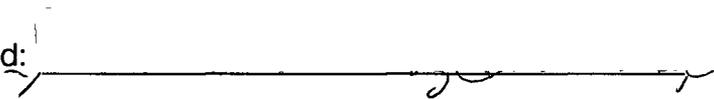


AN ABSTRACT OF THE THESIS OF

Edgar Eduardo Tello López for the degree of Master of Science in Food Science and Technology presented on February 18, 1994.

Title: Improved Moisture Permeability Determinations
for Packaging Films and Food Coatings

Abstract approved:



Dr. J. Antonio Torres

Equipment and procedures for the rapid measurement of the water vapor permeability of polymer films and food coatings has been evaluated. The method uses an electronic sensor to measure the concentration increase in water vapor diffusing through a film into a chamber of known volume. Air of known humidity is passed over each side of the film to establish a desired equilibrium relative humidity differential prior to each test. Experimental results showed that moisture vapor transmission rates of polymer packaging films and edible coatings could be determined in a range from 0.25 to 12 hours instead of the usual 24 hour period required by existing tests. Permeance values for Teflon, high density polyethylene (HDPE), polyethylene terephthalate (PET) and

three coating materials were measured at relative humidity differentials between 0 - 100% and temperatures between 5 and 30 °C. Results were found to be similar to values reported in the literature using standard measurement methods. This method allows the measurement of film and coating permeance values at temperature and relative humidity values close to actual food storage conditions.

Improved Moisture Permeability Determinations for
Packaging Films and Food Coatings

by

Edgar Eduardo Tello López

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

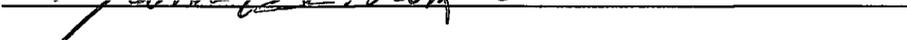
Master of Science

Completed February 18, 1994

Commencement June 1994

APPROVED:


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Dean of Graduate School

Date thesis is presented: February 18, 1994

Typed by EdgarEduardoTello

ACKNOWLEDGMENTS

I express my appreciation to the Latin American Scholarship Program for American Universities (Fulbright - LASPAU) for the opportunity that they have given me.

I express my gratitude to my major professor D. J. Antonio Torres for his guidance and effort in my thesis research, and to Dr, Daniel Farkas for his critical evaluation of my thesis work.

I dedicate this thesis to Ligia, Rennato Andres and Ana Marcela for their continued love, understanding and moral support.

TABLE OF CONTENTS

INTRODUCTION	1
LITERATURE REVIEW	7
Coating formulations	8
Edible coatings and agricultural commodities	11
Edible coatings and processed foods	11
Permeability Measurements	12
Theoretical considerations	13
Quantitative evaluation of coatings and films	16
Moisture permeability determination	18
<i>ASTM E96-80 test</i>	18
<i>Stagnant air correction method</i>	19
<i>Permatran-WTM test system</i>	20
<i>Continuous gravimetric method</i>	21
Oxygen permeability	22
Non-condensable gas permeability	23
Thickness measurements	24
Temperature effects on permeability	26
Determination of film moisture isotherms	27
Film orientation effects	28
Structural effects	29
MATERIALS AND METHODS	35
Permeability cell	35
Relative Humidity Sensing Probes	40
Experimental Procedures	41
Data Aquisition	43
Calculation procedures	44
Test films and coatings	49
Preparation of SRE-3 and CR-1 coatings	50
RESULTS AND DISCUSSION	51
Permeability Cell Evaluation	54
Measurement accuracy and precision	54
Source of error	54
Evaluation of Permeance Calculation Methods	56
Parameters Affecting RH Measurements	58
Permeability Cell Application	59
RH Affect on Permeance	59
Temperature effect on Film Permeance	60
Advantages of the Dynamic Method	60

CONCLUSIONS 62

REFERENCES 65

APPENDICES

 Appendix 1. Water vapor transmission rate (WVTR) data for each
 relative humidity (RH) and temperature point for different
 films and coatings (average of three values for each WVTR) 74

 Appendix 2. Description of electronic probes 77

LIST OF FIGURES

FIGURE 1. Location of relative humidity probes RH0 (high humidity) and RH3 (low humidity). RH2 is the humidity on the film surface in the low humidity chamber calculated from equation (24). RH1 is the humidity on the film surface in the high humidity chamber and is assumed to be the same as RH0 with 10 scfh of air flowing through the chamber.	36
FIGURE 2. Moisture permeability apparatus	38
FIGURE 3. Variation of permeance (P) with increasing air flow rate through the high humidity chamber for cellulose support material	40
FIGURE 4. Water vapor transmission rates (WVTR) calculated from low humidity chamber readings for the RH gradients indicated. Film PET, 3.6 mil, T = 30°C. The slope of the least square fit line is used to determine the permeance value (P) by equation (27) . .	47
FIGURE 5. Arrhenius plot of permeance values for Teflon, HDPE and PET films	48
FIGURE 6. Arrhenius plot of permeance values for SRE-3 and CR-1 coatings and EM-1100 edible film	49

LIST OF TABLES

TABLE 1. Suggested applications for edible coatings and films	7
TABLE 2. Variation coefficients of continuous versus discontinuous gravimetric determination of moisture permeability	21
TABLE 3. A comparison of film thickness measurement methods	25
TABLE 4. Characterization of films prepared with paraffin oils and paraffin waxes	32
TABLE 5. Permeance values (P) for different films calculated from experimental data taken at five relative humidity gradients and four temperatures	51
TABLE 6. Permeance values for different coatings calculated from experimental data taken at five relative humidity gradients and three temperatures	52
TABLE 7. Activation energy (E_a), constant ($\ln K_0$) and permeance (P) at 25 °C for films and coatings	53
TABLE 8. Reported permeance (P^*) comparison with values obtained experimentally at the same temperature and relative humidity gradient	55
TABLE 9. Permeance value calculated from experiments run for 15 min and a time necessary to increase RH by 5% in the low humidity chamber at temperatures shown	58

LIST OF APPENDICES TABLES

1a. TEFLON	74
1b. High Density Polyethylene (HDPE)	74
1c. Polyethylene terephthalate (PET)	75
1d. Film Support	75
1e. CRE-3 + Film Support	76
1f. CR-1 + Film Support	76
1g. EM-1100	76

TABLE OF SYMBOLS

Area	A
Atmospheric pressure	P_T
Coating Film (Carnauba)	CR-1
Coating Film (shellac)	SRE-3
Concentration of diffusant	C
Diffusion rate constant	$D_{x,i}$ or D
Energy of Activation	E_a
Flow of permeate i	$F_{x,i}$
Gas constant	R
Gradient of weight	Δw
Gradient of time	Δt
Height	h or z
High Density Polyethylene	HDPE
Mass	m
Moisture	M
Permeability	K
Permeance	P
Permeance values reported by literature	P^*
Permeate concentration	$p_{i,j}$
Polyethylene terephthalate	PET
Relative Humidity	RH
Respiratory quotient	RQ
Solubility coefficient	S
Temperature	T
Thickness	L
Vapor pressure	P_o
Volume	V
Water vapor transmission rate	WVTR
Water Activity	a_w

Improved Moisture Permeability Determinations for Packaging Films and Food Coatings

INTRODUCTION

A key factor limiting the profitability of fresh fruit and vegetable production is their relatively short shelf-life. Respiration, the process by which stored organic materials are broken down into simple end products to produce energy, is responsible for rapid quality losses. The reaction of oxygen with glucose to yield carbon dioxide and water represents one of many complex reactions responsible for ripening. In addition, produce and fruits stored at ambient conditions dehydrate. These water losses diminish fresh quality (Erbil and Muftugil, 1986). Estimates for postharvest losses in fresh fruits and vegetables range from 5 to 25% in developed countries and 20 to 50% in developing countries (Kader et al, 1985). Reducing these losses requires an understanding of biological and environmental factors and of the postharvest technologies available for delaying senescence and retaining quality. The term "quality" is somewhat subjective but firmness, color and fresh flavor are generally recognized to be important attributes (Knee, 1972, 1982; Banks, 1984a).

Refrigeration is the preservation method most frequently used in preserving postharvest quality. However, in some cases, it cannot retard fruit

ripening and prevent other undesirable changes such as microbial growth. In addition, prolonged refrigerated storage may induce physiological damage such as internal browning and softness (Smith et al., 1987). Early work by Kidd and West (1927) led to the development of controlled atmosphere storage (CAS), i.e. storage under controlled oxygen and carbon dioxide concentrations.

Refrigerated CAS is an expensive and sophisticated technique extending the life of fruits and vegetables more than refrigeration and CAS alone. A disadvantage of refrigeration and CAS is that removal from storage exposes the fruit or produce to ambient conditions immediately initiating the process of quality loss.

Water loss in fruits occur via active transport of water vapor through the dermal system which includes cells in the cuticle, epidermal cells, lenticels and trichomes layers. The cuticle, a thin layer covering the fruit epidermis, is composed of surface waxes, cutin embedded in wax, and a mixed layer of cutin, wax and polysaccharides (Banks, 1984; Kader, 1985; Solomos, 1987). The thickness of the cuticle is an important factor in fruits because fruits containing a heavy cuticle generally lose less moisture (Claypool, 1940). Edible coatings to enhance or replace the natural coatings lost during postharvest operations, particularly washing, are effective in preserving fresh fruits and vegetables (Dalal et al., 1971; Smith et al., 1987; Shetty et al., 1989; Hagenmaier and Shaw, 1992). Generally, coating costs are lower than other preservation techniques (Kester and Fennema, 1986; Guilbert, 1986).

An edible coating or film has been defined as a thin, continuous layer of edible material formed on, placed on, or between, foods or food components. It provides a barrier to mass transfer, serves as a carrier of food ingredients and additives, or provides mechanical protection (Torres et al., 1985; Torres and Karel, 1985; Kester and Fennema, 1986; Guilbert, 1986; Hatzidimitriou et al., 1987; Torres, 1987; Guilbert and Biquet, 1989; Vojdani and Torres, 1989a,b, 1990; Krochta et al., 1988, 1990a,b; Gennadios and Weller, 1990; Rico-Pena and Torres, 1990a,b, 1991; Hagenmaier and Shaw, 1990, 1991a,b; Avena-Bustillos, 1992; Martin-Polo et al., 1992a,b; Mahmoud and Savello, 1992, 1993; Gennadios et al., 1993).

The use of edible barriers, coatings or films, on foods is not a new technique. Coatings were used in China as early as the 12th and 13th century to prolong the storage life of oranges and lemons (Hardenburg, 1967; Kester and Fennema, 1986). Food coating processes using wax and gelatin were patented in the 1800s (Guilbert, 1986). In the 1930s hot-melt paraffin waxes became commercially available for the coating of citrus fruits. In the early 1950s, carnauba wax oil-in-water emulsion, were developed for coating fresh fruits and vegetables (Kaplan, 1986). Shellac wax has also been used since the beginning of this century as an edible coating and has been approved by the Food and Drug Administration (FDA) for some foods since 1939 (Hardenburg, 1967; Fisher, 1981).

A variety of ingredients are used to prepare edible films and coatings with functional properties which help to preserve foods. An understanding of the functional role of each ingredient and the interaction of these ingredients is essential to achieve the desired functionality. This functionality includes one or more of the following: (1) control of moisture transfer; (2) control of ingredient migration; (3) reduction of microbial activities and modification of biochemical and chemical reactions on food surfaces; (4) control of gas exchanges with the environment; (5) compatible appearance, texture, flavor and aroma; and (6) desirable mechanical properties including coating adhesion to food surfaces. Techniques traditionally used in packaging laboratories have been adapted to quantify these functional properties and include a variety of permeability determinations and mechanical tests. A complication in the formulation of a coating is the migration of food components into the coating. These can alter the expected performance of the coating. Also, few studies have reported sensory evaluations of edible coatings and films. The possibility of incorporating flavoring agents into coatings has been mentioned but not verified experimentally. The interaction between the coating or film and food have not been investigated. This is unfortunate since coatings can introduce flavor, taste and aroma changes (Nisperos-Carriedo et al., 1990).

Often, the functional property of interest in edible films and coatings is their resistance to the migration of moisture. Moisture losses represent an important economic loss and affect compliance with net weight product labeling.

In many processed foods, critical levels of water activity (a_w) must be maintained if the product, or a certain component of a multi-phase food, is to retain quality and safety. Critical a_w values are important not only to prevent microbial outgrowth but also in preventing texture degradation and minimizing deteriorative chemical and enzymatic reactions (Kester and Fennema, 1986).

Standard permeability methods are designed to determine the properties of synthetic polymer films. These methods assume negligible resistance to mass transfer in the gas phase on both sides of the test film as compared to resistance within the film. This is not the case with films having a high moisture permeability. In addition, few researchers have quantified the effect of storage relative humidity (RH) and temperature on the permeability of edible coatings and films. Permeability data for fruit and produce coatings in commercial use is generally lacking (Hagenmaier and Shaw, 1990, 1991a,b, 1992). Therefore, the principal objectives of this study were to:

- Design and construct a device to measure the water vapor transmission rate of edible and plastic polymer films at temperatures and RH values of interest in foods.
- Establish experimental and calculation procedures to measure water vapor transmission rates under changing conditions of RH.
- Compare experimental results with values published for similar conditions and materials.

- Determine the water vapor transmission rates for selected films and coatings under conditions not reported in the literature. Investigate relative humidity differential values other than 0 - 100% RH and temperatures other than 25°C.

LITERATURE REVIEW

Developments in edible coating formulations with a wide range of gas and moisture permeability characteristics have extended their potential applications to the stability of many processed foods (Table 1).

TABLE 1. Suggested applications for edible coatings and films¹

Control of moisture migration/losses
Control of gas exchanges (O ₂ , CO ₂ , C ₂ H ₄ , N ₂ .)
Control of oil and fat absorption and migration
Control of solute migration
Control of flavor and other volatile migration, exchange and losses
Carrier of flavor, color, antimicrobial and other allowed food additives
Prevention or control of photo degradation-oxidation
Improves/provides mechanical-handling properties of foods

¹ Adapted from Kester and Fennema (1986).

Oxygen barrier films are needed to prevent vitamin degradation, lipid oxidation, enzymatic browning and other oxidative reactions. Flavor exchange barriers are needed to retain the sensory individuality of food components. Light barrier films could protect pigments, flavors and nutrients from photodegradation. However, often the functional property of greatest interest in edible films and coatings is their resistance to the migration of moisture.

Only very recently, research has been initiated to obtain quantitative information on the permeability of "new" edible films. Independent of the

permeability properties of the film, another critical difficulty is the need to produce coatings and films of even thickness and reproducible properties. In coatings, additional issues are surface adhesion and the need to keep them as thin as possible to facilitate consumer acceptance. Coatings could be flavored to improve a consumer acceptance. Edible coatings or films must have desirable flavors and textures and be flexible so as not to crack or fragment during product handling and storage. Approved additives, such as plasticizers, flavors, antimycotic agents or antioxidant agents and light energy absorbers can be added to improve their mechanical, organoleptic, or protective properties over a wide range of storage conditions (Guilbert, 1986).

Coating formulations

Polysaccharide and protein chains can associate by hydrogen bonding and sometimes by electrostatic forces which contribute to film and coating formation. Polysaccharides used in edible films and coatings include hydroxypropyl amylose and the cellulose derivatives methylcellulose, carboxymethylcellulose, hydroxypropylcellulose, and hydroxypropyl methylcellulose. Due to the hydrophilic nature of these polymers, only minimal moisture barrier properties can be expected (Kester and Fennema, 1986). Less commonly used polymers are plant and microbial polysaccharides such as agar, carrageenan, alginate, pectin, dextran, gum ghatti, scleroglucan, pullulan and curdlan (Vojdani and Torres, 1989b). Proteins evaluated for films and

coatings include collagen, gelatin, wheat gluten, soy protein, casein, whey protein, and zein, a corn protein fraction. In contrast to polysaccharides, proteins and other synthetic polymers, hydrophobic substances such as waxes and triglycerides, form thicker and more brittle films and coatings. Hydrophobic substances are combined with polysaccharides and proteins to form improved films (Torres and Karel, 1985; Kester and Fennema, 1986; Hagenmaier and Shaw, 1990). Coatings and films from formulations containing lipids absorb less moisture and have much potential in the development of moisture, oxygen and carbon dioxide barriers (Kester and Fennema, 1986; Guilbert, 1986). Emulsion-based, bilayer and multilayer films are more effective than pure protein and polysaccharide films because the characteristics of the whole film are enhanced by the individual contribution of each component (Kester and Fennema, 1986). Acceptable lipids for film formulations include beeswax, carnauba wax, paraffin wax, fatty acids and acetylated glycerides (Krochta, 1992).

In general, increasing polymer chain length and polarity enhances film and coating cohesion (Kester and Fennema, 1986). A uniform distribution of polar groups along the polymer chain also enhances cohesion by increasing the likelihood of interchain hydrogen bonding and ionic interactions (Banker et al., 1966). Solvent systems for edible films or coatings are limited primarily to water, ethanol, or a combination of the two (Kester and Fennema, 1986). Plasticizers are added to films to reduce brittleness and increase flexibility through a decrease in film cohesion. The plasticizer can also increase film

permeability (Gontard et al., 1992; McHugh et al., 1993). Plasticizers must be compatible with polymers in the film and if possible be readily soluble in the solvent. Among the plasticizers used are mono-, di-, and oligo-saccharides (e.g. glucose, high fructose syrup and honey), polyols (e.g. sorbitol, glycerol, glycerol derivatives and polyethylene glycol), and lipids (e.g. fatty acids, monoglycerides and ester derivatives, phospholipids and surfactants) (Guilbert, 1986).

Extensive research is needed to relate information on molecular structure and properties to functional film and coating properties. Fluorescence microscopy studies have shown that starch-fatty acid films perform best as moisture barriers when the particle size distribution in the emulsion used to form the film is carefully controlled (Pennisi, 1992). Also, chitosan films combined with fatty acids were more effective moisture barriers when a 12-C fatty acid was used. Computer simulations showed that chitosan molecules assumed helical configurations when combined with fatty acids. The hydrophobic end of the fatty acid would occupy the center of the helix closing a gap through which water could move through the film. Fatty acids with chains longer than 12-C may force a wider spacing between chitosan molecules and thus increase film porosity (Pennisi, 1992).

Edible coatings and agricultural commodities

Artificial edible barriers may reduce water loss, lower internal oxygen and increase internal carbon dioxide and ethylene concentrations, reduce respiration rates and retard ripening processes (Edmond et al., 1964; Pascat, 1986; Guilbert, 1986; Avena-Bustillos, 1992; Hagenmaier and Shaw, 1992). The extent to which these factors may be manipulated are coating and fruit specific. The literature on fruit coating permeability to moisture and gases is limited and thus prediction of a coating performance for a given fruit and storage condition (temperature, RH and gas composition) is difficult.

Packaging films have been developed to create gas concentrations surrounding produce and fruits that approximate the beneficial effects of controlled atmosphere storage. Edible coatings as artificial barriers to gaseous diffusion could be used for the same purpose while reducing the risk of mechanical and microbial damage. These artificial barriers would not only reduce respiration, but also increase the carbon dioxide content of the internal coated product atmosphere (Smock, 1935; Edmond et al., 1964; Kester and Fennema, 1986; Chu, 1986; Smith et al., 1987; Edmond et al., 1991).

Edible coatings and processed foods

Moisture movement within food components and between food and the environment limits the storage stability of many foods, generating often complex packaging requirements. An example is the familiar cheese and cracker in

many consumer lunch boxes where these two components need to be packed separately to avoid hardening of the cheese and staling of the cracker (Pennisi, 1992). These complex packaging requirements are compounded by public concern for the environment and the valid, or invalid, association by consumers of food packaging waste with overflowing landfills. Aluminum is recycled the most because of energy savings possible when aluminum is obtained from recycled material instead of mineral ores. The process is considered generally safe because the high temperature of molten aluminum destroys bacteria and other toxic contaminants. Paper recycling has expanded but improvements to recovery technologies are necessary to reduce fiber damage, particularly fiber length. Waxed paper and cardboard is in little demand except from thermoelectrical plants where they are used as fuel. Plastic recycling is technologically difficult because it involves the separation of the multiple layers used to produce safe and effective packaging materials (Russell, 1989). Glass is recyclable but there are few intrinsic economic advantages in using recycled glass because of the cost of transportation and separating containers by glass type. An increasing in the use of edible films for food packaging could reduce solid packaging waste.

Permeability Measurements

The development of edible films and coatings to reduce moisture transfer, oxidation, or respiration in foods requires the evaluation of the

permeabilities of these films to water vapor, oxygen and carbon dioxide. These measurement techniques must take into account calculation assumptions, instrument detection limits, and control of experimental conditions with particular emphasis on temperature and relative humidity.

Theoretical considerations

In the absence of cracks or pinholes, diffusion is the primary mechanism for gas and vapor transfer through a film or coating. Diffusion depends on the molecular size and shape of the permeant with smaller size particles having higher diffusion values. In general, linear molecules diffuse faster than branched or cyclic molecules. Small differences in shape may cause important changes in permeability.

Diffusion equations (1) are used to evaluate mass transfer through films and coatings (Crank, 1956; Mannheim and Passy, 1985; Pascat, 1986; Loncin, 1986; Krochta, 1992):

$$F_{x,i} = -D_{x,i} \frac{\partial C_i}{\partial x} \quad (1)$$

where $F_{x,i}$ is the flow of permeant i in the direction x ; $D_{x,i}$ is an apparent diffusion rate constant; and $\partial C_i / \partial x$ the partial derivative is the permeant concentration gradient across the film or coating. The apparent diffusion rate constant is assumed to be independent of location within the film. Under

steady-state and with a diffusion rate constant it is possible to derive the following expression:

$$F_{x,i} = D_{x,i} \left(\frac{C_{i,1} - C_{i,2}}{L} \right) \quad (2)$$

where $C_{i,j}$ ($j = 1$ or 2) are the concentrations of the permeante at the "inside and outside" film surfaces, while L is the film or coating thickness. In the case of vapor and gas permeability measurements it is further assumed that an equilibrium exists between the film surface and the surrounding atmosphere (films) or bulk conditions in the food (coatings) and that heat of sorption is equal to that of desorption. Hysteresis with respect to sorption equilibrium, a fairly common phenomenon for hydrophilic polymers, is also neglected (Schwartzberg, 1986). The simplest expression and the one most often used assumes a linear concentration relation between the coating or film and the surrounding water vapor or gas pressure. This assumption is based on Henry's law:

$$C_{i,j} = S_i p_{i,j} \quad (3)$$

where S_i represents the solubility coefficient of permeant i in the film or coating, ($j = 1$ or 2) is the permeant concentration in the environment on both sides of the film or coating. This leads to the following modification of Eq. (2):

$$F_{x,i} = D_{x,i} \left(\frac{S_i p_{i,1} - S_i p_{i,2}}{L} \right) \quad (4)$$

which leads to the following expression:

$$F_{x,i} = K_i \left(\frac{p_{i,1} - p_{i,2}}{L} \right) \quad (5)$$

where $K_i = D_i S_i$ is the permeability coefficient for permeant i through the film or coating.

The solubility coefficient dependence with water vapor or gas pressure can be determined from the sorption isotherm for the film or coating and may deviate significantly from the linear relationship assumed above. Also, the diffusion constant may increase with water vapor or gas pressure due to plasticization of the film by absorbed molecules (Cairns et al., 1974). A further assumption in the above equations is negligible resistance to mass transfer in the surrounding environment as compared to mass transfer in the coating and films. Expressions have been developed to analyze the case when comparable mass transfer resistances exist on both sides of the film (Krochta, 1992). Therefore, permeability is not a universal film property and values should be reported with a careful description of testing conditions, particularly relative humidity and temperature.

The concept of permeance has been used often in the literature on the permeability of edible coatings and films and can be defined as follows (Hagenmaier and Shaw, 1992)

$$K_i = P_i L \quad (6)$$

where P_i is the permeance of a coating with permeability K_i and thickness L .

Permeance is considered a coating or film performance evaluation value and it is not a material property. It can be defined as the rate of water vapor or gas transmission through a unit area and induced by a unit of vapor or gas pressure difference separating the film or coating being tested (ASTM, 1992).

The following expression can be used to determine the permeance of multiple layers (Hagenmaier and Shaw, 1992):

$$\frac{1}{P_i} = \sum_{j=1}^n \frac{1}{P_j} \quad (7)$$

Quantitative evaluation of coatings and films

The advantages of a quantitative approach to food coating development were demonstrated by Hagenmaier and Shaw (1992) with the following example. Assuming a 170 g orange with a 150 cm² surface area, a respiration rate at 20 ± 5 °C temperature of 11 ml O₂ (STP) kg⁻¹ h⁻¹, and an internal O₂ concentration of 18%, the following peel permeance ($P_{O_2}^{peel}$) value was estimated:

$$P_{O_2}^{peel} = \frac{11 \left(\frac{ml(STP)}{kg \ h} \right) \left(\frac{kg}{10^3 \ g} \right) 170 \ (g) \left(\frac{24 \ h}{day} \right)}{150 \ (cm^2) \left(\frac{1 \ m^2}{10^4 \ cm^2} \right) (0.209 - 0.18) \ (atm)} \quad (8)$$

$$P_{O_2}^{peel} = 103,000 \left(\frac{ml (STP)}{m^2 \text{ day atm}} \right) \quad (9)$$

where 20.9% is the atmospheric O₂ concentration. If this fruit were to be coated using a wax with $P_{O_2}^{coating} = 40,000 \text{ ml (STP) m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$, the permeance of the coated peel could be determined as follows:

$$\frac{1}{P_{O_2}^{coated peel}} = \frac{1}{P_{O_2}^{peel}} + \frac{1}{P_{O_2}^{coating}} \quad (10)$$

$$P_{O_2}^{coated peel} = 29,000 \left(\frac{ml (STP)}{m^2 \text{ day atm}} \right) \quad (11)$$

This calculation procedure can also be used to determine the permeability of coatings and films that require a support. In this case, their permeability is determined using a permeable film as a support (e.g. Hagenmaier and Shaw, 1991a).

Given the tendency of the edible materials used for coatings and films to interact strongly with water vapor, D_i and S_i , and consequently K_i and P_i , are values affected by testing conditions. The permeability of hydrophilic films at high RH is several fold higher than values at low RH. This has been attributed to an increased hydration of the film matrix (Kamper and Fennema, 1984a,b, 1985; Hagenmaier and Shaw, 1991a). Therefore, permeability values should be measured near conditions of interest and it is surprising that most edible film and coating permeability values reported in the literature have been measured using large (0-100%) RH gradients. More relevant evaluations would have been

obtained if the RH gradient used in tests were smaller and were based on expected storage RH and the internal packaging RH or food water activity (a_w).

Moisture permeability determination. A variety of procedures have been reported to determine the moisture permeability of edible coatings and films. The following sections will discuss these procedures and where possible identify sources of error associated with their use.

ASTM E96-80 test. The most frequently used method to determine water vapor transmission rate (WVTR) is a discontinuous procedure (ASTM, 1992; Debeaufort et al., 1993). A container with either water, saturated salt solution, or desiccant is covered with the test film and then placed in a constant RH chamber. The container is removed periodically from the chamber and weighed to determine by weight the amount of moisture crossing the film in a certain amount of time. At equilibrium, the rate of weight loss becomes a constant which is then used in calculations of permeance (P_{water}) and permeability (K_{water}):

$$WVTR = \frac{\Delta w}{\Delta t A} \quad (12)$$

$$P_{water} = \frac{WVTR}{(p_1 - p_2)} \quad (13)$$

$$K_{water} = P_{water} L \quad (14)$$

where $\Delta w/\Delta t$ is the amount of moisture transferred per unit time, L is the film thickness, A is the area of film exposed to moisture transfer, p_i ($i = 1$ or 2) are the vapor pressures on either side of the film, and K_{water} is the moisture permeability of the film (Martin-Polo et al., 1992a). The recommended metric units for permeability are $(\text{amol m})/(\text{m}^2 \text{ s Pa})$ where $1 \text{ amol} = 10^{-18} \text{ g-mol}$ (Gennadios et al., 1993). Modifications to the gravimetric method have been introduced by several authors working on edible coatings (Kemper and Fennema, 1984a,b, 1985; Kester and Fennema, 1986, 1989a,b; Martin-Polo et al., 1992a,b; Gontard et al., 1992; Debeaufort et al., 1993).

Stagnant air correction method. The mass transfer coefficient above the cup can be increased by forced convection to ensure equal vapor pressure in the bulk chamber and in the air layer in contact with the film. If the mass transfer coefficient inside the cell is comparable to that in the film, the following measurement correction has been shown to be necessary (Krochta, 1992):

$$F_{w,x} = -\frac{PD_w}{RT} \left(\frac{dx_w}{dx} \right) + x_w F_{w,x} = \text{constant} \quad (15)$$

where x_w is the molar fraction of water in the air inside the cell at a pressure P and temperature T . Integration of Eq. (15) between conditions on the surface of the desiccant, solution or water inside the cell and those directly under the film yields the following expression:

$$p_{w,1} = P_T - (P_T - p_{w,c}) e^{\left(F_{w,x} \frac{RT h}{PD_w} \right)} \quad (16)$$

where $p_{w,1}$ is the corrected water vapor pressure under the film, $p_{w,c}$ is the water vapor pressure over the water, saturated solution or desiccant in the film-covered container, h is the distance between the surface of this container and the film, and D_w is the diffusion rate constant of water in still air.

Permatran-WTM test system. The MOCON Permatran-WTM system measures water vapor released into an air stream at 0%RH from a film covering a container, holding either a saturated salt solution or water, into an air stream at 0%RH. A disadvantage of the device is the limiting detection range of the infrared sensor measuring the amount of moisture permeating the film at equilibrium conditions (Fritsche, 1993). Therefore, only air at 0%RH can be used to flow over the film being tested and films with large water vapor permeabilities can not be measured with this device (Krochta, 1992). A serious

drawback is that edible films usually have a high moisture content and 0% humidity air is not a suitable testing condition.

Continuous gravimetric method. Frequent weighing of the container covered with the test film in the ASTM E96-80 procedure underestimates WVTR and moisture permeability (Debeaufort et al., 1993). These authors proposed the use of a continuous weighing system to determine moisture permeability and a ventilator to maintain a large flow rate within the chamber to minimize the time that internal RH conditions were affected by opening the chamber. A further advantage of the continuous measurement system was its significantly lower experimental variability as indicated in Table 2.

TABLE 2. Variation coefficients of continuous versus discontinuous gravimetric determination of moisture permeability ¹

Permeability range $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$	$\sigma_x/X \text{ avg}^1$	
	Continuous	Discontinuous
$> 10^{-11}$	<5%	10-45%
$< 10^{-11}$	<45%	>70%

¹ Adapted from Debeaufort et al. (1993).

Oxygen permeability. Oxygen permeability seems to be independent of the oxygen partial pressure but for most edible films and films in general it is strongly affected by the film or coating hydration. Oxygen permeability can be determined with the Mocon Ox-Tran 100™ permeability tester (Modern Controls, Minneapolis, MN) calibrated at 0% RH with reference films provided by the National Bureau of Standards (ASTM, 1981; Hagenmaier and Shaw, 1991a, 1992). Permeability measurements at conditions other than 0% RH can be accomplished by conditioning films prior to testing in desiccators at the desired RH. During testing, gases are passed through bubblers with saturated salt solutions to adjust them to the desired RH (Hagenmaier and Shaw, 1991a). Using a cell similar to the one described by Davis and Huntington (1977), Rico-Peña and Torres (1990b) placed films between two chambers to determine the effect of film moisture content on oxygen permeability. A RH-controlled N₂ flow through one chamber and a similarly adjusted oxygen flow through the other were used to adjust the film hydration status prior to permeability determinations. After 2 h, the inlet and outlet valves were turned off in the mentioned order to ensure equal pressure (atmospheric pressure) in the two chambers. At various times thereafter, samples were taken with a syringe from the N₂ flushed compartment. The increase in O₂ concentration was monitored using an oxygen head space analyzer (MOCON LC-700F, Minneapolis, MN). An amount of N₂ equal to the volume of gas removed was added back to minimize changes in total pressure during testing. Ideal gas

behavior was assumed to correct O₂ concentration measurements because of sampling and the N₂ added back to minimize pressure changes.

Films and coatings made from polymers containing hydroxy, ester and other polar groups tend to have a lower O₂ permeability than polymers with hydrocarbon and other nonpolar groups. Also, the presence of polar groups increases the RH effect on O₂ permeability (Ashley, 1985; Hagenmaier and Shaw, 1992). Rico-Peña and Torres (1990b) found a strong O₂ permeability dependence upon RH for hygroscopic films.

Oxygen permeability is important in the coating of agricultural commodities. Low O₂ permeability can lead to the development of off-flavors in respiring produce as it induces an anaerobic metabolism elevating internal ethanol and acetaldehyde concentrations (Erbil and Muftugil, 1986; Nisperos-Carreido et al., 1990; Hagenmaier and Shaw, 1992).

Non-condensable gas permeability. Carbon dioxide, C₂H₄ and other non-condensable gases can be measured simultaneously using mixtures of these gases on one side of the film and on the other an inert gas such as N₂ or helium. Both gas streams need to be adjusted to the test temperature and RH. Concentration increase in the inert gas stream is measured by a gas chromatograph attached usually to a thermal conductivity detector (Hagenmaier and Shaw, 1991a, 1992).

In the case of coatings for agricultural products, an additional parameter of interest is the ratio of non-condensable gases which varies less than the permeabilities themselves (Ashley, 1985). For example, the O₂ to CO₂ permeability ratio of emulsified polyethylene waxes used on agricultural commodities was 0.21 for several commercial formulations tested under a variety of experimental conditions; the same ratio for low density polyethylene film was 0.35 (Hagenmaier and Shaw, 1991a). This information can be combined with the respiratory quotient (RQ) and the desired internal oxygen (O₂ⁱ) and carbon dioxide (CO₂ⁱ) concentrations for a given fruit to obtain the following expression:

$$\frac{K_{CO_2}}{K_{O_2}} = \frac{20.9 - O_2^i}{(CO_2^i - 0.03) RQ} \quad (17)$$

where 20.9 and 0.03 are the O₂ and CO₂ concentration in air (Hagenmaier and Shaw, 1992).

Thickness measurements. An often ignored issue in permeability studies is the measurement of the coating or film thickness. The thickness of the films can be measured directly (Kester and Fennema, 1989a,b; Greener and Fennema, 1989a,b; Rico-Peña and Torres, 1991; Martin-Polo, 1992a; Gennadios et al., 1993; Debeaufort et al., 1993) or calculated from the net weight of the coating and the density of the material (Guilbert, 1986; Hagenmaier and Shaw, 1991b). Debeaufort et al. (1993) compared micrometer screw, electronic gauge and scanning

electronic microscopy measurements and found that if the two sides of the film were smooth, measured thicknesses were reproducible regardless of the method used. In their experimental tests (Table 3) this was the case for cellophane, pure methylcellulose, and laminated methylcellulose and paraffin wax films. Micrometer measurements yielded a larger standard deviation because of the instrument precision limitations. If the film surfaces were irregular, micrometer readings were about twice the value obtained with the electronic gauge which were similar to SEM measurements. Electronic gauge measurements were considered superior due to simplicity, precision and agreement with SEM measurements (Debeaufort et al., 1993).

TABLE 3. A comparison of film thickness measurement methods ¹

FILM TESTED	Contact Measurements		SEM ⁴
	Micrometer ²	Electronic ³	
Cellophane	25 ± 10	19.8 ± 0.6	20 ± 4
Methylcellulose	20 ± 10	16.8 ± 0.4	17 ± 1
w/emulsified paraffin wax	130 ± 30	71.6 ± 6.2	68
w/laminated paraffin wax	90 ± 15	90.1 ± 0.6	87 ± 15

¹ Adapted from Debeaufort et al. (1993).

² Palmer, 10 μm

³ Sodexim S.A., Reims, France, 0.1 to 1 μm

⁴ SEM JEOL JSM 35-CF, Tokyo, Japan.

Temperature effects on permeability. A film or coating is generally¹ Adapted from Debeaufort et al. (1993). formed by a network of macromolecular chains and interstices. The thermal motion of the chains or their terminal groups² Palmer, 10 μm yields cavities which may be filled and crossed by the diffusing substances. Diffusion depends not only on the number and dimensions of the³ Sodexim S.A., Reims, France, 0.1 to 1 μm cavities, but also on the energy of activation (E_a) which is needed for the diffusing molecules to cross the polymeric⁴ SEM JEOL JSM 35-CF, Tokyo, Japan. membrane. This phenomenon is described by an Arrhenius equation for a diffusant i as follows (Rogers, 1985):

$$K_i = K_{o,i} e^{\frac{-E_{a,i}}{RT}} \quad (18)$$

The activation energies for moisture and gas permeability can be determined from Arrhenius plots of $\ln K_i$ vs inverse absolute temperature (T) (Hagenmaier and Shaw, 1991a). The values obtained are generally in the range 0-15 kcal/g-mol (Vojdani and Torres, 1990; Taoukis, 1989; Hagenmaier and Shaw, 1991a; Gennadios et al., 1993). For example, the average E_a for oxygen permeating emulsified polyethylene waxes used as fruit coatings is 4.7 kcal/g-mol which means that permeability increases about 30% for a 10°C increase in temperature (Hagenmaier and Shaw, 1991a). Plasticizers added to coatings reduces polymer interchain attraction forces and thus can lower E_a values (Kester and Fennema, 1986).

Determination of film moisture isotherms. Water vapor sorption of edible films and coatings may result in swelling and conformational changes of the structural polymer (proteins or polysaccharides). Therefore, a determination and interpretation of the water sorption properties of edible films is necessary to develop effective edible films and coatings (Gennadios and Weller, 1991). Film samples cut into small pieces and brought to zero moisture by freeze drying or other suitable procedures can be exposed to constant RH and temperature. Constant RH environments can be generated using the saturated solutions recommended by the COST-90 project (Wolf et al., 1984). The weight gain of the samples is recorded to the nearest 0.1 mg until changes in moisture content are less than 0.001g water/g dry matter. Similar procedures can be used to determine the desorption isotherm (Labuza, 1984). Gennadios and Weller (1991) evaluated several equations to describe the absorption isotherm for corn zein, wheat gluten, and wheat gluten/soy protein isolate films and found that the three-parameter (M_o , C, K) 'G.A.B.' equation (Bizot, 1984) to predict film moisture content (M) as a function of its water activity (a_w):

$$M = \frac{M_o C K a_w}{(1 - K a_w) (1 - K a_w + C K a_w)} \quad (19)$$

showed the best fit for several films. The degree of fit was evaluated using a mean relative deviation modulus (DM):

where M_{pred} and M_{exp} are moisture content predicted with the G.A.B equation and measured experimentally, respectively. A $DM < 5$ indicates an extremely good fit,

$$DM = \frac{100}{n} \sum_{i=1}^n \frac{|M_{\text{exp},i} - M_{\text{pred},i}|}{M_{\text{pred},i}} \quad (20)$$

$5 < DM < 10$ corresponds to a reasonably good fit, while $DM > 10$ indicates a poor fit (Gennadios and Weller, 1991).

Film orientation effects. The moisture permeability properties of proteins and polysaccharides modified by the incorporation of hydrophobic materials (e.g. fatty acids) into the film exhibit significant film orientation effects. Films prepared by emulsification of these components are nonisotropic because of separation and creaming during film dehydration. For example, methylcellulose (MC) or hydroxypropyl methylcellulose (HPMC) suspensions containing lauric, palmitic, stearic or arachidic acids form films when cast on glass plates at 80-85 °C. The plates are left at room temperature to promote fatty acid orientation within the wet film and then placed in a convection oven at 80-85 °C for 15 min. SEM photomicrographs of such films after drying and cooling, show fatty acid crystals on the film surface as well as discrete lipid particles within the polysaccharide matrix (Vojdani and Torres, 1989a). Even more heterogenous films were prepared by casting HPMC and fatty acid emulsions on top of a pure preformed HPMC film leading to the formation of three layers, essentially pure HPMC, HPMC with discrete lipid particles and a surface layer of pure lipids (Vojdani and Torres, 1989a). The same emulsion instability was observed in whey protein films in spite

of the moderate ability of whey proteins to act as emulsifiers (McHugh and Krochta, 1993a). As in the polysaccharide films, discrete lipid particles remained within the protein matrix and a layer of lipids also formed on the film surface which appeared dull. Moisture permeability tests with the dull side facing the high relative humidity chamber resulted in significantly lower WVPRs compared to films tested when oriented in the opposite direction (McHugh and Krochta, 1993a). This demonstrates the importance of reporting orientation when evaluating the moisture permeability of films containing hydrophilic materials such as proteins, polysaccharides and lipids.

Structural effects. The barrier efficiency of multi-component coatings and films is affected by the distribution of the hydrophobic component on or within the film forming matrix (Kamper and Fennema, 1984, 1985; Martin-Polo et al., 1992a). The exact nature of the hydrophobic component and the polymer used as the structural matrix for the film needs to be further analyzed. Film preparation techniques needs to be interpreted in terms of their effect on this matrix-hydrophobic ingredients interaction.

Lipids, a material frequently used to increase the hydrophobicity of edible films, have different physical states depending upon their chemical composition, conformational structure, and molecular size (Martin-Polo et al., 1992b). Kamper and Fennema (1984) in their work on polysaccharide-based films demonstrated that an increase in the degree of saturation increased the moisture barrier

properties of the film. Films prepared with the emulsion technique were more moisture resistant when paraffin and beeswaxes were used instead of corn oil. These authors suggested that this difference was related to water vapor solubility in the lipid component and on differences in the molecular organization of the lipid. Differences in oxygen permeability could be explained in terms of the previous factors and the relative polarity of the support where these lipids are incorporated.

The role of paraffin waxes and oils in controlling moisture permeability in edible films has been recently examined by Martin-Polo et al. (1992a,b). In their work, three cellulose derivatives (methylcellulose, filter paper, and cellophane) were used to prepare films by dipping, casting and coating techniques. Disks of cellophane or filter paper were dipped for 30 s in molten paraffin wax (95 °C) or in paraffin oil at room temperature and then drained for 1 min. Paraffin wax and oil are mixtures of alkanes with different chain lengths. The major components in paraffin oil, $C_{16}H_{34}$ and $C_{14}H_{30}$, and in paraffin wax, $C_{26}H_{54}$ and $C_{40}H_{82}$, are responsible for the liquid-solid difference in physical state (Martin-Polo et al., 1992a). These two paraffins have similar hydrophobicity which means that solubility of water in the coatings thus prepared would be similar and negligible (Martin-Polo et al., 1992a). Coated disks were kept for 18 hr at 70 °C to remove excess wax and ensure a constant deposition of paraffin ($0.045 \pm 0.006 \text{ kg m}^{-2}$). The thickness of the coated filter paper was $190 \pm 10 \mu\text{m}$ and $80 \pm 10 \mu\text{m}$ for the coated cellophane. Methylcellulose (MC, 4.25 g), paraffin wax (4.25 g) and polyethylene glycol 400 (1.3 mL) were dissolved at 75 °C in 75 mL of a 1:2 (v/v)

mixture of distilled water and ethanol and used to cast films following the techniques described by Kester and Fennema (1989b). Cast emulsion films with a 1:0.025 methylcellulose to paraffin wax ratio and heated to 70°C were coated with molten paraffin wax preheated to 95°C. For all tested films, a significant decrease (1.3 to 62 times) in moisture permeability was observed when the paraffin oil or waxes were used (Table 4; Martin-Polo et al., 1992a). The most effective moisture barriers were the wax-coated cast films and the wax-dipped cellophane films (Table 4). This property could be explained by a continuous layer of paraffin wax covering these films as observed by SEM. The high permeability values for the MC-paraffin emulsion films are in some disagreement with the work by Kamper and Fennema (1984a) who found that emulsified films were more efficient than laminated ones when fatty acids were used in the methylcellulose emulsion. It was speculated by Martin-Polo et al. (1992a) that the fatty acids solidify forming spangles which are less efficient in providing a continuous hydrophobic surface.

TABLE 4. Characterization of films prepared with paraffin oils and paraffin waxes ¹

Film tested	Thickness μm	Contact Angle ² , °	Permeabilit K x 10 ¹¹ g m ⁻¹ s ⁻¹ Pa ⁻¹
a. Emulsion & emulsion/coated films			
Methylcellulose (MC)	70±10	28±1	10.8±1.6
MC/paraffin oil	130±20	51±2	9.1±1.0
MC/paraffin wax	200±20	62±3	9.6±2.0
MC/paraffin wax + paraffin wax	140±20	102±3	0.2±0.2
b. Dip coated films			
filter paper (FP)	180±10	--- ³	35.1±3.6
FP + paraffin oil	190±10	71±5	26.5±4.6
FP + paraffin wax	190±10	116±2	29.0±2.5
cellophane (CP)	30±10	8±1	5.7±0.4
CP + paraffin oil	80±10	n.m. ⁴	9.3±1.7
CP + paraffin wax	90±10	104±3	0.3±0.04

¹ Adapted from Martin-Polo et al. (1992a).

² Contact angle for water determined at 20 °C with the aid of a microscope equipped with a goniometric piece.

³ Water was absorbed on filter paper.

⁴ Not measured.

Further evidence of the role of the hydrophobic layer structure has been obtained by analyzing films composed of cellophane and a hydrophobic coating containing different proportions of a solid phase, paraffin wax or n-octacosane

($C_{28}H_{58}$), and a liquid one, paraffin oil or n-hexadecane ($C_{16}H_{34}$) (Martin-Polo et al., 1992b). The barrier properties of the n-alkanes were less than those of the paraffins. However, in both cases a significant increase in moisture permeability was observed when the mixture contained less than 25% w/w of the solid phase. SEM and X-ray diffraction (XRD) analysis suggested that the efficiency of 100% paraffin wax-coated films were related to a parallel orientation of the wax crystals to the base sheet of the cellophane. XRD analysis showed that the presence of a liquid phase (paraffin oil) did not influence the orientation of the wax crystals. The significant increase of moisture permeability when the paraffin wax proportion was less than 25% was interpreted as an indication that the quantity of crystals was so low that it did not cover the cellophane surface.

The barrier properties of n-alkane mixtures were less than those for paraffin waxes (~10 times less). When n-alkane coatings containing less than 25% octacosane were analyzed by XRD a unique orientation for the aliphatic chains perpendicular to the base sheet of the cellophane was observed. Other arrangements were observed at higher solid n-alkane proportions. For 100% octacosane clusters of needles were observed by SEM while stacking of separated flakes were apparent at 10%. In going from 50 to 100% octacosane the moisture permeability increased from 0.5×10^{-11} to 6.9×10^{-11} $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$. This abnormal behavior was interpreted on the basis of void regions in the crystalline structure which were filled with liquid n-hexadecane at lower octacosane concentrations. This would produce a greater resistance to the

passage of the water molecules than in the absence of a liquid hydrophobic phase. The absence of a sufficient number of crystalline structures at octacosane concentrations below 25% would explain the increase in moisture permeability in this region (Martin-Polo et al., 1992b).

Large differences were noted between the effectiveness of paraffin waxes and oils and between the substrate on which they were applied (Martin-Polo et al., 1992a). As expected, the highest permeability values were observed for films with smallest contact angle for the more polar supports (Table 4).

Permeability values estimated for the paraffin wax layer in the coated cast films and in the dipped cellophane films were 0.18×10^{-11} and 0.06×10^{-11} $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$, respectively. This difference was interpreted as an indication that wax applications on a non-porous substrate (cellophane) was more effective than over the cast MC-wax film. In porous filter paper, i.e. a model for some food surfaces, the paraffin oil or wax fills the pores, but the moisture transfer may still occur through the paper fibers free of the paraffins. The value for the paraffin oil on the cellophane film was estimated to be 15×10^{-11} $\text{g m}^{-1} \text{s}^{-1} \text{Pa}^{-1}$ which suggests a much lower effectiveness for liquid paraffin wax. Finally, in many food applications, the coating may interact and probably extract some food components that alter the effectiveness of the coating (Martin-Polo et al., 1992a).

MATERIALS AND METHODS

Permeability cell

The method used to determine the rate of flow of water vapor through a film or edible coating, requires the film or coating (usually on a supporting material) to be mounted between two independent chambers. Each chamber is fitted with a sensitive and responsive relative humidity measuring probe and temperature measurement device and is provide with its own flow of air capable of being adjusted to any relative humidity. Relative humidity values are selected to give the desired differential RH across the film and the system is equilibrated at a selected temperature until a constant flow of water vapor is established through the film.

When this flow has been established the flow of air to the lower humidity chamber is stopped and the rate of increase in the relative humidity of the air in the chamber is measured for an increase in relative humidity of five percent or for a time period which will yield enough data points to give an accurate and precise estimate of the rate of humidity increase in the chamber. The rate of humidity increase can be related to the flow of moisture through the film. This method allows a range of humidity differentials and a range of humidity values. For example a differential RH of 50% can be tested using RH values of 0 and 50%, 25 and 75%, or 45 and 95% RH in the chambers on either side of the film or coating.

The water vapor transmission cell (Figure 1) was custom built in Chile (Escuela Industrial, Valparaíso, Chile) and modified at Oregon State University.

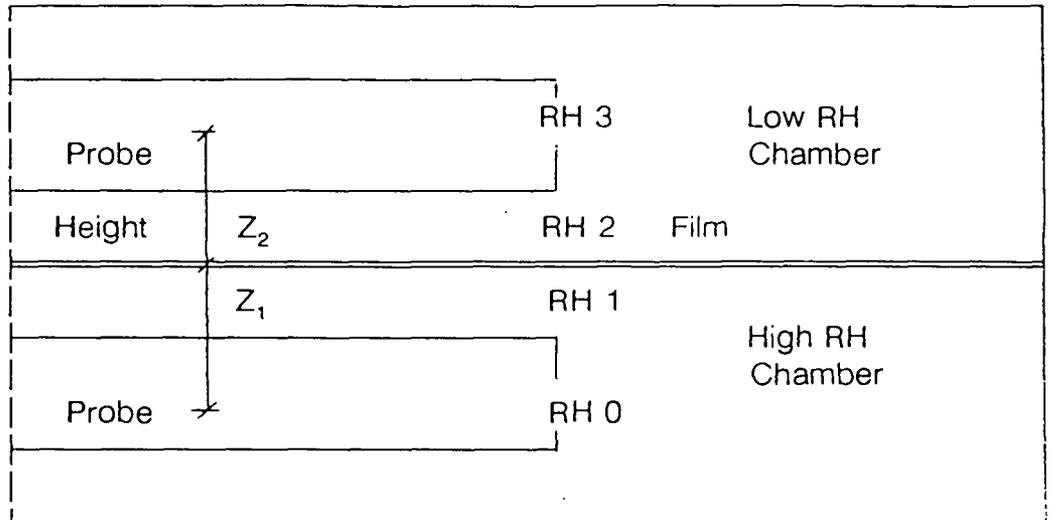


Figure 1. Location of relative humidity probes RH0 (high humidity) and RH3 (low humidity). RH2 is the humidity on the film surface in the low humidity chamber calculated from equation (24). RH1 is the humidity on the film surface in the high humidity chamber and is assumed to be the same as RH0 with 10 scfh of air flowing through the chamber.

The cell consisted of two cylindrical chambers sealed on one end and open on the other. The two chambers were stacked with the open ends facing each other. The film to be tested was clamped between the chambers and two neoprene O-rings and vacuum grease were used as sealing aids to prevent gas from leaking across the chambers. When assembled, the seals were tested by immersing the cell in a water bath. The chambers have a diameter of 0.150 m with the height of the lower and upper chambers being 0.029 m and 0.048 m

respectively. The test film area was 0.018 m^2 and the volumes of the lower and upper chambers were $522 \times 10^{-4} \text{ m}^3$ and $864 \times 10^{-4} \text{ m}^3$ respectively.

The lower and upper chambers were equipped with RH sensors (Model HMP35C, Campbell Scientific Inc., Logan, UT) reaching from the side approximately to the center of each compartment. The probe includes a thermistor for temperature measurements (see specifications in appendix 2). Probe readings recorded with an electronic datalogger (Model 21X, Campbell Scientific, Inc.) were transferred to an IBM personal computer (Figure 2).

Description Figure 2:

1. Compressed air tank
2. Flowmeters
3. High humidity conditioning bottles
4. Low humidity conditioning bottles
5. Lower relative humidity chamber
6. Higher relative humidity chamber
7. Cell
8. Bottles with oil
9. Datalogger
10. Personal Computer
11. Temperature controlled cabinet

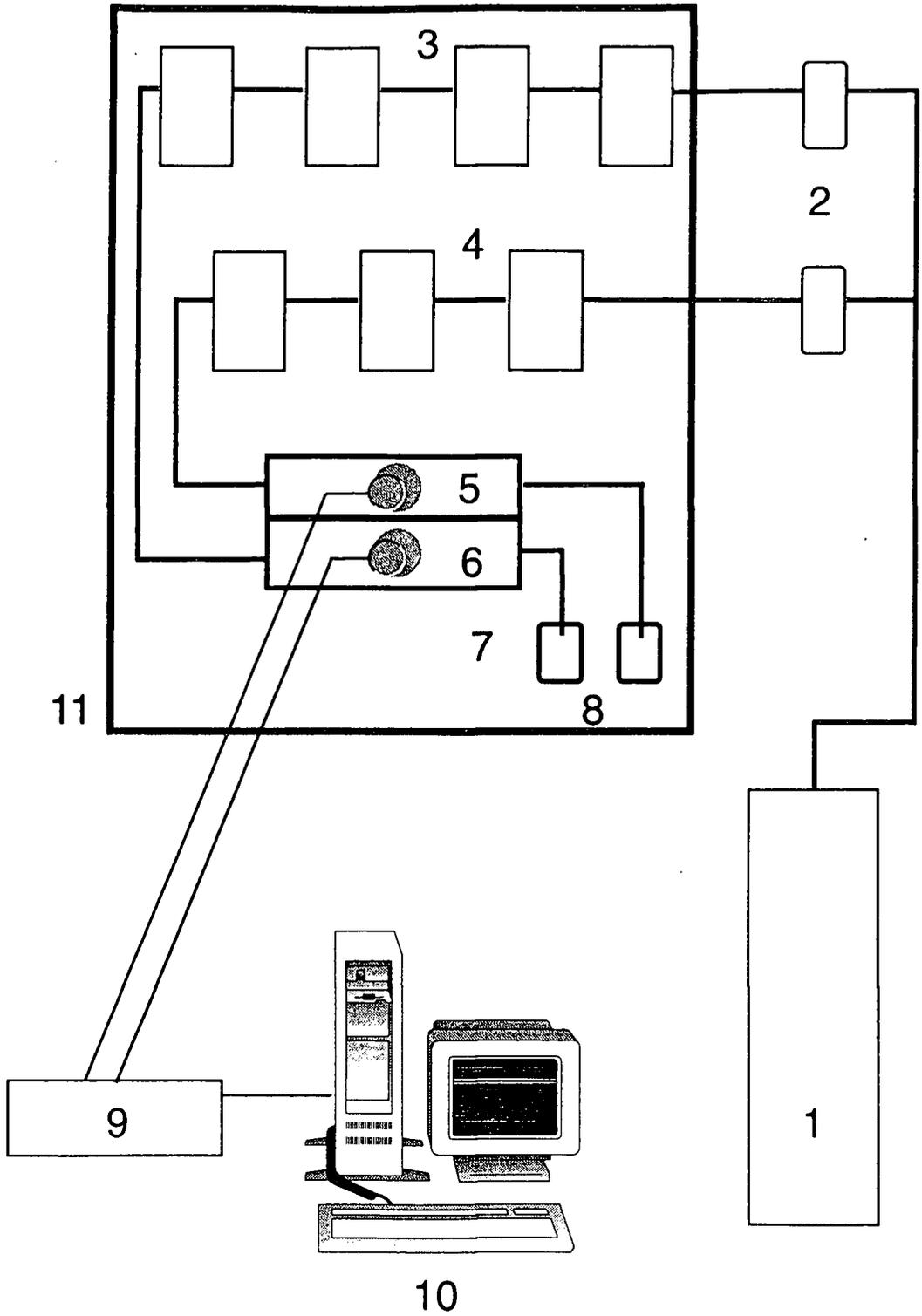


Figure 2. Moisture Permeability Apparatus.

All studies on the permeability of films were conducted using pure air. Constant RH air was generated by passing pure air (USP, Industrial Welding, Corvallis, OR) through a series of gas washing bottles. Air for the lower compartment (high RH) was obtained by passing air through water, a saturated salt solution twice (or additional water if desired RH was 100%), and finally fiber glass to remove solution carryover into the cell. Air for the upper compartment (low RH) was obtained by passing air twice through a saturated salt solution (or Drierite™ if desired RH was 0%) and then through fiber glass. Solution (or water) levels were kept constant for all experiments. Saturated salt solutions used were (Analytical Reagent, Mallinckroad Inc., Paris, KY) $\text{Mg}(\text{NO}_3)_2$ (approximately 53%RH) and NaCl (approximately 75%RH). Flowmeters (Catalog No. 7906, Alltech Associates Inc, 2951, Waukegan Road, Deerfield, IL, 60015-1899) measured the gas flow rate into each compartment. The gas flow rate was kept constant at a flow of 10 scfh, standard cubic feet per hour, ($7.86 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$) to each compartment. This flow rate was found to allow the RH sensor probes to respond in a reproducible manner to RH changes (Figure 3). Pressure in both cells was kept constant by discharging the air into two 250 ml Erlenmeyer flasks filled to the same height with 200 ml of high vacuum oil. The permeability cell and gas washing bottles were kept in a constant temperature cabinet ($\pm 1^\circ \text{C}$, Model 30, Hoffman Manufacturing Co., Albany, OR).

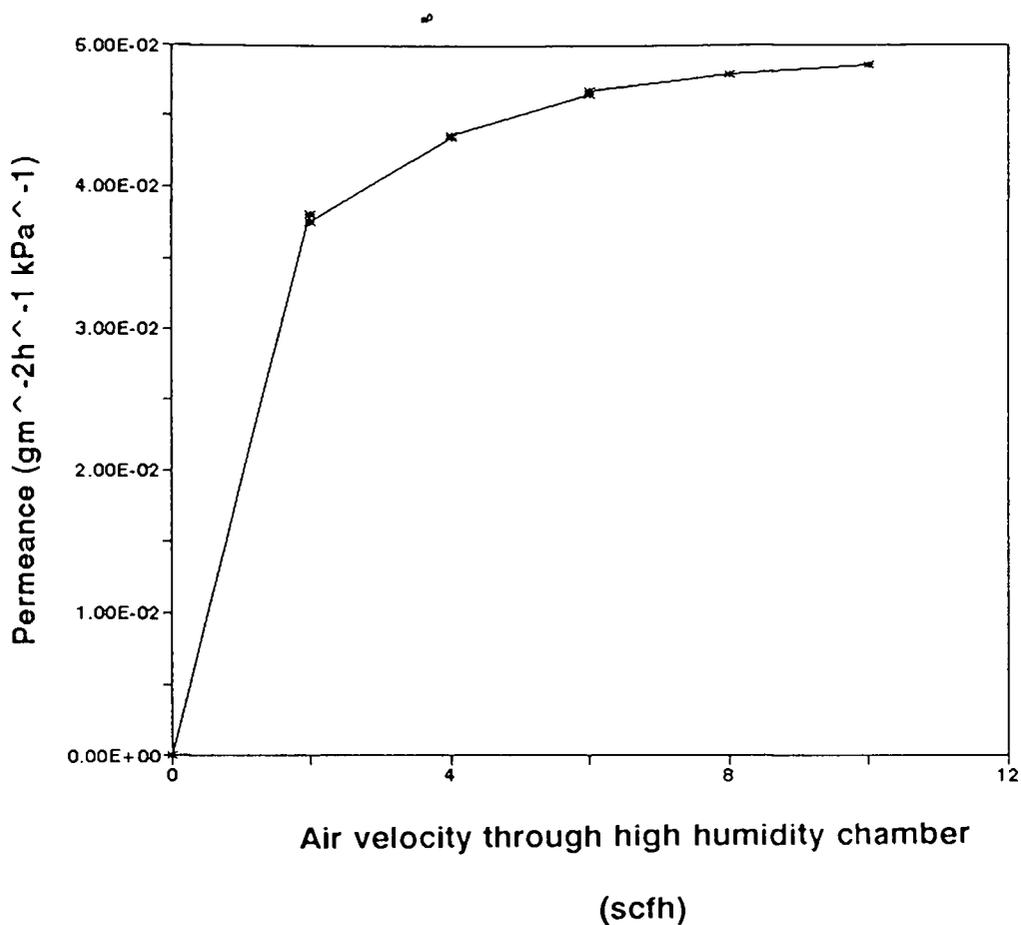


Figure 3. Variation of permeance (P) with increasing air flow rate through the high humidity chamber for cellulose support material.

Relative Humidity Sensing Probes

The RH sensor was selected to give fast, and accurate response to relative humidity with the temperature, gas, and humidity conditions encountered in food packaging. The principle of operation was based on changes in the capacitance of the probe with RH (see appendix 2)

Each RH sensor probe was calibrated at an air flow rate of 10 scfh through the cell against salt solutions of known concentrations and temperature. Further, the built-in thermometer in each probe was calibrated against a previously calibrated glass thermometer. Both probes agreed to within 0.5% RH for RH values between 0 and 100% when simultaneously exposed to the same RH presented in flowing air. Air flow rate was varied over a ten fold range (1-10 scfh) and did not appear to affect probe RH response. However, a value of 10 scfh was required to measure a reproducible probe response to changes in RH in the upper and lower chambers during test runs with high permeance coatings.

All experiments were carried out at a flow rate of 10 scfh during equilibration and during permeability measurements for this reason.

Experimental Procedures

Experimental variables were film moisture as a function of upper and lower chamber relative humidity, temperature, and air relative humidity in the upper and lower chambers. Film hysteresis was not considered and all tests were run starting from the lowest RH gradient (0-53%RH). Four RH values were selected to provide five differential RH values across each film; 0% RH (calcium sulfate), 53% RH (magnesium nitrate), 75% RH (sodium chloride), and 100% RH (distilled water). The number of bottles and the volume of saturated solution in each bottle to achieve the desired RH in the air flowing at 10 scfh was

determined by trial and error until the desired RH was obtained in a reproducible manner.

The following relative humidity differential and temperature combinations were used to evaluate the permeance of Teflon, high density polyethylene (HDPE), and polyethylene terephthalate (PET); 0-50%, 0-75%, 0-100%, 53-100%, and 75-100% RH. Temperatures used were 5, 14, 21, and 30°C.

The following relative humidity differentials and temperature combinations were used to evaluate the permeability of coatings SRE-3 and CR-1, the cellulose support material, and coating film EM 1100; 0-53%, 0-75%, 0-100%, 53-100% and 75-100% RH. Temperatures used were 5, 15, and 25°C.

A typical run required time to allow the adjustment of cell temperature and film moisture to an initial 0-53%RH gradient where 0% RH was maintained in the upper compartment and 53% RH was maintained in the lower compartment. In subsequent runs, the film was equilibrated to increasingly higher values of RH (0-75, 0-100, 53-100 and 75-100 %).

Film moisture and temperature conditioning began by setting the cabinet temperature and allowing it to equilibrate for a minimum of eight hours with RH-adjusted gas flowing into both cell compartments. Permeability determinations were made by stopping the air flow into the low RH compartment while keeping the flow into the high RH compartment at 10 scfh. Changes in RH in the low RH compartment were recorded every 15 s for a minimum of 15 min or until a 5% RH increase was observed. Replicate measurements were conducted after

flushing both compartments with constant RH air for a minimum of 20 min. When the experimental conditions were changed to a different RH gradient both chambers were flushed with gas at the new controlled RH condition for a minimum of 2 h. When experimental conditions required a change in temperature eight hours was allowed for the apparatus to equilibrate.

Data Acquisition

The experimental apparatus was equilibrated to a selected temperature and RH differential across the film sample. At time zero, the air flow in the chamber with the lower humidity was stopped by diverting it to a flowmeter and RH readings were taken in the chamber every 15 seconds for a period of 15 minutes or until a 5% increase in the RH was measured. After 15 minutes or when an increase of 5% in RH was recorded, the flow of lower humidity air was reestablished in the test cell and continued for 20 minutes to reequilibrate the system. Three replicate runs were made at each temperature and RH difference value. When a new humidity difference was tested at one temperature a time of two hours was used for equilibration. The apparatus was equilibrated at the next higher temperature over an eight hour period when all humidity studies were completed at the lower temperature.

A series of experiments was carried out to compare the accuracy of data collected over 15 minutes with data collected over a 5% RH increase which for Teflon could require up to 8 hours. This experiment was done to determine if

shorter data acquisition times were possible with films of low moisture permeability. Results indicated that data taken over a 15 minute period could predict the permeance of a low permeance film if the RH increase was at least 1% in that time period.

Calculation procedures

When the flow of air in the low humidity chamber is stopped the film continues to release moisture to the air trapped in the fixed volume of the low humidity chamber ($8.5 \times 10^{-4} \text{ m}^3$). The moisture increases the relative humidity in the chamber at a rate proportional to the rate of diffusion through the film. For small increases, the rate of increase in RH in the chamber can be shown to be a linear function of the diffusion rate through the film and the RH at the film surface can be related to the RH measured by the probe above the film. The rate measured over a 5% increase in RH was used to calculate the permeance. For some conditions the rate could be determined in as little as 15 minutes.

Film permeance was calculated from recorded the humidity changes in the low relative humidity chamber over time after the flow of air was stopped. The humidity in the high relative humidity chamber, the air flow, and the temperature in both chambers was held constant during data acquisition.

The rate of moisture increase at the probe location in the low RH compartment was assumed equal to the film water vapor transmission rate (WVTR). The calculation procedure used published values of the water vapor

pressure (P_o) at the test temperature. These were refined by statistical modeling of tabulated values in the 0-30 °C range (Table 3-5, p. 3-45, Perry, 1984) using equation (21)

$$P_o = 2,018.7 - 14.815 T + 0.027253 T^2 \quad (21)$$

where T (K) is the average absolute temperature ($r^2 = 0.999$). The water diffusion constant in still air was estimated as (Bretsznajder, 1971):

$$D = 2.6 \cdot 10^{-5} \left(\frac{273.15 + T}{298.15} \right)^{1.8} \quad (22)$$

Other values required were the exposed area of the film ($A = 0.018 \text{ m}^2$), volume of the low RH compartment ($V = 0.00085 \text{ m}^3$), probe height above the film ($z_2 = 0.024 \text{ m}$), total pressure ($P_T = 101.325 \text{ kPa}$), and gas constant ($R = 8,314.4 \text{ J/kg mol K}$).

Assuming ideal gas behavior for any time point:

$$\text{water vapor mass} = \frac{18 P_o RH3 V}{100 R T} \quad (23)$$

where RH3 is the relative humidity value determined by the probe in the low humidity chamber.

Equations proposed by Krochta and others to estimate the effect of the stagnant air layer above the test film (Krochta, 1992; McHugh and Krochta, 1993a) allowed an estimation of the actual RH gradient across the film. In

equation (24) RH2 is the relative humidity on the film and RH3 is the RH at the probe in the low humidity chamber. RH2 was needed for actual WVTR calculations.

$$RH2 = \frac{100}{P_o} \left(P_T - \frac{P_T - \frac{RH3}{100} P_o}{\exp\left(\frac{WVTR R T z_2}{18 P_T D}\right)} \right) \quad (24)$$

where P_T is total pressure and P_o is the pressure of the water vapor.

WVTR was calculated directly from a plot of RH2 against time using

$$\text{Corrected water vapor mass} = \frac{18 P_o RH2 V}{100 RT} \quad (25)$$

$$WVTR = \frac{\text{corrected watervapormass}}{\text{time} * A} \quad (26)$$

$$P = \left(\frac{100}{P_o} \right) \left(\frac{WVTR}{RH1 - RH2} \right) \quad (27)$$

RH1 is the humidity at the surface of the film in the high humidity chamber and is assumed to be equal to the value recorded by the probe in the high humidity chamber with air flowing at 10 scfh.

The permeance (P) of each film and coating was estimated from equation (27) by using the slope of a least squares plot of the WVTR against RH differential as shown in Figure 4.

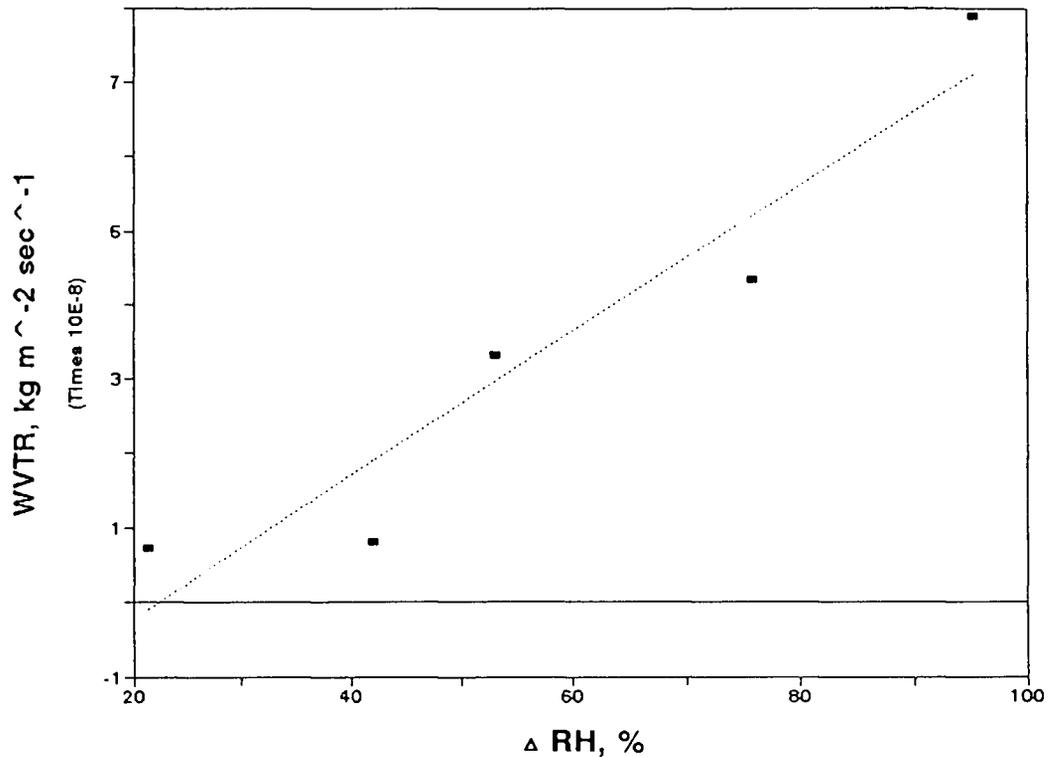


Figure 4. Water vapor transmission rate (WVTR) calculated from low humidity chamber readings for the RH gradients indicated. Film PET, 3.6 mil thickness, $T = 30 \text{ }^\circ\text{C}$. The slope of the least square fit line is used to determine the permeance value (P) by equation (27).

Finally an Arrhenius plot of permeance values was prepared to allow comparison with literature values reported at various temperatures as shown in Figures 5 and 6.

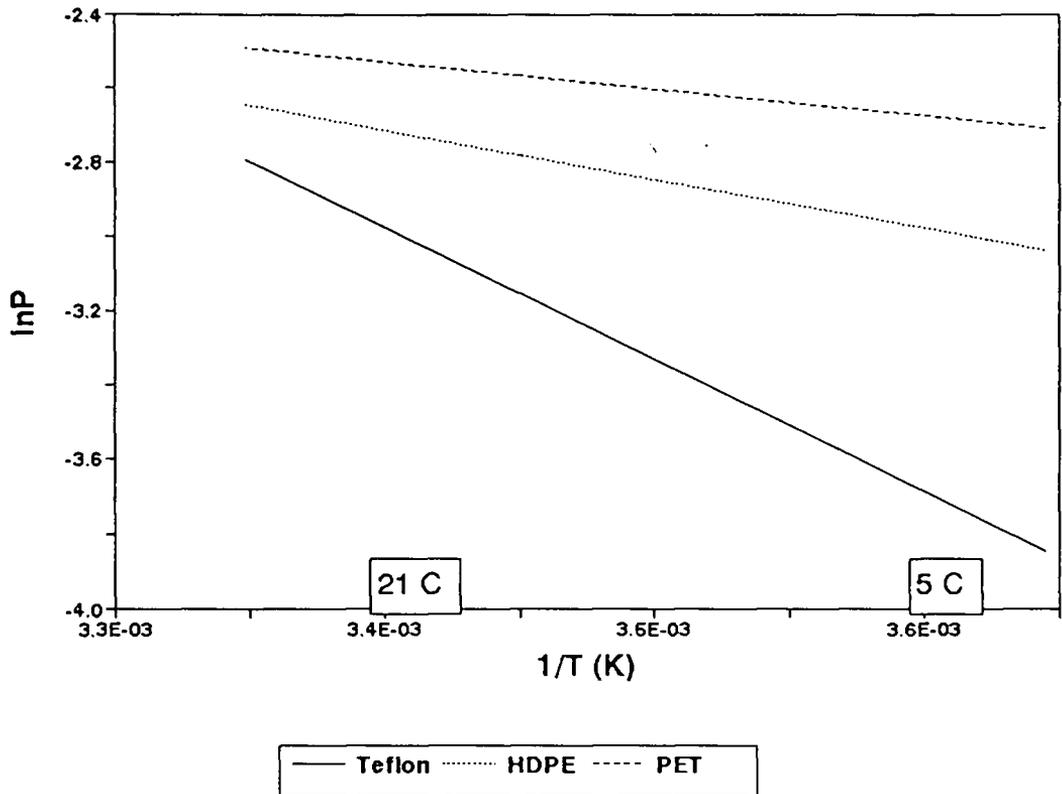


Figure 5. Arrhenius plot of permeance values for teflon, HDPE and PET films.

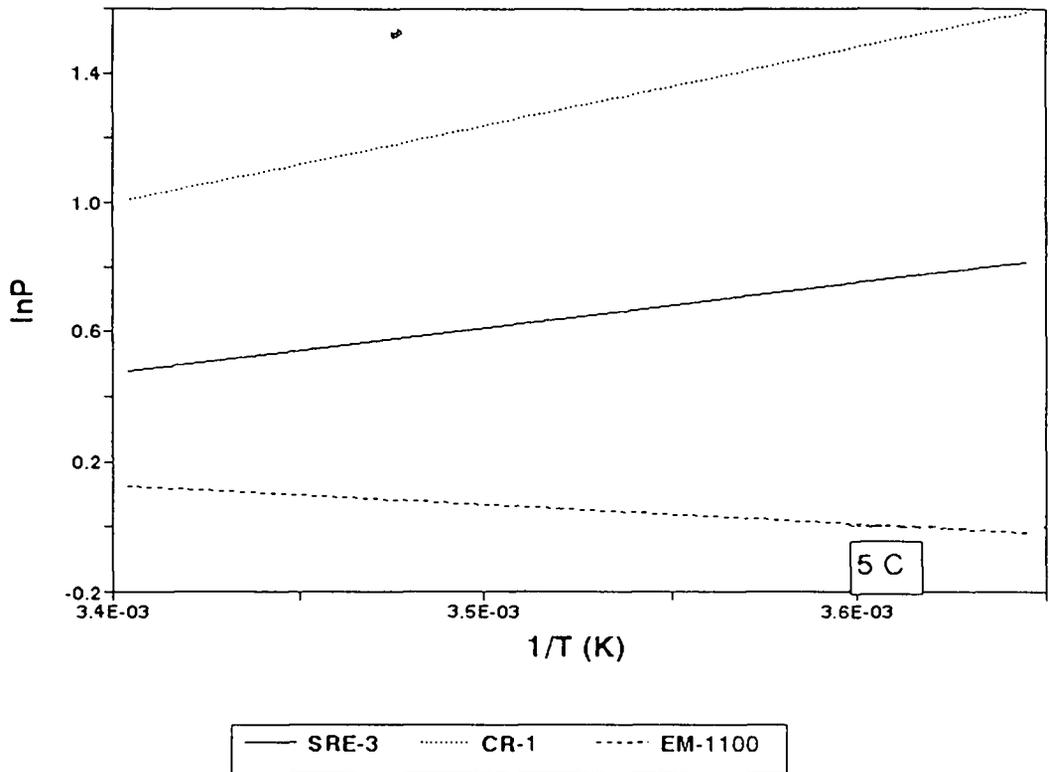


Figure 6. Arrhenius plot of permeance for SRE-3 and CR-1 coatings and EM-1100 edible film.

Test films and coatings

A variety of films and coatings were used in evaluating the performance of the experimental permeability cell, the flexibility of the operating procedures, and the reliability of calculation methods. Teflon and high density polyethylene (HDPE) films were obtained from the Dept. of Food Science and Technology at the University of California (Davis, CA) and polyethylene terephthalate (PET) was obtained from the Technology Center at Kraft General Foods (Glenview, IL). Coating solutions tested were provided by FMC (Lakeland, FL) and included

SRE-3 with shellac and rosin as main components and CR-1, a carnauba based formulation. Both coatings were tested on a regenerated cellulose support. The water vapor permeability of the support was determined independently so that the permeance of the coating could be determined. Also tested was a commercial edible film (EM-1100, Polymer Film Inc., Rockville, CT). Micrometer (Browne and Sharpe, model 599-579-14, North Kingston, RI, 02852) readings at 7 locations were averaged and used to estimate film thickness. Thickness measurements were done after permeability tests to avoid film damage. The micrometer was used in this study since it was the only measuring device available.

Preparation of SRE-3 and CR-1 coatings

SRE-3 and CR-1 solutions were applied on the cellulose film stretched over glass plates using a thin layer chromatography spreader (thickness fixed to 1 mm). The spreader (C. Desega, model DS200/0.3 Heidelberg, West Germany) was filled with 5 ml of solution and moved over the cellulose support at a constant speed ($\approx 0.04 \text{ m s}^{-1}$). Coated film supports were dried at room temperature (20-25°C) for 24 hr before the films were detached from the plates. Prior to permeability determinations, coated films were stored in desiccators at 0%RH. All permeability determinations were completed with the coated side facing the high RH compartment and the cellulose film support facing the low RH compartment.

RESULTS AND DISCUSSION

Tables 5 and 6 summarize permeance values found using the dynamic method. Permeance values in the 5-30 °C range were determined for Teflon, HDPE, PET. Permeance values in the 5-25 °C range were determined for the cellulose film support, SRE-3, CR-1 and EM-1100 coating materials.

Permeance values are calculated using a least square fit at each temperature for moisture gradients of 0-53, 0-75, 0-100, 53-100, and 75-100 %RH.

Table 5. Permeance values (P) for different films calculated from experimental data taken at five relative humidity gradients and four temperatures

		Temperature, °C			
		5	14	21	30
Film	Thickness, mil	P _*	P	P	P
Teflon	5.3	2.2	2.9	4.5	6.3
HDPE	5.4	5.0	5.4	5.9	7.5
PET	3.6	6.7	7.0	7.9	8.2

* Permeance values are expressed as $10^{-2} \text{ g m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$.

Table 6. Permeance values for different coatings calculated from experimental data taken at five relative humidity gradients and three temperatures

		Temperature °C		
		5	15	25
Film	Thickness, mil	P*	P	P
F. Support	1.8	69	73	93
SRE3+F.Supp	2.5	52	53	58
SRE-3	0.7	219	200	157
CR1 + F. Supp	2.5	60	62	69
CR-1	0.7	477	383	266
EM-1100	2.1	94	114	108

* Permeance values are expressed as $10^{-2} \text{ g m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$.

An Arrhenius equation was used to convert permeance values to the same temperature as literature values, and to 25 °C as reported in Table 7. Table 7 includes parameters E_a and $\ln k_0$ at 25 °C.

Table 7. Activation energy (E_a), constant ($\ln K_0$) and permeance (P) at 25 °C for films and coatings

Film	P*	Ea**	$\ln K_0$
Teflon	5	7.07	8.9
HDPE	6	2.63	1.72
PET	8	1.46	-0.06
Film Support	90	2.48	4.1
SRE-3	160	-2.7	-4.15
CR-1	274	-4.8	-7.1
EM-1100	113	1.16	2.08

* Permeance values are expressed as $10^{-2} \text{ g m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$.

** Activation energy is expressed as kcal g-mol^{-1}

Permeability cell evaluation

Measurement accuracy and precision

Source of Error Films and coatings used to verify the accuracy of moisture permeance determinations were selected based on their reported literature values. These values ranged from 2.27×10^{-2} (Teflon) to 3.98 (CR-1) $\text{g m}^{-2} \text{hr}^{-1} \text{kPa}^{-1}$ (Table 8). Comparisons were complicated by the wide variability of reported permeance values (Teflon and HDPE), failure of previous workers to report variability (PET, SRE-3 and CR-1), the use of different test temperatures (23, 25 and 30 °C). Experimental permeance data were converted to various temperatures using the Arrhenius equation (5-30 °C range) to allow comparison to values reported in the literature. However, differences in the method of preparation of coated supports may have affected our ability to compare our results with work by Hagenmaier and Shaw (1992). For example, the composition of the solutions provided by FMC were similar but not identical to those used by these authors.

TABLE 8. Reported permeance (P^*) comparison with values obtained experimentally at the same temperature and relative humidity gradient¹

Film	Δ %RH	T, °C	P^* a,b,c	P
Teflon (a)	0 - 50	23	2.3 \pm 5.8	4.7
HDPE (a)	0 - 50	23	3.7 \pm 6.4	6.4
PET (b)	0 - 100	25	14.7	15.8
Cellulose Support	0 - 100	30		96.0
SRE-3^{(c)**}	0 - 100	30	218.0	153.1
CR-1^{(c)**}	0 - 100	30	398.0	258.5

** Note: Permeance values for each coating were corrected for the cellulose support by assuming.

$$\frac{1}{P_{\text{coating}}} = \frac{1}{P_{\text{observed}}} - \frac{1}{P_{\text{support}}}$$

¹Experimental permeance was calculated using the Arrhenius expression to obtain values at the same temperature as the values reported by (a) Toas (1985), (b) Kester and Fennema (1986) and (c) Hagenmaier and Shaw (1992). Values are expressed as 10^{-2} g m^{-2} h^{-1} kPa^{-1} .

Permatran cells used to determine the reported permeance of PET, SRE-3 and CR-1 have RH-adjusted air flow on both film sides and need no correction for diffusion limitations. The stagnant air layer is a source of error in the ASTM cup method only for high permeance films. This is not the case for Teflon and HDPE (Table 8). The dynamic method used in this study can be affected by the stagnant air layer on each side of the film. Corrections were in the range of two percent for the value of the RH indicated by the probe and the value at the film surface.

The dynamic method to determine permeance, i.e., changes in RH measured during 15 minutes or for the time required for a 5% RH increase, demonstrated an accuracy comparable to established methods (Table 8). The probe used in this study was found to react to a 0-100%RH humidity change in <15 s (Campbell Scientific Inc.). This was adequate to measure the much slower RH changes involved in this dynamic method.

Evaluation of permeance calculation methods.

Permeance values for hydrophobic films were comparable to those published in the literature. Permeance values for coatings based on a full range of moisture contents were found to be 65-70% of published values. The testing time required in the dynamic method is faster than those used in other methods. Only 15 min are needed to determine a WVTR value with coating films such as SRE-3, CR-1, EM-1100, and film support. However, more hydrophobic

films such as Teflon, HDPE, and PET were found to require very long times to reach an RH increase of 5% in the low humidity chamber at low temperatures and low humidity differentials. For example, the time for a 5% increase ranged from 15 min ($T = 30\text{ }^{\circ}\text{C}$ and 0-100%RH) to over 12 h ($T = 5\text{ }^{\circ}\text{C}$ and 75-100%RH). WVTR measurements for Teflon and HDPE were very difficult to measure at an RH different of 75-100% because the rate of moisture transmission through the film was very slow. A time greater than 12 h was needed to reach a 5% increase in RH at $30\text{ }^{\circ}\text{C}$ and 75-100%RH. Therefore, the WVTR of Teflon and HDPE were not analyzed at 75-100%RH by the dynamic method because of the time required to measure a significant increase in the RH. WVTR values for 15 min runs were compared with those with a time necessary to increase RH by 5%. Table 9 indicates that permeance values could be estimated quite well in 15 minutes for the conditions shown.

Table 9. Permeance values calculated from experiments run for 15 min for a time necessary to increase RH by 5% in the low humidity chamber at temperatures shown

Film	Δ %RH	Temp °C	P*	time min	P	%RH increase
Teflon	0 - 50	23	2.3	15	5.1	1.2
				90	4.7	5.0
HDPE	0 - 50	23	3.7	15	6.9	2.0
				55	6.4	5.0
PET	0 - 100	25	14.7	15	16.0	4.7
				16	15.8	5.0

Permeance values (P) are expressed as $10^{-2} \text{ g m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$.

P* permeance values reported by the literature.

Parameters Affecting RH Measurements

The wide range of permeance values resulting from the wide range of films tested required several approaches to data acquisition. Films with a very high WVTR yielded a 5% increase in RH in less than 15 min. High WVTR

values could be handled by reprogramming the datalogger to record RH changes at a higher frequency to get more points during a 5% RH increase. Low WVTR values could be measured using an RH change of less than 5% if sufficient points could be collected for a 1% RH increase. Thus if the probe used in this study could detect accurately changes in RH to 0.1 %, ten points could be determined for an RH increase of 1%.

Permeability cell applications

RH effect on permeance

WVTR increases as the difference in RH increases across a film due to an increase in the moisture vapor concentration differential (Karel, 1975). However, it was thought that the WVTR of some films and coatings may be higher for the same RH differential when high RH values are present on both sides of the film. This maybe due to an increase in film or coating moisture content. WVTR results for Teflon, HDPE and PET for 53-100%RH were lower than values at 0-53% RH at all temperatures. Additional studies will be needed to determine the effect of relative humidity and thus film moisture content on permeability for hydrophobic films. The cellulose support and coatings appear to show about the same WVTR with an increase in RH.

Temperature effect on film permeance

Permeance and other diffusion controlled phenomena are generally characterized by activation energies in the range 0-15 kcal/g-mol (Karel, 1975). Hagenmaier and Shaw (1991a) reported values < 4 kcal/g-mol and < 6 kcal/g-mol for the moisture and oxygen permeance of six emulsified polyethylene wax coatings, respectively. The E_a values shown in table 7 range from a negative value of -4.8 for CR-1 to 7.1 for Teflon. The coatings SER-3 and CR-1 showed a decrease in permeance with increasing temperature. Teflon, HDPE and PET showed an increase in permeance with increase in permeance with increase in temperature.

Advantages of the dynamic method

A major advantage of the dynamic method used for measuring film permeance values was the significant time reduction for determinations. After overnight temperature adjustment and film moisture equilibration several RH gradients could be tested in a single day. Measurement time was reduced because there was no need to hold the film for moisture equilibration. In the ASTM cup method and with Permatran measurements the time required to obtain a single measurement range approximately from 1 to 7 days.

Permeance values reported from the literature in Table 8 were measured with the ASTM cup method (Teflon and HDPE) or with a MOCON PermatranTM (PET, SRE-3 and CR-1). These two procedures determine water transfer

through the film under equilibrium and for a fixed relative humidity gradient. The ASTM method does not correct for the stagnant air layer effect, however it is unlikely to have affected the permeance of the low permeance films such as Teflon and HDPE. The Permatran cell maintains an air flow rate on both sides of the film and does not require the diffusion correction suggested by Krochta and others. However, the infrared sensor used to detect the moisture change works only at very low air humidity and restricts the low RH side of the film to 0%RH testing conditions. This is not a limitation of the ASTM cup method nor of the dynamic method evaluated in this study.

CONCLUSIONS

- * A dynamic method has been tested for determining the permeance value of packaging films over a wide range of relative humidities and for temperatures between 5 and 30 °C. Results for film were found to be in agreement with values published using standard testing methods such as the MOCON Permatran and ASTM cup method. Results for coatings were 65-70% of those reported in the literature.

- * Replicate runs at a single humidity gradient could be made at 20 minute intervals with test data being taken in as little as 15 minutes.

- * Data acquisition time was found to depend on the sensitivity of the relative humidity (RH) measuring probe. In this study the probe was sensitive to a 0.1% change in RH. Thus the time for data acquisition depended on the rate of humidity change in the detection chamber. For low humidity gradients (75-100% RH differential) and low temperatures (5 °C) a test run could be greater than 12 hours to obtain a change of 1% RH in the test chamber (10 data points) for Teflon or HDPE. For this reason the system was less suitable for moisture impermeable barriers.

- * Films with high water vapor transmission rate (WVTR) could be evaluated in several hours at any one temperature. An eight hour period was required to achieve temperature equilibrium when a change in the experimental temperature condition was made.

- * Data on a variety of films (Teflon, HDPE, PET) showed that the WVTR values for RH gradients between 0 - 53% RH were higher than values for 53-100% RH. Higher values of RH were expected to give a higher WVTR value for these films since their moisture content was higher.

- * Data on edible coatings (EM-1100 and SRE-3 and CR-1 on a cellulose support) showed closer WVTR values at 0-53% RH and 53-100% RH.

- * Permeance values taken in the range 5 - 30 °C were used to calculate the activation energy associated with moisture transmission. The values for Teflon, HDPE and PET were found to be in agreement with values in the literature and were in the range of 1 to 7 kcal/g-mol. Values for the coating materials SRE-3 and CR-1 were found to be negative indicating a reduction in permeance with an increase in temperature.

- * This work shows the dynamic method has promise as a quicker and more accurate method for measuring the permeability of edible coatings for foods. It

has potential as a method requiring less time for films with low moisture transmission rate. This method allows the evaluation of WVTR over a range of films moisture contents by allowing a wide range of relative humidity values to be used on either side of the film to create a humidity differential.

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APPENDIX 1. Water vapor transmission rate (WVTR) data for each relative humidity (RH) and temperature point for different films and coatings (average of three values for each WVTR).

1a. TEFLON

Thickness: 5.3 ± 0.06 mil

Δ RH		Temperature °C			
Nominal %	Real %	5	14	21	30
0 - 53	52.4	2.04	4.69	8.14	15.5
0 - 75	74.7	2.76	5.86	11.0	33.9
0 - 100	95.3	3.69	8.8	21.9	44.8
53 - 100	42.0	0.46	1.17	2.96	5.98

WVTR is expressed as 10^{-9} kg m⁻² sec⁻¹

1b. High Density Polyethylene (HDPE)

Thickness: 5.3 ± 0.06 mil

Δ RH		Temperature °C			
Nominal %	Real %	5	14	21	30
0 - 53	53.3	2.27	7.18	1.39	28.0
0 - 75	75.6	4.68	11.7	21.7	46.0
0 - 100	96.0	7.16	15.5	27.7	54.7
53 - 100	42.3	0.62	1.88	3.83	6.54

1c. Polyethylene terephthalate (PET)Thickness: 3.6 ± 0.06 mil

Δ RH		Temperature °C			
Nominal %	Real %	5	14	21	30
0 - 53	53.0	4.6	10.4	18.1	33.2
0 - 75	75.3	6.1	13.5	24.3	43.3
0 - 100	96.2	13.0	26.9	45.1	79.0
53 - 100	42	1.2	2.68	4.65	8.18
75 - 100	21.4	1.1	2.38	4.2	7.28

1d. Film SupportThickness: 1.8 ± 0.007 mil

Δ RH		Temperature °C		
Nominal %	Real %	5	15	25
0 - 53	52.8	60.5	123.0	276
0 - 75	73.7	94.8	180.0	400.0
0 - 100	94.3	127.0	274.0	719.0
53 - 100	41.0	39.8	71.9	182
75 - 100	20.0	4.73	17.1	65.2

1e. CRE-3 + Film SupportThickness: 2.5 ± 0.008

Δ RH		Temperature °C		
Nominal %	Real %	5	15	25
0 - 53	54.0	35.2	83.3	195.0
0 - 75	76.2	70.4	145.00	350.0
0 - 100	94.0	100.0	202.0	415.0
53 - 100	40.5	20.3	54.4	132.0
75 - 100	19.5	8.53	19.4	42.7

1f. CR-1 + Film SupportThickness: 2.5 ± 0.005 mil

Δ RH		Temperature °C		
Nominal %	Real %	5	15	25
0 - 53	53.1	49.2	108.0	239.0
0 - 75	75.4	89.1	176.0	382.0
0 - 100	95.0	115.0	232.0	498.0
53 - 100	41.3	27.5	74.8	161.0
75 - 100	19.4	8.63	20.1	43.3

1g. EM-1100Thickness: $21. \pm 0.007$ mil

Δ RH		Temperature °C		
Nominal %	Real %	5	15	25
0 - 53	53.5	116.0	257.0	582.0
0 - 75	75.2	169.0	370.0	781.0

TEMPERATURE AND RELATIVE HUMIDITY PROBE

1. GENERAL

The Model HMP35C probe contains a Vaisala capacitive relative humidity sensor and a Fenwal Electronics UUT51J1 thermistor. The probe is designed to be housed in the 41002-2 12 Plate Gill Radiation Shield; a ten foot lead length is standard. Longer lead lengths are available up to 1000 feet. Voltage drop in the longer lead lengths will lower the RH reading by approximately 0.6% RH per 100 feet of cable. Do not extend lead lengths by adding wire to the pigtail (connection) end or measurement errors will result.

2. ACCURACY - TEMPERATURE SENSOR

The overall probe accuracy is a combination of Fenwal's interchangeability specification, the precision of the bridge resistors, and the polynomial error. In the "worst case" all errors add to an accuracy of $\pm 0.4^{\circ}\text{C}$ over the range of -33°C to $+48^{\circ}\text{C}$. The error is typically less than the specification and, if desired, can be reduced with a single point calibration. The major error component is the $\pm 0.2^{\circ}\text{C}$ interchangeability specification of the thermistor from 0 to 60°C ($\pm 0.5^{\circ}\text{C}$ at -40°C). The interchangeability error is predominantly offset and can be determined with a single point calibration. Compensation can then be done with an offset entered in the measurement instruction.

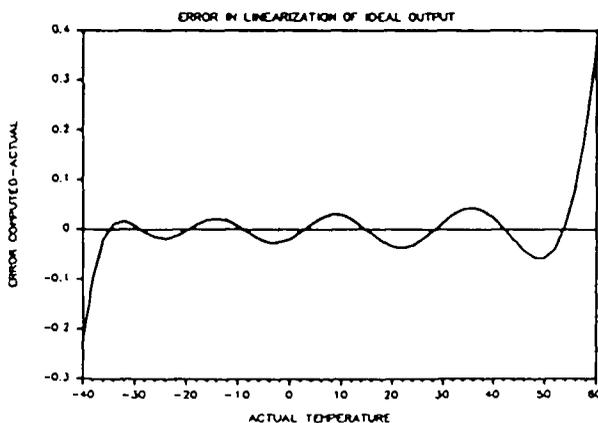


FIGURE 1. Temperature Probe Polynomial Error Curve

The bridge resistors are 0.1% tolerance with a 10ppm temperature coefficient. Polynomial errors are plotted in Figure 1.

3. RH SENSOR – SPECIFICATIONS

The following relative humidity sensor specifications are provided by Vaisala, Inc.

TABLE 1. RH Sensor Specifications

Measurement Range	0 to 100 % RH
Output Signal Range	0.002 to 1 VDC
Accuracy (at 20°C , including nonlinearity and hysteresis)	
against factory references	$\pm 1\%$ RH
against field references	$\pm 2\%$ RH, 0 to 90% $\pm 3\%$ RH, 90 to 100%
Temperature dependence	$\pm 0.04\%$ RH/ $^{\circ}\text{C}$
Typical long term stability	better than 1% RH per year
Response time (at 20°C , 90% response)	15 s with membrane filter
Settling time	1.5 s*
Supply voltage (via CSI switching circuit)	12 VDC
Current consumption	≤ 4 mA
Operating temperature	-20 to $+60^{\circ}\text{C}$

* 1.5 seconds is Campbell Scientific's recommendation.

4. WIRING

Connections to the datalogger for the HMP35C are shown in Figure 2. The probe requires two single ended analog measurements, the green (RH) and the orange (temp.) leads can be inserted into either HI or LO inputs.

The black thermistor excitation lead connects to any excitation channel. The yellow lead is used to control switching 12 volts to the relative humidity sensor and is normally connected to an excitation channel, although a control port could be used with a different program in the datalogger. The number of HMP35C probes per excitation channel is physically limited by the number of lead wires that can be inserted into a single excitation terminal (approximately ten).

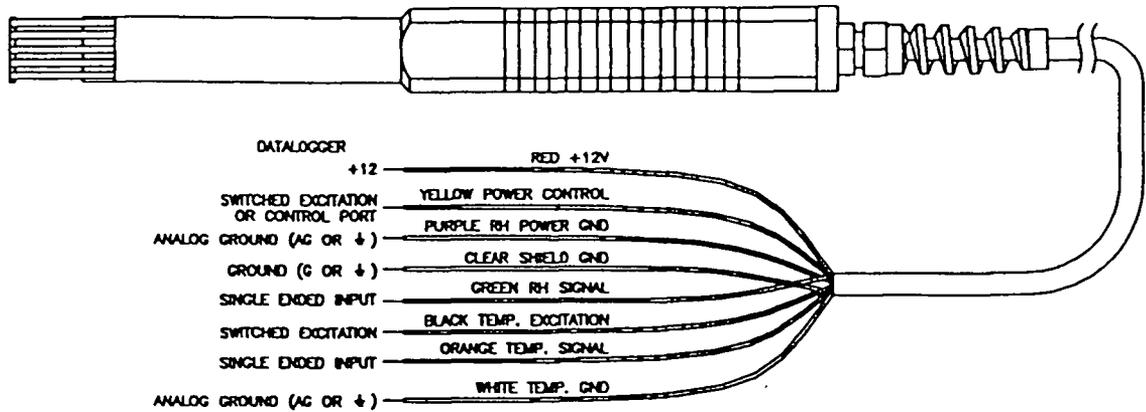


FIGURE 2. HMP35C Probe Datalogger Connections

NOTE: Do not connect the power control lead and the temperature excitation to the same excitation channel. The power control will slow the response of the excitation and result in temperature errors.

The white lead connects to Analog Ground. Analog Ground, labeled "AG" on the CR10, is the same as Ground for the 21X and CR7. The clear lead is the shield which connects to Ground (G) on the datalogger.

5. PROGRAMMING

Instruction 11 is used to measure temperature and instruction 4 is used to measure relative humidity.

Instruction 11 provides AC excitation, makes a single ended voltage measurement, and calculates temperature with a fifth order polynomial. A multiplier of 1.0 and an offset 0.0 yields temperature in Celsius. If Fahrenheit is desired, use a multiplier of 1.8 and an offset of 32.

Instruction 4 sets an excitation voltage which switches 12 volts to the probe, waits a specified time and makes a single ended voltage measurement. Because the probe is calibrated to have an output of 0 to 1000 millivolts for the 0 to 100% RH range, a multiplier of 0.1 and an offset of 0.0 provides relative humidity in percent.

Example 1 shows the use of instruction 11 and 4.

EXAMPLE 1. Sample 21X Instructions for HMP35C Probe

01:	P	11	Temp 107 Probe
01:		1	Rep
02:		1*	IN Chan
03:		1	Excite all reps w/EXchan 1
04:		1*	Loc [:Air Temp.]
05:		1	Mult
06:		0	Offset
02:	P	4	Excite,Delay,Volt(SE)
01:		1	Rep
02:		5**	5000 mV slow Range
03:		2*	IN Chan
04:		2*	Excite all reps w/EXchan 2
05:		15	Delay (units .01sec)
06:		5000**	mV Excitation
07:		2*	Loc [:RH]
08:		.1	Mult
09:		0	Offset

* Proper entries will vary depending on the program and datalogger channel usage.
 ** On CR10 the 2500 mV input range and 2500 mV excitation are used.

6. MAINTENANCE

The HMP35C Probe requires minimal maintenance. Monthly, check to make sure the radiation shield is free from debris. The screen on the sensor should also be checked as often. Annually, check the calibration of the probe. (It

should be sent to Campbell Scientific, Inc. if recalibration is needed and facilities to do so are unavailable.)

7. INSTRUCTION 11 DETAILS

Reading this section is not necessary for general operation of the HMP35C Probe with Campbell Scientific's dataloggers.

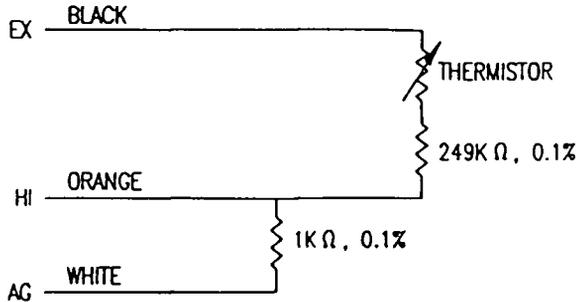


FIGURE 3. 107 Thermistor Probe Schematic

Instruction 11 outputs a precise 4V AC excitation (2V with the CR10) and measures the voltage drop due to the sensor resistance (Figure 3). The thermistor resistance changes with temperature. Instruction 11 calculates the ratio of voltage measured to excitation voltage (V_s/V_x) which is a direct function of resistance, as shown below.

$$V_s/V_x = f(R_s) = R_f/(R_s + R_f) = 1000/(R_s + 250000)$$

where, V_x/V_x = ratio of measured to excitation voltage, R_f = fixed resistance, and, R_s = sensor resistance.

Instruction 11 then calculates temperature using a fifth order polynomial equation developed by correlating V_s/V_x with temperature. The polynomial coefficients are given below; input to this equation is $(V_s/V_x) * 8000$.

TABLE 2. Polynomial Coefficients

Coefficient	Value
C0	-53.4601
C1	9.08067
C2	-8.32569 x 10-01
C3	5.22829 x 10-02
C4	-1.67234 x 10-03
C5	2.21098 x 10-05

Table 3 displays resistance and datalogger output at several temperatures.

TABLE 3. Temperature, Resistance, and Datalogger Output

TEMPERATURE ° C	RESISTANCE OHMS	OUTPUT ° C
-40.0	4015500	-39.0
-38.0	3503500	-37.4
-36.0	3062000	-35.7
-34.0	2680400	-33.9
-32.0	2350200	-32.0
-30.0	2064000	-30.1
-28.0	1815500	-28.1
-26.0	1599400	-26.1
-24.0	1411100	-24.0
-22.0	1246900	-22.0
-20.0	1103400	-20.0
-18.0	977910	-17.9
-16.0	867910	-15.9
-14.0	771370	-13.9
-12.0	686530	-12.0
-10.0	611870	-10.0
-8.0	546070	-8.0
-6.0	488000	-6.0
-4.0	436680	-4.1
-2.0	391270	-2.1
0.0	351020	-0.1
2.0	315320	2.0
4.0	283600	4.0
6.0	255390	6.0
8.0	230260	8.0
10.0	207850	10.1
12.0	187840	12.1
14.0	169950	14.1
16.0	153950	16.0
18.0	139610	18.0
20.0	126740	20.0
22.0	115190	22.0
24.0	104800	23.9
26.0	95447	25.9
28.0	87022	27.9
30.0	79422	29.9
32.0	72560	32.0
34.0	66356	34.0
36.0	60743	36.0
38.0	55658	38.1
40.0	51048	40.1
42.0	46863	42.1
44.0	43062	44.1
46.0	39605	46.0
48.0	36458	47.9
50.0	33591	49.8
52.0	30976	51.6
54.0	28590	53.4
56.0	26409	55.1
58.0	24415	56.7
60.0	22590	58.3