This is to certify that the

thesis entitled

BLACK PEPPER AROMA IN PLASTIC POUCHES

presented by

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has been accepted towards fulfillment
of the requirements for

M.S. degree in PACKAGING

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Date June 6, 1979

O-7639

BLACK PEPPER AROMA IN PLASTIC POUCHES

By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

School of Packaging

1979

ABSTRACT

BLACK PEPPER AROMA IN PLASTIC POUCHES

BY

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In order to achieve cost reduction of a black pepper package, a plastic pouch was proposed.

Aroma was the least stable factor in a black pepper storage test. So, it was assumed that the most critical factor for black pepper shelf life was its volatile oil loss. The critical volatile oil loss was predicted by a combination of a mathematical-experimental model and a sensory test. This result was confirmed by a chemical analysis and another sensory test using an expert panel.

These results indicated that the volitile oil loss was a critical factor and that it would be a reliable predictor of black pepper shelf life. By considering the critical volatile oil loss, it should be possible to develop plastic packages which will provide adequate shelf life for black pepper.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation and gratitude to the following individuals and organizations:

Dr. Hugh E. Lockhart, Department of Packaging, under whose inspiring supervision and unselfish contribution of time and encouragement this research was completed.

Dr. Steven W. Gyeszly, Department of Packaging, who served as a thesis committee member. To Dr. Gyeszly is owed a great deal of appreciation for his overall guidance in the field of permeability and shelf life.

Dr. Jerry N. Cash, Department of Food Science, who, in addition to being a constant source of guidance in the field of food science, served as a thesis committee member.

Dr. Jack R. Giacin, Department of Packaging, for time so graciously allotted for consultation and advice in the field of analytical aspects of packaging.

Mr. Daniel J. Goeke Jr., whose valuable assistance in the field of spice science provided the author with the tools to accomplish this task.

The Lion Dentifrice Co., Ltd., for granting educational leave and their financial support during the course of study.

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INTRODUCTION

Packages for black pepper are mostly glass bottles and metal cans. Plastic pouches can be marketed for reasons of cost reduction and resource conservation. The cost of a glass bottle (1.75 oz), a cap and labels is estimated at 7.4¢. A printed metal can (4 oz) is estimated to cost 10.1¢.[65] Compare these costs with the cost of a preprinted pouch estimated at 0.74¢.[18] The filling and closing cost with glass bottles or metal cans is also more than the filling and closing cost with form fill sealed plastic pouches.[65] In this study, a plastic pouch is considered a refill package, not intended for dispensing. If plastic pouches are used as refill packages, this eliminates the need for glass or metal packages, which results in resource conservation to the extent that the overall cost of the plastic is cheaper in terms of energy required to make, ship and use. The market of black pepper is not small, which makes this cost reduction more attractive. In recent years, the average annual world exports of pepper have amounted to about $38.5 million, or just over 25 percent of the total volume of net world exports of all spices.[53]

The main requirements for black pepper packages are given in Table 1. Protection of black pepper against certain environments is essential for adequate shelf life. The other factors in Table 1 must be established during packaging development, but only the protection function is considered in this study.

Table 1. The Main Requirement for a Black Pepper Package

1. Safety as a food package
2. Product quality protection against the following environments
   - A. Chemical Environment
     - Volatile oil permeation and chemical reaction
     - Non-volatile oil permeation and chemical reaction
     - Moisture effect
   - B. Physical Environment
     - Light
     - Shock, vibration and compression
   - C. Insect and Microbiological Environment
3. The least possible cost
4. Communication to consumers (convenience, labeling, and appearance)
5. Containment function
6. Disposability

Black pepper, Piper nigrum L., has two characteristics which affect the quality. One is the aromatic odor contributed by an essential oil. This essential oil contains these compounds: α-pinene, β-pinene, and limonene.[46]

The essential oil is commonly referred to as volatile oil. The other characteristic is the sharp pungent taste contained in the oleoresin, which consists of piperine, chavicine and piperidine.[53] These are referred to as non-volatile oil.

The Food and Drug Administration (F.D.A.)[68] and the American Spice Trade Association (A.S.T.A.)[2] specify a standard of identity for black pepper. It is given in Table 2. This standard lists volatile oil and non-volatile oil along with other elements. The maximum moisture content is specified in the regulation because microbial spoilage readily occurs when the moisture exceeds twelve percent. This can be considered in water sorption isotherm of black pepper. The other factors, ash, acid insoluble ash, and crude fiber, are considered as the secondary concern for black pepper shelf life because they are more stable than the primary concern: volatile and non-volatile oil.

Table 2. Specification for Black Pepper*

Volatile Oil	Min	2.0 ml/100g
Non-volatile oil	Min.	7.0% (Methylene Chloride)
Moisture	Max.	12.0%
Ash	Max.	7.0%
Acid Insoluble Ash	Max.	1.0%
Crude Fiber	Max.	11.0%

*U.S. Food and Drug Administration, Food and Drug No. 2, 1962.

The effect of light should be considered for transparent plastic pouches. Wrolstad et al.[71] reported that light causes certain photochemical changes that are evidenced by a decrease in at least one fraction of volatile oil, and an increase in another. Their experimental method was with direct sunlight exposure for seven weeks. In real life, black pepper is exposed to fluorescent light in supermarkets, but not to sunlight. Therefore, their experimental method can be considered too stringent and probably not applicable. The fluorescent light effect was considered in earlier work and found to be negligible.[66]

Another factor is insect and microbiological spoilage. Several leading spice processors exercise quality control programs to assure themselves and their industrial consumers that their spices are microbiologically acceptable.[56] For this reason, the insect and microbiological spoilage consideration is eliminated from this study.

Considering these factors, volatile oil and nonvolatile oil are the primary concern for black pepper shelf life in plastic pouches. The effect of moisture for black pepper shelf life can be considered in water sorption isotherm.

LITERATURE REVIEW

According to the Food Stability Survey by Rutgers University in 1971, the shelf life of ground black pepper in a metal can is three years.[56] They also reported that quality loss factors for black pepper during storage were aroma and flavor. It is well known in the spice industry that aroma and flavor are contributed by volatile and non-volatile oils.[53] Comparing these volatile and non-volatile oils in a stability test, Yugami et al.[74] reported that the critical factor for black pepper shelf life was the volatile oil, rather than the non-volatile oil. This implies that the non-volatile oil is more stable than the volatile oil. Using gas chromatography he found that black pepper in a metal can, stored for 3 months at 40^{o}C, lost its volatile oil constituents: α-pinene and β-pinene due to the relatively low boiling points of these compounds. He also reported that the top note* of the pepper aroma was diminished after the storage.

The volatile oil conposition of black pepper has been studied by several investigators. Hasselstrom et al.[22] isolated the monoterpenes. Using gas chromatogrraphy and

*Top note: Initial intensity of aroma.

infrared spectroscopy, Jennings et al.[30] identified the monoterpene α-pinene, β-pinene and limonene. Ikeda et al.[29] analyzed pepper oil in their study of a number of essential oils and found 29 compounds including α-pinene, β-pinene and limonene. Wrolstad and Jennings[72,73] also found these 29 components by gas chromatography, infrared and ultraviolet spectroscopy. Muller et al.[43,44] and Russel et al.[54] identified 16 new compounds. Russel and Jennings[31,55] and Richard and Jennings[51] investigated oxygenated compounds of black pepper oil by infrared and mass spectroscopy, and nuclear magnetic resonance spectroscopy. Debrauwere et al.[14,15,16] in 1975 and 1976 reported several other new compounds in the essential oil of black pepper. All investigators agree that α and β-pinene, and limonene are in volatile oil. In discussing the composition of volatile oil, Lewis et al.[39] state that these new volatile oil constituents may be explained by the fact that the content of individual monoterpenes in black pepper oil depends on the variety of pepper and on the manner of storage of the starting material. Therefore, it is important to specify the variety of black pepper to be tested because many varieties which are recognized in the spice trade. These are usually identified by the ports from which the goods are exported or the region where the pepper is grown. The varieties of black pepper are: Lampong, Malabar, Tellichery, Sarawak, Brazilian, Singapore, Penang, and Saigon.[47,53] Orgonoleptic evaluation, as well as chromatographic techniques, can be applied to the qualitative analysis of volatile oil. Speight[60] conducted a sensory evaluation of black pepper to compare the flavor retention after microwave and conventional heating. Pangborn[45] reported that the organoleptic evaluation was more sensitive than the chromatographic technique in detecting the aroma change of black pepper.

For moisture sensitive products, several mathematical models have been applied for shelf life prediction. These equations are based on the water sorption isotherms of the product and the water vapor permeation rate through the package. Wink et al.[70] in 1950 developed an experimental approach to measure the sorption isotherm. The importance of the sorption isotherm was discussed by Labuza et al.,[33,34] Rockland[52], and Heiss et al.[24] Labuza[36,37] used the water sorption isotherm to study the nutrient loss of dehydrated foods. Caurie[8] studied a single layer moisture absorption theory in dehydrated foods. A multilayer adsorption equation was described by Iglesias et al.[26,27,28] Chirife and Iglesias[10,11] compiled and discussed several isotherm equations which were reported in the literature for fitting water sorption isotherms of foods. These sorption isotherm theories were applied to shelf life prediction of crackers,[38] ground beef,[57] kidney beans,[57] mashed potato flakes,[62] wheat flour,[64] cassava[25] and potato.[25] Recently, the effect of moisture on nonenzymatic browning was studied as an extension of the sorption isotherm concept. Resnik et al.[50] considered the nonenzymatic browning in dehydrated apple. Mizrahi et al.[42] successfully predicted the extent of browing in dehydrated cabbage.

Mathematical models of permeability have been used for a hundred years.[40] Using a permeability equation, Felt et al.[19] compared the shelf life results of packaged cereal obtained from field studies and by calculation. Cairns et al.[7] also discussed permeability theory and real life complications. Gyeszli[20] used the theory to compare the internal partial pressure change of a gas or vapor in a double wall package and in a single wall package. Uno[67] applied the theory to a package for soy sauce. All these investigators obtained good agreement between experimental and calculation results.

Quest et al.[48,49] and Karel[32] simulated the shelf life of foods by using sorption isotherm theory and permeability theory. The combined theory of sorption isotherm and permeability was applied to the shelf life prediction of packaged foods, such as crackers,[23] salted peanuts,[13] tea,[35] dry milk solid,[35] seed,[21] and cereal.[12,41] Manathunya[41] dealt with packaged cereal and reported that the predicted results of its shelf life showed good agreement with the experimental data.

From the above review, the following three conclusions can be drawn. First, volatile oil may be the most critical factor in a stability test of black pepper. Secondly, sensory evaluation can be applied to a qualitative analysis of black pepper. Finally, moisture content of black pepper in a plastic pouch can be predicted with a mathematical model.

THEORETICAL BASIS

Sensory Evaluation

Statistical analysis can be applied to sensory evaluation if there is rigid control of the factors which influence the propriety of laboratory sensory panels.[3,59] These factors are given in Table 3. The triangle test and paired comparison test are the most common testing methods for organoleptic comparison of two different products.[61] In the trinagle test, the judge is informed that two of the three stimuli are identical and one is different, and that the odd sample must be identified. The two stimuli can be presented in six different arrangements (AAB, ABA, BAA, BBA, BAB, ABB), and the probability of selecting the odd sample by chance alone is 1/3. The chi-square ($\chi 2$) distribution is used to compare the observed frequency with the theoretical frequency.[3] Following is the equation for χ^2 for the triangle test,

$$\chi^2 = ((|4X_1 - 2X_2 | -3)^2/8n \qquad (1)$$

where

χ^2 is the value of chi-square,

X_1 is the number of opinions favorable to sample 1,

X_2 is the number of opinions favorable to sample 2,

Table 3. The Critical Factors for Adequate Sensory Evaluation*

A. Panel Selection

Careful selection of judges is essential in order to achieve maximum discriminability.

B. Size of Panel

C. Panel Morale

D. Environmental Conditions

Air conditioning, lighting, seating comfort, and distractions need to be controlled during testing.

E. Control of Sample Variability and Number of Samples

Intensity of a specific taste or aroma characteristic will influence the design of the experiment. Masking, usually of color is sometimes used to eliminate judgments on unimportant criteria. A test for an inexperienced panel should be limited to two samples per test. Otherwise, psychological effect or fatigue will influence the results.

F. Proper Preparation of Foods

It is necessary to give attention to proper preparation of foods, cooking procedures, methods of detecting flavor pick-up, and the standard used.

G. Service Procedures

These factors must be closely controlled: Control of appearance, sample size (e.g. 2 g for serving), temperature, utensils, coding, order of serving, and clear instructions to judges.

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*Amerine, Maynard A. et al. "Principles of Sensory Evaluation of Food," 1965.

and n is the total number of trials.

The calculated value of χ^2 must exceed 2.71 for significance at the 5% level, 5.41 for significance at the 1% level, and 9.55 for significance at the 0.1% level.

In the paired comparison test, the probability of a judge identifying by chance a particular sample in each of the several trials is 1/2. The value of χ^2 is shown in the following equation.[3]

$$\chi^2 = (|X_1 - X_2| - 1)^2/n \qquad (2)$$

Actually, the number of correct identifications (one tailed) necessary for significance in each case can be determined directly from statistical tables. Table 20 for triangle test and Table 21 for paired comparison test are given in Appendix A. The entries of Tables 20 and 21 represent the actual values of X_1 of each of several value of n which are required to achieve significance.

Moisture Weight Prediction by a Mathematical Model

A moisture weight prediction will be necessary to correct for moisture content while determining volatile oil loss.

The total amount of moisture in a closed package (M) is the sum of the weight of water in the product (M_1) and the weight of the water vapor in the headspace (M_2).[12]

$$M = M_1 + M_2 \qquad (3)$$

If we make several assumptions, Equation (3) can be changed to

$$M = \frac{W}{100}\,(a + b \cdot Hi(t)) + 18\,\frac{V}{R.T} \cdot Ps \cdot \frac{Hi(t)}{100} \qquad (4)$$

where

w is the weight of the dry product in the package,

a is the intercept of sorption isotherm,

b is the slope of sorption isotherm, which is assumed to be a straight line,

Hi(t) is the relative humidity inside the package at the time = t,

V is the headspace of the package,

R is the gas constant,

T is the temperature, and

Ps is the saturated water vapor pressure at T temperature.

The derivation of Equation (4) is given in Appendix B. The required assumptions for this mathematical model are the following:

A. The permeability constant of a package depends on temperature but not on wall thickness or pressure difference.

B. Permeation is a steady state process.

C. Interchange between outside and inside environments is done only by permeation, not by flow through pinholes.

D. Moisture in the product and water vapor in the headspace are always in equilibrium.

E. There is no chemical reaction between package and environments, package and product, or product and environment.

F. The Ideal Gas Law is applicable to water vapor.

G. The wall thickness of a package and headspace volume are constant.

H. The package is perfectly sealed.

I. The temperature is constant and is the same inside and outside of the package.

J. The outside relative humidity is constant.

K. The water sorption isotherm is fitted by a straight line within a certain range, and that within this range, product quality is acceptable.

Since the temperature inside and outside the package is the same, the permeation rate can be obtained from Fick's Law and Henry's Law. This derivation is given in Appendix C.

$$\frac{dM}{dt} = \overline{P} \cdot \frac{A}{\ell} \cdot \frac{Ps}{100} (He - Hi(t)) \qquad (5)$$

where

$\overline{P}$ is the permeability constant of the packaging material,

A is the surface area of the package,

ℓ is the thickness of the package wall, and

He is the relative humidity outside the package.

From Equation (4) and (5),

$$\bar{P} \cdot \frac{A}{\ell} \cdot \frac{Ps}{100} (He - Hi(t)) = \frac{d}{dt} (\frac{W}{100} (a + b \cdot Hi(t)) + 18 \frac{V}{R \cdot T} \cdot Ps \cdot \frac{Hi(t)}{100}) \quad (6)$$

Since everything is constant except Hi(t), Equation (6) can be integrated.

$$Hi(t) = He - (He - Hi(0)) e^{-J \cdot t} \quad (7)$$

where

Hi(0) is the relative humidity inside the package at time = 0,

t is the time, and

$$J = \frac{\bar{P} \cdot A \cdot Ps}{\ell \ (18 \ Ps \cdot V/R \cdot T + b \cdot W)} \quad (8)$$

The derivation of Equation (7) is given in Appendix D. Using Equation (7), the relative humidity at any time can be obtained.

The moisture weight change after a certain storage period (ΔWm) can be calculated from Equation (4).

$$M(0) = \frac{W}{100} (a + b \cdot Hi(0)) + 18 \frac{V}{R \cdot T} Ps \frac{Hi(0)}{100} \quad (9)$$

$$M(\alpha) = \frac{W}{100} (a + b \cdot Hi(\alpha)) + 18 \frac{V}{R \cdot T} \cdot Ps \cdot \frac{Hi(\alpha)}{100} \quad (10)$$

where

M(0) is the total weight of moisture in the closed package at time = 0,

Hi(0) is the relative humidity inside the package at time = 0,

$M(\alpha)$ is the total weight of moisture in the closed package at the time = α, and

$Hi(\alpha)$ is the relative humidity inside the package at time = α.

ΔWm is the difference of M(0) and $M(\alpha)$, then

$$\Delta Wm = M(\alpha) - M(0) \tag{11}$$

so

$$\Delta Wm = \left(\frac{b \cdot W}{100} + \frac{18\ Ps \cdot V}{100\ R \cdot T}\right)\ (Hi(\alpha) - Hi(0)) \tag{12}$$

$Hi(\alpha)$ can be obtained from Equation (7)

$$Hi(\alpha) = He - (He - Hi(0))e^{-J \cdot \alpha} \tag{13}$$

Plug Eguation (13) into (12),

$$\Delta Wm = \left(\frac{b \cdot w}{100} + \frac{18\ Ps \cdot V}{100\ R \cdot T}\right)\ (He - (He - Hi(0)) \cdot e^{-J \cdot \alpha} - Hi(0)) \tag{14}$$

Where J is given in Equation (8).

Using Equation (14), the weight change of moisture after any storage period can be calculated. This calculation will be used to obtain volatile oil loss.

Assumption for Volatile Oil Weight Change

Under a constant temperature and a constant relative humidity, the total weight change of black pepper in a package after a certain storage period (ΔW_T) is assumed to be the sum of the weight change of moisture (ΔW_m) and the weight change of volatile oil ($\Delta Wv.o.$) when the weight change of the package is negligible.*

$$\Delta W_T = \Delta Wm + \Delta Wv.o. \tag{15}$$

ΔW_T can be measured by an experimental method.

ΔWm can be calculated by a mathematical model. Thus, $\Delta Wv.o.$ can be obtained as a balance in Equation (15).

To consider black pepper shelf life in plastic pouches, determination of the critical volatile oil loss is the primary concern. For the purpose of this study, the critical volatile oil loss is defined as the volatile oil weight change when the aroma is found to be significantly different from the control aroma by a sensory test. The critical volatile oil loss can be obtained from Equation (15) combined with the sensory test results.

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*Negligible weight change occurs in polyolefin.

EXPERIMENTAL METHODS AND RESULTS

In order to obtain the critical volatile oil loss, the following experiments were conducted.

Determination of the Total Weight Change (ΔW_T)

Ground black pepper in a 4 oz can, packaged on December 19, 1977, was used. The variety of this black pepper was a combination of Lampong, Malabar, and Sarawak. The black pepper was weighed within the range of 1.2 to 1.4 g, and was packed in pouches made of 1 mil low density polyethylene (LDPE) film or 0.5 mil M-24 film. The M-24 is polyethylene terephthalate film with polyvinylidene chloride copolymer coating on one side.[17] These pouches were four side impulse sealed with dimensions 4 cm x 5 cm.

These specimens were placed in closed containers with saturated sodium bromide (NaBr) solution in contact with excess dissolved crystals. The NaBr solution maintains constant relative humidity at constant temperature. One container was stored in a temperature controlled chamber (100^{o}F). The other container was stored at room temperature (77^{o}F average). In the containers, the relative humidities were maintained at 58.5% (77^{o}F) and 53.7% (100^{o}F).[70] The specimens were weighed periodically with an analytical balance which had a sensitivity of 10^{-4} g. Five replications were used for each film and each condition. The weight change results, expressed in g/100g·dry product, are given in Table 4. We will use these values later on in evaluating Equation (15).

The LDPE pouches and M-24 pouches (without the products) were weighed during exposure to 55% RH for 14 days at 77°F and 100°F. The change in weight never exceeded 0.0004 g. Therefore, it can be concluded that the weight change of the packages is negligible--a necessary condition for Equation (15) to be valid.

Sensory Evaluation for Black Pepper Aroma

Sensory tests were conducted to determine the critical aroma loss of black pepper in plastic pouches.

Designing of the Sensory Test

The triangle test was selected for the following two reasons. First, the procedure is simple. An inexperienced panel can easily follow it. Secondly, statistical analysis can be applied to the triangle test results. The size of a panel was twenty-four. This size is commonly used for sensory evaluation because it is very convenient to manipulate the factors and it also satisfies the statistical analysis.[3] All panelists were college students or faculty members, and only people who were interested in pepper and who had good physical health were selected. The test was conducted in mid-morning or mid-afternoon. The test room

Table 4. The Weight Change of Black Pepper in Plastic Pouches*

Storage Period			(g/100g·dry product)				
			26 hr	61 hr	84 hr	122 hr	146 hr
77°F 58.5% RH	M-24	1	.084	.144	.243	.380	.486
		2	.090	.165	.241	.383	.481
		3	.094	.167	.253	.391	.492
		4	.099	.182	.244	.380	.472
		5	.110	.169	.250	.397	.500
		$\bar{X}$	.095	.165	.246	.386	.486
	LDPE	1	.216	.460	.579	.725	.760
		2	.267	.577	.707	.873	.880
		3	.304	.602	.747	.899	.962
		4	.214	.368	.541	.748	.742
		5	.362	.656	.777	.957	.998
		$\bar{X}$	.273	.533	.670	.840	.868
100°F 53.7% R.H.	M-24	1	.258	.537	.700	.938	1.098
		2	.242	.531	.672	.900	1.085
		3	.157	.456	.579	.803	.977
		4	.236	.512	.654	.876	1.035
		5	.253	.519	.672	.891	1.054
		$\bar{X}$	.229	.511	.655	.882	1.050
	LDPE	1	.500	.673	.694	.694	.639
		2	.465	.714	.707	.721	.680
		3	.577	.754	.761	.754	.699
		4	.479	.736	.702	.702	.653
		5	.511	.729	.701	.722	.633
		$\bar{X}$	.506	.721	.713	.719	.661

*The weight change in this table, expressed in g/100g·dry product, was calculated by ((Final Weight - Initial Weight)/(Initial Weight - Initial Moisture Content)) x 100.

had a quiet atmosphere, good lighting, comfortable seating, and controlled temperature at $75^{o}F$. A test was limited to two samples per panelist to avoid psychological effect or fatigue. As a vessel, an amber glass bottle was used so that the amber color would mask any difference in appearance. The glass bottle was reclosed after each test, thus minimized the aroma lost during a test. Coding and order of serving were closely controlled. An example of coding and serving sequence is given in Figure 1. An example of the report form is in Figure 2.

Procedure for the Triangle Test

Ground black pepper in plastic pouches was stored at $77^{o}F$, 58.5% RH and $100^{o}F$, 53.7% RH, which was described in the section labeled Determination of Total Weight Change. After a certain period of storage, the black pepper in the pouches was transferred into 22 cc amber Boston round glass bottles. Each bottle contained 0.5 g of ground black pepper and the bottles were closed with caps. Three replications were prepared from each storage condition. These three replications were coded randomly (e.g. R, Z and E). A black pepper control against the stored sample was prepared from an unopened can which had the same manufacturing code as the stored sample. The same amount of the black pepper control, 0.5 g each, was transferred into the same kind of glass bottle. Three replications were prepared for each test. These were also coded randomly

Ground Black Pepper

Date ______________

I ______________ II Control ______________ Correct Total ________

Name	Sampling Sequence	Code I	Code II	Panelist's Response: Old Sample	Panelist's Response: Comment
	II		I		
1.	I	R			
	II		B		
	I	Z			
2.	II		Q		
	II		I		
	II		B		
3.	II		Q		
	I	E			
	I	R			
4.	II		I		
	I	Z			
	I	E			
5.	I	R			
	II		B		
	II		Q		
6.	I	Z			
	I	E			
	II		I		
7.	I	R			
	II		B		
	I	Z			
8.	II		Q		
	II		I		
	II		B		
9.	II		Q		
	I	E			
	I	R			
10.	II		I		
	I	Z			
	I	E			
11.	I	R			
	II		B		
	II		Q		
12.	I	Z			
	I	E			

Figure 1. Triangle Test Design Sheet

Set ____________

Name ____________ Date ____________

1. Which sample (odor) is different?

2. Which sample(s) contain(s) the greater odor?

3. A complete description of the odor of each sample.

Samples	(1) Different Sample	(2) Stronger Odor	(3) Description of each
I R B			
O J M			

Figure 2. The Report Form of the Triangle Test

(e.g. I, B, and Q).

A panelist had three samples (e.g. I, R, and B), in which two of them were identical (I and B) and the other (R) was different, and he was told that the odd sample must be identified. According to the test design in Figure 1, twenty-four panelists tested the same set in different coding combinations and order. Total correct numbers were counted, and the significance in aroma difference between the stored sample and the control was determined by Table 20 in Appendix A. After completing the triangle test, each panelist performed the directed triangle test, in which he answered the question: Which sample (or samples) has (have) stronger odor. The probability of selecting the stronger sample(s) by chance alone is 1/2. So, the statistical table for the paired comparison is applied for the significant difference. This is Table 21 in Appendix A. These results are given in Table 5.

Determination of the Moisture Weight Change (ΔWm)

To calculate ΔWm, the following experiments were conducted.

Determination of the Initial Moisture Content

Initial moisture content of black pepper was determined by phosphorus Pentoxide (P_2O_5) method. 1.5 g to 1.6 g of ground black pepper were weighed into aluminum dishes then placed over P_2O_5 in a closed container. Five specimens were stored at 75^{o}F. They were periodically weighed until

Table 5. Sensory Test Results for Black Pepper Aroma in LDPE Pouches (Triangle Test)

		1 day	2 day	3 day	5 day	7 day
$77^{o}F$	Ratio of Correct Replies	9/24	10/24	10/24	11/24	22/24**
58.5% RH	Control> Test	8/9	8/10	6/10	6/11	22/22**
$100^{o}F$	Ratio of Correct Replies	11/24	12/24	15/24*	--	19/24**
53.7%	Control> Test	9/11	8/12	13/15*	--	18/19**

*Significance at 99% Confidence Level

**Significance at 99.9% Confidence Level

Control> test: Ratio that the control aroma was found to be stronger than the stored sample aroma.

no weight change was noticed. The results, expressed in g/100g·dry product, and in g/100g·product, are in Table 6.

Determination of the Sorption Isotherm

The sorption isotherm was determined by using saturated salt solutions in contact with excess undissolved crystals. At constant temperature, the solutions maintain constant humidities in closed containers.[70] Approximately 1.5 g of each black pepper were weighed into aluminum dishes then placed into containers where the salt

Table 6. The Initial Moisture Content of Black Pepper

Sample No.	Initial Moisture Content	
	dry basis (g/100g·dry product)	wet basis (g/100g·product)
1	6.87	6.43
2	6.77	6.34
3	6.69	6.27
4	6.45	6.06
5	6.52	6.13
$\overline{X}$	6.660	6.246
S	0.155	0.135

solutions were set. The containers were stored at 75^{O}F (average) and at 100^{O}F. The black pepper samples were periodically weighed until they reached equilibrium. The averages of three-replication results expressed in unit of g/100g·dry product, are given in Table 7. From the equilibrium moisture content in Table 7, the sorption isotherms for the black pepper were drawn in Figure 3.

As shown in Figure 3, the sorption isotherms were fitted by straight lines within the range of 30% to 70% RH with reasonable accuracy. The straingt lines were determined by linear regression analysis, and their intercepts and slopes are given in Table 8.

Table 7. The Salt Solutions and Equilibrium Moisture Content of Black Pepper

Salt* Solution	75°F		100°F	
	% RH	g/100g· dry product	% RH	g/100g· dry product
$(NH_4)_2SO_4$	80.6	10.679	79.5	10.385
NaCl	75.5	9.349	75.6	8.181
$NaNO_2$	65.3	7.424	62.0	6.254
NaBr	58.5	6.619	53.7	5.154
$Mg(NO_3)_2$	53.5	6.246	--	--
KNO_2	49.0	5.831	46.5	4.486
K_2CO_3	--	--	43.0	3.984
$MgCl_2$	33.0	4.404	32.0	2.912

*Wink and Sears, 1950.

Table 8. The Intercept (a) and Slope (b) of the Sorption Isotherms for Black Pepper

Temperature	a (g/100g·dry product)	b (g/100g·dry product/%RH)
75°F	1.315	0.0925
100°F	-0.655	0.1096

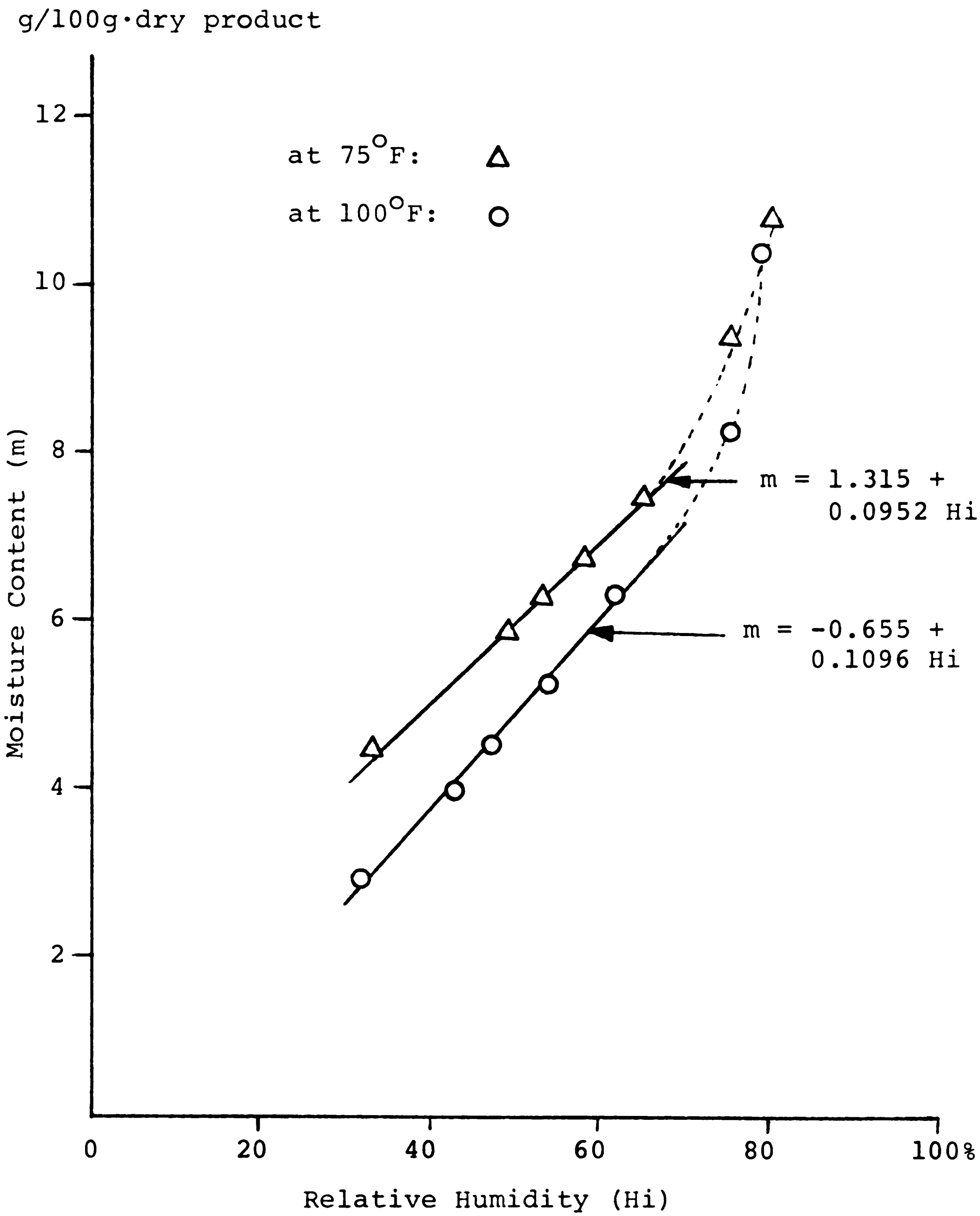

Figure 3. Sorption Isotherms of Black Pepper

Determination of the Permeability Constant

Water vapor transmission rates of LDPE and M-24 were determined by the dish method with desiccant, which is described in ASTM E96-66, Procedure A. These rates were converted to permeability constant, expressed in $g \cdot mil/cm^2/hour/\Delta atm$. The averages of three-replication results are given in Table 9.

Table 9. The Water Vapor Transmission Rate (WVTR) and Permeability Constant ($\bar{P}$) of Films

		WVTR $g/cm^2/hr$			$\bar{P}$ $g \cdot mil/cm^2/hr/\Delta atm$
78°F	M-24	0.4285×10^{-5}	78°F	M-24	1.407×10^{-4}
47% RH	LDPE	1.2010×10^{-5}		LDPE	7.890×10^{-4}
100°F 80% RH	M-24	2.8013×10^{-5}	100°F	M-24	2.707×10^{-4}
	LDPE	7.0625×10^{-5}		LDPE	13.650×10^{-4}

Calculation of the Moisture Weight Change (ΔWm)

ΔWm can be calculated from Equations (14) and (8).

$$\Delta Wm = \left(\frac{b \cdot w}{100} + \frac{18\ Ps \cdot V}{100\ R \cdot T}\right) (He - (He - Hi(0)\ e^{-J \cdot \alpha} - Hi(0)) \quad (14)$$

$$j = \frac{\bar{P} \cdot A \cdot Ps}{\ell\ (18\ Ps \cdot V/R \cdot T + b \cdot W)} \quad (8)$$

The following variables were obtained from the experiment.

$W = 1.3$ g

R is the gas constant $= 82.05 \frac{(cc)\ (atm)}{(^{o}K)\ (moles)}$

$A = 40$ cm^2

$Hi(0) = 44\%$

$T = 298.0\ ^{o}K\ (77^{o}F)$, $T = 310.8^{o}K\ (100^{o}F)$

$Ps = 0.03126$ atm $(77^{o}F)$[69], $Ps = 0.06468$ atm $(100^{o}F)$[69]

$He = 58.5\%\ (77^{o}F)$, $He = 53.7\%\ (100^{o}F)$

The thickness was measured and found to vary $\pm$ 10% or less.

$\ell = 1 \pm 0.1$ mil (LDPE), $\ell = 0.5 \pm 0.05$ mil (M-24)

The headspace volume (V) was estimated because this value is small and is not so critical in Equations (14) and (8).

$V = 8$ cc

The permeability constant ($\overline{P}$) is obtained from Table 9. However, since the room temperature was $78^{o}F$ during WVTR measurement, $\overline{P}$ (at $78^{o}F$) should be converted to $\overline{P}$ (at $77^{o}F$). By using Arrhenius Equation[40]

$$\overline{P} = \overline{P}o \cdot e^{-\beta/T} \qquad (16)$$

Where

$\overline{P}o$ is the permeability constant (independent on temperature), and

β is the constant.

Plug $\overline{P}$ and T results (from Table 9) into Equation (16).

For M-24

$$1.407 \times 10^{-4} = \overline{P}o \cdot e^{-\beta/298.56} \qquad (17)$$

$$2.707 \times 10^{-4} = \bar{P}o \cdot e^{-\beta/310.78} \tag{18}$$

Solve $\bar{P}o$ and β from Equations (17) and (18)

$\bar{P}o = 2362.3$

$\beta = 4966.85$

So, Equation (16) becomes

$$\bar{P} = 2362.3e^{-4966.85/T} \tag{19}$$

For LDPE using the same manner,

$$\bar{P} = 872.8e^{-4154.87/T} \tag{20}$$

Therefore, when $T = 77^{\circ}F = 296.9^{\circ}K$

$\bar{P}$ (M-24) = 1.364×10^{-4} g·mil/cm^2/hr/Δatm

$\bar{P}$ (LDPE) = 7.690×10^{-4} g·mil/cm^2/hr/Δatm

When $T = 100^{\circ}F = 310.8^{\circ}K$

$\bar{P}$ (M-24) = 2.71×10^{-4} g·mil/cm^2/hr/Δatm

$\bar{P}$ (LDPE) = 13.65×10^{-4} g·mil/cm^2/hr/Δatm

From Table 8 the slope of sorption isotherm, b, can be obtained. However, the room temperature was 75°F, so b (at 75°F) should be converted to b (at 77°F). By using proportional allotment,

$$b(\text{at } 77^{\circ}F) = 0.0925 + (0.1096 - 0.0925) \times \frac{77-75}{100-75}$$

$$= 0.0939 \text{ g/100g·dry product/\% RH, and}$$

$$b(\text{at } 100^{\circ}F) = 0.1096 \text{ g/100g·dry product/\% RH.}$$

From all of the above inputs, ΔWm can be calculated in Equation (14). The results are given in Table 10.

Table 10. The Moisture Weight Change of Black Pepper in Plastic Pouches (ΔWm) Using a Mathematical Model

		ΔWm(g/100g·dry product)				
		26 hr	61 hr	84 hr	122 hr	146 hr
77°F	M-24	.125	.277	.372	.511	.595
	LDPE	.331	.674	.859	1.094	1.213
100°F	M-24	.316	.623	.779	.968	1.055
	LDPE	.664	1.007	1.212	1.318	1.348

Calculation of the Volatile Oil Weight Change ($\Delta Wv.o.$)

By using Equation (15) $\Delta Wv.o.$ can be obtained since ΔW_T is given in Table 4 and ΔWm is given in Table 10. The results are given in Table 11 comparing with the sensory test results for black pepper aroma.

Correlation Between Sensory Evaluation and Chemical Analysis

In this study, it was assumed that the shelf life of black pepper in plastic pouches was determined by the critical volatile oil loss. The volatile oil weight change was calculated in Equation (15) and the critical aroma loss was determined by the sensory test. However, there are two questions concerning this approach. First, even though Yugami et al.[74] reported that the volatile oil loss is the

Table 11. The Volatile Oil Weight Change (ΔWv.o.) and the Sensory Test Results of Aroma for Black Pepper in Plastic Pouches

		ΔWv.O. (g/100g·dry product)				
		26 hr	61 hr	84 hr	122 hr	146 hr
77°F	M-24	.030	.108	.126	.125	.109
58.5%	LDPE	.058	.141	.189	.254	.345**
100°F	M-24	.087	.112	.124	.086	.005
53.7%	LDPE	.158	.286	.499*	.599^{S}	.687**

*,**: Sensory test results showed that the aroma of the stored sample was significantly weaker than the aroma of the control at 99% confidence level (*), and at 99.9% confidence level (**).

S: Sensory test was not conducted for this sample.

most critical factor for black pepper shelf life, the volatile oil affects only the aroma of black pepper, not its flavor. In other words, the pepper's taste might not be acceptable even when the volatile oil loss is still acceptable. Therefore, the flavor of black pepper should be tested by a sensory test after a certain storage period. Secondly, the volatile oil weight change, obtained from Equation (15), was based on several assumptions. It is desirable, therefore, to confirm the results by other methods (e.g. chemical analysis).

Considering these factors, the following experiments were designed and conducted.

Preparation of Black Pepper Specimens in M-24 Pouches

Ground black pepper in a 4 oz can, packaged on December 19, 1978, was used. The variety of this black pepper was a combination of Lampong and Brazilian. The black pepper weight was between 1.4 g and 1.5 g, and was packed in 0.5 mil M-24 pouches. These pouches were four side impulse sealed with dimensions 4 cm x 5 cm.

Sensory Test for Pepper Aroma by Inexperienced Panels

The prepared specimsns were stored at 75°F, 50% RH (average) and 100°F, 80% RH. After certain storage periods, the specimens were transferred into 22 cc amber Boston round glass bottles. Each bottle contained 0.5 g of ground black pepper and the bottles were closed with caps. Also 0.5 g of black pepper used as a control was prepared from an unopened can which had the same manufacturing code as the experimental pepper. Three replications of the storage sample and three replications of the control were coded randomly. Three samples, a combination of the stored sample(s) and the control(s), were presented to each panelist. According to the triangle test design in Figure 1, twenty-four panelists tested the same set in different coding combinations and orders. The report form, given in Figure 2, was used. Total correct numbers were counted, and the significance in aroma difference was determined by Table 20 in Appendix A. The panelists also answered a question: which sample(s) has (have) stronger odor? Since this was the paired comparison test, Table 21 in Appendix A was applied to determine any significant differences. These results are given in Table 12.

Table 12 shows that there was a significant difference between the aroma of the control and the aroma of the sample which was stored at 100°F, 80% RH for five weeks or longer. However, there was no significant difference between the aroma of the control and the aroma of the sample which was stored at 75°F, 50% RH for less than nine weeks. The following two experiments were designed based on these results.

Sensory Test for Pepper Flavor by Experienced Panels

The black pepper in M-24 pouches stored for seven weeks at 100°F, 80% RH and 75°F, 50% RH, was used. Here, the stored sample at 100°F, 80% RH represented the black pepper whose aroma was found to be significantly different from the control aroma by the triangle test. On the other hand, the stored sample at 75°F, 50% RH represented the black pepper whose aroma was found to be not significantly different from the control aroma. The sensory evaluation for black pepper flavor (the paired comparison test) was conducted in a spice company.* Both stored samples were

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*Both sensory test and chemical test were conducted in laboratories of the spice company. The sensory panelists were trained in the spice company for evaluation of spice. The name of the company is not disclosed here, but it is available upon the personal contact with the author.

Table 12. Sensory Test Results for Black Pepper Aroma in M-24 Pouches with Inexperienced Panels (Triangle Test)

Stored Condition		2 weeks	5 weeks	7 weeks	9 weeks
$75^{o}F$	Ratio of correct replies	9/24	11/24	--	7/24
50% RH	Control> test	5/9	3/11	--	3/7
$100^{o}F$	Ratio of correct replies	11/24	15/24*	17/24**	--
80% RH	Control> test	2/11	4/15	4/17	--

Control> test: Ratio that the control aroma was found to be stronger than the stored sample aroma.

*Siginficance at 99% confidence level.

**Significance at 99.9% confidence level.

Table 13. Sensory Test Results for Black Pepper Flavor in M-24 Pouches with Expert Panels (Paired Comparison Test)

Stored Condition	Initial Pepper Flavor	Pepper Heat	Total Pepper Flavor
$75^{o}F$			
50% RH	8/23	11/24	9/24
$100^{o}F$			
80% RH	16/24	19/24*	16/24

Figures are the ratio that the control was found to be stronger than the stored sample.
*Significance at 99% confidence level.

compared directly to the control in two separate tests on the same day. For each test, the samples were evaluated in potato soup media by twenty-four experienced panelists. The ingredients of the potato soup media, the cooking procedure, and the serving procedure are given in Appendix E. The ballot used in the paired comparison test is in Figure 4. These results are given in Table 13.

Chemical Analysis for Volatile and Non-Volatile Oil

The black pepper in M-24 pouches stored for seven weeks at 100°F, 80% RH and 75°F, 50% RH was presented to a spice company.* They analyzed the volatile oil content by the steam distillation method specified in the standard of the American Spice Trade Association.[6] The non-volatile oil was determined by the solvent extraction method. These procedures are in Appendices F and G. The results are given in Table 14.

NAME ____________________

DATE ____________________

BLACK PEPPER FLAVOR

Please try these two samples from left to right and answer the following questions:

1. Which sample has more initial flavor (the characteristic initial flavor which occurs before the throat heat)?

   Is the difference in initial flavor:

   Slight _________ Moderate_________ Strong _______

2. Which sample has more heat? _________________

   Is the difference in heat:

   Slight _________ Moderate _______ Strong _______

3. Which sample has more total pepper flavor (initial flavor plus heat)?

   ____

   Is the difference in total flavor:

   Slight _________ Moderate ________ Strong _______

THANK YOU!

Figure 4. The Ballot for Black Pepper Flavor (Paired Comparison Test)

Table 14. The Chemical Analysis Results of Volatile and Non-Volatile Oil for Black Pepper

Stored Condition	No.	Volatile Oil (ml/100g·product)	Non-Volatile Oil (g/100g·product)
75°F	1	2.33	7.98
50% RH	2	2.32	7.98
	$\overline{X}$	2.325	7.98
100°F	1	2.17	7.91
80% RH	2	2.17	7.79
	$\overline{X}$	2.17	7.85

The samples were stored in M-24 pouches for 7 weeks.

DISCUSSION

The shelf life of black pepper was assumed in the study to be determined by the critical volatile oil loss. The critical volatile oil loss was obtained by a combination of the calculation-experimental method and sensory evaluation using the triangle test. These results were compared with the chemical analysis results and the sensory evaluation results with experienced panels. Before discussing the experimental results, several assumptions which were made for the mathematical model are considered.

Consideration of the Assumptions Used in the Mathematical Model

Several assumptions were made in the section labeled Moisture Weight Prediction by a Mathematical Model in the chapter on Theoretical Basis. Unless these assumptions are valid, we cannot use Equation (15) for volatile oil weight loss. The following is a discussion of the assumptions.

The permeability constant was assumed to depend only on temperature, not on wall thickness or pressure difference.

The effect of material thickness on a permeability constant has been discussed by many investigators. Scopp et al.[58] in 1958 and Briston[6] in 1970 reported that the permeability constant is not independent of the material thickness. However, they used material ranging from one to twenty mils thick. All other investigators referenced in this study tested a range from one to five mils and found no dependence of permeability constant on material thickness. In this study, 0.5 mil and 1 mil films were used. So, the effect of permeability constant is considered to be independent of material thickness.

The effect of pressure difference was also discussed in several works. Barrer[4] in 1951 and Briston[6] in 1970 noted in their work that in hydrophilic materials there existed a strong dependence of the solubility coefficient upon partial pressure differential when exposed to water vapor. In this study, the weight changes of LDPE and M-24 films were tested and found to be negligible. This indicates that the films are not hydrophilic. Therefore, the permeability constants of these films are independent of the partial pressure difference.

It was assumed that the temperature was constant and was the same inside and outside of the package, and the outside relative humidity was constant. These assumptions may not be exactly true. However, laboratory records indicated that during the period of test, fluctuations of temperature and humidity were small and regular. Therefore, the variations can be ignored.

We did not consider mass interchange between outside and inside environments by flow. With packaging materials, mass flow occurs through pinholes, cracks, and discontinuous seals. With modern materials, pinholing or cracks and discontinuous seals, which lead to mass flow, are considered to be defects. These defects were eliminated by care in selection of materials and construction of pouches.

It was assumed that moisture in the product and water vapor in the headspace are always in equilibrium. This is true when permeation through a film is slower than diffusion into a product. In this study LDPE and M-24 films were used, and both have relatively low permeability constants against water vapor.

Permeation was assumed to be a steady state process. There is a lag time before reaching a steady state process, and the lag time can be calculated in Equation (21)[63]

$$L = \frac{\ell^2}{6D} \tag{21}$$

where

L is the lag time,

ℓ is the film thickness, and

D is the diffusion coefficient

In this study, 1 mil LDPE and 0.5 mil M-24 were used. The literature values for diffusion coefficients of LDPE and M-24 films against water vapor are about 0.2 mil^2/min and 0.02 mil^2/min. Plugging these data into Equation (21), we can obtain L = 0.8 min (LDPE) and L = 2.1 min (M-24). Therefore, the time lags can be ignored.

It was assumed that there were no chemical reactions among product, package and environment. There is a possibility for volatile oil in black pepper to interact with a film. The volatile oil would act as a plasticizer, and increase the permeability of the film. This problem must be left for future study. Since LDPE and M-24 were relatively inert against volatile oil,[66] and the storage period was only one week, the mathematical model can be assumed to be valid in this study.

The Ideal Gas Law was assumed to be applicable to water vapor. There are no real gases which obey the Ideal Gas Law. Van Der Waal's Equation represents the behavior of ordinary gases more correctly than the Ideal Gas Law. However, Van Der Waal's Equation is more complicated and the error introduced by using the Ideal Gas Law is considered to be negligible.[12]

It was assumed that the wall thickness of a package and headspace volume were constant. This assumption will be validated by error analysis in a later section.

We assumed that the sorption isotherm was fitted by a straight line within a certain range. From Figure 3, it can be found that the experimental results were on straight lines within the range of 30 to 70% RH with good agreement.

Considering all of the above assumptions, the model was concluded to be valid with its error analysis.

Discussion of the Experimental Results

The purpose of the experiment was to obtain the critical volatile oil loss. For this reason, the validity of Equation (15) is essential.

$$\Delta W_T = \Delta Wm + \Delta Wv.o. \qquad (15)$$

This equation is valid when the weight change of the package is negligible. The weight change of LDPE and M-24 films were less than 0.0004g in any storage conditions. This satisfies the condition for Equation (15), that is, the weight change of the film is negligible.

In Table 4, we can find that ΔW_T at 77°F, 58.5% RH (0.486g/100g·dry product) was smaller than ΔW_T at 100°F, 53.7% RH (1.050g/100g·dry product) in M-24 pouches while ΔW_T at 77°F, 58.5% RH (0.868g/100g·dry product) was larger than ΔW_T at 100°F, 53.7% RH (0.661g/100g·dry product) in LDPE pouches after seven days storage. The results in M-24 pouches can be explained by the permeability constant ($\bar{P}$) and the saturated partial pressure (Ps). Table 9 shows that $\bar{P}$ for M-24 at 100°F is about double $\bar{P}$ at 78°F. This means that twice as much water vapor can penetrate through M-24 film at 100°F as at 78°F. The saturated partial pressure (Ps) at 100°F is also larger than Ps at 77°F. So, the results in Table 4 can be explained as follows: ΔW_T at 100°F, 53.7% RH gained more moisture than ΔW_T at 77°F, 58.5% RH because of the higher $\bar{P}$ and Ps. In the case of LDPE pouches, $\bar{P}$ at 100°F was also about double $\bar{P}$ at 78°F.

However, ΔW_T at $100^{o}F$, 53.7% RH was even smaller than ΔW_T at $77^{o}F$, 58.5% RH. This can be explained by the following: black pepper lost something at $100^{o}F$, 53.7% RH. We assumed it was a volatile oil. These results had an important meaning in this study. That is, the weight change of volatile oil can be measured by an analytical balance with a reasonable sensitivity.

In order to calculate ΔWm, the initial moisture content, the equilibrium moisture content, and the water vapor transmission rate were measured. Table 6 shows the initial moisture content results by the P_2O_5 method. Actually, these results are not only the moisture loss, but also the volatile oil loss. So, some correction is necessary in order to use these figures. There was the same problem in the measurement of the equilibrium moisture content (the salt solution method). The results in Table 7 are the sum of the moisture weight change and the volatile oil loss. In both the P_2O_5 method and the salt solution method, the black pepper samples in aluminum dishes were stored for more than twenty days. It was noticed that the aroma of the pepper was totally gone after the storage. In other words, the volatile oil might be completely diminished in both experiments. Since the same amount and the same origin of black pepper was used in both measurements, it is reasonable to assume that the same amount of volatile oil was missing. In Figure 3, the sorption isotherms for black pepper are drawn. The isotherms were obtained from the initial moisture content measurement and the equilibrium moisture content measurement. So, the isotherms are the sum of the moisture weight change and the volatile oil loss. Since we assumed that the same amount of volatile oil was lost in all relative humidity conditions, the actual water sorption isotherms would be parallel to the sorption isotherms drawn in Figure 3. This means that the slopes of the actual water sorption isotherms are the same as the slopes in Figure 3. Therefore, we can use the same slope (b) in Equation (14) for the ΔWm calculation.

The critical volatile oil loss can be determined in Table 11. From the table, the significant aroma differences will be found when $\Delta Wv.o.$ is more than 0.345 g/100g·dry product, and the significant aroma differences will not be found when $\Delta Wv.o.$ is less than 0.286g/100g·dry product. So, the critical volatile oil loss will be between 0.286 and 0.345g/100g·dry product.

To confirm the critical volatile oil loss, two other experiments were conducted. One was the sensory test for pepper flavor with experienced panels. The other was the chemical analysis to confirm the critical volatile oil loss. Table 12 shows the sensory test results for black pepper aroma with inexperienced panels. In the table, the aroma of black pepper, stored in M-24 pouches for seven weeks at $100^{\circ}F$, 80% RH, shows a significant difference from the aroma of the control. However, the aroma of black pepper, stored in M-24 pouches at $75^{\circ}F$, 50% RH for the same period, does not show a significant difference from the aroma of the control. Using these two samples, the paired comparison test for the pepper flavor was conducted with experienced panels. The results in Table 13 show that in one important factor there was a significant difference between the control and the sample. The pepper heat* of the control was found to be significantly stronger than the pepper heat of the sample stored at 100°F, 80% RH. This result has two meanings. First, this result for flavor is pretty much the same as the triangle test result for aroma. The pepper heat of the stored sample at 100°F, 80% RH was found to be significantly different, and the pepper aroma of the same sample was also found to be significantly different at the same storage period. Secondly, the significance in the pepper heat might be a symptom of total pepper flavor deterioration in the future. The fact that total pepper flavor was not found significant for either sample supports the hypothesis that the aroma test should be a reliable predictor of total flavor.

The results of the chemical analysis for volatile oil and non-volatile oil are given in Table 14. There was a difference in the amount of volatile oil between the pepper stored at 75°F, 50% RH (2.325 ml/100g·product) and the pepper stored at 100°F, 80% RH (2.17 ml/100·product). There might be a difference in the amount of non-volatile

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*Pepper heat: Hot taste after the initial flavor.

oil between the pepper stored at 75°F, 50% RH (7.98 g/100g· product) and the pepper stored at 100°F, 80% RH (7.85g/100g· product). However, the sample stored at 100°F, 80% RH showed a large range so that we cannot conclude a significant difference between these two stored samples. Three conclusions can be drawn from the results in Table 14. First, the critical volatile oil loss can be calculated. The average volatile oil in pepper is 2.5 ml/100g, and the specific gravity of the volatile oil is 0.9.[53] So, the weight loss at 75°F, 50% RH storage is

$$(2.5 - 2.325) \times 0.9 = 0.157 \text{ g/100g·product}$$

The weight loss at 100°F, 80% RH storage is

$$(2.5 - 2.17) \times 0.9 = 0.297 \text{g/100g·product}$$

The critical volatile oil loss is between 0.157 and 0.297 g/100g·product. In Equation (15) we also obtained the critical volatile oil loss between 0.286 and 0.345g/100g· dry product. However, we cannot compare these results directly because the units were different. The unit conversion will be shown later in this study.

The second conclusion from Table 14 is the possibility of non-volatile oil weight change. The weight change of the non-volatile oil cannot be concluded from Table 14 because of the large range of data. However, if there exists a non-volatile oil weight change, Equation (15) must be changed to

$$\Delta W_T = \Delta Wm + \Delta Wv.o. + \Delta Wn.v.o. \qquad (22)$$

where

ΔWn.v.o. is the weight change of the non-volatile oil.

This upsets the original hypothesis: The measurement of volatile oil loss, and thus aroma loss, is the most critical factor in black pepper shelf life. Since this is an important factor, it should be left for future study. This is also true;

$\Delta Wv.o. > \Delta Wn.v.o.$

however, we do not know by how much ΔWv.o. is larger than ΔWn.v.o.

The third conclusion is that the results in Table 14 are all within the limits specified by the F.D.A. and A.S.T.A. (Table 2). This indicates that the sensory test is more stringent than the chemical analysis.

Consideration of the Critical Volatile Oil Loss

The values for critical volatile oil loss were obtained from the chemical analysis and Equation (15). They also have different dimensions. In order to unify both units, the actual initial moisture content should be determined. From Table 6 the initial moisture content is 6.246 g/100g·product. This value includes the moisture loss and the volatile oil loss. We made the assumption that all volatile oils were diminished. Since the specific gravity of the average volatile oil is 0.9 and pepper contains 2.5 ml/100g·product volatile oil, the actual initial moisture content can be calculated.

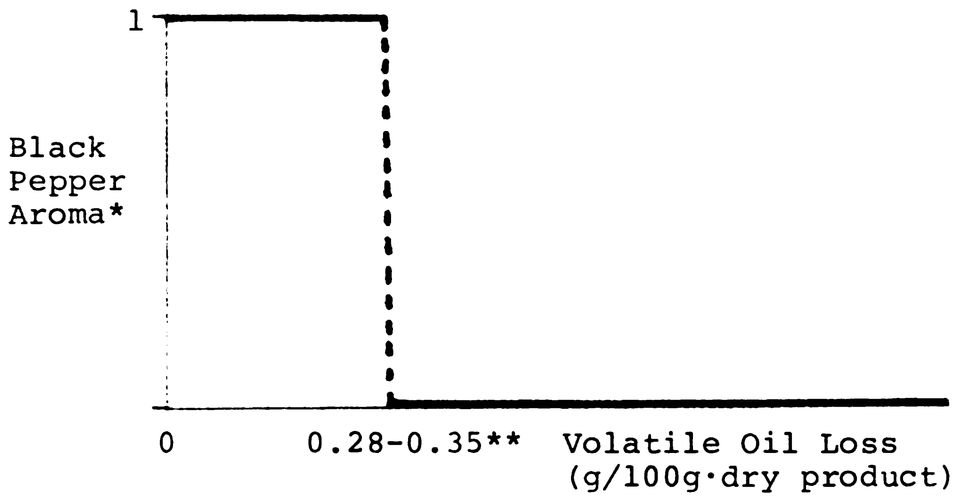
Initial Moisture Content = 6.246 + (2.5 x 0.9) = 8.50g/100g·product. Therefore, the volatile oil loss by chemical analysis can be

$0.157 \div (1-0.085) = 0.172$g/100g·dry product (at 75°F, 50% RH)

$0.297 \div (1-0.085) = 0.325$g/100g·dry product (at 100°F, 80% RH)

Comparing these figures to the sensory test results, the aroma of the sample stored at 100°F, 80% RH was found to be significantly different from the aroma of the control. So, the critical volatile oil loss is 0.325g/100g·dry product or less. This result satisfies the predicted critical volatile oil loss range, 0.286 to 0.345g/100g·dry product.

From all of the above discussions, the relationship between the volatile oil loss and the black pepper aroma can be concluded. The range for critical volatile oil loss was found to be 0.28 to 0.35g/100g·dry product. The relationship between the aroma and $\Delta W_{v.o.}$ is drawn in Figure 5. The graph is a discontinuous curve because the pepper aroma cannot be represented on a numerical scale. So, a significant difference from the control is designated by 0, and an insignificant difference is designated by 1 on the graph.



*Black Pepper Aroma
1: Insignificant difference from the control by the sensory test.
0: Significant difference from the control by the sensory test

**The critical volatile oil loss range is 0.28 to 0.35g/100g·dry product in this study

Figure 5. Black Pepper Aroma VS Volatile Oil Loss

Consideration of Moisture Effect

The specifications for black pepper given by the F.D.A. and A.S.T.A. are in Table 2. Maximum moisture content is specified because microbial spoilage readily occurs when the moisture exceeds twelve percent. This can be considered in the sorption isotherm. Figure 3 shows a pseudo sorption isotherm. We made an assumption that this pseudo isotherm includes the volatile oil loss and is parallel to the actual sorption isotherm. Because the volatile oil loss is 2.25g/100g·product and the actual initial moisture content is 8.50g/100g·product, the actual water sorption isotherm can be drawn. The unit of the pseudo isotherm was converted to g/100g·product and the volatile oil loss (2.25g/100g·product) was added to this value. This is given in Figure 6 and is labeled "Revised Sorption Isotherms for Black Pepper." In the graph, when the equilibrium moisture content is 12g/100g·product, which is the limit specified by the F.D.A. and the A.S.T.A., the relative humidity is about 80%. This means that the relative humidity in the package is allowed to be as high as 80%. In other words, no package is necessary for moisture protection reasons if the relative humidity is less than 80%. In real life, black pepper is stored in a warehouse or in a supermarket where the relative humidity is usually less than 80%. Therefore, it can be concluded that the moisture effect for black pepper shelf life is not as important as volatile or non-volatile oil.

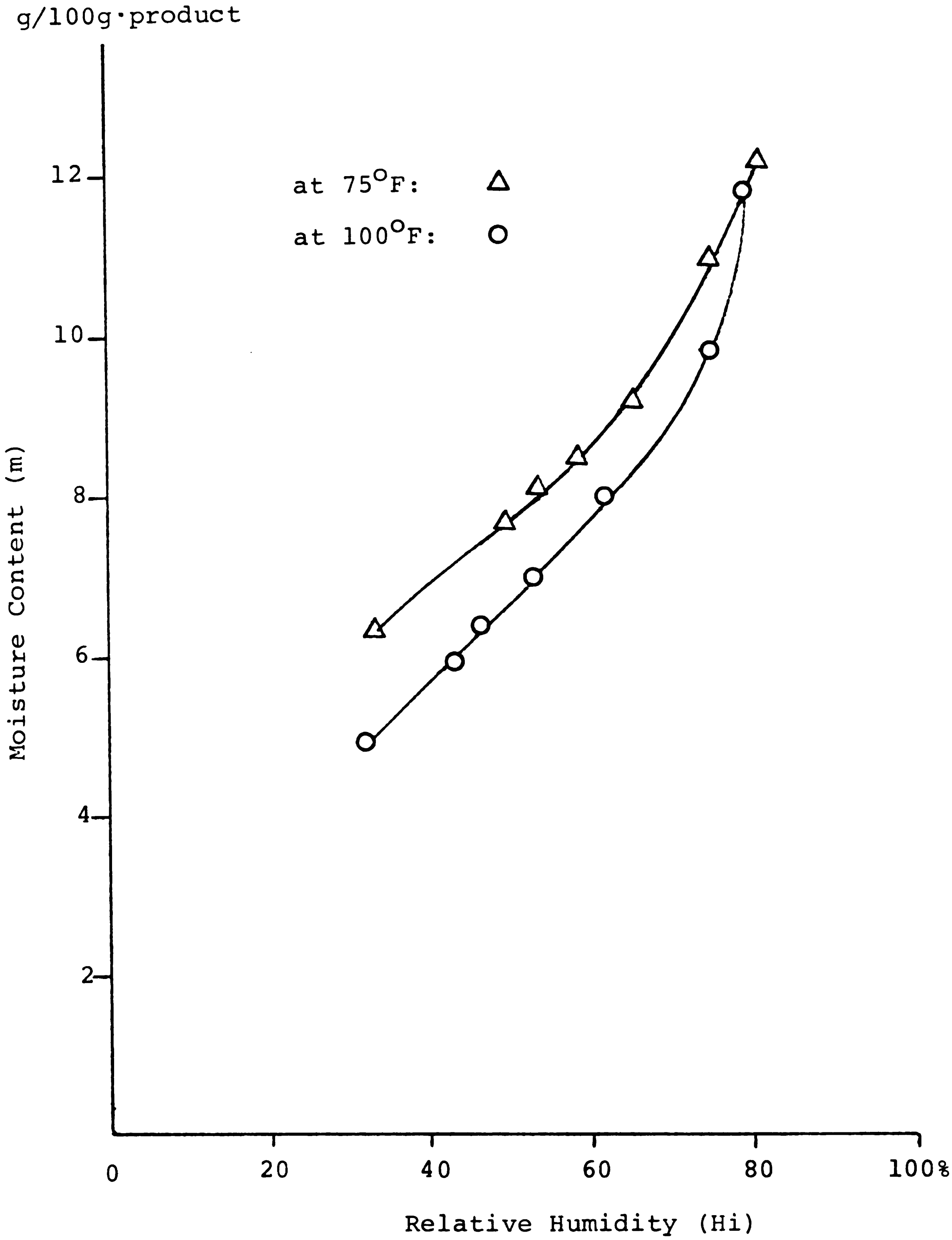


Figure 6. Revised Sorption Isotherms for Black Pepper

Error Analysis

Several errors are involved in the experimental methods. They are considered in the following.

Temperature (T) is the first factor to be considered. The fluctuation of the temperature in the laboratory was observed to be $\pm$ $2^{o}F$ during the test. Even though this fluctuation is not large, its effect on the calculation of the moisture weight change (ΔWm) should be analyzed. The temperature influences the following factors: the saturated partial pressure, the external relative humidity by the saturated salt solution method and the permeability constant of film. It may also influence the slope of the sorption isotherm because our experimental result for the sorption isotherm (Figure 3) shows that the higher temperature has the steeper slope. Considering all of these factors, ΔWm in Equation (14) was recalculated. Table 15 shows the effect of temperature ($77 \pm 2^{o}F$, $100 \pm 2^{o}F$) on the moisture weight change (ΔWm) of black pepper after seven days storage. In the table, it will be found that the maximum error is 0.064g/100g·dry product. The ratio of this error to ΔWm is

$$\frac{0.064}{1.348} = 4.7\%$$

This should not be ignored. We can reduce this error by increasing the sensitivity. For example, if we use 130g of black pepper for each sample instead of 1.3g, the error can be reduced by a factor of 100.

Table 15. The Effect of Temperature (T) Fluctuations on the Moisture Weight Change (ΔWm) of Black Pepper

		ΔWm (g/100g·dry product)				
Film	T	75°F	76°F	77°F	78°F	79°F
M-24	ΔWm	0.548	0.569	0.595	0.621	0.642
	Er*	0.047	0.026	--	0.026	0.047
LDPE	ΔWm	1.160	1.183	1.213	1.241	1.261
	Er	0.053	0.030	--	0.028	0.048
Film	T	98°F	99°F	100°F	101°F	102°F
M-24	ΔWm	1.064	1.074	1.055	1.095	1.106
	Er	0.009	0.019	--	0.040	0.051
LDPE	ΔWm	1.412	1.401	1.348	1.375	1.363
	Er	0.064	0.053	--	0.027	0.015

*Er (Error at temperature T): Difference between the values at 77°F and the values at T°F or difference between the values at 100°F and the values at T°F.

The saturated salt solution method was used to maintain the constant relative humidity. According to Wink and Sears[70] in 1950, the following factors are essential to obtaining a stable relative humidity: the purity of the salt, the use of distilled water, a large solution surface area, a small headspace, and a stable temperature. These factors were well controlled in the experiment, but no attempt was made to measure the actual relative humidity inside the container. Assuming that the fluctuation of relative humidity was $\pm$ 1% during the test, the moisture weight change of black pepper after 7 days storage can be calculated in Equation (14). The results are in Table 16. In Table 16, it will be found that the maximum error is 0.139g/100g dry product. The ratio of this error to ΔWm is

$$\frac{0.139}{1.348} = 10.3\%$$

This value indicates that the external relative humidity is an important factor in the mathematical model. However, this value also can be reduced by increasing the mass of the pepper sample.

The permeability constant ($\bar{P}$) also includes several errors because it is based on a WVTR (water vapor transmission rate) measurement by the dish method. The fluctuation of temperature and relative humidity and the measurement of exposed film surface area are the possible factors giving rise to an uncertainty in $\bar{P}$. The tolerance in $\bar{P}$ is estimated to be $\pm$ 3% g·mil/cm^2/hr/Δatm. The results are

Table 16. The Effect of Relative Humidity (RH) Fluctuations on the Moisture Weight Change (ΔWm) of Black Pepper

		ΔWm (g/100g·dry product)					
		77°F			100°F		
Film	RH	57.5%	58.5%	59.5%	52.7%	53.7%	54.7%
M-24	ΔWm	0.554	0.595	0.636	0.947	1.055	1.164
	Er*	0.041	--	0.041	0.108	--	0.109
LDPE	ΔWm	1.129	1.213	1.296	1.209	1.348	1.487
	Er*	0.084	--	0.083	0.139	--	0.139

*Er (Error at relative humidity RH): Difference between the values at 58.5% and the values at RH% or difference between the values at 53.7% and the values at RH%.

in Table 17. The maximum error in ΔWm was found to be 0.020g/100g·dry product. This is a relatively small error.

The film thickness is the next factor to be considered. The film thickness varied by $\pm$ 10% in the experiment. The error was analyzed assuming this range. The results are in Table 18. The maximum error in ΔWm was found to be 0.068g/100g·dry product.

The other factors; the surface area, the volume of headspace, the slope of the sorption isotherm, and the weight of black pepper were also considered as error factors. However, these errors are found to be negligible. A summary of the error ΔWm assuming maximum uncertainties for these minor contributing factors is found in Table 19.

Table 17. The Effect of Permeability Constnat ($\bar{P}$) Difference on the Moisture Weight Change (ΔWm) of Black Pepper

		ΔWm (g/100g·dry product)					
		77°F			100°F		
Film	$\bar{P}$*	1.314	1.364	1.414	2.61	2.71	2.81
M-24	ΔWm	0.575	0.595	0.621	1.037	1.055	1.072
	Er	0.020	--	0.017	0.018	--	0.017
Film	$\bar{P}$	7.49	7.69	7.89	13.25	13.65	14.05
	ΔWm	1.195	1.213	1.230	1.343	1.348	1.353
	Er	0.018	--	0.017	0.005	--	0.005

*P: (X 10^{-4} g·mil/cm^2/hr/Δatm)

Table 18. The Effect of Film Thickness (ℓ) Variation on the Moisture Weight Change (ΔWm) of Black Pepper

		ΔWm (g/100g·dry product)					
		77°F			100°F		
Film	ℓ	0.45 mil	0.5 mil	0.55 mil	0.45 mil	0.5 mil	0.55 mil
M-24	ΔWm	0.647	0.595	0.550	1.104	1.055	1.009
	Er	0.052	--	0.045	0.049	--	0.046
Film	ℓ	0.9 mil	1 mil	1.1 mil	0.9 mil	1 mil	1.1 mil
LDPE	ΔWm	1.281	1.213	1.151	1.361	1.348	1.334
	Er	0.068	--	0.062	0.013	--	0.014

Table 19. Maximum Errors in ΔWm by the Effect of A, V, W, and b

	Estimated Range	Max Error in ΔWm
A	40 ± 1 cm^2	0.017 g/100g·dry product
V	8 ± 1 cc	0.001
W	1.30 ± 0.05 g	0.020
b* (77°F)	0.0939 ± 0.001	0.006
(100°F)	0.1096 ± 0.001	0.011

*b: Slope of the sorption isotherm, g/100g·dry product/% RH.

A: The surface area.

V: The volume of headspace.

W: The weight of dry product.

From all of the above considerations, three important error factors were found. They were the temperature, the relative humidity, and the film thickness. The cumulative effect of these three important errors is estimated to be 0.167g/100g·dry product in the following calculation.

$$((0.064)^2 + (0.139)^2 + (0.068)^2)^{1/2} = 0.167$$

Calculating the ratio of this maximum possible error to ΔWm in LDPE

at 77°F $\frac{0.167}{1.213} = 13.8\%$, and

at 100°F $\frac{0.167}{1.348} = 12.4\%$

These errors should not be ignored. However, these are the maximum possible errors. So, our results still can be considered to be valid. These errors also can be decreased by increasing the mass of black pepper samples.

CONCLUSION

The critical volatile oil loss was predicted by a combination of the mathematical-experimental model, and the sensory test. The result was confirmed by the chemical analysis and the sensory test with expert panels. Both results agreed that the critical volatile oil loss was between 0.28 and 0.35g/100g·dry product. The sensory test results and the chemical analysis result indicated that the volatile oil loss would be a reliable predictor of black pepper shelf life.

It should be possible to develop a plastic package for black pepper by considering the critical volatile oil loss.

Future Work

When developing a plastic package for black pepper, the following problems must be considered.

A. The stability of non-volatile oil should be considered since this is another important factor for black pepper shelf life.

B. It is a good idea to study the permeability of a plastic film against volatile oil. This will help the shelf life prediction in the future.

C. The sensitivity of the experiment should be improved by increasing the mass of black pepper.

D. Black pepper has many varieties by its origin. Each variety might have critical volatile oil loss different from others.

E. The possibility of chemical reaction should be considered. Volatile oil might interact with a plastic film and act as a plasticizer. This results in increasing the permeability of the film.

SUMMARY

In order to achieve cost reduction of a black pepper package, a plastic pouch was proposed. The most essential requirement for the plastic package was to provide adequate shelf life. Three factors were considered in this study. These were volatile oil, non-volatile oil and moisture. Because aroma was the least stable factor in a black pepper storage test, the following hypothesis was made: the most critical factor for black pepper shelf life in a plastic package was its volatile oil loss. The critical volatile oil loss was predicted by a combination of mathematical-experimental model and a sensory test for black pepper aroma. This critical volatile oil loss was confirmed by a chemical analysis and a sensory test using an expert panel. These results indicated that volatile oil loss would be a reliable predictor of black pepper shelf life.

In the sensory test with the expert panel, it was found that there was a significant difference in pepper heat between a stored sample and the control, but there was no significant difference in the total flavor between them. This meant that non-volatile oil was another important factor to be considered in black pepper shelf

life, but it was more stable than volatile oil.

The moisture effect was also considered. Using the sorption isotherm of black pepper, it can be concluded that the factor of moisture was not as important as volatile or non-volatile oil.

By using the critical volatile oil loss as a predictor, it should be possible to consider the shelf life of black pepper in plastic pouches.

APPENDICES

APPENDIX A

TABLE FOR SIGNIFICANCE IN THE TRIANGLE TEST AND IN THE PAIRED TEST

APPENDIX A

TABLE FOR SIGNIFICANCE IN THE TRIANGLE TEST AND IN THE PAIRED TEST

Table 20. Table for Significance in the Triangle Test* (p = 1/3)

Number of Judges or Judgments	Minimum correct judgments to establish significant differentiation		
	Significance level 0.05	Significance level 0.01	Significance level 0.001
5	4	5	5
6	5	6	6
7	5	6	7
8	6	7	8
9	6	7	8
10	7	8	9
11	7	8	10
12	8	9	10
13	8	9	11
14	9	10	11
15	9	10	12
16	9	11	12
17	10	11	13
18	10	12	13
19	11	12	14
20	11	13	14
21	12	13	15
22	12	14	15
23	12	14	16
24	13	14	16
25	13	15	17
26	14	15	17
27	14	16	18
28	14	16	18
29	15	17	19
30	15	17	19
31	16	17	20
32	16	18	20
33	16	18	21
34	17	19	21
35	17	19	21
36	18	20	22

*Sensory Testing Method, "Encyclopedia of Industrial Chemical Analisis," 1973.

Table 21. Table for Significance in the Paired Test* (P = 1/2)

Number of judges or judgments	Minimum correct answers necessary to establish significant differentiation (one-tailed test)		
	Significant level 0.05	Significant level 0.01	Significant level 0.001
7	7	7	-
8	7	8	-
9	8	9	-
10	9	10	10
11	9	10	11
12	10	11	12
13	10	12	13
14	11	12	13
15	12	13	14
16	12	14	15
17	13	14	16
18	13	15	16
19	14	15	17
20	15	16	18
21	15	17	18
22	16	17	19
23	16	18	20
24	17	19	20
25	18	19	21
26	18	20	22
27	19	20	22
28	19	21	23
29	20	22	24
30	20	22	24
31	21	23	25
32	22	24	26
33	22	24	26
34	23	25	27
35	23	25	27
36	24	26	28

*Sensory Testing Method, "Encyclopedia of Industrial Chemical Analysis," 1973.

APPENDIX B

THE DERIVATION OF EQUATION (4)

APPENDIX B

THE DERIVATION OF EQUATION (4)

The Derivation of Equation (4)*

$$M = M_1 + M_2 \tag{3}$$

If W is the weight of the dry product in the package and m is the moisture content,

$$M_1 = m \cdot \frac{W}{100} \tag{3.1}$$

When the water in the product has reached equilibrium, m is given by the water isotherm, which is assumed to be a straight line.

$$m = a + b \cdot Hi(t) \tag{3.2}$$

From Equations (3.1) and (3.2)

$$M_1 = \frac{W}{100}\,(a + b \cdot Hi(t)) \tag{3.3}$$

Assuming the Ideal Gas Law is applicable to water vapor,

$$Pi \cdot V = n \cdot R \cdot T \tag{3.4}$$

where

Pi is the pressure inside the package,

V is the volume of the headspace,

n is the number of water vapor molecules in the headspace,

R is the gas constant, and

T is the temperature.

Since one mole of water vapor weighs 18g, and the water

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*Clifford, Wayne H., et al., 1977.

vapor pressure can be expressed in terms of relative humidity,

Equation (3.4) can be expressed as

$$M_2 = 18 \cdot Ps \cdot \frac{Hi(t)}{100} \cdot \frac{V}{R \cdot T} \tag{3.5}$$

From Equations (3.3) and (3.5),

$$M = \frac{W}{100} (a + b \cdot Hi(t)) + 18 \frac{V}{R \cdot T} \cdot Ps \cdot \frac{Hi(t)}{100} \tag{4}$$

APPENDIX C

THE DERIVATION FROM FICK'S LAW AND HENRY'S LAW TO EQUATION (5)

APPENDIX C

THE DERIVATION FROM FICK'S LAW AND HENRY'S LAW TO EQUATION (5)

The Derivation from Fick's Law and Henry's Law to Equation (5).*

Fick's first law is

$$F = -D \cdot \frac{\partial c}{\partial x} \tag{5.1}$$

where

D is the diffusion coefficient,

C is the concentration,

X is the space coordinate measured to the section,

F is the flux (the rate of transfer per unit area of section).

but,

$$\frac{\partial c}{\partial x} = -\frac{C_1 - C_2}{\ell} \quad (C_1 > C_2) \tag{5.2}$$

where

C_1 is concentration of side 1,

C_2 is concentration of side 2, and

ℓ is the thickness of the material.

so

$$F = D \cdot \frac{C_1 - C_2}{\ell} \tag{5.3}$$

---

*Barrer, R. M., 1951.

From Henry's Law

$$C = P \cdot S \tag{5.4}$$

where

P is the pressure, and

S is the solubility coefficient.

Plug (5.4) into(5.3).

$$F = D \cdot S \cdot \frac{P_1 - P_2}{\ell} \tag{5.5}$$

where

P_1 is the pressure of side 1,

P_2 is the pressure of side 2, and

$P_1 > P_2$.

but,

$$D \cdot S = \overline{P} \tag{5.6}$$

so

$$F = \overline{P} \cdot \frac{P_1 - P_2}{\ell} \tag{5.7}$$

F is the rate of transfer per unit area of section.

$$F = \frac{\Delta M}{\Delta t \cdot A} \tag{5.8}$$

where

ΔM is the moisture weight change,

Δt is the time period, and

A is the unit area of section.

Consider the limit of $(\frac{\Delta M}{\Delta t})$ when Δt approaches zero.

$$\lim_{\Delta t \to 0} \left(\frac{\Delta M}{\Delta t}\right) = \frac{dM}{dt} \tag{5.9}$$

P_1 and P_2 can be expressed in terms of relative humidity.

$$P_1 = \frac{Ps \cdot He}{100} \tag{5.10}$$

$$P_2 = \frac{Ps \cdot Hi(t)}{100} \tag{5.11}$$

Here $He > Hi(t)$

From Equations (5.7), (5.8), (5.9), (5.10) and (5.11),

$$\frac{dM}{dt} = \overline{P} \cdot \frac{A}{\ell} \cdot \frac{Ps}{100} \cdot (He - Hi(t)) \tag{5}$$

APPENDIX D

THE DERIVATION OF EQUATION (7)

APPENDIX D

THE DERIVATION OF EQUATION (7)

The Derivation of Equation (7).*

$$\overline{P}\cdot\frac{A}{\ell}\cdot\frac{Ps}{100}(He - Hi(t)) = \frac{d}{dt}\left(\frac{W}{100}(a + b\cdot Hi(t)) + 18\frac{V}{R\cdot T}\cdot Ps\cdot\frac{Hi(t)}{100}\right) \tag{6}$$

$$\frac{dHi(t)}{dt} = \frac{\overline{P}\cdot\frac{A}{\ell}\cdot\frac{Ps}{100}}{\frac{bw}{100}+\frac{18Ps\cdot V}{100R\cdot T}}\cdot(He - Hi(t)) \tag{6.1}$$

Let

$$\frac{\overline{P}\cdot\frac{A}{\ell}\cdot\frac{Ps}{100}}{\frac{bw}{100} + \frac{18Ps\cdot V}{100R\cdot T}} = \frac{\overline{P}\cdot A\cdot Ps}{\ell(18Ps\cdot V/R\cdot T + b\cdot W)} = J \tag{8}$$

Integrate Equation (6.1)

$$\int\frac{dHi(t)}{He - Hi(t)} = \int Jdt \tag{6.2}$$

Let

$$He - Hi(t) = K \tag{6.3}$$

Differentiate (6.3)

$$-dHi(t) = dK \tag{6.4}$$

From Equations (6.2), (6.3) and (6.4),

$$-\int\frac{dK}{K} = \int J\cdot dt \tag{6.5}$$

---

*Manathanya, Vallop, 1976

$$\ln K + \text{constant (1)} = -J \cdot t \tag{6.6}$$

$$K = \text{constant (2)} \cdot e^{-J \cdot t} \tag{6.7}$$

$$He - Hi(t) = \text{constant (2)} \cdot e^{-J \cdot t} \tag{6.8}$$

when $t = 0$

$$\text{Constant (2)} = He - Hi(0) \tag{6.9}$$

From Equation (6.8) and (6.9),

$$Hi(t) = He - (He - Hi(0)) \cdot e^{-J \cdot t} \tag{7}$$

APPENDIX E

SENSORY TEST FOR PEPPER FLAVOR: COOKING PROCEDURE FOR THE MEDIA AND SERVING PROCEDURE

APPENDIX E

SENSORY TEST FOR PEPPER FLAVOR: COOKING PROCEDURE FOR THE MEDIA AND SERVING PROCEDURE

The potato soup media consisted of the following ingredients.

200g Chicken broth

200g Water

300g Milk

300g Cooked White Potatoes

The soup was blended for one minute on the stir speed and for one minute on the mix speed of a blender. The black pepper was diluted in the soup to 0.125% and allowed to stand for 20 minutes.

Panelists were served 20 ml of each sample in coded medicine cups. Sample order of presentation was rotated to avoid bias and red lights masked color differences.

APPENDIX F

VOLATILE OIL CONTENT OF BLACK PEPPER

BY STEAM DISTILLATION

APPENDIX F

VOLATILE OIL CONTENT OF BLACK PEPPER BY STEAM DISTILLATION

Reagents and Apparatus

Flask - 1 liter, round-bottom, short neck

Electric Heating Mantle

Oil Traps - 5.0 ml distilling trap, Clevenger type, boiling flask, and finger condenser

Condenser - Drip-tip, 400 mm long

Pipet - 5 ml

Antifoam

Boiling Chips

Salt-crystals

Detergent - 3% V/V aqueous solution

Wire - copper

Procedure

1. Grind sample.
2. Weigh 50.0 g of the sample.
3. Transfer the sample quantitatively to the distilling flask.
4. Add 500 ml of water, two drops antifoam boiling chips and thoroughly mix the contents.
5. Clean the dilution trap immediately before use by filling with boiling 3% aqueous solution of detergent for 10 minutes, then rinse well but do not dry.

6. Connect oil trap to the flask and add water to the graduated portion of the trap.
7. Connect to condenser and distill overnight.
8. Cool and determine volume (ml) of oil collected.

Calculation

$$\frac{\text{Corrected Volume of Oil (ml)} \times 100}{\text{Sample Weight (g)}}$$

= % V/W Volatile Oil

APPENDIX G

NON-VOLATILE OIL OF BLACK PEPPER DETERMINED BY SOLVENT EXTRACTION

APPENDIX G

NON-VOLATILE OIL OF BLACK PEPPER DETERMINED BY SOLVENT EXTRACTION

Reagents and Apparatus

Methylene Chloride - A.C.S. grade

Extractor - standard continuous extraction apparatus

Extraction Thimbles - paper

Oven - 110°C circulating air type

Aluminum Dish - 70 x 10 mm

Procedure

1. Weigh approximately 2.000 g of sample in a paper extraction thimble of medium porosity.
2. Place the thimble in the extraction apparatus and extract 20 hours with Methylene Chloride.
3. Transfer the extract, using several solvent washes to a tared aluminum dish and evaporate the solvent on a steam bath in a forced draft hood.
4. Place the dish in a drying oven at 110°C $\pm$ 2°C and weigh hourly until the difference in consecutive weighings is not more than 1 mg.

Calculation

$$\frac{\text{Weight of Residue in Dish (g)} \times 100}{\text{Sample Weight (g)}}$$

= % Non-Volatile Extract

Report as percent Non-Volatile Methylene Chloride Extract.

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