membranes and membrane laminates showed an excellent correlation with an existing water vapor transport apparatus that uses hygroscopic polymer film capacitance sensors. The diode laser spectrometer eliminates sorption hysteresis artifacts present in the capacitance sensors.

14. SUBJECT TERMS

MASS TRANSFER	SORPTION	PERMEATION
CLOTHING	WATER VAPOR	DIODES
SPECTROSCOPY	DIFFUSION	MEMBRANES

15. NUMBER OF PAGES

26

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

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PREFACE

This report evaluates the performance of a diode laser spectrometer (DLS) in a water vapor permeation apparatus that is used for measuring the transport properties of protective clothing. This work was funded by the U.S. Army In-House Independent Research (ILIR) program, and the Office of the Secretary of Defense (OSD) Chemical and Biological Protection program; further assistance and support was provided by the U.S. Army Research Office and the University of Arizona Optical Sciences Center.

MEASUREMENT OF WATER VAPOR DIFFUSION THROUGH LAMINATED FABRICS AND MEMBRANES USING A DIODE LASER SPECTROSCOPE

1. INTRODUCTION

Protective clothing systems for industrial, military, and agricultural applications require materials with barrier properties against toxic chemicals in vapor, liquid, and aerosol form. For many situations, these materials must also have high permeability to water vapor to allow evaparative cooling for the humans wearing them, otherwise the protective clothing system imposes an intolerable thermal burden upon the user. Convenient and accurate laboratory vapor permeation test methods are required to develop and test new materials for protective clothing.

The aim of the work presented here was to evaluate the usefulness of a diode laser spectrometer (DLS) in an existing water vapor permeation apparatus [1-3] the Dynamic Moisture Permeation Cell (DMPC). The results of this evaluation will be used to refine the prototype DLS and suggest modifications to the design and associated software and instrumentation. The eventual objective is to add the ability to determine the concentrations of multiple gases of various compositions, including water vapor, to create a vapor permeation apparatus capable of measuring multicomponent steady-state and transient mass transport across various protective membranes and membrane laminates.

The diode laser spectrometer has potential advantages over the existing water vapor concentration measurement transducers in the DMPC, which are based on electrical capacitance measurements of a thin hygroscopic polymer film. These transducers are vulnerable to attack from organic vapor components in a multicomponent gas diffusion test. They are not designed for measurements at very low concentration levels, and may sometimes give misleading results due to factors such as sorption hysteresis in the hygroscopic polymer film portion of the transducers. Because the DLS system is a non-contact optical method, it also has the potential to give better response times to vapor concentration changes than the polymer film transducers, since the polymer takes some time to absorb the vapor and come to a new equilibrium state before the local vapor concentration can be measured.

2. EXPERIMENTAL METHOD

DMPC DESCRIPTION

A schematic of the DMPC apparatus, including the DLS, is shown in Figure 1.
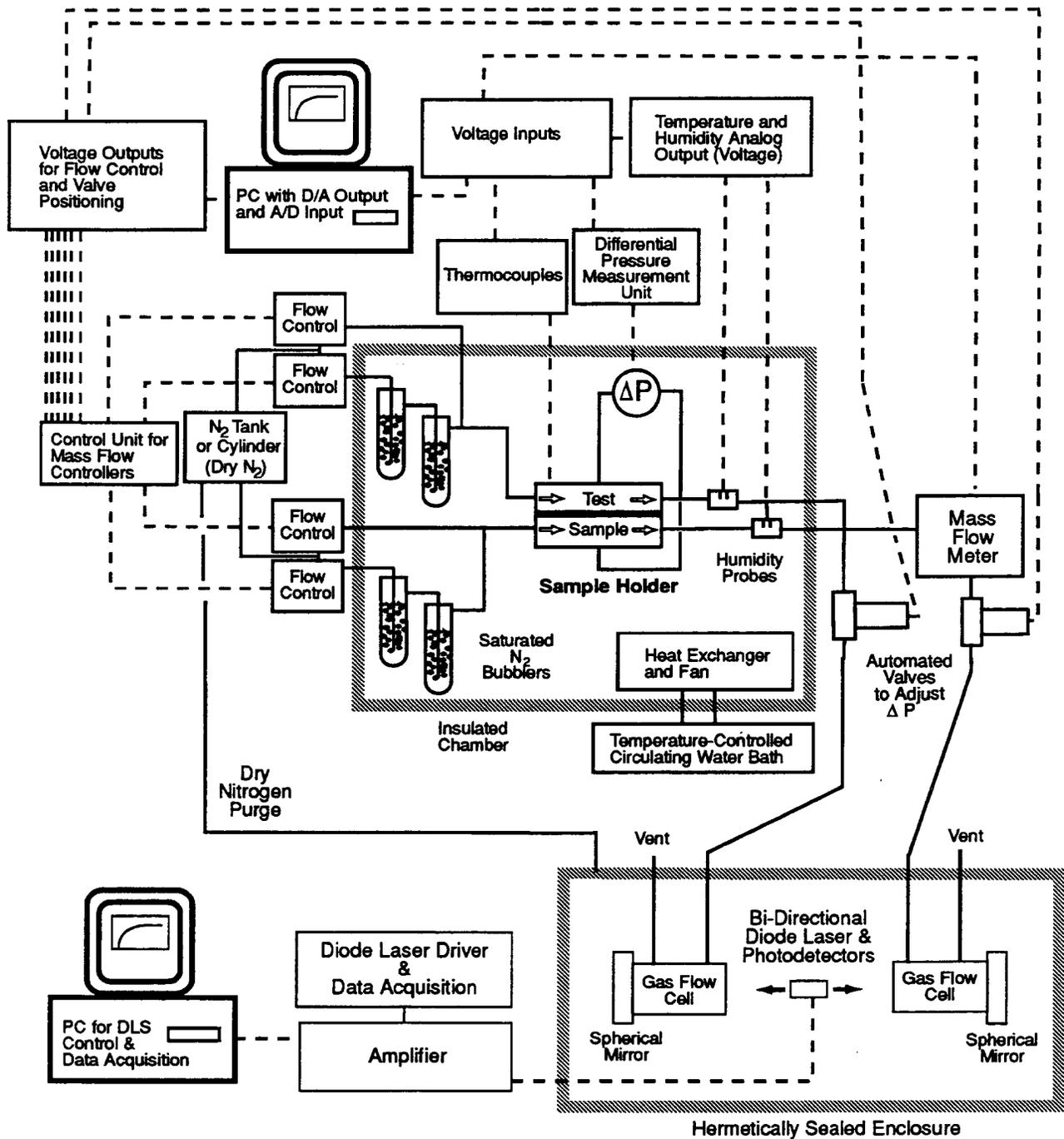

Figure 1. Schematic of Dynamic Moisture Permeation Cell (DMPC) Apparatus with Addition of Diode Laser Spectroscope (DLS).

Nitrogen streams consisting of a mixture of dry nitrogen and water-saturated nitrogen are passed over the top and bottom surfaces of the sample. The relative humidity of these streams is varied by controlling the proportion of the saturated and the dry components. By knowing the temperature and water vapor concentration of the entering nitrogen flows, and by measuring the temperature, water vapor concentration, and flow rates of the nitrogen flows leaving the cell, one may measure the fluxes of gas and water vapor transported through the test sample.

With no pressure difference across the sample, transport of vapor proceeds by pure diffusion, driven by concentration differences. If a pressure difference across a porous sample is present, convective transport of vapor adds to or subtracts from the diffusive flux, depending on the direction of the convective gas flow. In this paper, the DMPC is only used to determine water vapor diffusion properties of several membrane-based materials under the condition of no convective flow, as a method to evaluate the performance of the DLS water vapor concentration measurement system.

Review of Water Vapor Diffusion Test Method

The use of the DMPC for determining water vapor diffusion properties will be reviewed first, followed by a description of the DLS. The following equations for calculating water vapor flux apply to either the top or bottom flows in the cell. Strictly speaking, only one measurement on one side of the cell is necessary; the use of two separate humidity transducers for the top and bottom flows allows two measurements of water vapor flux to be made at the same time, using the equations given below for either the top or bottom flow, as appropriate. Further details may be found in References [1-3].

For this type of test, the mass flow rate of water vapor diffusing through the test sample from one side of the cell to the other is given by:

$$\frac{\dot{m}}{A} = \frac{Q(\delta C)}{A} = \frac{Q(C_2 - C_1)}{A} \tag{1}$$

$\dot{m}$ mass flux of water vapor across the sample [kg/s]
A area of test sample [m²]
Q volumetric flow rate through top or bottom portion of the cell [m³/s]
δC $= C_2 - C_1$, water vapor concentration difference between incoming stream (C_1) and outgoing stream (C_2) in top or bottom portion of the moisture permeation cell [kg/m³]

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The incoming water vapor concentration is determined by the ratio of the mass flows of the saturated and the dry nitrogen streams. The mass flow rates are controlled by MKS model 1259C mass flow controllers, with a Model 247C 4-Channel Readout (MKS Instruments, Inc.). These mass flow controllers can control mass flow rate at an accuracy of ±0.8% of full scale, with a response time of less than two seconds. At constant mass flow, the true volumetric flow rate will vary with temperature; the flow rate set by the MKS controllers is indicated in terms of volumetric flow rates at standard conditions of 0°C and atmospheric pressure (1.01325×10^5 Pa) The actual volumetric flow rate at different temperatures may be found from the mass flow rate, the temperature, and the pressure of the actual flow.

For water vapor diffusion, the critical measurement is the outgoing flow water vapor concentration C_2, which can be measured in a variety of ways. In the work reported here, capacitance-type relative humidity probes (Vaisala HMI 32 or 38) with Type HMP 35 or 37 sensors were used (Vaisala Inc.), which are adequate for materials which have significant vapor flux across them. The advantage of these probes is that they have a relatively fast response time (5 to 30 seconds: response time increasing with humidity), which is useful for transient studies. The probes are listed by the manufacturer as having an accuracy of ±1% from 0 to 90% relative humidity, and ±2% from 90 to 100% relative humidity. The measurement accuracy of these probes may be improved to ±0.5% by determining a calibration curve *in situ*. This is done by placing an impermeable aluminum foil sample in the cell and varying the relative humidity of the gas flow in the top and bottom of the cell by means of the flow controllers. The resulting curves (at increments of 10% r.h.) of measured relative humidity versus true relative humidity (set by the flow controllers) are used as calibration factors to correct the measured relative humidity for subsequent tests. Sorption hysteresis of the hygroscopic polymer used in the capacitance probe make any further improvements in probe accuracy difficult. For test materials which have small vapor fluxes, requiring measurements at very low concentrations, an 1100DP Dew Point Hygrometer (General Eastern Instruments, Inc.) may be used. For the highest accuracy, an M200 Gas Chromatograph (MTI Analytical Instruments, Inc.) has also been used as the concentration measurement device, but this is much less convenient in the practical sense of a routine test, because of its relatively long sampling time.

To obtain the water vapor concentration in the outgoing air stream, one must be able to convert from the known values of relative humidity and temperature to water vapor concentration. The vapor pressure of saturated water vapor in air is obtained from an empirical formula (or tables) as a function of temperature, and then converted to concentration using the perfect gas law.

We may express the water vapor transmission rate in terms of the indicated volumetric flow rate at standard conditions, the humidity difference, and the temperature:

$$\frac{\dot{m}}{A} = \frac{\delta\phi Q_s p_s M_w}{ART_s} \qquad (2)$$

M_w molecular weight of water vapor [18.015 kg/kmole]
Q_s volume flow rate at standard conditions of 0°C and atmospheric pressure [m³/s]
R universal gas constant [8314.5 N-m/kg-°K]
T_s reference temperature at standard conditions of 0°C in degrees K (273.15 K)
p_s saturation vapor pressure of water [Pa]
$\delta\phi$ $= \phi_2 - \phi_1$, relative humidity difference between incoming stream (ϕ_1)
       and outgoing stream (ϕ_2) in top or bottom portion of the moisture permeation cell
ϕ $= p_v/p_s$, relative humidity
p_v vapor pressure of water [Pa]

Various sample holders are available, which have different test sample measurement areas, and which have different downstream locations from the flow inlet. In this study, the sample measurement area was 1.0 x 10⁻³ m², with the sample located equidistant from the inlet and outlet ports of the cell, and a volumetric flow rate of 3.33 x 10⁻⁵ m³/s (2000 cm³/min). The dimensions of the DMPC were chosen to assure flow velocities of at least 0.5 m/s over the sample to minimize the contribution of boundary air layer resistances to the test measurements. Details of the sample holder are shown in Figure 2.

Differential Pressure Measurement Ports

Flow Inlet or Outlet

Upper Half of Flow Cell (Identical to Lower Half)

Measurement Area (typical)= 0.001 m^2 (size and location may vary depending on sample holder in use)

Sample Clamping Plate

Test Sample

Sample Clamping Plate

Duct Width = 0.025 m
Duct Height = 0.0025 m or 0.0050 m
(two different cells available)
Duct Length = 0.13 m

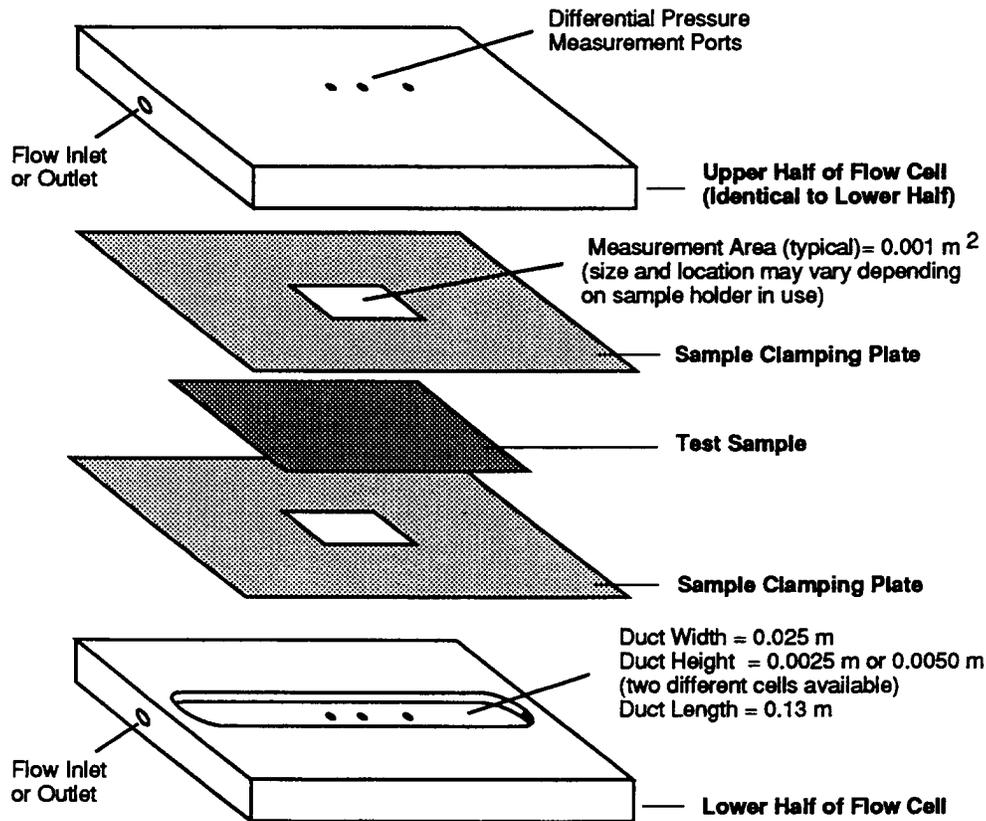**Flow Inlet or Outlet**

Lower Half of Flow Cell

Figure 2. Schematic and Dimensions of the Sample Holder for the DMPC.

The sample sizes are kept quite small to make it possible to evaluate developmental membranes and laminates, which are often produced in quantities too small for testing by some of the standard water vapor diffusion test methods. Sample mounting methods vary according to the material being tested. Some thin materials, such a laminates and woven cloth, were originally tested with rubber sealing gaskets to prevent leakage, but the sealing proved to be unnecessary for most materials; the clamping force provided by the mounting bolts is sufficient to prevent leakage in the absence of a gasket. Thick materials that are highly permeable require special sealing methods such as edge sealing by molten wax, or the use of a curable sealant. The testing of thicker materials also requires a larger sample area to minimize factors such as edge effects.

Diffusion Test Procedure

The actual test is conducted under the control of a personal computer (PC) connected to the flow controllers, automated valves, and the various measurement transducers through input and output boards (see Figure 1). Various options exist within the software for operator input setpoint information, or preset files containing the setpoint information. The computer applies the proper setpoint voltage to each controller to produce the desired relative humidity in the upper and lower gas streams entering the DMPC. The A/D board in the PC reads analog voltage outputs of the relative humidity, RTD, thermocouples, differential pressure transducer, mass flow meters, etc., records the data on disk, calculates parameters of interest, and plots results to the PC screen. The software applies operator-determined equilibration criteria to determine when equilibration has been reached for that setpoint. Once equilibration is reached, the results (humidity, calculated flux, etc.) are output to a printer and to a data file on disk. The computer then proceeds to the next setpoint and repeats the process.

The pressure drop across the sample is monitored by means of a MKS Baratron Type 398 differential pressure transducer, with a Type 270B signal conditioner (MKS Instruments, Inc.). For measurement of pure diffusion, especially for materials such as fabrics, which may be quite permeable to convective flows, it is important to make sure that the pressure drop across the sample is zero, so that transport takes place only by pure diffusion. The pressure drop is continuously monitored and displayed, and is controlled by means of two automated valves at the outlets of the cell. For the permeable fabrics, this system also allows one to do testing under controlled conditions of a defined pressure drop across the sample, so that transport takes place by both diffusion and convection (which will be described later). This makes it possible to determine an air permeability value from the apparatus, in addition to the water vapor diffusion properties of the test sample.

Materials that have a constant mass transfer coefficient show a linear slope on plots of flux versus concentration difference across the sample. These materials do not change their transport properties as a function of water content or test conditions.

For materials that do not have a constant slope, the data points for a test series will not superimpose, but will form a set of curves for each test condition. From an evaluation of the flux versus concentration difference curve at various points we can calculate values for the material diffusion resistance, which will be a function of the concentration of water in the material.

We define a total resistance to mass transfer as the simple addition of an intrinsic diffusion resistance due to the sample (R_i) and the diffusion resistance of the boundary air layers (R_{bl}):

$$\frac{\dot{m}}{A} = \frac{\Delta \overline{C}}{(R_i + R_{bl})} \tag{3}$$

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$$R_i = \left[\frac{\Delta \overline{C}}{\left(\dfrac{\dot{m}}{A} \right)} \right] - R_{bl} \qquad (4)$$

$\dot{m}$ = mass flux of water vapor across the sample (kg/s)

A = area of test sample (m²)

$\Delta \overline{C}$ = log mean concentration difference between top and bottom nitrogen streams (kg/m³)

R_i = intrinsic diffusion resistance of sample (s/m)

R_{bl} = diffusion resistance of boundary air layers (s/m)

The log mean concentration difference across the sample is appropriate since there is a significant change in the concentration of the gas stream both below and above the sample. In addition, the gas streams may not necessarily be in parallel unidirectional (cocurrent) flow, but may be run in counter flow to maintain a more constant concentration gradient across the sample. The log mean concentration difference [4] is defined as:

$$\Delta \overline{C} = \frac{\Delta C_a - \Delta C_b}{\ln(\Delta C_a / \Delta C_b)} \qquad (5)$$

ΔC_a = concentration difference between the two gas streams at one end of the flow cell (kg/m³)

ΔC_b = concentration difference between the two gas streams at the other end of the cell (kg/m³)

For parallel cocurrent flow, the concentration differences are between the top and bottom incoming flow at one end of the cell (ΔC_a), and the difference between the top and bottom outgoing flows at the other end of the cell (ΔC_b). For countercurrent flow, the concentration differences are between the incoming and outgoing flows at one end of the cell (ΔC_a), and the incoming and outgoing flows at the other end of the cell (ΔC_b).

DIODE LASER SPECTROSCOPY

A diode laser based analyzer was developed to overcome some of the limitations of the humidity measurement transducers mentioned previously. A near infrared diode laser spectrometer has sufficient sensitivity to provide an accurate humidity measurement using a simple two pass optical cell. The analyzer consists of an electronic driver, laser temperature controller, amplifiers and two equivalent gas flow cells, mounted on opposite sides of the laser. Radiation at 1.36×10^{-6} m (1360 nm) emitted by the diode laser in two opposite directions is reflected by spherical mirrors to two Germanium photodiodes located near the diode laser. The length of the cell is 5 cm, and the radiation passes through the cell twice making the optical path 10 cm. One of the cells can serve as a reference channel with a known humidity concentration (for low concentration measurements), or as a second analytic channel. The analyzer is mounted in a hermetically sealed box flushed with dry nitrogen. This prevents detection of the local ambient air humidity, which is inline between the laser and the gas flow cells.

The diode laser is mounted on a copper holder soldered to one side of a thermoelectric element that controls the laser temperature and thus the wavenumber of emitted radiation to within approximately 30 cm^{-1}. The laser temperature is controlled by two diodes fixed on the copper holder and can be stabilized near the absorption frequency line with an accuracy of better then 10^{-2} K

A pulse technique is used for absorption line detection. In this method the diode laser is driven by current pulses of approximately sawtooth form that register a small portion of the spectrum that includes the absorption line. The pulse duration (20 - 1000 msec), the slope of the pulse (which determines the portion of spectra to be observed), and the interval between the pulses are determined experimentally to find the optimum signal-to-noise ratio. The signals from the photodetectors are amplified and filtered by two high pass (10 kHz) and one low pass filter (45 kHz) in the main amplifier and sent to the data acquisition module by two transient recorders (20 MHz, 8 bit, 4 K). The data acquisition module accumulates and averages the data to increase accuracy. The data processing time mainly depends on transmission line (Com port) speed, accumulation number and number of points in the spectral range used for calculations and varies from 10 s to 30 s depending on the number of accumulations (1 -255).

The prototype DLS gas analyzer is completely automated by a PC, and is independent from the DMPC instrumentation. An operator can set the duration, amplitude, and slope of laser current pulses (reproducibility of all current's parameters is better than 10^{-4}), as well as the laser temperature, and observe device output as a recorded spectral line at the monitor. For measurements, the analytic signal near the absorption line is compared with the reference file previously stored in computer memory. The computer program calculates a correlation function to get a value that is proportional to measured gas concentration. It should be noted that even small changes of laser temperature shift the recorded spectra with respect to the reference file, which could lead to serious errors in concentration calculations. To prevent this, the computer program shifts the recorded spectra until the peaks in it and the reference

file coincide. This program follows the absorption line position with high accuracy (corresponding to 10^{-5} K) and fails only if the absorption line is completely lost. Concentration versus time information is displayed on the PC monitor screen as well as written to a file on disk.

MATERIALS

Four materials, which exhibit a 100-fold range in transport properties, were chosen to evaluate the performance of the DLS. These materials are of interest for various types of protective clothing systems. They include a porous and a nonporous polymer membrane, as well as two commercially available polymer membrane/fabric laminates used in items such as gloves, boots, and cold weather parkas, and are described below.

Material "A" is a microporous polytetrafluoroethylene (PTFE) membrane. This membrane is typically laminated to a textile fabric to produce a clothing layer that is quite windproof and resists liquid water penetration. This is due to the extremely small pore size and the hydrophobic surface properties of the PTFE. The membrane is very thin and porous, so that it presents very little resistance to the diffusion of water vapor through the interconnected pores.

Material "B" is a commercially available perfluorosulfonate ionomer membrane. Material "B" also has very low water diffusion resistance, but the transport mechanism is different from Material "A" since the water vapor molecules must be absorbed into the bulk polymer and then diffuse through the polymer structure. Material "B" is quite hygroscopic, and the transport behavior is dependent on the amount of water contained in the polymer matrix.

Material "C" is a commercially available membrane laminate. The membrane is composed of an expanded PTFE membrane that has been partially infiltrated on one side with a polyalkylene-oxide polyurethane-urea coating. The coating forms a continuous layer of a hygroscopic polymer component in the membrane. The membrane is adhesively laminated to an outer woven nylon shell fabric and inner knit nylon fabric.

Material "D" is another commercially available membrane laminate. The membrane in this case is a monolithic polymer layer composed of a hygroscopic copolymer of polyester and polyether. The polymer membrane is also adhesively laminated to an outer woven nylon shell fabric and inner knit nylon fabric.

3.   RESULTS AND DISCUSSION

To evaluate the DLS against the polymer film sensors incorporated in the DMPC, the DLS was attached to the outlets of the DMPC system, and the test procedures altered as little as possible. The same calibration procedures and test conditions were used for the DLS sensors as are normally used in the current version of the DMPC. This allowed simultaneous determination of properties using both the hygroscopic polymer film sensors and the DLS sensor. Issues concerning DLS calibration, sensitivity, measurement of water vapor flux, and calculation of mass transfer resistances, are dealt with in the following sections.

CALIBRATION AND SENSITIVITY

The DLS concentration measurement system may be operated in two modes. In the first mode, a reference gas mixture of known composition flows through one cell to serve as a reference, while the other cell serves as the analytic cell where the measured concentration is compared to the concentration in the reference cell. This is the most accurate mode of operation, and gives a direct concentration measurement. The DMPC system is designed to obtain a concentration or relative humidity measurement in both gas flow streams. This could be done by switching each gas flow outlet of the DMPC sequentially into the analytic cell of the DLS; however, this requires constant operator attention because this function is not yet automated in the current DLS software.

The second mode of operation is to use each DLS gas flow cell as an independent analytic cell, and use calibration data stored in the computer to determine the actual vapor concentration measured in each cell. This mode is most similar to the normal DMPC operation. A potential problem is that the calibration data is taken for only a single concentration value at a temperature and pressure that may not be identical to those used for the test. Also, because the DLS optical flow cells are at room temperature, the concentration measurement is taken at a temperature different than that in the DMPC system. Room temperature variations over the course of a test can also affect the measured vapor concentration values slightly. These small effects can be corrected for, but it would be preferable to have the DLS at the same temperature as the rest of the system.

For these reasons, a multi-point calibration procedure identical to the one used for the hygroscopic polymer sensors is also applied to the DLS [5]. A series of 21 setpoints, starting at 0% relative humidity, and working up to 100% r.h. and then back to 0% r.h, using increments of 10%, is run through the DMPC and DLS systems as described in the DMPC review section. This multi-point calibration provides a reference file for both the DLS and the hygroscopic polymer sensors, in terms of relative humidity outputs.

A typical humidity calibration sequence for the DLS is shown for both cell outputs in Figure 3. The final output relative humidity from the DLS is compared to the input relative humidity, and a calibration file is generated to correct subsequent measurements.
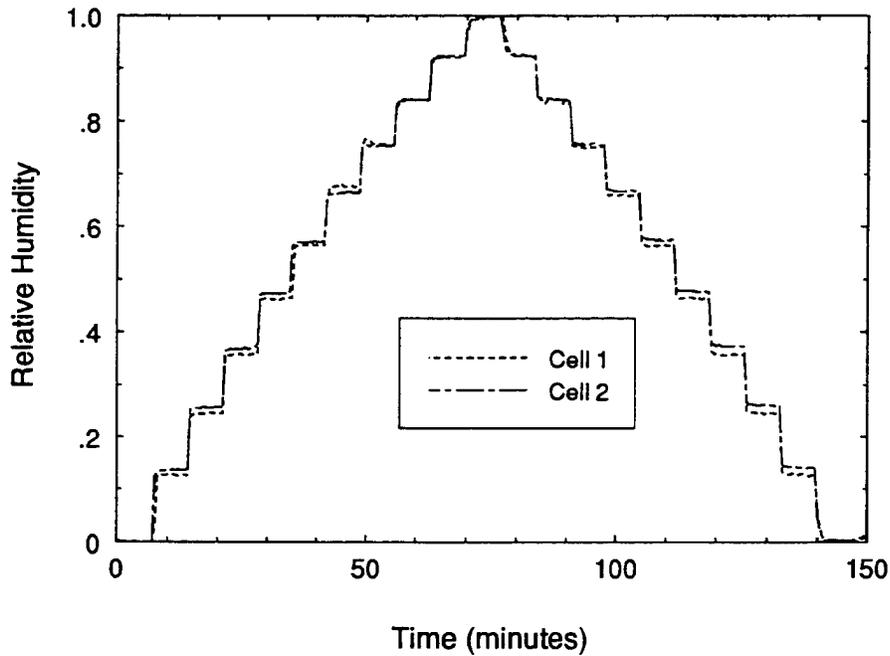

Figure 3. Humidity Calibration.

The observed sensitivity and limits of error of the DLS system are affected by the non-optimum conditions in which it is used in the DMPC. For example, the DLS system is placed downstream of the hygroscopic film sensors (which themselves are absorbing and releasing water vapor), the mass flow meter, the control valves, several long lengths of tubing, valves, and tubing connectors. In addition, a minimum number of spectra were sampled to make it possible to output data points approximately once every 30 seconds. The small number of spectral samples, plus the factors mentioned above, combined to give a resolution of +/- 0.0025 in relative humidity (+/- 0.25% r.h.). This is an improvement over the maximum resolution of the hygroscopic polymer film sensors (usually about +/- 0.005), but is more variation than we expected of the DLS. Minor design improvements should be able to improve the sensitivity and error range of the DLS system significantly. Figure 4 shows the typical variation in measured relative humidity outputs of the two DLS gas flow cells for a baseline flow of dry nitrogen gas (0% r.h.).
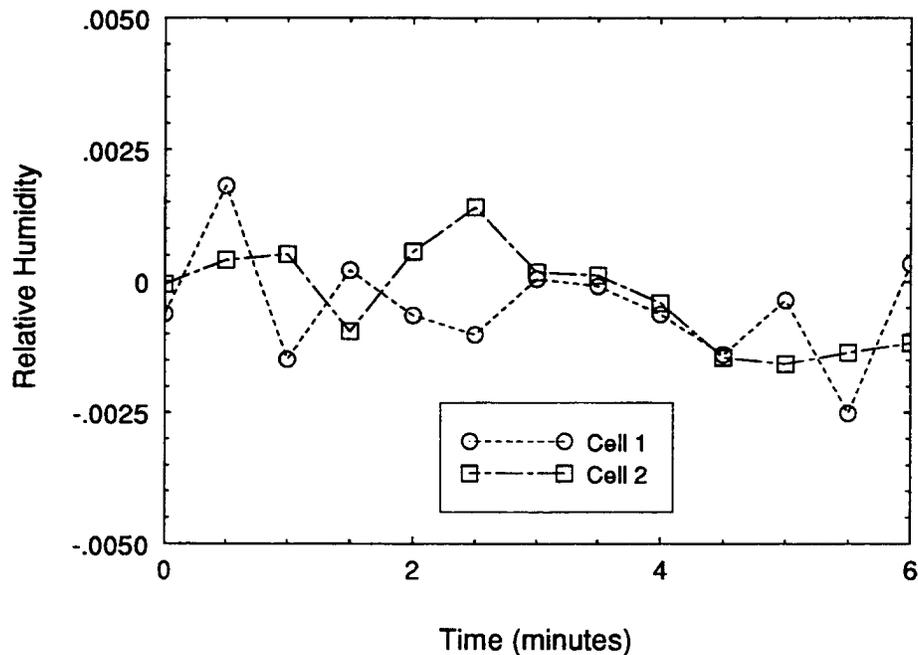
Figure 4. Typical Sensitivity.

We also note that the DLS sensor should have an improved response time to changes in vapor concentration. In practice, the prototype device suffers in respect to the response time of the original polymer film capacitance transducers because of the long tubing length between the outlet of the sample holder and the DLS system, the overly large gas flow cell volume, and the slow data processing speed of the PC and data acquisition system. Design changes to address these deficiencies are simple to implement; however, the response time is adequate for the primary purpose of the present system, which is the steady-state determination of water vapor diffusion properties.

WATER VAPOR DIFFUSION RESISTANCE MEASUREMENTS

Vapor transport across nonporous hygroscopic polymer membranes and films is often highly dependent on the amount of water present in the polymer. Many commercially available semipermeable membrane laminates exhibit this concentration-dependent behavior to varying degrees. The DMPC, when operated in the pure vapor diffusion mode (no pressure drop across the sample) is capable of showing this concentration-dependent transport behavior [1-4,6].

A standard set of test conditions was used for the four test materials. The test temperature was 20°C and nominal gas flow rate was 2000 cm³/min. The sequence of test setpoints began at low mean relative humidity and worked systematically up to high mean humidities, so that the samples were absorbing water vapor. The setpoints were then repeated in reverse order so the samples were desorbing water vapor. A constant humidity gradient of 0.50 (50% r.h.) was maintained across all the samples to allow direct comparison of water vapor fluxes for the different setpoints. Table 1 presents the sequence of setpoints used for each sample. The initial and final setpoints of 0% relative humidity allowed a baseline check for the DLS system.

Table 1. Humidity Test Setpoints (at 20°C)

Setpoint #	Input Relative Humidity Cell 1	Input Relative Humidity Cell 2	Mean Relative Humidity
1	0	0	0
2	0.5	0	0.25
3	0.6	0.1	0.35
4	0.7	0.2	0.45
5	0.8	0.3	0.55
6	0.9	0.4	0.65
7	1	0.5	0.75
8	1	0.5	0.75
9	0.9	0.4	0.65
10	0.8	0.3	0.55
11	0.7	0.2	0.45
12	0.6	0.1	0.35
13	0.5	0	0.25
14	0	0	0

Water vapor transport results are shown in terms of the "mean relative humidity", which is simply the average of the humidity on the two sides of the sample. The analogy is to the sorption isotherm, which is the equilibrium water content of a hygroscopic polymer as a function of relative humidity. The mean relative humidity has proven to be useful in showing the mass transport behavior in terms of concentration dependence of the permeability coefficient [1-4,6].

Figure 5 shows the apparent water vapor diffusion resistance of the four materials as determined from DLS data for the "desorption sequence" (setpoints 8-13) of Table 1. The diffusion resistance given in Figure 5 is the sum of the intrinsic material resistance (R_i) plus the boundary layer resistance (R_{bl}), as defined in equations 4 and 5. In this paper we present the combined resistances as a single value, but procedures exist for separately determining the intrinsic material mass transfer and boundary layer resistances [1-3, 6]. The results show the expected increase in water transport with humidity for the three materials with a hygroscopic polymer component.
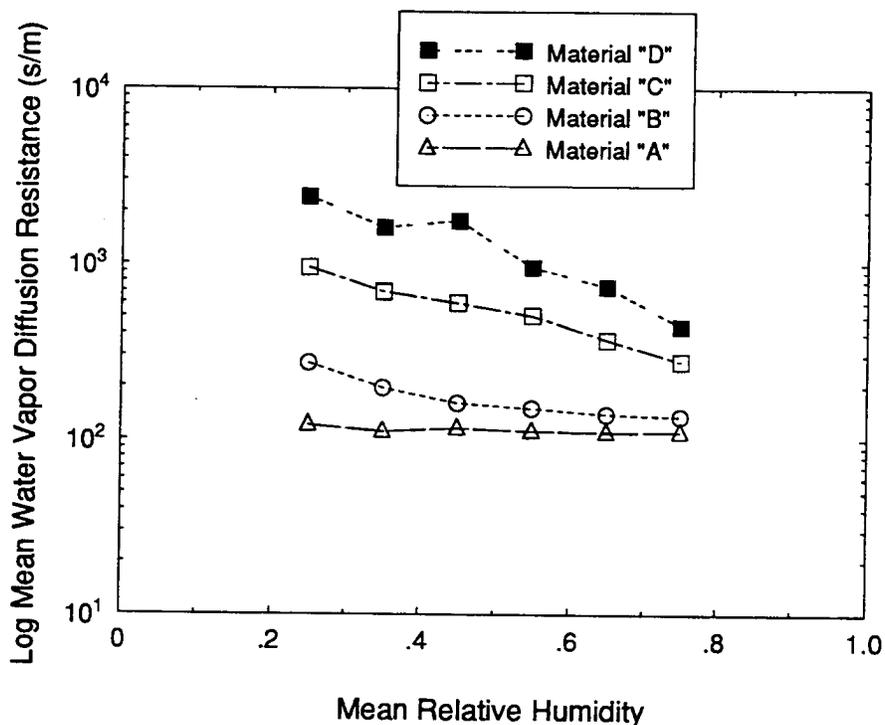

Figure 5. Water Vapor Diffusion Resistance Determined by DMPC with DLS.

Figure 6 shows the water vapor fluxes across the four samples, again in terms of the "mean relative humidity." Figure 6 shows that the water vapor transport behavior of the four materials varies by at least an order of magnitude. Again, Material "A", the porous PTFE membrane, shows no concentration dependence, while the other three materials with hygroscopic polymer layers show much greater water vapor transport under conditions of high water content in the polymer layer.
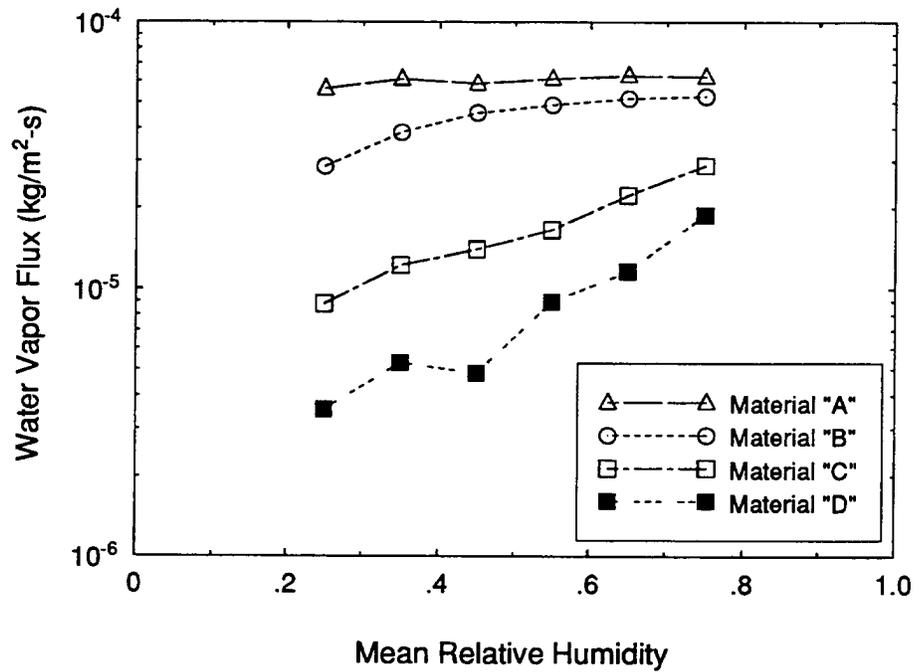

Figure 6. Water Vapor Flux Determined by DMPC with DLS.

CORRELATION OF DLS AND HYGROSCOPIC POLYMER SENSOR MEASUREMENTS

The DMPC tests were conducted with both the hygroscopic polymer sensors and the DLS system simultaneously. It is therefore possible to directly compare the measurements obtained using the two different concentration measurement devices. The correlation of water vapor diffusion resistance determined by the two systems are shown in Figure 7.
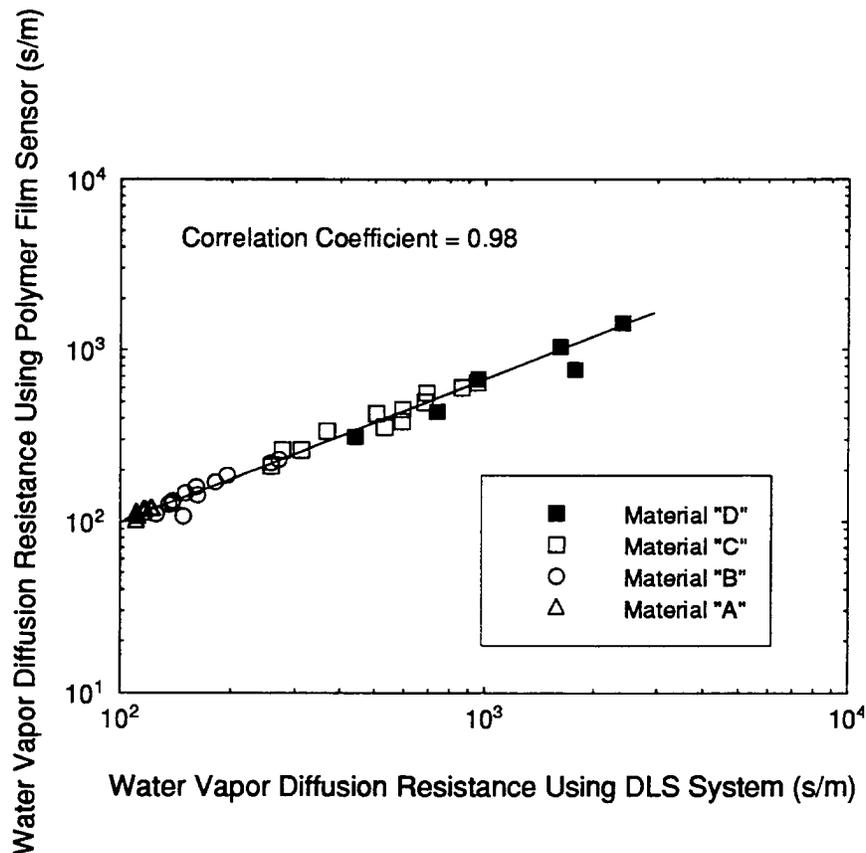

Figure 7. Correlation of Water Vapor Diffusion Resistance
as Determined by Two Different Sensor Types.

Material "D" exhibited less water permeation for the "sorption" sequence than for the "desorption" sequence of setpoints. Examination of the time-dependent data showed that this was due to insufficient time allowed for equilibration during the sorption sequence; therefore, data from setpoints 2-7 for Material "D" are omitted from Figure 7 and the remaining discussion. If these setpoints are included, the correlation coefficient becomes 0.89.

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Figure 7 shows an excellent correlation of steady-state water vapor diffusion properties measured by the two types of sensors. The correlation is quite good even despite a systematic error due to sorption hysteresis of the hygroscopic polymer sensor, which is discussed in the next section.

ELIMINATION OF APPARENT HYSTERESIS DUE TO HYGROSCOPIC POLYMER SENSORS

Water vapor permeability measurements made using the DMPC apparatus sometimes show hysteresis in plots of water vapor diffusion resistance or flux as a function of mean relative humidity. This is expected given the known hysteresis in water vapor sorption isotherms of many polymers. Due to the nature of the hygroscopic polymer film sensors, it was difficult to determine how much of the measured hysteresis effect was due to the tested sample response, and how much was due to sorption hysteresis in the sensor itself. The DLS system is not prone to these hysteresis effects and lends itself to determining if observed hysteretic phenomena are a sensor artifact, or if they reflect physical processes occurring in the sample.

An example of observed hysteresis in the transport curves for Materials "B" and "C" is shown in Figure 8. Both materials contain hygroscopic polymer components, and would theoretically be expected to show some kind of sorption hysteresis phenomena.
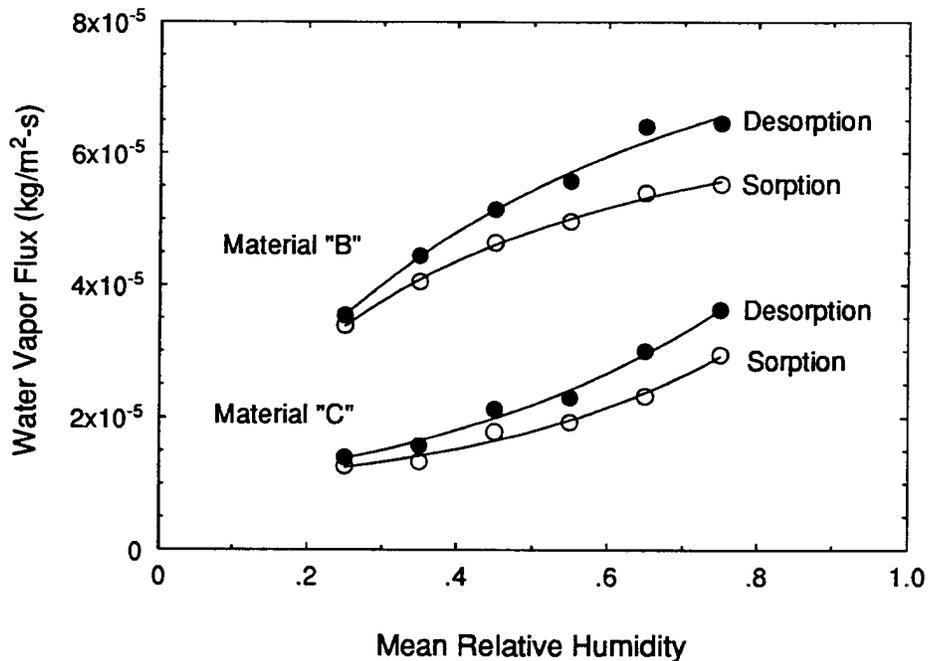

Figure 8. Apparent Hysteresis in Measured Water Vapor Flux
due to Hygroscopic Film Sensor Response.

However, when the water vapor flux is obtained using the DLS analysis system, most of this apparent sorption hysteresis disappears, as shown in Figure 9.
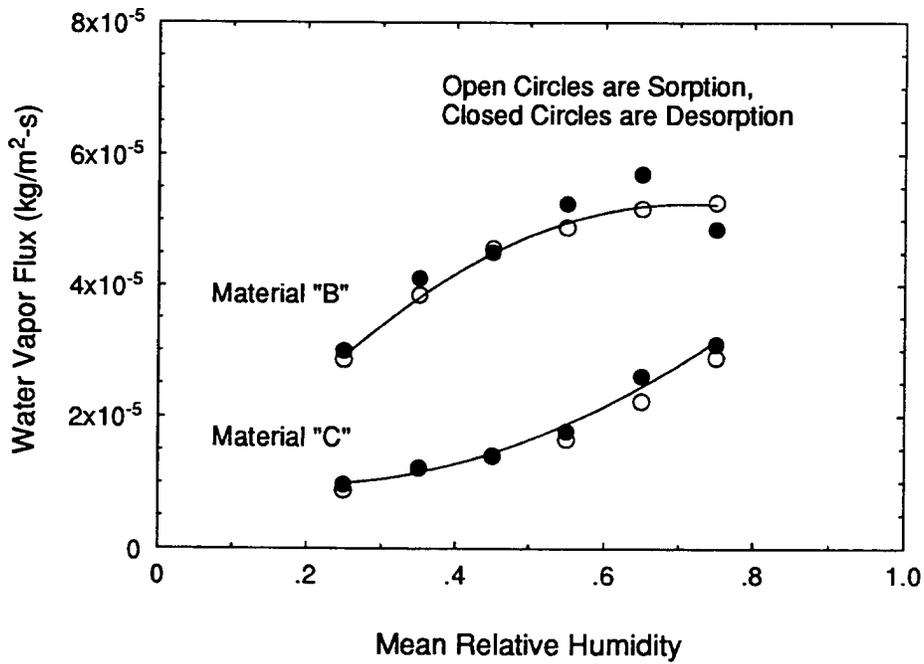

Figure 9. DLS Sensor Reduces Hysteresis in Measurement
due to Hygroscopic Polymer Film Sensor.

The absence of pronounced hysteresis in the DLS results indicate that the hygroscopic polymer film sensors themselves are producing an artifact which masks the much smaller hysteresis associated with the tested materials.

4. CONCLUSIONS

The prototype diode laser spectrometer (DLS) has proven to be useful for measuring water vapor transport through polymer membranes and membrane laminates. Measurements of water vapor diffusion through four materials using the DLS showed an excellent correlation with measurements made using polymer film capacitance sensors in an existing water vapor transport apparatus. The DLS was shown to eliminate a systematic error of the existing humidity transducers caused by sorption hysteresis in the hygroscopic polymer film sensor.

Hardware and software design changes will increase sensitivity, resolution, and response time of the prototype DLS. Extension to other wavelengths will permit multicomponent gas transport testing of protective clothing materials. Chemical vapor transport across membranes and films will vary depending on factors such as the ambient temperature and the amount of water contained in a swollen hygroscopic polymer layer. The DLS should provide a realistic assessment of the transport properties of membrane laminates that are designed to be barriers to toxic chemical vapors while still allowing high water vapor fluxes.

5.   REFERENCES

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