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MATHEMATICAL MODEL PREDICTION OF MOISTURE CONTENT FOR DRY FOOD PRODUCTS STORED AT CHANGING ENVIRONMENTAL CONDITIONS

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MATHEMATICAL MODEL PREDICTION OF MOISTURE CONTENT FOR DRY FOOD PRODUCTS STORED AT CHANGING ENVIRONMENTAL CONDITIONS

By

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ABSTRACT

MATHEMATICAL MODEL PREDICTION OF MOISTURE
CONTENT FOR DRY FOOD PRODUCTS STORED AT
CHANGING ENVIRONMENTAL CONDITIONS

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The shelf life of packaged food products often depends on the product's moisture content. The proper selection of packaging materials will result in maintaining a product's moisture content below a critical level for an extended period. The ability to predict a product's moisture content over time can be a valuable tool in selecting a packaging material.

There are several methods utilized throughout the food industry to predict shelf life based on moisture absorption. The most scientific methods include mathematical models that utilize data for the product and package along with environmental conditions to predict moisture content under constant storage conditions.

The research described herein has attempted to predict a packaged products moisture content under varying storage conditions. This research has shown that a product's moisture content can be determined for constantly changing storage conditions by using a mathematical model.

DEDICATION

This thesis is dedicated to my family, especially my parents, in appreciation and thanks for their assistance and guidance through all my academic endeavors. Also, to my wife for her patience and support throughout this work.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Bruce Harte for his efforts and guidance while serving as major advisor. Thanks are also due to Dr. Dennis Heldman and Dr. Jack Giacin for their criticisms and suggestions as members of the thesis committee.

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INTRODUCTION

Shelf life can be defined as the length of time that a product remains of acceptable quality. A product's shelf life can be dependent on numerous factors. One of the most important is the loss of quality due to absorption of moisture from the external environment. In this case, the proper selection of packaging materials is required to provide a barrier between the internal and external environment.

There are numerous methods used throughout the food industry to determine a product's shelf life. Many of these methods attempt to predict moisture absorption, by the product, to a critical level. One commonly used method is accelerated shelf life testing. This technique subjects a product to stressed temperature and humidity conditions. It is assumed that storage under these conditions is equal to a longer storage period under actual distribution conditions. This method often leads to erroneous results and costly overpackaging (Manathunya, 1976).

Another method of shelf life prediction has been the use of mathematical models. The models are based on calculations utilizing experimental data for packaging materials, moisture absorption properties of the product and storage conditions to predict shelf life.

A model has been developed to predict moisture absorption of dried food product under constant storage conditions (Kliment, 1978). This study subjected the package to constant conditions for a defined time period. At the end of the time period the package was transfered into different storage conditions. This sequence was defined as a time-step. The model was used to calculate moisture content upon completion of each time-step. The model closely predicted moisture content for a time-step at constant conditions. However, error was introduced due to drastic changes in storage conditions between time-steps.

The objective of this study was to utilize a similar calculation to predict moisture content under actual distribution conditions. Storage conditions were constantly monitored throughout the study. The model utilized gradual fluctuation for temperature and relative humidity, therefore, reducing the potential for error noted in previous models under simulated storage conditions. The model was used to predict moisture content under known storage conditions for two products. Each product was repackaged in two packaging materials.

LITERATURE REVIEW

The proper selection of packaging materials is critical to ensure a product's quality throughout distribution. Several techniques are commonly used by the food industry to aid in the selection of packaging materials. Most methods are based on determining the amount of protection offered by various packaging materials. The amount of protection is commonly measured by the product's moisture content increase versus time.

Due to the length of time required for many products to complete the distribution cycle, actual shelf life testing can be prohibitive. Thus, predictive methods have been developed to expedite the evaluation and selection of packaging materials.

Accelerated shelf life testing was used to reduce the time required for selecting packaging materials (Easter, 1953). This method subjects a product, packed in various packaging materials, to stress conditions of temperature and relative humidity. The product's quality at accelerated conditions is measured and compared to product quality under normal storage conditions. Product quality can be measured by several techniques including moisture content and analytical methods to measure chemical changes within the product. Once the product under accelerated conditions was judged unacceptable a correlation can be drawn between quality at accelerated conditions versus normal conditions. The product's shelf life can then be predicted by assuming a direct relationship of reactions which determine product quality at normal and accelerated conditions. In many cases this assumption is invalid (Manathunya, 1976).

An extension of this method to further reduce time required to select packaging materials, can be the selection of materials for products "similar" to a product previously tested under accelerated conditions. This method was based on the assumption that deterioration reactions will occur at similar rates for "similar" products. Again, in many cases this assumption is invalid (Manathunya, 1976).

Another method for shelf life prediction has been the use of mathematical models. A significant amount of research has been conducted and published in this area. In most cases, the models are based on experimental data generated on the food product, packaging material and storage environment. The primary advantage of mathematical models is the ability to significantly reduce the time required to make shelf life predictions.

Dried food products can deteriorate through several mechanisms depending upon composition and storage conditions. Deteriorative mechanisms include, lipid oxidation, nonenzymatic browning, degradation of proteins and textural change such as the loss of crispness and caking (Mizrahi et al., 1970; Quast and Karel, 1972; Labuza et al., 1972). The rate of deteriorative reactions often depends upon the atmosphere surrounding the product. Therefore, a major function of packaging materials is to provide a barrier between the internal and external environment. By knowing the deteriorative mechanism of the product versus the internal environment and equations to determine the rate of permeation from the external environment a shelf life model can be developed.

Numerous studies have been conducted to develop models based on the absorption of moisture to a critical level (Charie et al., 1963; Mizrahi et al., 1970; Iglesias et al., 1975). Labuza et al. (1972) reviewed mathematical models based on deteriorative mechanisms and packaging material properties for space rations.

This work was extended to include the effect of various storage temperatures on water absorption by Iglesias and Chirife (1976). In this work an equation was developed for several food products to be used in predicting shelf life at different storage temperatures. Manathunya (1976) developed a model that predicted the moisture content of cereals at two constant storage conditions. The model was based on package permeability and sorption isotherm data generated at the known storage conditions. The model developed proved to be more accurate than accelerated shelf life predictions.

Several models have been developed to predict shelf life of product that deteriorate through two mechanisms. Quast and Karel (1972) studied potato chip deterioration due to oxidative rancidity and textural changes due to moisture absorption. Karel et al. (1971) developed a similar model to study dehydrated cabbage.

Mizrahi and Karel (1977a) developed an accelerated testing method for predicting the extent of deterioration of moisture sensitive products. The method used data generated from an accelerated test to predict deterioration of the same product for any given package and moisture content combination. The method was later extended to include storage at various temperatures by Mizrahi and Karel (1977b).

Kliment (1978) developed a mathematical model to predict moisture content under changing storage conditions. The study used a time-step sequence and subjected packaged products to a range of simulated storage conditions. The simulated storage conditions were constant during each time-step. The model was based on data generated for the product and packaging materials over the range of storage conditions.

Labuza (1979) reviewed mathematical equations to predict shelf life under fluctuating temperatures in distribution. Zero and first order reaction rates were reviewed. Riemer and Karel (1977) used mathematical models to study vitamin retention of dehydrated tomato juice as a function of time, temperature and moisture content. Villota et al. (1980) extended this work by developing an equation correlating shelf life of dehydrated vegetables with storage conditions. Labuza (1982) studied the quality loss in whey powders during steady and nonsteady state storage. A comparison was made between the amount of browning and protein quality loss during storage.

Aquerre et al. (1983) studied desorption isotherms of rice stored at various temperatures. An equation was reviewed to take temperature into account for sorption isotherms.

Paredes et al. (1983) studied the influence of storage on quality of maize meal. The study included comparisons of product quality stored under accelerated humidity conditions.

EXPERIMENTAL METHODS

The calculation of moisture content based on varying storage conditions requires data generated on the product, package and storage conditions. In most cases, this information can be determined through generally accepted laboratory test methods used throughout the food industry.

Initial Moisture Content

Numerous acceptable methods exist for determining the moisture content of food products. Most techniques involve removal of water held by the product. Moisture content can be calculated based on weight change. Vacuum oven drying was selected for this work. This technique is widely used throughout the food industry due to the lower oven temperature required. Therefore, the chance of driving off volatile components of the product is reduced.

The moisture content was determined for four samples of each product. Approximately ten grams of each sample was weighed into an aluminum dish, and placed into the vacuum oven at 70°C for sixteen hours. The moisture content was calculated from the weight change of the sample. The average moisture content was determined for each product and expressed as $\frac{\text{gms moisture}}{\text{100 gms dry product}}$. Results are reported in Table 1. The following calculation was used to determine the initial moisture content.

$$\frac{W_I - W_F}{W_F} \times 100 = M_i$$

Where

W_I is the initial sample weight, gms.

W_F is the sample weight after drying, gms

M_i is the initial moisture content,

$\frac{\text{gms moisture}}{\text{100 grams dry product}}$

Sorption Isotherms

A products sorption isotherm can be described as a plot of the amount of water absorbed or desorbed as a function of the equilibrium relative humidity. Two methods of determining sorption isotherms were reviewed. These included, equations for fitting sorption isotherms of foods (Chrife et al., 1978), and determination of sorption isotherms above saturated salt solutions, Wink et al., 1950. The latter method was selected for this work. Approximately 5 grams of each sample was weighed into an aluminum dish and placed over the super saturated salt solution.

The initial samples had a moisture content equal to the initial moisture content of product used for experimental testing. The samples would either lose or gain moisture depending upon the surrounding relative humidity. Therefore, the isotherms for this work are actually a mixed absorption/desorption isotherm. Sorption isotherms were determined at three temperatures.

The following calculation was used to determine moisture content for the sorption isotherm. The initial dry weight of the sample is determined by,

$$W_d = \frac{W_i}{1 + \frac{M_i}{100}}$$

Table 1--Initial Moisture Content

	% Moisture for experimental testing and sorption isotherms $\frac{\text{g moisture}}{\text{100 g dry product}}$	Package Fill weight gms
Product A	4.010	520
Product B	.645	450

Where

W_d is the dry weight of the sample, gms.

W_i is the initial weight of the sample, gms.

M_i is the initial moisture content,

$$\frac{\text{gms } H_2O}{\text{100 gm dry mix}}$$

. The moisture content for the sorption isotherm, upon equilibrium can now be determined by:

$$M_c = \frac{W_f - W_d}{W_d} \times 100$$

where

W_f is the sample weight after equilibrium, gms.

W_d is the initial dry weight of the sample gms.

M_{ct} is the moisture content $\frac{\text{gms moisture}}{\text{100 gms dry mix}}$

Results are plotted in Figures 1 and 2. The salt solutions and corresponding relative humidities are listed in the Appendix in Table 5 .

Package Fill Weight

Average package fill weight of product for the pouches were used. Results are reported in Table 1.

Moisture Vapor Transmission Rates

The Moisture Vapor Transmission Rates (MVTR) were determined for each packaging material at four temperatures. A Mocon IRD-2 Infrared Diffusometer was used following ASTM F372-73. Results are in Table 2.

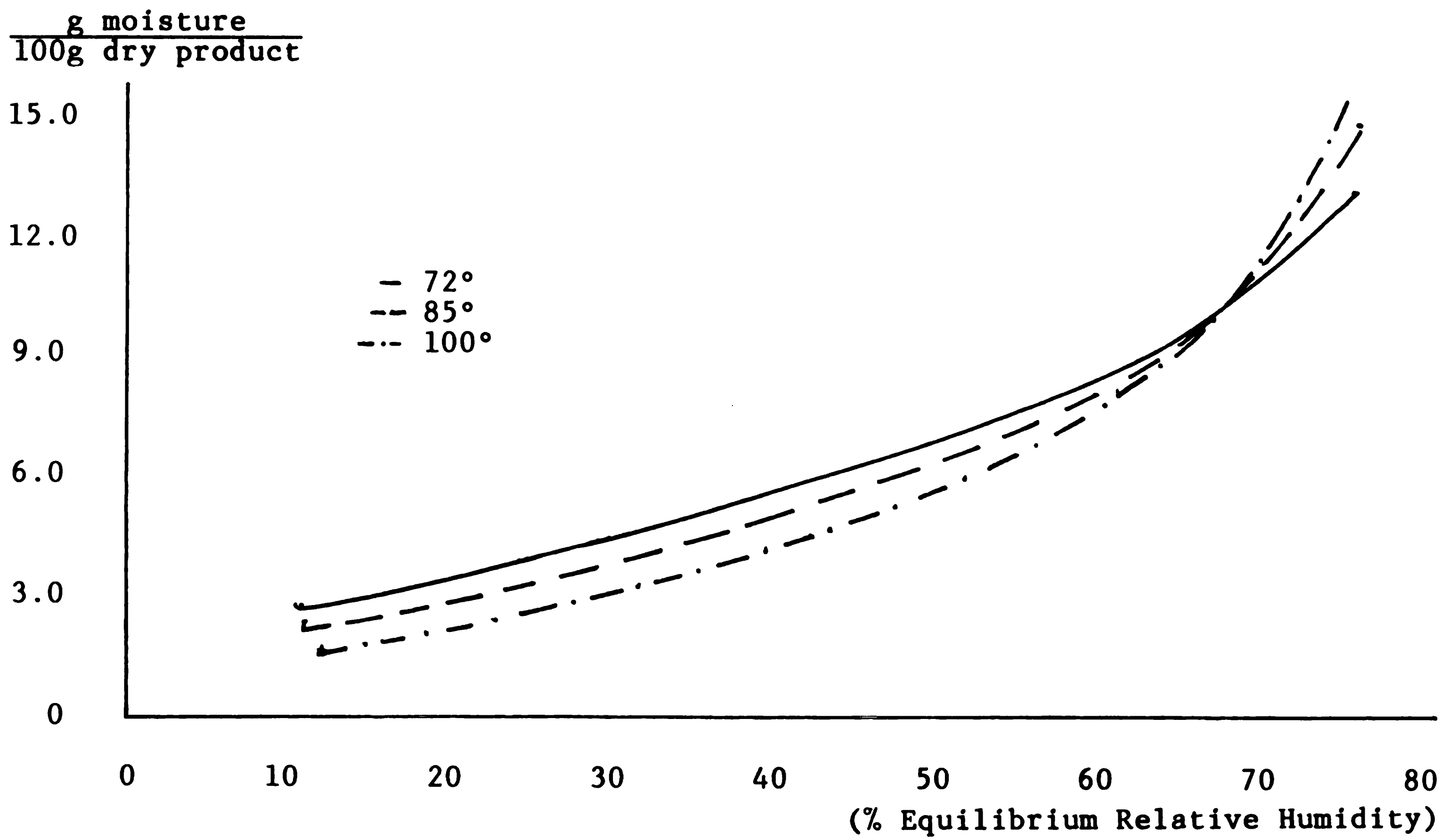

Figure 1. Sorption isotherm--Product A

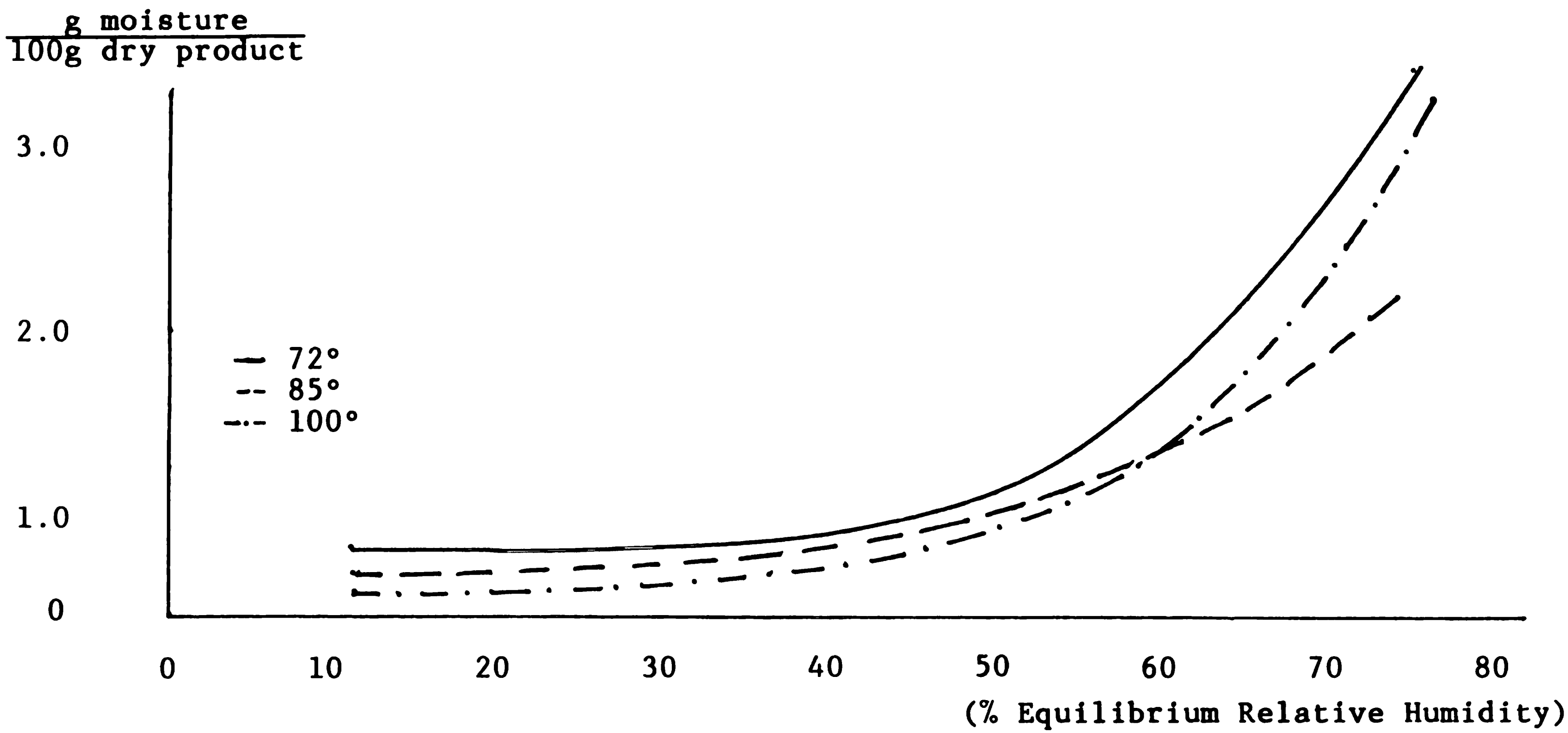

Figure 2. Sorption isotherm--Product B

Table 2--Moisture Vapor Transmission Rates

	Temp (°F)	RH (%)	MVTR* (g/100in^2/24 hrs)	Package Permeability g/hr/mm dif
Material I	100	90	0.41	$4.21\text{x}10^{-4}$
	90	90	0.30	$4.02\text{x}10^{-4}$
(104 in^2)	80	90	0.19	$3.47\text{x}10^{-4}$
	70	90	0.12	$3.09\text{x}10^{4}$
Material II	100	90	0.15	$1.49\text{x}10^{-4}$
	90	90	0.11	$1.48\text{x}10^{-4}$
(108 in^2)	80	90	0.08	1.46x10
	70	90	0.05	$1.29\text{x}10^{-4}$

* Average of 5 material samples.

Calculation of Package Permeability

The package permeability was determined from the moisture vapor transmission rates. These values were determined at four temperatures and expressed as gms H_2O/hr./mm of water vapor pressure differential/package. Results are in Table 2.

The following is the permeability calculation procedure.

$$\frac{\text{MVTR}}{24\text{ hr.}(\Delta P)} \times \frac{\text{Package Area (in}^2\text{)}}{100}$$

Preparation of Shelf Life Samples

Two commercially available dry mix products were selected for this work. Both products had relatively low initial moisture contents and varied significantly in composition. Therefore, the product would be expected to absorb moisture from the surrounding atmosphere at differing rates.

Product A was a bakery mix product, while B was a dessert topping mix. The primary mode of failure for both products was the absorption of moisture to a critical level.

Two packaging materials were selected to be used with each product. Material II was four mil coextrusion of high density and low density polyethylene. Material I was a two mil low density polyethylene coextrusion. Since one objective of the study was to determine shelf life of each product in various packaging materials, the product had to be repacked in manually designed packages. Therefore, the study did not take into account the affect of packaging equipment and distribution handling on finished package quality.

Four sets of samples were produced and labeled, AI and AII and BI and BII. A set included six manually designed heat sealed pouches. To ensure consistent product mixture prior to producing the test packages, each product was thoroughly mixed and weighed to the approximate declared commercial net weight. Initial product samples were taken for analytical analysis. Finished package weight of each pouch was measured on a top loading balance and recorded to the nearest one hundredth of a gram.

Experimental Shelf Life Testing

The finished packages were transferred to an ambient storage area for actual shelf life testing. Under these conditions, temperature and relative humidity are constantly changing. Therefore, the packages would be expected to gain, and possibly lose moisture at varying rates. The packages remained at ambient conditions for one month.

Storage temperature and relative humidity conditions were continuously monitored with a Honeywell

(Model 612X0-HT-00-60-7M-L) recorder. Periodically throughout the test, the samples were weighed for the determination of moisture gain or loss, then returned to the ambient storage area.

Calculation of Experimental Moisture Content

To calculate the moisture content at each weighing, the dry weight of the package must be determined at time t=0. The moisture content at t=0 is equal to the initial moisture content. The dry weight at t=0 can be determined by:

$$W_d = \frac{W_i}{1 + \frac{M_i}{100}}$$

where

W_i is the initial weight of product in the package, and M_i is the initial moisture content of the product at t=0,

$\frac{\text{g moisture}}{\text{100 g dry product}}$

W_d is the dry weight of product in the package at time t=0, grams.

The moisture content M_c at each weighing can be determined by:

$$M_c = \frac{W_f - W_d}{W_d} \text{ X } 100$$

where

W_f is the weight of product in the package at time t, grams

W_d is the dry weight of product in the package at time t=0, grams.

M_c is the moisture content of the product at any weighing time t,

$$\frac{\text{g moisture}}{\text{100 g dry product}}$$

MATHEMATICAL MODEL FOR MOISTURE ABSORPTION BASED ON VARYING STORAGE CONDITIONS

The stability of many food products depends largely on the product's moisture content. As the moisture content approaches a critical level (an amount above which delivers a product of unacceptable quality) the reaction rates for various spoilage mechanisms increase.

There are numerous methods available to inhibit spoilage due to high moisture content. Several commonly used food processing techniques include drying, freezing, addition of chemical agents along with many others. In these applications, the preservation method revolves around making water unavailable for the moisture related reactions to occur. In many cases these techniques are used for products with an initial moisture content close to or above the critical level.

For many food products, the initial moisture content is below the critical level. For product in this category, the proper selection of packaging material is often an economical means of maintaining a moisture content below the critical level.

Numerous methods are available to aid in the selection of packaging materials. These methods range from actual shelf life testing to the use of mathematical models. These techniques evaluate the ability of a package to maintain a product below the critical level.

The use of mathematical models is a more scientific, economical and less time consuming method to evaluate the functionality of a package as compared to actual or accelerated shelf life testing (Manathunya, 1976). The models take into consideration certain aspects of the product, package and external environmental conditions to predict a product's shelf life (the length of time required for a product to reach the critical moisture content). The mathematical equations for these models have been widely reported throughout the food industry.

External storage conditions, temperature and relative humidity, are constantly changing during distribution and warehousing. Additionally, the internal conditions are constantly changing as the system tries to reach equilibrium. By knowing the internal and external storage conditions for a period of time the change in moisture content of the product can be determined. This research reviews a model developed for determining moisture content of a product stored under actual distribution conditions. The model calculates moisture content for a defined period of storage time. The period of time was defined as a time step.

The calculation is based on the following assumptions:

(i) The moisture in the product and headspace of the package is in equilibrium.

(ii) The seal is perfect and there is no damage to the side wall of the package.

(iii) The external conditions for each time step are constant.

The rate of water vapor permeation through a packaging material at a given time as expressed by Gyeszli (1971),

$$\frac{dM}{dt} = \bar{P}(P_o - P_i) \qquad (1)$$

where

M = weight of water permeated into the package, gms.

t = time, hours

$\bar{P}$ = Permeability constant of the package (gms H_2O/hr/mm pressure difference)

p_o = partial pressure of water in air outside the container (mg Hg)

p_i = partial pressure of water in air in the container (mg Hg)

In many cases it is easier to measure percent relative humidity than to measure the water vapor pressure.

Selection of Time Step t, hours

↓

Select Temp and RH Conditions for Time Step

↓

Determine initial conditions for moisture,
sorption isotherms

↓

Calculate slope of sorption isotherm at Temp. (T)

↓

Recall data required for calculation, Partial Pressure
of Water, package permeability at Temp (T) and
weight of dry mix

↓

Calculate Internal Relative Humidity (Water Activity)*
at the end of time step

↓

Determine moisture content at end of time step
based on sorption isotherm

↓

If upper critical limit has not been reached
return to initial step.

*Internal Relative Humidity can be used interchangedly with water activity

Flow Diagram: Model for Predicting Moisture Content Under Varying Storage Conditions.

This relationship can be expressed by Equation (2)

$$p = \frac{P_{ST}}{100} \bullet H$$

where

p = Water vapor pressure at a temperature (mm Hg)

H = % Relative Humidity

P_{ST} = Saturated vapor pressure of water at temperature (T), (mm Hg)

the rate of permeation can be expressed by Equation (3),

$$\frac{dM}{dt} = \bar{P}\,\frac{P_{sT}}{100}(H_o - H_i)$$

where

H_o = percent relative humidity outside the package

H_i = percent relative humidity inside the package.

The water vapor that has permeated into the package will be absorbed by the food. A very small amount will be contained in the package headspace. Assuming that the water within the package reaches equilibrium between the product and the headspace, the moisture content will be function of the internal relative humidity (H_i).

This function can be described by the sorption isotherm of the product. The sorption isotherm can be described as the amount of water absorbed or desorbed plotted against the equilibrium relative humidity (Labuza, 1968).

There are numerous ways to express an absorption isotherm. For most dry food products the curve is constant over the critical range (from the initial moisture content to the critical moisture content). In this case the sorption isotherm can be expressed by the slope of the line, $\frac{dm}{dH}$.

Where

dm = difference between the initial and critical moisture content (percent)

dH = difference between the initial and critical equilibrium relative humidity (percent).

The amount of water vapor absorbed (K_1) by the product over time can be expressed as:

$$\frac{dK_1}{dt} = \frac{W_d}{100} \cdot \frac{dm}{dH} \cdot \frac{dH_i}{dt} \tag{4}$$

where

W_d is the dry weight of the product (grams)

The remainder of water vapor within the package (K_2) will be contained within the headspace. By using the ideal gas law the weight of water within the headspace can be expressed by the equation,

$$K_2 = 18 \cdot P_s \frac{H_i}{100} \cdot \frac{v}{RT} \tag{5}$$

where

K_2 = Amount of water in the headspace gms

P_S = Saturated water vapor inside the package (mm Hg)

H_i = Relative humidity inside the package

V = volume of headspace in the package (cm^3)

R = gas constant

T = absolute temperature, °K

18 = molecular weight of water.

The amount of water gain at any time can be expressed as:

$$K_T = K_1 + K_2$$

where

K_T = amount of water gain within the package

K_1 = amount of water gain within the product

K_2 = amount of water gain within the headspace

Previous studies have found that the amount of water vapor contained in the headspace is negligible (Kliment, 1978). Therefore, for this work the total amount of water within the package at any point in time was assumed to be absorbed by the product. Thus,

$$K_T = K_1 \tag{7}$$

Substituting Equation (7) into Equation (4) and solving for K_T gives:

$$\frac{dK_T}{dt} = \frac{W_D}{100}\frac{dm}{dh} \cdot \frac{dH_i}{dt} \qquad (8)$$

The rate of water vapor permeation equals the change in water vapor content within the package, or,

$$\frac{dM}{dt} = \frac{d_{KT}}{dt}$$

From equations (3) and (8), we have,

$$\bar{P} \cdot \frac{P_{sT}}{100}(H_o - H_i) = \frac{dH_i}{dt}\left(\frac{dm}{dH}\cdot\frac{Wd}{100}\right) \qquad (9)$$

The equilibrium relative humidity inside the package is the only factor that changes with time, so,

$$\bar{P} \quad \frac{P_{sT}}{100}\ (H_o - H_i) = \frac{d_m W_d}{dH100} \cdot \frac{dH_i}{dt} \qquad (10)$$

By rearranging Equation (10) gives

$$\frac{dH_i}{dt} = (H_o - H_i)\ \left(\frac{\bar{P}\ P_{sT} dH}{Wd\ dm}\right)$$

Let

$$B = \frac{\bar{P}\ P_{sT}\, dH}{W_d\ dm}$$

so $\frac{dH_i}{dt} = B\ (H_o - H_i)$ (11)

$$\frac{dH_i}{H_o - H_i} = Bdt$$

Integrate H_i from 0 to t hours,

$$\int_{H_i}^{Hf} \frac{dH_i}{H_o-H_i} \Big|_o^t = Bdt$$

$$\frac{H_o-H_i}{H_o-H_f} = e^{Bt}$$

Where

H_f = final relative humidity at the end of the time step.

or

$$\frac{H_o-H_f}{H_o-H_i} = e^{-Bt}$$

Solving for H_f gives:

$$H_f = H_o-(H_o-H_i)e^{-Bt} \qquad (12)$$

By knowing the internal equilibrium relative humidity at the end of the time step for the given temperature, the moisture content can be determined from the sorption isotherm. If the calculated moisture content is less than the critical moisture content the calculation can be repeated for the next time step.

The following is a sample calculation using the model to determine moisture content.

Sample Calculation

Determine the moisture content of variable B/I stored at 80°F and 60% relative humidity. Length of the time step is 12 hours.

$$H_f = H_o - (H_o - H_i)e^{-Bt}$$

where H_f = Final internal relative humidity at the end of the time step, (%)

H_o = External relative humidity (%)

t = length of the time step (hours)

$$B = \frac{\bar{P}\, ps_T}{W_d}\,\frac{dH}{dm}$$

where $\bar{P}$ = Total package permeability, gms/hr/mm vapor pressure differential/package

$\frac{dH}{dm}$ = Inverse of the slope for the sorption isotherm

ps = Saturated vapor pressure of water at temp (T).

W_d = Weight of dry mix in the package, gms.

So,

H_o = 60%

H_i = 38.50%, from sorption isotherm at a moisture content of .671%

t = 12 hours

$\bar{P}$ = .000347 gms/hr/mm vapor pressure differential package

ps = 26.221 mm

W_d = 450 gms

$dH = 10\%$ (Δ equilibrium relative humidity from sorption isotherm)

$dm = .11\%$ (Δ moisture content from sorption isotherm)

Therefore

$$B = \frac{.000347\ (26.221)}{450} \ \frac{10}{.11}$$

$$= 1.838 \times 10^{-3}$$

Now

$$H_F = 60-(60-38.50)e^{-1.838x10^{-3}(12)}$$

$$H_F = 60-(21.5)e^{-.022050}$$

$$H_F = 60-(21.5) \quad .978$$

$$H_F = 38.97$$

The moisture content at the end of the time step can be determined from the sorption isotherm. In this case, the moisture content corresponding to an equilibrium relative humidity of 38.97% is .679%.

Since the critical moisture content has not been attained the calculation is repeated for the next time step.

RESULTS AND DISCUSSION

The moisture content for all variables was calculated for each time step. The length of a time step varied depending upon the magnitude of change for the storage conditions. As seen from Tables 6,7,8 and 9 the duration of a time step ranged from 6 hours up to 38 hours. Storage conditions were continuously monitored and recorded every two hours.

There is some judgment required to determine the length of a time step under changing conditions. In general, a time step was defined as the length of time required for a temperature change of approximately 10°F. The temperature and relative humidity recordings over the period were averaged to arrive at the storage conditions for that time step. Generally, the length of a time step was within the range of 8 to 14 hours.

The calculated moisture contents for the products compared very well with the experimental results. The results for these values over the storage period can be seen in Tables 6,7,8 and 9, and plots are in Figures 3,4,5 and 6. The difference between the average experimental and calculated moisture contents can be seen in Table 3. The results are plotted in Figures 3,4,5 and 6.

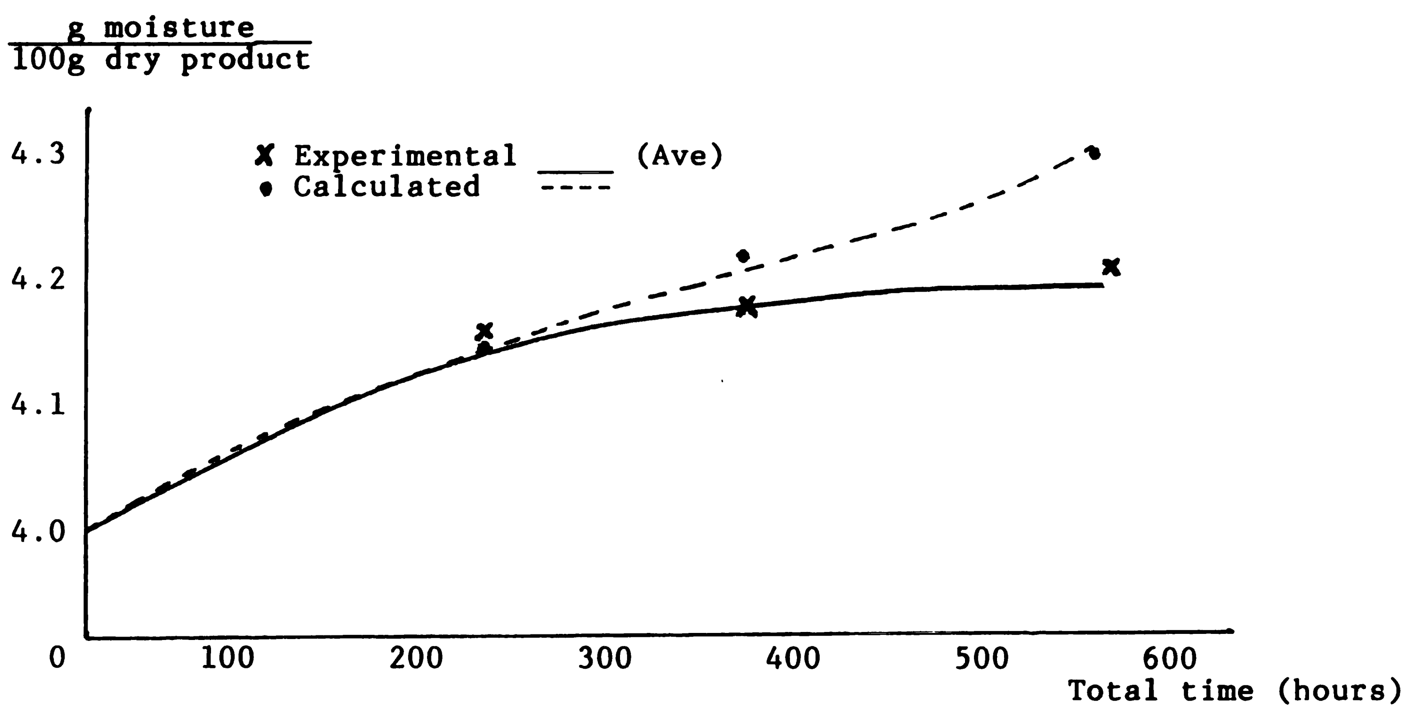

Figure 3. Experimental and calculated moisture contents - Product A/Material I

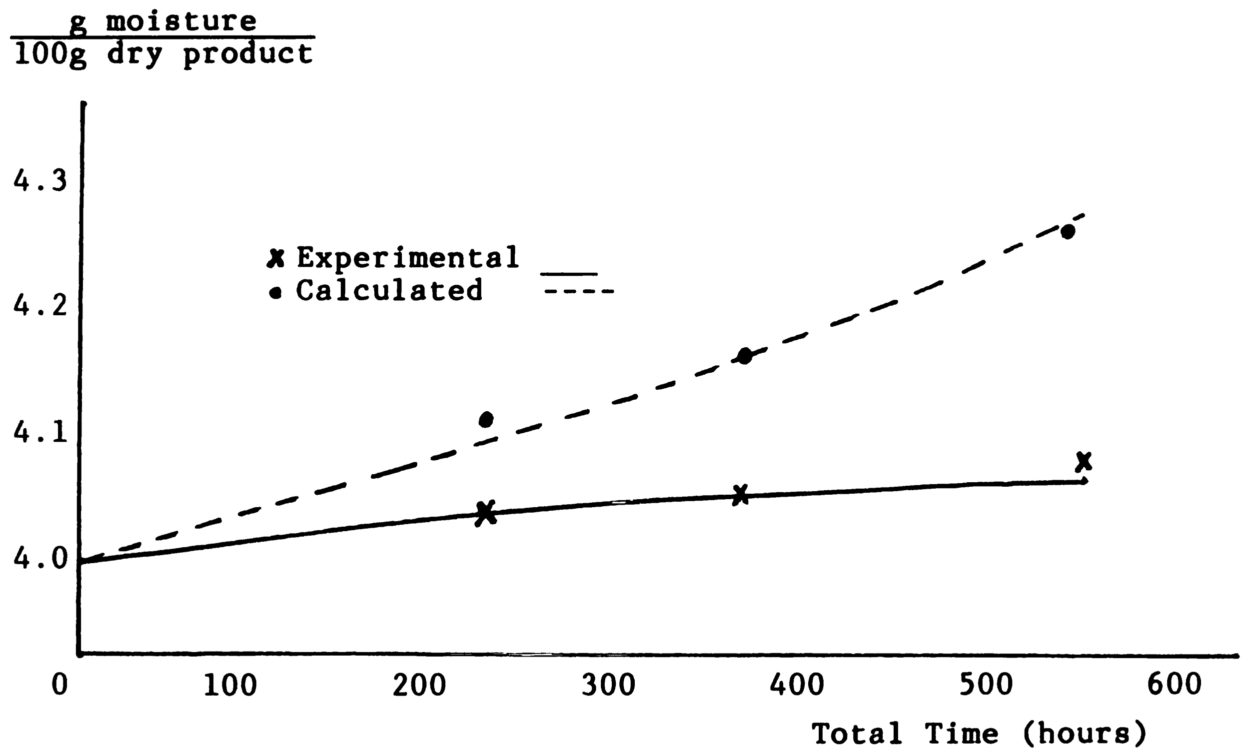

Figure 4. Experimental and calculated moisture contents - Product A/Material II

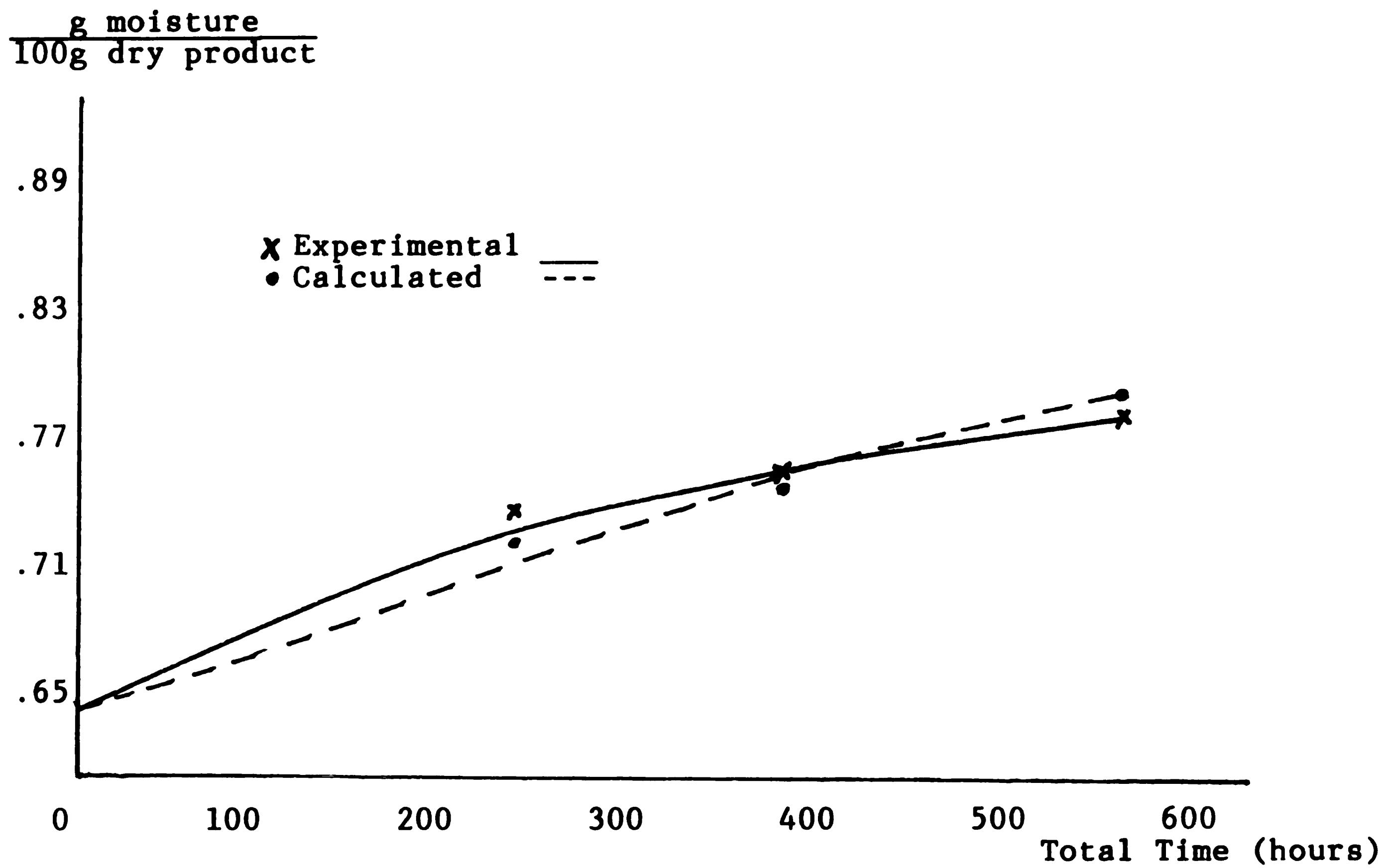

Figure 5. Experimental and calculated moisture contents - Product B/Material I

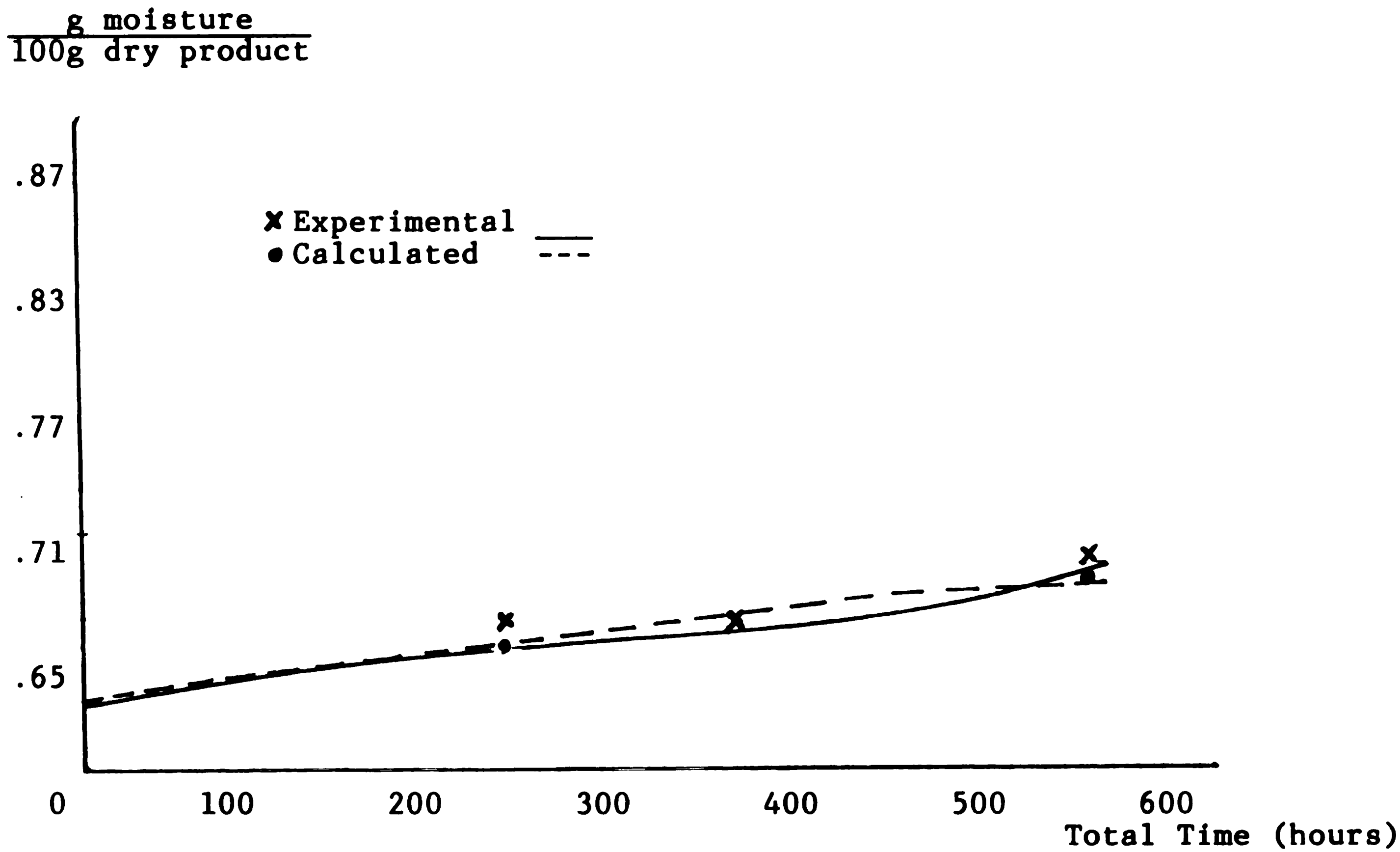

Figure 6. Experimental and calculated moisture contents - Product B/Material II

Table 3: Difference Between Experimental and Calculated Results

Product/ Material	Final % Moisture Cal.	Exp	% Difference $\frac{K_{exp}-K_{cal}}{K_{exp}} \times 100$
A/I	4.325	4.214	2.63
A/II	4.254	4.103	3.68
B/I	.785	.780	.64
B/II	.717	.724	.97

The calculated moisture content increases were very small between time steps for all products. A more significant percentage increase was noted for the overall storage period due to the additive effect of storage time. The percentage increase for each interval for the four variables can be seen in the appendix in Tables 6,7,8 and 9.

The overall moisture content increases can be seen in Table 4. The percent difference between experimental and calculated moisture content can also be calculated by determining the percent increase from the initial moisture content. These results can be seen in Table 4.

Table 4: Overall Moisture Content Increases as Percent of Original

Product	Av. Exp. Moisture Content Increase (%) $\frac{M_i - M_{exp}}{M_i} \cdot x\ 100$			Calc. Moisture Content Increase (%) $\frac{M_i - M_{calc}}{M_i} x\ 100$	Difference between Calc. and Experimental Moisture Content Increases (%) $\frac{(M_{cal} - M_I) - (M_{exp} - M_I)}{(M_{exp} - M_I} x\ 100$
	Low	Ave	High		
A/I	4.44	5.09	5.81	7.85	54
A/II	2.02	2.32	2.54	6.08	162
B/I	19.70	20.90	21.90	21.71	3.87
B/II	10.9	12.20	14.70	11.20	8.20

The moisture gains within a set of packages was very close. This can be exemplified by Product A/II, where the experimental moisture content increase ranged from a low of 2.02% to a high of 2.54%.

The calculated moisture content increases corresponded to the experimental results for Products B/I and B/II, however, not as close for product A/I and A/II. This is further demonstrated in Table 4 by calculating the percent difference between the calculated and experimental moisture content increases.

Calculating percent difference by this method results in a greater difference for all products as compared to the previous method. It is the author's opinion that calculating a percent difference based on total moisture content is more realistic than calculating the difference based upon the moisture content increase. In many cases the moisture content increase is quite small and may well be within the experimental error for determining moisture contents. Therefore, this method will result in a greater percentage difference between experimental and calculated results.

As expected, Material II provided a superior moisture barrier to both products when compared to Material I. This was illustrated in Table 4.

SUMMARY AND CONCLUSION

In many cases, a product's moisture content is a critical factor in determining the product's shelf-life. This is most important when an increase in moisture content leads to a reduction in shelf-life. The ability to predict the moisture content of a product enables a packaging scientist to properly select materials that will maintain a moisture content below a critical level.

The mathematical model discussed in this work proved to be a good method for predicting a product's moisture content under changing storage conditions. The model used actual storage conditions for temperature and relative humidity along with laboratory data for the product and packaging materials to calculate the moisture content increases for a defined time step. By knowing a product's critical moisture content the time required to reach this level can be determined.

The model provides a quick, inexpensive means of determining moisture content when compared to commonly used food industry methods such as, accelerated shelf-life and actual storage testing. These methods are often quite time consuming and can inhibit a company's ability to rapidly introduce new products. A result of this time constraint may lead to the selection of packages that provide a moisture barrier far greater than required for a product.

The model can also be utilized to evaluate the effectiveness of packaging materials for existing products, in addition to being used to design packages for new products. In this case, the scientist can readily evaluate numerous products to identify potential cost saving opportunities. Alternate packaging materials can be laboratory tested to determine the package permeability. These data can be used in the model to determine the ability to maintain a moisture content below the critical level.

Temperature and relative humidity data must be gathered for the distribution system. For this work storage conditions were continuously monitored and recorded every two hours. Selecting the length of a time step involves some subjectivity on the part of the scientist. Several factors must be taken into consideration when selecting a time step. This is necessary because of the assumption that all conditions are constant during a time step. Factors to be considered include; the length of time required for a product to cycle through the distribution system and fluctuation of temperature and relative humidity over time.

Shorter time steps will result in a more gradual fluctuation of storage conditions. Therefore, a shorter time step will reduce error because it will be more likely that all conditions will be constant. For products that require a significant amount of time (1-2 years) to cycle through distribution, an enormous number of time steps could be required. The feasibility for accumulating the necessary temperature and relative humidity data for the model must be determined. The length of a time step can then be determined.

A product that cycles through distribution in a much shorter time frame would require a shorter time step because of the greater potential for error. In both cases the scientist must take into consideration the amount of fluctuation for temperature and relative humidity. The greater the fluctuation in a storage environment the shorter time step would be required to minimize error.

Future Research

This application of shelf life modeling to constantly changing storage conditions is new. The following identifies several areas for future studies utilizing mathematical models to determine the effect on a product's quality.

1. Shelf life modeling for reaction rates that are moisture related, such as mold and microbial growth

and enzymatic activity.

2. Modeling of deteriorative reactions that are not moisture related, such as, vitamin degradation due to temperature fluctuations.

3. Effect of secondary, tertiary and unitized packages on the model for constantly changing storage conditions.

4. Developing a similar model to predict moisture loss for high moisture or liquid food type products.

5. Identify and evaluate alternate means of determining storage conditions for ambient distribution systems, such as United States Weather Bureau data.

6. Develop a mathematical model to predict shelf life based on multiple modes of failure.

APPENDIX

Appendix

Table 5: Test Conditions, Salt Solutions, and Equilibrium Moisture Content Results for Sorption Isotherms

Temperature (°F)	Salt Solution	Relative Humidity (%)	Equilibrium Moisture Content* $\frac{\text{g moisture}}{\text{100g dry product}}$ Product A	B
100°	NaCl	75	15.74	3.20
	NaNO	63	7.3	1.25
	$Mg(NO_3)_2$	51	6.04	.75
	K_2CO_3	41	5.26	.60
	$MgCl_2$	32	4.38	.51
	$K_2C_2H_3O_2$	23	3.52	.45
	LiCl	11	2.00	.25
85	NaCl	75	12.36	2.15
	$NaNO_2$	64	7.64	1.38
	$Mg(NO_3)_2$	52	6.16	.95
	K_2CO_3	42	5.26	.71
	$MgCl_2$	32	4.60	.60
	$KC_2H_3O_2$	23	3.95	.50
	LiCl	11	2.20	.35

* Average of three samples

Table 5: continued

Temperature (°F)	Salt Solution	Relative Humidity (%)	Equilibrium Moisture Content* $\frac{\text{g moisture}}{\text{100g dry product}}$ Product A	B
72	NaCl	75	12.36	3.4
	$NaNO_2$	65	8.70	1.6
	$Mg(NO_3)_2$	52	6.83	1.05
	K_2CO_3	44	6.38	.82
	$MgCl_2$	33	5.26	.70
	$KC_2H_3O_2$	23	4.38	.60
	LiCl	11	2.25	.50

* Average of three samples.

Table 7: Experimental Test Conditions, Results of Experimental* and Calculated Moisture Contents -- Product A/I

Interval	Temp (°F)	Relative Humidity (%)	Total Time (Hours)	Experimental Moisture Content (% Dry Basis)			Calculated Moisture Content (% Dry Basis)
				Low	High	Average	
0			0			4.01	
1	86	57	12				4.015
2	76	67	18				4.021
3	85	53	36				4.024
4	74	62	48				4.029
5	86	56	60				4.03
6	93	40	60				4.03
7	83	67	72				4.035
8	92	56	84				4.041
9	80	60	96				4.047
10	92	42	102				4.050
11	75	62	114				4.061
12	85	54	126				4.07
13	75	55	138				4.08
14	85	49	150				4.085
15	78	49	150				4.091
16	84	55	177				4.104

Table 7: continued

17	73	60	188				4.11
18	83	53	198				4.12
19	73	65	236	4.112	4.144	4.128	4.124
20	80	56	249				4.150
21	70	58	269				4.160
22	69	54	287				4.163
23	82	43	299				4.17
24	71	54	311				4.175
25	89	55	323				4.177
26	73	68	337				4.180
27	82	53	345				4.185
28	69	56	361				4.19
29	79	39	369				4.20
30	67	54	383	4.156	4.20	4.176	4.22
31	80	53	397				4.225
32	72	63	411				4.230
33	80	57	419				4.241
34	70	63	431				4.145
35	83	42	443				4.25
36	74	56	455				4.255
37	84	56	467				4.26
38	74	61	477				4.27
39	83	49	491				4.275
40	71	58	501				4.28
41	84	53	517				4.29
42	81	55	529				4.31
43	69	62	541	4.188	4.293	4.214	4.325

* Average of six samples

Table 6: Experimental Test Conditions, Results of Experimental* and Calculated Moisture Contents -- Product A/II

Interval	Temp (°F)	Relative Humidity (%)	Total Time (Hours)	Experimental Moisture Content (% Dry Basis)			Calculated Moisture Content (% Dry Basis)
				Low	High	Average	
0				0		4.010	4.010
1	86	57	0				4.015
2	76	67	18				4.02
3	85	53	36				4.03
4	74	62	48				4.035
5	86	56	54				4.04
6	93	40	60				4.04
7	83	67	72				4.05
8	92	56	84				4.055
9	80	60	96				4.065
10	92	42	102				4.065
11	75	62	114				4.07
12	85	54	126				4.08
13	75	55	138				4.08
14	85	49	150				4.09
15	78	60	168				4.095
16	84	55	177				4.099

Table 6: continued

17	73	60	188				4.10
18	83	53	198				4.108
19	73	65	236	4.047	4.069	4.056	4.115
20	80	56	249				4.118
21	70	58	269				4.12
22	69	54	287				4.12
23	82	43	299				4.125
24	71	54	311				4.130
25	84	55	323				4.14
26	73	68	337				4.144
27	82	53	345				4.15
28	69	56	361				4.155
29	79	39	369				4.16
30	67	54	383	4.069	4.09	4.078	4.164
31	67	54	397				4.175
32	72	63	411				4.18
33	80	57	419				4.185
34	70	63	431				4.186
35	83	42	443				4.20
36	74	56	455				4.21
37	84	56	467				4.22
38	74	61	477				4.22
39	83	49	491				4.23
40	71	58	501				4.23
41	84	53	517				4.24
42	81	55	529				4.25
43	69	62	541	4.091	4.112	4.103	4.254

*** Average of six samples**

Table 8: Experimental Test Conditions, Results of Experimental* and Calculated Moisture Contents -- Product B/I

Interval	Temp (°F)	Relative Humidity (%)	Total Time (Hours)	Experimental Moisture Content (% Dry Basis) Low	High	Average	Calculated Moisture Content (% Dry Basis)
0			0		.645	.645	
1	86	57	12				.647
2	76	67	18				.649
3	85	53	36				.655
4	74	62	48				.659
5	86	56	54				.663
6	93	40	60				.661
7	83	67	72				.669
8	92	56	84				.671
9	80	60	96				.679
10	92	42	102				.674
11	75	62	114				.679
12	85	54	126				.683
13	75	55	138				.685
14	85	49	150				.689
15	78	60	168				.695
16	84	55	177				.698

Table 8: continued

17	73	60	188				.703
18	83	53	198				.705
19	73	65	236	.729	.737	.734	.725
20	80	56	249				.726
21	70	58	260				.732
22	69	54	287				.735
23	82	43	299				.740
24	71	54	311				.739
25	84	55	323				.743
26	73	68	337				.745
27	82	53	345				.753
28	69	56	361				.754
29	79	39	369				.756
30	67	54	383	.754	.764	.759	.755
31	80	53	397				.757
32	72	63	411				.76
33	80	57	419				.765
34	70	63	431				.766
35	83	42	443				.772
36	74	56	455				.770
37	84	56	467				.773
38	74	61	477				.775
39	83	49	491				.780
40	71	58	501				.780
41	84	53	517				.783
42	81	55	529				.784
43	69	62	541	.772	.7886	.780	.785

* Average of six samples

Table 9: Experimental Test Conditions, Results of Experimental* and Calculated Moisture Contents -- Product B/II

Interval	Temp (°F)	Relative Humidity (%)	Total Time (Hours)	Experimental Moisture Content (% Dry Basis)			Calculated Moisture Content (% Dry Basis)
				Low	High	Average	
0			0		.645		
1	86	57	12				.646
2	76	67	18				.647
3	85	53	36				.65
4	74	62	48				.652
5	86	56	54				.652
6	93	40	60				.652
7	83	67	72				.655
8	92	56	84				.656
9	80	60	96				.658
10	92	42	102				.657
11	75	62	114				.658
12	85	54	126				.659
13	75	55	138				.660
14	85	49	150				.661
15	78	60	168				.663
16	84	55	177				.666

Table 9: continued

17	73	60	188				.668
18	83	53	198				.670
19	73	65	236	.675	.702	.691	.672
20	80	56	249				.675
21	70	58	269				.676
22	69	54	287				.682
23	82	43	299				.683
24	71	54	311				.686
25	84	55	323				.688
26	73	68	337				.690
27	82	53	345				.693
28	69	56	361				.693
29	79	39	369				.695
30	67	54	383	.690	.715	.704	.695
31	80	53	397				.696
32	72	63	411				.698
33	80	57	419				.701
34	70	63	431				.702
35	83	42	443				.703
36	74	56	455				.703
37	84	56	467				.705
38	74	61	477				.708
39	83	49	491				.71
40	71	58	501				.711
41	84	53	517				.714
42	81	55	529				.716
43	69	62	541	.715	.740	.724	.717

* Average of six samples

Integration Procedure

From Equation (10)

$$(Wd \bullet \frac{dm}{dH}) \frac{dH_i}{dt} = \underline{\bar{P}\ P_s(T)}H_o - (\underline{\bar{P}\ P_s(T)}) \bullet H$$

Let

$$A = Wd \bullet \frac{dm}{dH}$$

$$B = \bar{P}\ P_s(T)H_o$$

$$C = \bar{P}\ P_s(T)$$

Equation (10) can be rewritten

$$A \quad \frac{dH_i}{dt} = B - CH$$

Dividing by A gives

$$\frac{dH_i}{dt} = \frac{B}{A} - \frac{C}{A} H$$

or

$$\frac{dH_i}{dt} = \frac{C}{A} (\frac{B}{C} - H)$$

Now multiplying by dt and dividing by $(\frac{B}{C} - H)$ gives,

$$\frac{dH_i}{\frac{B}{C} - H} = \frac{C}{A}\, dt$$

Let

$$\frac{C}{A} = \frac{\bar{P}\ P_s(T)}{W_d\ dm/dH}$$

$$\frac{B}{C} = \frac{\bar{P}\ P_s(T)\ H_o}{\bar{P}\ P_s(T)} = H_o$$

Solving for $\dfrac{d\ H_i}{\frac{B}{C} - H}$

$$\int_{H_i}^{H_f} \frac{dH}{\frac{B}{C} - H} = -\ln(H_o - H)\Big|_{H_i}^{H_f}$$

$$= -\ln(H_o - H_f\ ) + \ln(H_o - H_i)$$

Now

$$\ln = \frac{H_o - H_i}{H_o - H_f} = \frac{C}{A}\ (t_2 - t_1)$$

Substituting for $\frac{C}{A}$ gives

$$\ln \frac{H_o - H_i}{H_o - H_f} = \frac{\bar{P}\ P_s(T)}{Wd\ dm/dH}\ (t)$$

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