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INTERACTION OF POLYMERIC PACKAGING MATERIALS WITH FLAVOR COMPONENTS FROM AN ONION/GARLIC FLAVORED SOUR CREAM

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INTERACTION OF POLYMERIC PACKAGING MATERIALS WITH FLAVOR COMPONENTS FROM AN ONION/GARLIC FLAVORED SOUR CREAM

By

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ABSTRACT

INTERACTION OF POLYMERIC PACKAGING MATERIALS WITH FLAVOR COMPONENTS FROM AN ONION/GARLIC FLAVORED SOUR CREAM

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Permeation and sorption studies were performed on a high impact polystyrene (HIPS) package containing onion/garlic flavored sour cream. For comparison, sorption studies were also conducted using high density polyethylene (HDPE) and polypropylene (PP). Dimethyl disulfide and dipropyl disulfide were chosen as probe compounds. Permeation studies were conducted using a quasi-isostatic technique, while a gravimetric method was used for sorption studies.

No detectable permeation of probe compounds through the HIPS container was observed. Sorption studies show the solubility of probe compounds in HIPS to be substantially higher than in HDPE or PP. A model was developed to predict sorption of probes in the actual product. Based on this model, none of the three test materials would reach saturation levels during storage of the product. Sensory analysis showed that panelists were unable to detect off odors or flavors in unflavored products stored adjacent to the onion/garlic flavored sour cream.

DEDICATION

This thesis is dedicated to my parents in appreciation of their love and acceptance.

Also, to Beth Waggoner whose friendship was a source of support and inspiration throughout this work.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Plastics are enjoying widespread popularity in food packaging. The value of all rigid and semi-rigid plastic containers manufactured in the U.S. was 3.77 billion dollars in 1985 (Friedman, 1985). The properties which make plastics distinct from other materials also make them attractive alternatives for use with many food products. Plastics offer several advantages to the consumer and manufacturer. Improved processing methods continue to decrease costs, while an increasing variety of plastics is available to suit specific needs. Other important advantages of plastics include resistance to breakage and its lightweight (as compared to glass and metal) (Hanlon, 1984). With the increased use of plastics, a need to characterize interactions between polymeric packages and the contents of these packages has arisen. Possible alteration of product quality and polymer properties may result from these interactions. Gaining a better understanding of the phenomena involved will aid in the appropriate selection of packaging systems to optimize product quality.

The aroma barrier properties of a package system are important because retention of aroma and flavor

constituents and exclusion of off odors or flavors is directly related to product quality and shelf life. Loss of volatile aroma or flavor constituents may occur by two packaging related mechanisms:

(1) The mass transfer of vapor into or out of the package.

(2) Sorption of organic volatiles by the packaging material.

This study was designed to determine the specific interactions between a package (polystyrene container) and product whose quality is associated with retention of volatile flavor and aromas. The product studied was an onion/garlic flavored sour cream dip susceptible to the following package interactions:

(1) Loss of flavor or aroma due to permeation through the package or sorption by the package wall.

(2) Absorption of off odors or flavors from products stored in the same area.

To monitor permeation and sorption of volatile constituents, probe compounds were selected based on their contribution to the aroma and flavor profile of the product. Dipropyl disulfide and dimethyl disulfide were used as probes because of their prominence in the aroma/flavor profile of the product, their ease of analysis, and availability.

A quasi-isostatic method of analysis was developed to determine the transmission rate of probe compounds through the test material (high impact polystyrene). To quantify permeating volatile constituents, gas chromatographic analysis was performed on samples taken from the free volume of the permeation cell. Sorption of probe compounds by the test materials (high impact polystyrene, high density polyethylene, and polypropylene) was determined using a gravimetric technique. Studies were conducted over a range of temperatures for each test material and probe compound. Desorption of probe compounds by each test material was also determined.

Sensory analysis was conducted to evaluate the extent of off flavor absorption by unflavored sour cream samples which had been stored under controlled conditions in close contact with onion/garlic flavored sour cream.

LITERATURE REVIEW

SORPTION AND PERMEATION BEHAVIOR OF FOOD CONTACTING POLYMERS

The ability of a packaging system to prevent loss of volatile, low molecular weight organic compounds from foodstuffs directly influences product quality and shelf life. Organic vapors such as aroma compounds often exist in food products at low concentrations, yet contribute extensively to the product flavor profile (Parliment, 1987). Loss of these constituents may adversely affect flavor intensity. Knowing the solubility of flavor and aroma compounds in polymer structures is essential to avoid "flavor scalping" or loss due to sorption (Hernandez et al., 1986). Since volatile aroma compounds may normally exist at very low concentrations in foodstuffs, there is the potential for loss of flavor and aroma constituents due to absorption by the contacting packaging material (i.e., solubilization). Further, knowledge of both permeation and sorption more completely describes the transport properties of volatile aroma constituents to polymeric packaging materials. The importance of both permeability and sorption to product quality is emphasized in recent studies describing penetrant/

polymer interactions (Berens, 1978; DeLassus, 1985; Mohney, 1986). It is possible for sorption interaction to be important and sometimes even dominant in food/polymer interactions (DeLassus, 1985).

Limonene has often been used as a probe compound in sorption/permeation studies. Limonene is a common flavor component present in citrus products and has a relatively high solubility in polyolefins (Mohney, 1986). DeLassus (1985) determined the effect of barrier location on sorption and permeation using limonene as the permeant compound. He found that the sorption interaction could be minimized by placing the barrier layer on the inside surface of the container. Hirose (1987) studied the influence of limonene absorption on the mechanical and barrier properties of polyethylene and two types of Surlyn®. Absorption of limonene was found to affect modulus of elasticity, tensile strength, percent elongation, seal strength, impact resistance, and oxygen permeability of the film. Mohney (1986) performed permeability and solubility tests on cereal package liners using limonene as the penetrant vapor. Both permeability and sorption were important in loss of limonene vapor from the intact package. Berens (1978) found that absorption of limonene by polyolefin structures caused swelling of the polymer matrix. This swelling altered diffusion, permeability, and solubility properties of the material.

Unlike inert gases such as oxygen and carbon dioxide, organic vapors exhibit non-ideal diffusion and solubility due to interaction with packaging materials. Swelling of the polymer matrix by sorbed organic vapors alters the configuration of polymer chains, resulting in concentration dependent diffusion (Bagley and Long, 1958; Fujita, 1961; Crank, 1975; and Berens, 1977).

Permeability of the polymer must be described as a function of penetrant diffusion (D) and penetrant solubility (S). The diffusion coefficient (D) represents a measure of the ease with which a penetrant molecule moves through a membrane, while (S) describes the number of penetrant molecules permeating the barrier (Crank and Park, 1968). For fixed or noninteractive gases, the permeability coefficient ($\overline{P}$) is related to two fundamental mass transfer parameters by:

$$\overline{P} = D \times S$$

This relationship is not applicable to organic permeants or multilayer laminant structures. Concentration dependency caused by swelling of the polymer matrix results in non-ideal diffusion and solubility properties (Bagley and Long, 1958; Fujita, 1961; Crank, 1975; and Berens, 1977). For such systems it is necessary to characterize diffusion, solubility, and permeability behavior to completely describe mass transfer between organic vapors (such as aroma compounds) and polymeric barrier structures.

HIGH IMPACT POLYSTYRENE: CHARACTERISTICS

High impact polystyrene is used extensively for protecting, storing, and serving many different food products (Monte and Landau-West, 1982). The wide range of physical properties and available formulations make polystyrene an attractive alternative to more expensive resins (Swett, 1986).

In Appendix I, Table 6, the physical properties of HIPS are shown. Polystyrene is the most widely used resin in packaging with an estimated 838MM lb consumed or 46% of the 1985 total resin consumption for miscellaneous plastic containers. A major portion of this resin is converted into tubs used to package such foods as cottage cheese, sour cream, margarine, and delicatessen foods (Rauch, 1985). Impact polystyrene has most of the advantages of polystyrene such as rigidity, ease of fabrication, and color and granule size availability. In addition, impact polystyrene has proven to be both tough and resistant to abuse (Herman et al., 1964). To enhance its toughness, high impact polystyrene usually contains 5-10% polybutadiene or styrene-butadiene copolymer.

Bergen (1968) investigated the effect of solvent contact on stress cracking in styrene polymers. Stress cracking can be defined as external or internal cracks in a plastic caused by tensile stresses less than that

of its short-time mechanical strength. The development of such cracks is frequently accelerated by the environment to which the plastic is exposed (Beckman et al., 1979). To reduce stress cracking and improve overall strength, Bergen suggested use of a rubber copolymer with a particle size of 2-5 microns.

Some contacting substances may cause substantial change in the structure and properties of HIPS. vom Bruck et al. (1981) found that interactions between HIPS and fat containing foods are so intense that under stress the containers often suffer from stress cracking. In vom Bruck's et al. research the presence of stress cracks indicated a definite interaction with a food component (i.e., fat). The reverse situation, no stress cracking, no interaction, cannot be assumed. Monte and Landau-West (1982) have shown certain foods to be incompatible with polystyrene. This incompatibility was due to the dissolution of polystyrene by certain essential oils present in the foods. Phillips (1979) inferred that polystyrene was dissolved by the essential oils in a lemon flavored tea to such an extent that those who drank this mixture from a polystyrene container "will also consume an appreciable amount of the container itself in solubilized form." Monte and Landau-West (1982) found that citronella, terpinene, and limonene (constituents of many flavor oils) were excellent

solvents for polystyrene. At room temperature these compounds solubilized almost half a gram of polystyrene per gram of solvent. D-limonene was one of the most active of the solvents tested. Lemon oil in low concentrations such as in lemon tea, was absorbed almost completely by the contacting polystyrene. Rapid loss of certain flavor components from orange juice packaged in polystyrene was shown by Durr et al. (1981). Orange juice packaged in glass experiences a much lower rate of flavor loss.

ONION FLAVOR COMPONENTS

The flavor compounds found in onion are extremely complex. Abraham et al. (1976) described a total of 74 compounds identified in fresh and processed onion. Members of the genus Allium (onions, garlic, leeks, chives, etc.) possess strong characteristic aromas and flavors not found in other vegetables. Stoll et al. (1951) found that the characteristic odor of onion is produced by volatiles enzymatically produced when injury occurs. Most members of this genus have no odor unless the plant tissue is cut or damaged in some way. The most important volatile flavor and aroma constituents of onion have been identified as sulfur containing compounds (Wahlroos and Virtanen, 1965; Bernhard, 1966).

Whitaker (1976) noted that 26-34 sulfur compounds have been isolated from intact onion. Of these, 8 account for 90% of the total sulfur content of onion. Saghir et al. (1964) and Bernhard (1968), found that the di- and tri-sulfides are the primary flavor components of the Allium family. Bernhard (1968), was able to quantify the disulfide volatiles in fresh onion and reported the results in descending order of concentrations: di-n-propyl, n-propyl allyl, methyl-n-propyl, methyl allyl, dimethyl, and diallyl. Bernhard (1968) found this order to be markedly altered in dehydrated onion. Methyl-n-propyl was the principal disulfide, followed by dimethyl, methyl allyl, di-n-propyl, n-propyl allyl, and diallyl. Not only was the prominence of each sulfur compound altered, but the total quantity of volatiles was significantly decreased. Total disulfide loss ranged from 89.0% to 99.70%. Loss of all volatiles (including disulfide) averaged 98% (Bernhard, 1968). Loss in flavor intensity of dehydrated onion has been directly related to the decrease in concentration of the highly odorous dipropyl disulfide (Mazza et al., 1979; Yagami et al., 1980). Even with such significant losses, there is still a sufficient concentration of volatile components remaining in the dehydrated product to be readily detected by the human nose.

In Appendix II the approximate composition of fresh and dehydrated onion (Table 7) and physical characteristics of toasted chopped dehydrated onion (Table 8) are shown. The major loss of volatiles from dehydrated onion occurs during the slicing and/or chopping operations and is not associated with drying (Stephenson, 1949). Mazza and LeMaguer (1978) found that dipropyl disulfide was lost almost exclusively after chopping and before the onion reached a critical moisture content during dehydration. Many factors influence the retention and behavior of onion volatiles. Processing and initial concentration of solids and volatiles are among these factors (Mazza and LeMaguer, 1978). Several studies have investigated the effect of processing methods on dehydrated onion and garlic products (Pruthi et al., 1959; Bhatti and Asaghar, 1965; Mazza and LeMaguer, 1978). Accelerating the drying rate and increasing air temperature were found to enhance percent volatile retention. Saimbhi et al. (1970) studied the effect of onion variety on dehydration traits and concluded that a fresh onion with a high degree of pungency, good flavor, pure white flesh, and a low drying ratio (pounds of fresh produce to 1 lb dry) was the best candidate for dehydration.

Several methods have been developed to identify volatile components in onion. Mazza et al. (1980) used headspace sampling of dehydrated onion and gas chromatographic

analysis. All major volatile constituents found in fresh onion were retained in the dehydrated sample. Constituents with low retention times (12-15 minutes) were difficult to detect. Dipropyl disulfide was not detectable unless sufficiently rehydrated prior to analysis. Loss of dimethyl disulfide was not as great as loss of other volatiles. It remains in amounts adequate to become the dominant disulfide component of dehydrated onion (Bernhard, 1968). The measured total disulfide content of fresh and dehydrated onion differs by 89%. However, this has not adversely affected the use of dehydrated onion. They are sufficiently flavored to be used in place of raw onions by most food processors (Bernhard, 1968).

METHODS OF ANALYSIS

The fraction responsible for the aroma and flavor of foods is often composed of very low levels of compounds with widely different polarities, solubilities, and volatilities. Difficulties in analysis may result due to volatile levels which may be in the subparts per million (ppm) range. Presence of soluble and insoluble solids, as well as lipid materials, and large amounts of water may add to the problems of sample collection and preparation (Parliment, 1987). Early studies used direct

gravimetric analysis to measure loss of odor and flavor compounds from products packaged in plastic lined containers (Becker et al., 1983). In the last two decades much more effective means of flavor and aroma analysis have been developed. Sample preparation techniques for flavor analysis can be classified as follows (Parliment, 1987):

(1) Headspace sampling

(2) Headspace concentrating

(3) Distillation/extraction

(4) Direct analysis of aqueous samples

(5) Direct adsorption of aqueous samples

(6) Direct extraction of aqueous samples

A method commonly used to separate volatile compounds from foods and beverages is steam distillation followed by extraction wih an organic solvent (Parliment, 1987). The Likens-Nickerson extraction apparatus can be used to continuously and concurrently steam distill and solvent extract organic volatiles. A volatile aroma concentrate is produced which can be further concentrated for gas chromatographic analysis. Great care must be taken when concentrating the sample since losses of low-boiling volatiles and concentration of solvent impurities may result (Parliment, 1987). Mazza et al. (1980) found that headspace sampling, when compared to solvent extraction procedures, does not reliably quantify the higher boiling

point constituents of onion. The level of aroma compounds in the gaseous environment over foods is often very low. Preconcentration is often required to achieve suitable analytical sensitivities (Olafsdottir et al., 1985). This is particularily necessary if onions have been pickled, canned, boiled, fried, dehydrated, or freeze-dried, since such processing is accompanied by considerable flavor loss (Freeman and Whenham, 1974). Adsorption of volatiles onto a porous solid is a commonly used procedure to concentrate samples for analysis by gas chromatography. Tenax-GC (2-6 diphenyl-paraphenylene oxide polymer) has emerged as a widely used porous polymer for these applications (Olafsdottir et al., 1985). A headspace concentration technique was developed by Olafsdottir et al. (1985) which employed Tenax-GC adsorption of volatile compounds followed by ether extraction. Wyatt (1986) used this same technique to study off odors in foods which were present due to migration from contacting polymeric packages. Using new instrumentation, concentration of samples can be fully automated. A dynamic headspace analysis technique has been developed which significantly enhances recovery of volatiles. The Tekmar Model 4000 concentrator system (Tekmar Co., Cincinnati, OH) is designed for this application (Westendorf, 1984). Figure 1 presents a general schematic of the Tekmar gas flow system.

In dynamic headspace analysis the sample is purged with an inert gas (i.e., bubbling through a liquid sample or sweeping the headspace of a solid sample) driving volatiles into the gas phase. The purge gas is then passed through a short column containing a porous polymer adsorbent (typically Tenax-GC). The adsorbent selectively retains the sample compounds while allowing the purge gas and any water vapor to pass through. By purging in this manner, the entire organic contents of the vapor phase can be analyzed by gas chromatography. Further partitioning of the volatiles into the vapor state is accomplished by continual removal of the purge gas from above the sample. After the purge step is completed the adsorbent column is heated to desorb the organic compounds. The sample is then backflushed to the GC via a 6-port valve. A cryogenic trap is used to focus the sample prior to injection into the capillary column. Utilizing this method, detection limits of low part-per-billion levels are obtainable with a good reproducibility. The use of this technique has experienced rapid growth in recent years and is now in routine use in a number of laboratories (Westendorf, 1984).

Quantification of aroma and flavor compounds is most commonly achieved by means of flame ionization detector (FID) systems, such as that used in gas chromatographic analysis. Ionization detectors operate on the principle

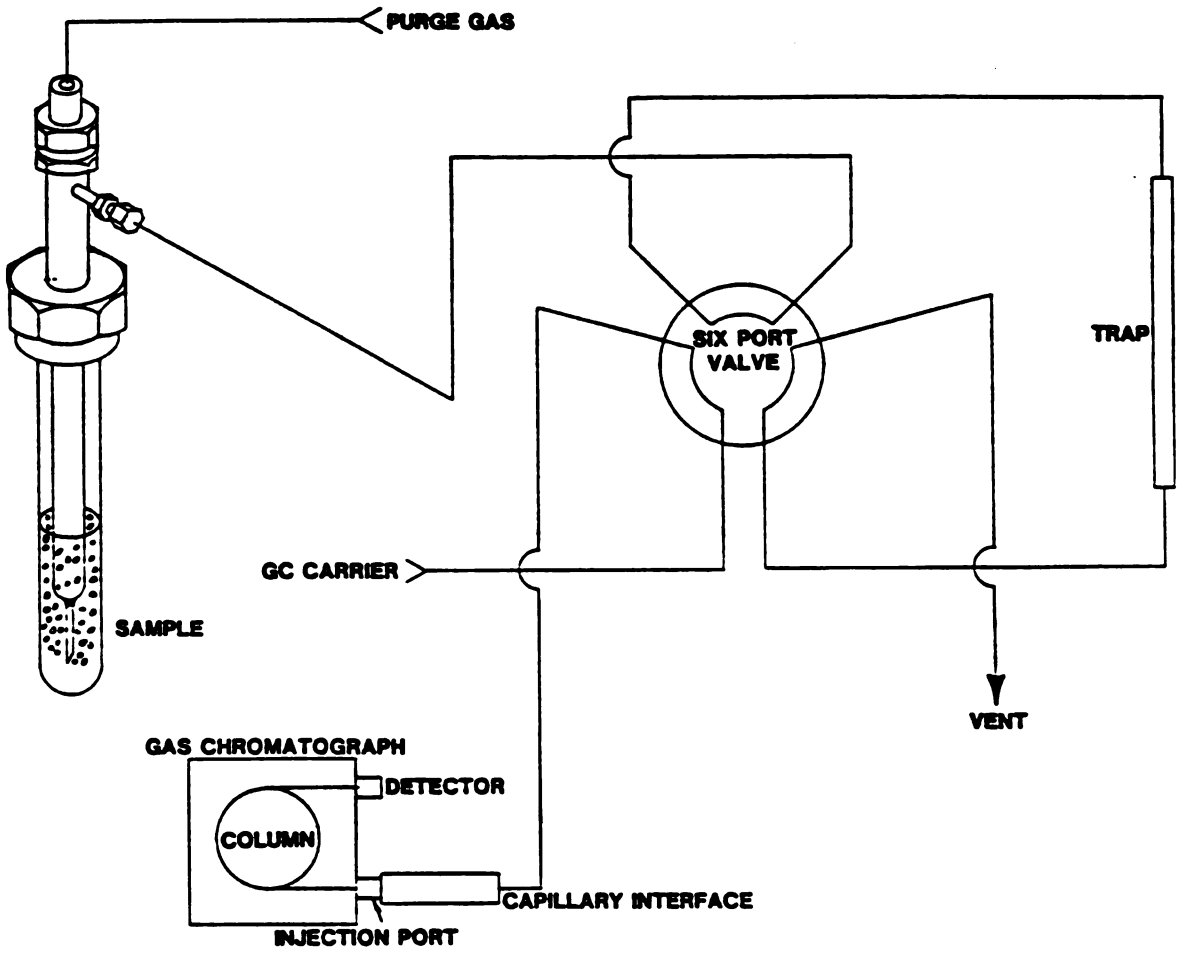


Figure 1. Tekmar Gas Flow System

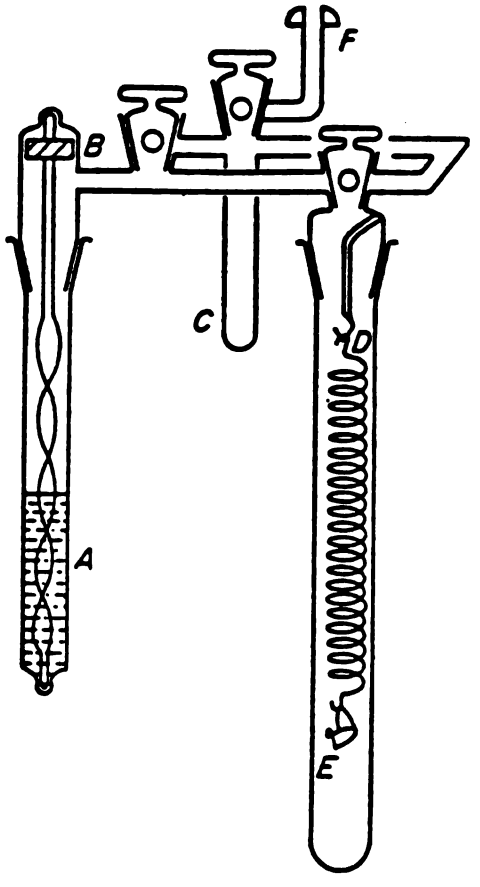
that the electrical conductivity of charged particles is directly proportional to the concentration of charged particles within the gas (Giacin, 1986). The effluent (flowing out or forth) gas from the column is mixed with hydrogen and burned in air or oxygen. The FID responds to virtually all organic compounds. The lack of response to air or water make a FID especially suitable to headspace analysis of aqueous samples. Use of gas chromatography/ mass spectometry (GC/MS) has allowed the separation and identification of over 70 flavor constituents in onion. The combination of gas chromatography and mass spectrometry provides unequivocal identificaton of compounds. The basic principle of the mass spectrometer involves exposing a sample to an energy source which can be converted into measurable products which are characteristic of the original molecule. When the energy source is a beam of electrons, a total mass spectrum is recorded. The relative abundance of positive ions created as the beam bombards the sample is displayed versus the ion mass (Giacin, 1986).

Methods of sorption measurement are quite varied. The simplest method is to weigh the polymer before and after sorption has occurred (Crank and Park, 1968). A specimen of known shape and size is held in an atmosphere of constant penetrant vapor pressure and is withdrawn and

weighed at various time intervals. Interruption of the sorption process at weighing produces errors and has resulted in the development of more accurate procedures. Polymer mass can be directly measured by suspension from a quartz spring. A schematic diagram of this test apparatus is shown in Figure 2. The mass of a specimen of known dimensions is obtained from the length of the quartz spring. Vapor pressure in the system can be adjusted by controlling the temperature of the liquid penetrant (Crank and Park, 1968). Recording electrobalances are also available which continuously record weight changes over time (Cahn Instruments Inc., Cerritos, CA). A schematic diagram of this test apparatus is shown in Figure 3. In this method the polymer film sample is suspended directly from one of the arms of the electrobalance. A constant concentration of penetrant vapor is continually flowed through the sample tube so that the polymer is completely surrounded by vapor. Gain in weight of the sample is monitored until the system attains a steady state (Hernandez et al., 1986).

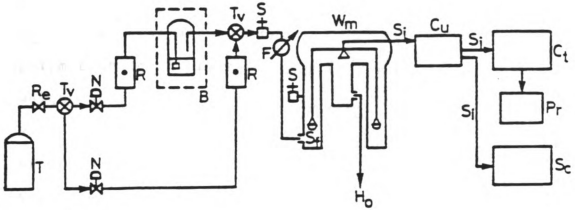
A solubility coefficient can be calculated from sorption experiments by using the following expression:

$$S = \frac{M_\infty}{\omega \cdot b}$$



A - Stirred Vapor Source
B - Magnetic Stirrer
C - Cold Thimble for Desorption
D - Quartz Spring
E - Polymer Specimen
F - Ball Joint to Vacuum System

Figure 2. Quartz Spring Sorption Apparatus



B	- Water bath, generation of permeant Vapor phase diluted in Nitrogen	R	- Rotameter
		R_e	- Regulator
		S	- Sample port
C_t	- Computer terminal	S_f	- Sampling film
C_u	- Control unit	S_c	- Strip chart
F	- Gas flow bubble meter	S_i	- Electrical input/ output signal
H_o	- Hood		
N	- Needle valve	T_v	- Three way valve
P_r	- Printer	W_m	- Cahn electrical balance
T	- Nitrogen tank		

Figure 3. Electrobalance Sorption/Desorption Apparatus

where S is the solubility coefficient expressed as mass of vapor sorbed at equilibrium per mass of polymer per driving force concentration or penetrant partial pressure. M_∞ is the total amount (mass) of vapor absorbed by the polymer at equilibrium for a given temperature. ω is weight of the polymer sample being tested, and b is a value of the penetrant driving force in units of concentration or pressure. This expression can be applied to organic vapors exhibiting non-ideal diffusion, as well as non-interacting penetrants (Hernandez et al., 1986).

SENSORY ANALYSIS

The analysis of onion flavor has proven to be extremely complex. Whitaker (1976) pointed out that for the Allium species, terms such as flavor, aroma, and pungency have no universally recognized meaning. Pungency is most often related to the eye-tearing or lachrymal effect raw onions induce when they are being disintegrated. Flavor and aroma are a reflection of the quantitative and qualitative alkyl and alkenyl di- and tri-sulfide and thiosulfonate composition of Allium, modified by soluble sugar composition, aldehydes and alcohols (Whitaker, 1976). Saghir et al. (1964) and Bernhard (1968) made quantitative correlations between subjective measurements of onion pungency and actual disulfide content. Dimethyl disulfide

was described as having a strong cabbage-like odor, while dipropyl disulfide had an odor typically associated with the common onion (Bernhard, 1968). Boelens et al. (1971) determined threshold levels for several onion compounds dissolved in water. Dipropyl disulfide was found to have a threshold value of 3.2 parts-per-billion (minimum detectable level). Other research has indicated that this is not the most sensitive organoleptic threshold measurement. Parker and Stabler (1913) have shown the sense of smell to be much more highly developed than the sense of taste. The human sense of smell can readily detect the quality of a food product, but unfortunately odors cannot be quantitatively measured by the nose (Mohney, 1986).

Sensory evaluation has been defined as "a scientific discipline used to evoke, measure, analyze, and interpret reactions to those characteristics of foods and materials as they are perceived by the senses of sight, smell, taste, touch, and hearing" (IFT, 1981). The selection of appropriate individuals for participation in trained (analytical) panels is essential to obtain effective panel performance (Larmond, 1977). Highly trained panelists are useful for evaluating product quality. Untrained panelists may be more effective in predicting the response of a typical consumer to a product. Since randomly selected and untrained panelists are variable

in their judgments, large panels are needed to yield significant results (Amerine et al., 1965).

Several precautions must be taken during sensory evaluation. Thirty minutes prior to testing, panel members should avoid such things as coffee, mints, smoking, perfume, and any other substance which might reduce sensitivity to product flavor (Larmond, 1977). The sensory evaluation room should be properly ventilated, odor free, well illuminated, and partitioned between individual panelists. The number of samples presented to the panelist must be controlled to prevent sensory fatigue (Larmond, 1977).

The type of sensory test to be performed must be chosen with care. Appropriate panelists and method of sample evaluation must be controlled to gain meaningful results. One of the most commonly occuring industrial applications of sensory analysis is evaluation of samples for storage stability.

Product stability during transportation, warehousing, retailing, and during storage in the home is essential to consumer satisfaction (IFT, 1981). To establish information regarding product shelf life, representative samples are subjected to controlled storage conditions and evaluated at specific time intervals. Generally, comparision is made to a control which has been held under conditions known to maintain the original product quality

(IFT, 1981). Difference and descriptive tests may be used simultaneously to characterize and/or quantify changes occurring during storage. Both tests are often used effectively with untrained panelists.

There are several types of difference, sensory evaluation tests (Amerine et al., 1965). These include:

(1) Paired-comparison

(2) Duo-Trio

(3) Triangle

(4) Ranking

(5) Rating difference/scalar difference from control

These tests are described as follows (IFT, 1981):

(1) Paired-comparison -- two coded samples are evaluated simultaneously or sequentially in a balanced order of presentation. There are two variations to this test:

   a. Simple difference -- the panelist indicates whether there is a difference between the samples. The panelist is told beforehand that the samples in each trial set to be tested may be identical or different. Complete randomness of presentation is essential so that the panelist responds to each trial set independently.

b. Directional difference -- the panelist chooses the sample within each pair that has the greater amount of a specified characteristic. A forced choice (no indeterminate answers) is required. The chance probability of selecting one sample over another within individual pairs is one-half.

(2) Duo-Trio -- this test employs three samples, two identical and one different. One sample is identified as the standard and presented first, followed by two coded samples, one of which is identical to the standard. The panelist must identify the sample which matches the standard. A forced choice is required. The chance probability of selecting the matching sample is one-half.

(3) Triangle -- this test employs three coded samples, two identical and one different. All samples are presented simultaneously. The panelist must determine which of the three samples presented differs from the other two. A forced choice is required. The probability of choosing the different or odd sample by chance alone is one-third.

(4) Ranking -- this test is used to make simultaneous comparisons of several samples on the basis of a single characteristic. Samples are presented simultaneously and ranked according to intensity of the characteristic designated; no ties are allowed. Rank totals or average ranks are obtained for each sample.

(5) Rating Difference/Scalar Difference from Control -- this test is used when a control sample is available for comparison with one or more experimental samples. All samples are presented simultaneously. Samples are rated on a scale typically ranging from "no difference from control" to "very large difference from control." Statistical analysis of the data is used to show whether the degree of difference from the control is significant.

Statistical interpretation of data obtained from sensory analysis must be handled with care. Sensory experiments yield measures of human judgment and are called subjective or sensory data (Gacula and Singh, 1984). In tests where a control sample is presented, statistical analysis is used to show whether the degree of difference from the control is significant (IFT, 1981). One commonly used statistical method is the Student's t Test. This test determines whether the means of scores

from two samples are significantly different (O'Mahoney, 1980). The t Test cannot be used if the sample deviates too much from a normal population. An alternative statistical procedure is called analysis of variance. This method is often used for large quantities of data. Analysis of variance partitions the total variation in data into various components and assigns them to respective causes (Gacula and Singh, 1984). Statistical evaluation may also be based upon the Chi-square test. This test can be used to determine whether or not the proportions of panelist responses to a control and test sample are the same or different. A null hypothesis is formulated (H_o) which sets the predicted panelist response (i.e., the proportions of responses for both control and test samples are the same) for the null hypothesis to be accepted. If the test results show the same proportions, then the assumption can be made that panelists do not perceive a difference in control vs. test samples. In all cases the null hypothesis is assumed to be true unless the test data proves otherwise (Bhattacharyya and Johnson, 1977).

MATERIALS AND METHODS

MATERIALS

Product/Package

The product/package system utilized in this study was Land O' Lakes Lean Cream, packaged in HIPS tubs. Plain and flavored (onion/garlic) Lean Cream was obtained directly from the manufacturer (Land O' Lakes, Minneapolis, MN) and from retail sources. Ingredients in each product were as follows:

Lean Cream - plain: Cultured sour cream, whey protein concentrate, skim milk, lactic acid, water, food starch-modified, natural flavor, agar, potassium sorbate, vitamin A palmitate.

Lean Cream - onion/garlic: Cultured sour cream, whey protein concentrate, skim milk, dehydrated onion and garlic, salt, hydrolyzed vegetable protein, monosodium glutamate, dextrose, spice, disodium inosinate and guanylate, lactic acid, water, food starch-modified, natural flavor, agar, potassium sorbate, vitamin A palmitate.

The product was contained in thermoformed, rigid high impact polystyrene cylindrical 8 ounce (236.56 ml) or 16 ounce (473.12 ml) tubs. Sandusky Plastics Inc. produced the tubs using extrusion grade resin (Chevron EA 6750) manufactured by Chevron Chemical Company (Houston, TX). Polypropylene and high density polyethylene were also obtained for sorption studies. The polypropylene was taken from portions of an 8 ounce (236.56 ml) margarine tub provided by Land O' Lakes. In Appendix III, Table 9, are listed the package specifications for the polystyrene and polypropylene tubs. Polypropylene resin for this tub was supplied by Shell Chemical Company (Houston, TX). The high density polyethylene was taken from portions of a one-half gallon (1.89 ℓ) unused milk container supplied by Soltex Polymer Corporation (Houston, TX). In Appendix III, Table 10, are listed the properties of the polypropylene and high density polyethylene materials (see Appendix I for polystyrene properties).

Probe Compounds

The principal flavoring constituent of the product to be tested is from onions. Review of pertinent literature indicated that the characteristic odor and flavor of onions is due to volatiles consisting mostly of sulfur

compounds. A Likens-Nickerson (Parliment, 1987) extraction was performed on the flavored product and toasted, chopped, dehydrated onion ingredient obtained from Land O' Lakes. A 1.5 ul sample of each extract was analyzed using GC to identify the predominate peaks (see Methods and Materials Analytical Section for conditions of analysis). Several sulfur compounds were investigated as possible probes. By spiking the extract with a small quantity (amount varied for each compound) of sulfur probe and analyzing by GC, the corresponding peak response could be identified. Two sulfur compounds were chosen as probes based on their contribution to the product flavor profile, chromatographic results, ease of analysis, and availability. Dipropyl disulfide and dimethyl disulfide were used for both permeation and sorption studies. Extracted onion/garlic samples were submitted for GC/MS analysis to provide unequivocal identification of the probe compounds in the product. These samples were not sufficiently concentrated to produce measurable GC/MS results for the probe compounds in question. The extract of the dehydrated onion ingredient produced a GC/MS response that enabled the positive identification of dipropyl disulfide and dimethyl disulfide in the product. In Appendix IV, Figure 23, the GC/MS scan of the two probe compounds is given (see Methods and Materials Analytical Section for conditions

of analysis). Analytical grade dipropyl disulfide was obtained from Pfaltz and Bauer, Inc. (Waterbury, CT). Dimethyl disulfide was obtained from Eastman Kodak Company (Rochester, NY). In Appendix IV, Table 11, are also listed some of the properties of these compounds.

EXPERIMENTAL METHODS

Extraction Methods

A steam distillation technique was used to separate volatiles from the test product. The Likens-Nickerson (Parliment, 1987) extractor apparatus (Figure 4) was employed to continuously steam distill and solvent extract organic volatiles from sour cream and dehydrated onion. Isopentane (2-methyl-butane) was chosen as the solvent because of its low boiling point which minimizes thermal decomposition. The nonpolar nature of this solvent minimizes mercaptan-disulfide exchange reactions (Carson and Wong, 1961). A known quantity of product (50-100 g) was placed in a 2,000 ml round-bottom flask with approximately 500 ml distilled water. The distilled water functions to disperse solid samples and aid heating. Duplicate samples may be simultaneously extracted. The contents of the flask were heated at 65^{o}C until the sample began to boil (approximately 1 hour). After boiling, the temperature was decreased to 50^{o}C and the

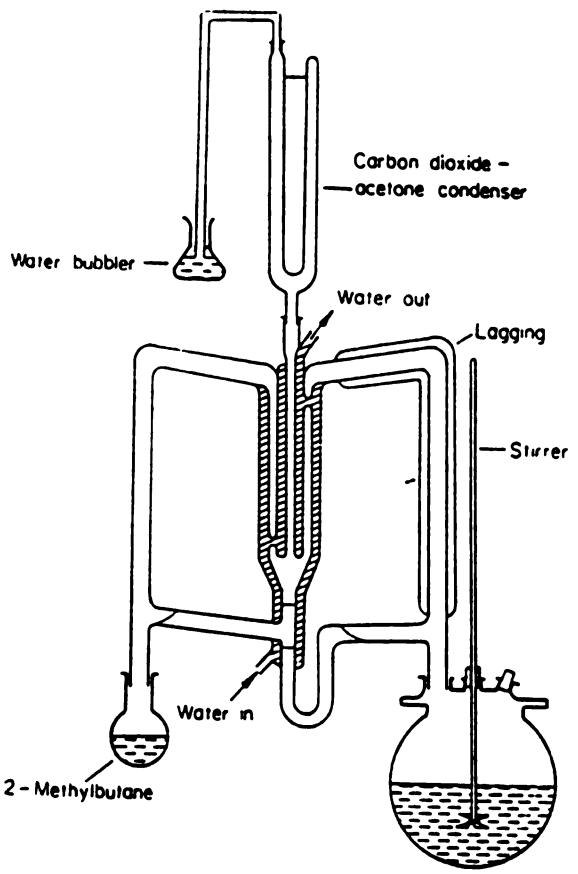


Figure 4. Modified Likens-Nickerson Distillation Apparatus

contents allowed to distill for 4-6 hours. Condensing coils were maintained at 20^{o}C throughout the extraction process. During the distillation process the sample was monitored to prevent excessive boiling. Samples of unflavored sour cream experienced a great deal of foaming during the extraction process. To decrease foaming, addition of an antifoam agent such as dimethyl polysiloxane (silicone oil) can be used to reduce surface tension created by heating (Fennema, 1976). After heating, the distillate was passed through glass wool and/or sodium anhydride to remove impurities. This procedure was used successfully to remove volatiles from samples of sour cream and dehydrated onion. An analytical evaporator providing a constant flow of nitrogen (Meyer N-EVAP, Organomation, Northborough, MA) was used to concentrate samples to 1.5 ml prior to GC analysis. Loss of probe volatiles due to extraction and concentration was quantified by determining percent recovery for each sulfur compound. Dipropyl disulfide (.56 g) and dimethyl disulfide (5.63 x 10^{-4} g) were added to the sour cream and water solution before extraction. After the distillation is completed, a 1.0 ul sample of extract is analyzed using GC. A unit area response is obtained which can be compared to the unit area response of the probe compound before extraction. Based on this comparison, percent recovery

can be calculated to show the loss of volatiles due to extraction. By concentrating the same sample extract to 1.5 ml prior to GC, percent loss due to concentration was determined. Using both methods, a percent recovery was calculated for each probe compound to account for volatiles lost during extraction and/or concentration.

Sorption Measurements

A gravimetric procedure was employed to determine sorption of probe compounds by test materials. Specimens of a known initial weight were cut from HIPS and polypropylene tubs and high density polyethylene milk containers. Glass jars (250 ml capacity) with threaded screw cap closures were used to contain the sample and probe solution. A sufficient quantity of solution was added to cover the bottom of the jar to insure that a constant saturated vapor pressure was maintained. Each test sample was suspended over the probe solution by attachment to a metal hook secured to the jar cap. Samples were withdrawn and weighed at various time intervals. The gain in weight of the sample due to penetrant (i.e., dimethyl disulfide, dipropyl disulfide) vapor sorption was monitored using a Mettler AE 160 analytical balance (Hightstown, NJ) until the system attained a steady state. This procedure was repeated

for both probe compounds for each test material over a range of temperatures as follows:

High impact polystyrene -	-17°C±2°C, 5°C±2°C, 26°C±1°C, and 35°C±1°C
Polypropylene -	5°C±2°C, 26°C±1°C, and 35°C±1°C
High density polyethylene -	26°C±1°C

All samples were weighed at room temperature which was 24°C±3°C. Percent sorption for each probe and test material combination was determined. Following attainment of steady state, desorption of test materials was measured for each material-probe combination.

Samples were removed from the jar and suspended in a well-ventilated area at room temperature (24°C±3°C). The decrease in weight of the sample due to penetrant desorption was monitored until the sample weight remained constant. Percent desorption for each probe and test material was thus determined.

Equilibrium Vapor Pressure

Equilibrium vapor pressure for the pure probe compound and the probe in a simulant system (unflavored sour cream) was determined at several temperatures and concentrations. Simulant systems were prepared by adding 20 ppm, 100 ppm, and 1,000 ppm of pure probe compound to the unflavored sour cream. Extracts of the flavored sour cream were

analyzed by GC to obtain unit area responses for each probe. The peak responses for dimethyl disulfide and dipropyl disulfide were identified by spiking the extract with a small quantity of each probe. By reference to a standard curve, (Appendix V, Figures 24 and 25) quantities (expressed as parts-per-million) of the probes in the actual product were determined. Compensation was made for volatile losses due to extraction and concentration.

Glass, 35 ml septa seal vials were filled with the unflavored sour cream and probe to within one-half of their volume and sealed with an aluminum crimp closure and Teflon®/silicone sampling septum. Samples were stored at $5^{o}C \pm 2^{o}C$ ($278^{o}K$), $26^{o}C \pm 1^{o}C$ ($299^{o}K$), and $35^{o}C \pm 1^{o}C$ ($308^{o}K$). After allowing the system to equilibrate (approximately 1 week), a 500 ul sample from the headspace volume was withdrawn with a gastight syringe. The sample was analyzed by GC to determine unit area responses. By reference to standard curves for each probe, equilibrium vapor pressures (expressed as parts-per-million) were determined for each system. Successive samples were withdrawn over time to insure that the system had reached equilibrium. A sufficient number of vials were prepared so that each sample was removed from a vial which had not been previously punctured.

Permeation Measurements

A quasi-isostatic method of analysis was employed to determine the transmission rate of the probe compounds through the HIPS test package. A glass permeation apparatus was designed to contain the intact package and allow direct sampling of the free volume surrounding the container. A picture of this apparatus is presented in Figure 5. Glass was utilized to construct the permeation cell to minimize surface adsorption of volatile components. Methyl ethyl ketone, an aggressive organic vapor, was used to determine integrity of the cell. The cell was flushed with methyl ethyl ketone vapor to obtain concentrations measurable by GC analysis. Samples were then taken over time to monitor the concentration of vapor remaining in the cell. A 500 ul sample was withdrawn from the sample port using a glass, gastight 500 ul syringe (Hamilton Co., Reno, NV). The samples were analyzed by GC to quantify vapor concentration. This method was used to test several different cell closures to determine which was the most effective. For each closure system, a relationship between percent methyl ethyl ketone vapor loss and time was developed. Results for each closure system are presented in Figure 6. The Teflon® gasket was chosen as the method of closure to use for permeation

Figure 5. Permeation Cell


LAND-O-LAKES
HALF THE FAT, ALL THE FLAVOR
NET WT. 8 OZ

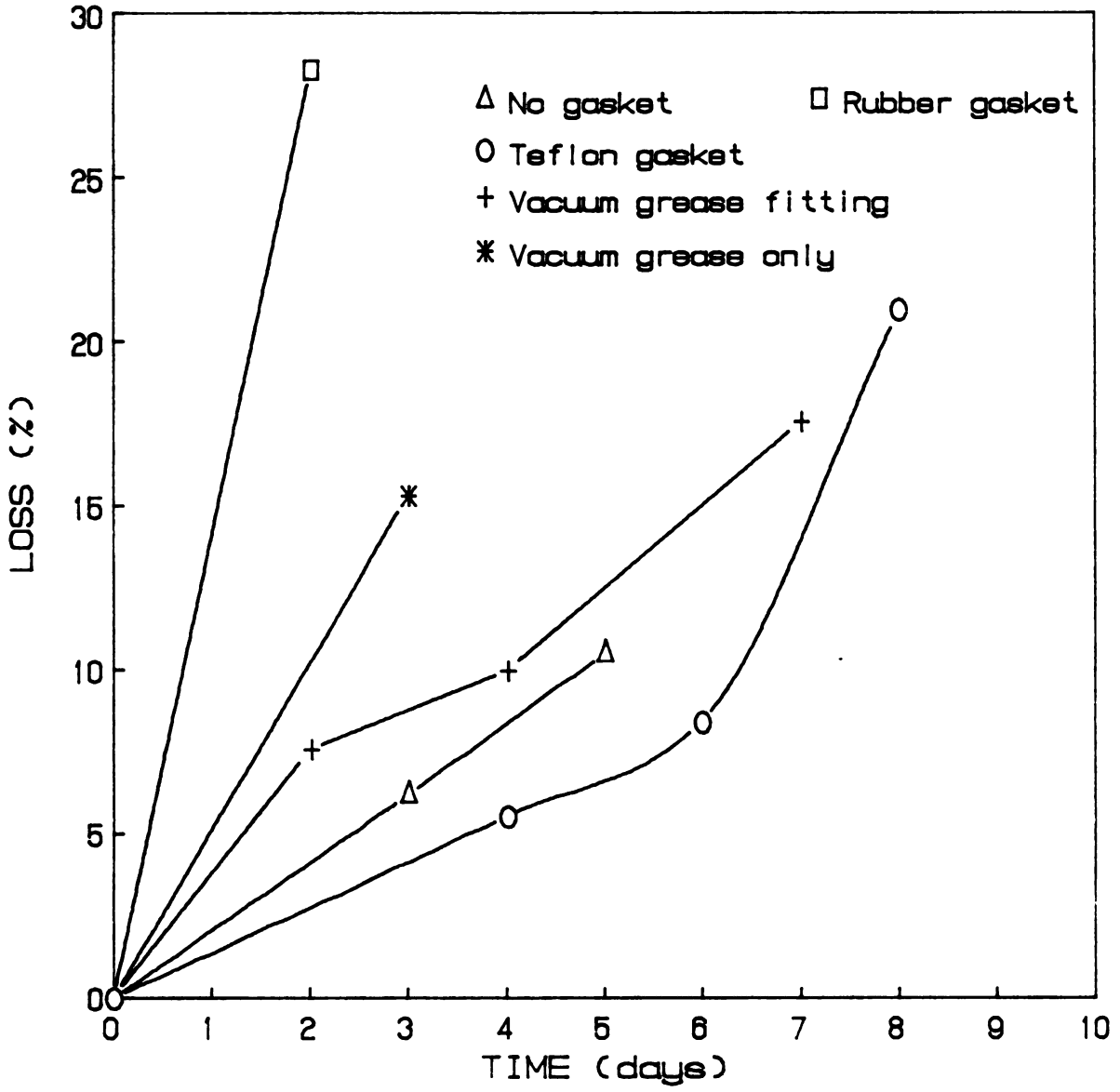


FIGURE 6. *PERMEATION CELL INTEGRITY TEST*

studies because it allowed the least amount of leakage over the initial testing period (0-6 days).

The onion/garlic product packaged in a HIPS tub was placed in the cell. 500 ul samples were withdrawn as a function of time to monitor compounds permeating through the package into the surrounding free volume. Without preconcentration of samples it was not possible to detect any permeating vapors by GC analysis. Tests were conducted over a period of 8 weeks at room ($24^{o}C/75.2^{o}F$) and refrigeration ($5^{o}C/41^{o}F$) temperatures.

To concentrate samples prior to GC analysis, Tenax (Anspec Co. Inc., Ann Arbor, MI) traps were fitted to the effluent sample port to collect volatile compounds from the cell. The permeability cell was then flushed with nitrogen for several hours (6-48). The Tenax traps were fabricated from 9-inch Pasteur disposable pipettes. Glass wool was used to position the Tenax in the pipette. Once the cell was flushed, the trapped compounds were eluted from the Tenax by washing with a suitable solvent. In this study, 1 ml of isopentane was gradually added and allowed to penetrate the Tenax. The trap was then centrifuged (IEC Clinical Centrifuge, Needham Hts., MA) at 650 rpm for approximately 1 minute or until the solvent collected in the bottom of the sample tube. This process was repeated 2-3 times. The 2-3 ml of collected extract

was then concentrated to 1.5 ml using an analytical evaporator (Meyer N-EVAP, Organomation, Northborough, MA).

Samples were injected into the GC using a precooled standard glass 10 ul syringe (Hamilton Co., Reno, NV). Sample sizes ranged from 1-2 ul depending on the concentration and amount of the collected extract.

ANALYTICAL

Gas Chromatography

For each probe compound, a standard curve of response vs. penetrant concentration was constructed from standard solutions of known concentration. In Appendix V are the standard curves for dimethyl disulfide (Figure 24) and dipropyl disulfide (Figure 25). Standard solutions were prepared by the addition of a known volume of isopentane to a known volume of probe compound. A 1.0 ul sample at each concentration level was analyzed by GC to obtain peak responses. By reference to the standard curves, penetrant concentrations were quantified.

A Hewlett Packard gas chromatograph, Model 5890A equipped with dual flame ionization detection (FID) and splitless injection port was used for all analyses. GC conditions were as follows:

Column - 60 meter

0.25mm I.D.

Fused silica capillary

Polar bonded stationary phase

Supelcowax 10 (Supelco, Inc., Bellefonte, PA)

Carrier gas - Helium at 30 ml/min

Oven temperature setpoint - 40°C

Injector temperature - 200°C

Detector temperature - 275°C

Initial temperature - 40°C

Initial time - 10.0 min

Temperature program-rate - 2.0°C/min

Final temperature - 180°C

Final time - 45.0 min

Gas Chromatography/Mass Spectrometry

Samples of onion/garlic flavored product and a dehydrated onion extract were submitted to a mass spectrometry laboratory (Mich. St. U.) for analysis to confirm the presence of dipropyl disulfide and dimethyl disulfide probe compounds in the flavored sour cream. Samples of the pure probe compounds were analyzed to determine retention times.

The GC/MS conditions were as follows:

Gas Chromatograph - Shimadzu GC-9A (Columbia, MD) - splitless injection port

Mass Spectrometer - Model LKB 2091 Magnetic Sector Electron Impact Ionization/70eV

Column - 15 meter

0.53mm I.D.

DB-1 Megabore Capillary

J&W (Anspec, Ann Arbor, MI)

1.5 ul Film Coating

Carrier gas - Helium at 20 ml/min

Injector temperature - 100^{o}C

Detector temperature - 325^{o}C

Initial temperature - 40^{o}C

Initial time - 10.0 min

Temperature program-rate - 2.0^{o}C/min

Final temperature - 180^{o}C

Final time - 80.0 min

Dehydrated onion extract samples were analyzed under the same conditions.

SENSORY ANALYSIS

Flavored and unflavored sour cream packaged in 8 ounce (236.56 ml) HIPS containers were stored for 14 days at 37.5^{o}C±2.5^{o}C. The storage cubicle was cleaned

before using so that no contaminants were present. The products were arranged on a pallet with cases of unflavored sour cream in direct contact with cases of onion/ garlic flavored sour cream. Containers were not removed from shipping cases for storage (twelve 8 ounce containers per case). After 2 weeks of storage, the unflavored product was evaluated to determine if it had absorbed any off flavors or odors. For comparison, unflavored product was obtained that had not been exposed to other flavored products. An untrained panel of 534 participants evaluated the unflavored sour cream and the control sample. The sensory evaluation took the form of a paired-comparison/simple difference test.

In Appendix VI, Figure 26, is an example of the consent form and questionnaire presented to each panelist. Two duplicate sets of coded samples were evaluated by each panelist. In each set a test sample and control were randomly presented. The panelist indicated whether the samples were the same or different. If the samples were different, a description of the difference was requested. The sensory evaluation was conducted in a well illuminated, properly ventilated, odor free environment. Partitions separated individual panelists.

Statistical evaluation of sensory analysis results was based on the Chi-Square Test. A contingency table analysis of responses for test and control samples was prepared and the Chi-Square value determined.

RESULTS AND DISCUSSION

PRODUCT CHARACTERIZATION

Likens-Nickerson extractions performed on the onion/garlic flavored product, unflavored product, and dehydrated onion allowed characterization of the sour cream flavor components by GC analysis. A typical chromatograph for the onion flavored sour cream extract is present in Appendix VII, Figure 27. Peak responses for the two probe compounds used (dimethyl disulfide and dipropyl disulfide) were positively identified in the extracts of onion flavored sour cream and dehydrated onion. Comparison of flavored sour cream extracts spiked with the probe compound to those unspiked extracts made tentative identification possible by GC analysis. Extracts of dehydrated onion were analyzed by GC/MS. The mass spectrum of dehydrated onions contained scans which were identified as those of dimethyl disulfide and dipropyl disulfide (Appendix IV, Figure 23). The GC retention times for each probe compound were determined to be the following:

Dimethyl disulfide - 17.8 minutes

Dipropyl disulfide - 42.7 minutes

Loss of probe volatiles due to extraction and concentration of the extract was determined for each probe compound. Recoveries of dimethyl disulfide and dipropyl disulfide are presented in Table 1. Values are taken from the average results of 4 extractions performed for each standard. In Appendix VIII, Tables 12-15, are shown the data used to derive the recoveries. The total amount of each probe compound (express in ppm) in the product was determined by taking into account percent recoveries following extractions and concentration. The actual probe concentrations in the sour cream are presented in Table 1.

PERMEATION

Several closure systems were tested to determine which would most effectively seal the glass permeation cell. Methyl ethyl ketone vapor was used as the test permeant. Percent vapor loss as a function of time was quantified by GC analysis. Results for each closure system are presented in Figure 6 (Methods and Materials). Comparison of percent vapor loss for the seven closures indicated that the Teflon® gasket provided the most effective seal during the initial testing period (0-6 days). After 6 days, approximately 8% vapor loss had occurred using the Teflon® gasket. Closures tested at 8 days had experienced vapor losses of 18 and 28%. During the entire 10 day

Table 1

Recoveries of Dimethyl Disulfide and Dipropyl Disulfide from Onion Flavored Sour Cream

Probe Compound	Loss Due to Extraction	Loss Due to Concentration	Total Loss	% Recovery	Probe Concentration in Sour Cream
Dimethyl Disulfide	73.5%	8.5%	82%	18%	80.1 ppm
Dipropyl Disulfide	42.0%	16.8%	58.8%	41.2%	8.95 ppm

testing period, percent vapor loss continued to increase for all closures. Equilibrium vapor loss was not achieved, therefore it was not possible to determine a reproducible error that would account for leakage.

Following permeation cell integrity testing, permeation studies were conducted using the Teflon® gasket closure system over a time period of 6 days. The HIPS tub containing the onion/garlic flavored sour cream was placed in the cell at room ($24^{o}C/75.2^{o}F$) and refrigeration temperatures ($5^{o}C/41^{o}F$). After 6 days, no measurable permeation of probe compounds at either temperature could be detected by GC analysis. By extending the test period to 8 weeks and preconcentrating the samples using the Tenax procedure, detection of permeant compounds was possible. The peak responses could not be identified as either of the probe compounds; therefore, quantification of permeants was not possible. It was not apparent after the 8 week test as to whether permeation occurred through the container wall or whether there was leakage through the seal area. Distribution time for the sour cream normally requires less than 4 weeks (Campbell, 1987). Retention of volatiles during this time period is most crucial to maintain product quality. Since permeation (from the seal and/or through the package wall) could not be detected in this time period, it was not considered to be a primary mechanism of volatile flavor loss. Subsequent studies were focused on package/volatile sorption interactions.

SORPTION

The results of absorption and desorption studies for the 2 probe compounds (dimethyl disulfide and dipropyl disulfide) and the 3 test materials (HIPS, PP, and HDPE) are summarized in Figures 7-12. Studies were conducted at several temperatures using saturated vapor pressures for each of the probe compounds. Percent absorption and desorption were determined by quantifying the gain or loss of probe by the polymer per unit of initial polymer weight.

Absorption and desorption were monitored as a function of polymer weight change. The probe compounds were highly soluble in HIPS over the range of test temperatures ($-17^{o}C$, $5^{o}C$, $24^{o}C$, and $35^{o}C$). At $35^{o}C$, HIPS became pliable and difficult to handle after 4 days of exposure to dipropyl disulfide and after only 7 hours of exposure to dimethyl disulfide. After this time period these samples were completely dissolved in the penetrant solutions. All HIPS samples eventually dissolved in the dipropyl disulfide and dimethyl disulfide solutions; therefore, equilibrium sorption of the two probe compounds in HIPS was not obtained. This effect appeared to be independent of temperature. Probe compounds were not as soluble in the PP and HDPE polymer samples. In Table 2 times required for HIPS samples to reach maximum absorption before dissolving in dimethyl disulfide and dipropyl disulfide

penetrant solutions are given. These materials did not soften and remained intact throughout the sorption studies.

In Figure 7 is shown the absorption of dipropyl disulfide by HIPS at 4 temperatures (-17°C, 5°C, 24°C, and 35°C). Desorption of dipropyl disulfide by HIPS is shown at 24°C. Absorption and desorption of dipropyl disulfide by HDPE is also shown at 24°C. Maximum absorption of dipropyl disulfide by HIPS was 43.5% (wt/wt) after 13 days at 5°C. Further measurements were not possible since polymer samples dissolved in the penetrant solutions. At 24°C the HIPS sample desorbed 69.6% of the sorbed dipropyl disulfide. 30.4% of the probe compound initially sorbed by HIPS was retained.

Table 2

Time Required for HIPS Samples to Reach Maximum Absorption Before Dissolving in Penetrant Solutions

Temperature	Dimethyl disulfide	Dipropyl disulfide
35°C	8 hr	120 hr
24°C	8 hr	240 hr
5°C	8 hr	312 hr
-17°C	28 hr	1,020 hr

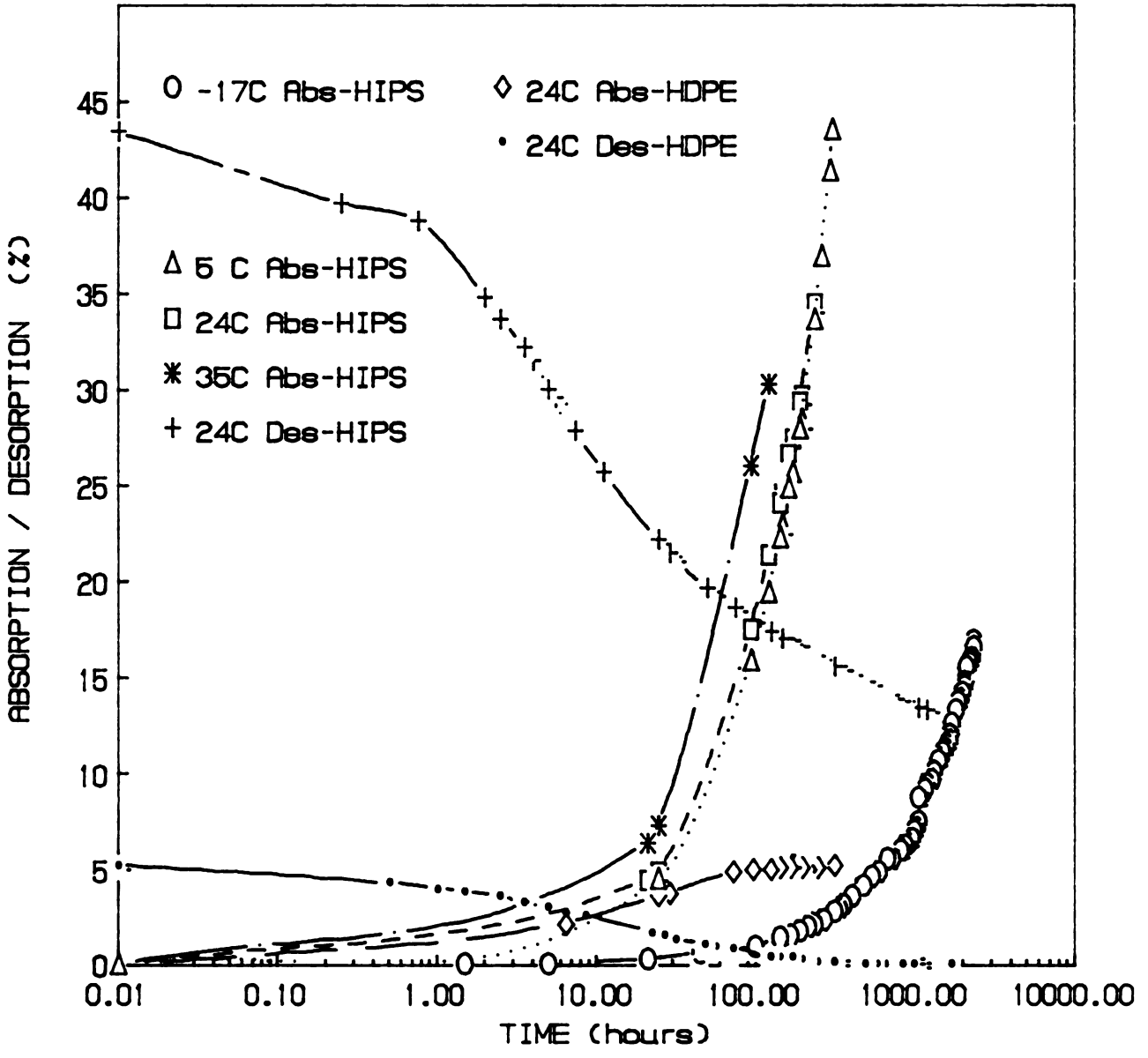


FIGURE 7. *ABSORPTION / DESORPTION OF DIPROPYL DISULFIDE BY HIPS AND HDPE*

In comparison, the HDPE sample absorbed a maximum of 5.2% (wt/wt) at 24°C and desorbed an equivalent amount. None of the probe compound was retained by the polymer.

In Figure 8 is shown the absorption of dipropyl disulfide by HIPS at -17°C, 5°C, 24°C, and 35°C. The only storage temperature which had a significant effect on the absorption rate was -17°C. The samples at 5°C, 24°C, and 35°C experienced similar absorption rates. Several investigators have established a relationship between solubility and temperature. Monte and Landau-West (1982) found a direct correlation between temperature and solubility of polystyrene in several solvents. As temperature was decreased, the solubility of polystyrene also decreased. Penetrant vapor pressures decrease with decreased temperatures. More of the penetrant will remain in the liquid phase. This results in fewer vapor molecules for the polymer to interact with; therefore, absorption rates are lowered. The HIPS sample at -17°C absorbed only 12% of the probe compound after 69 days of exposure (Figure 7). The maximum absorption at 35°C was 30% achieved in only 5 days of exposure. This comparison illustrates the dynamic effect temperature can have on absorption.

In Figure 9 is shown the absorption of dimethyl disulfide by HIPS at 4 temperatures (-17°C, 5°C, 24°C, and 35°C). Desorption of dimethyl disulfide by HIPS

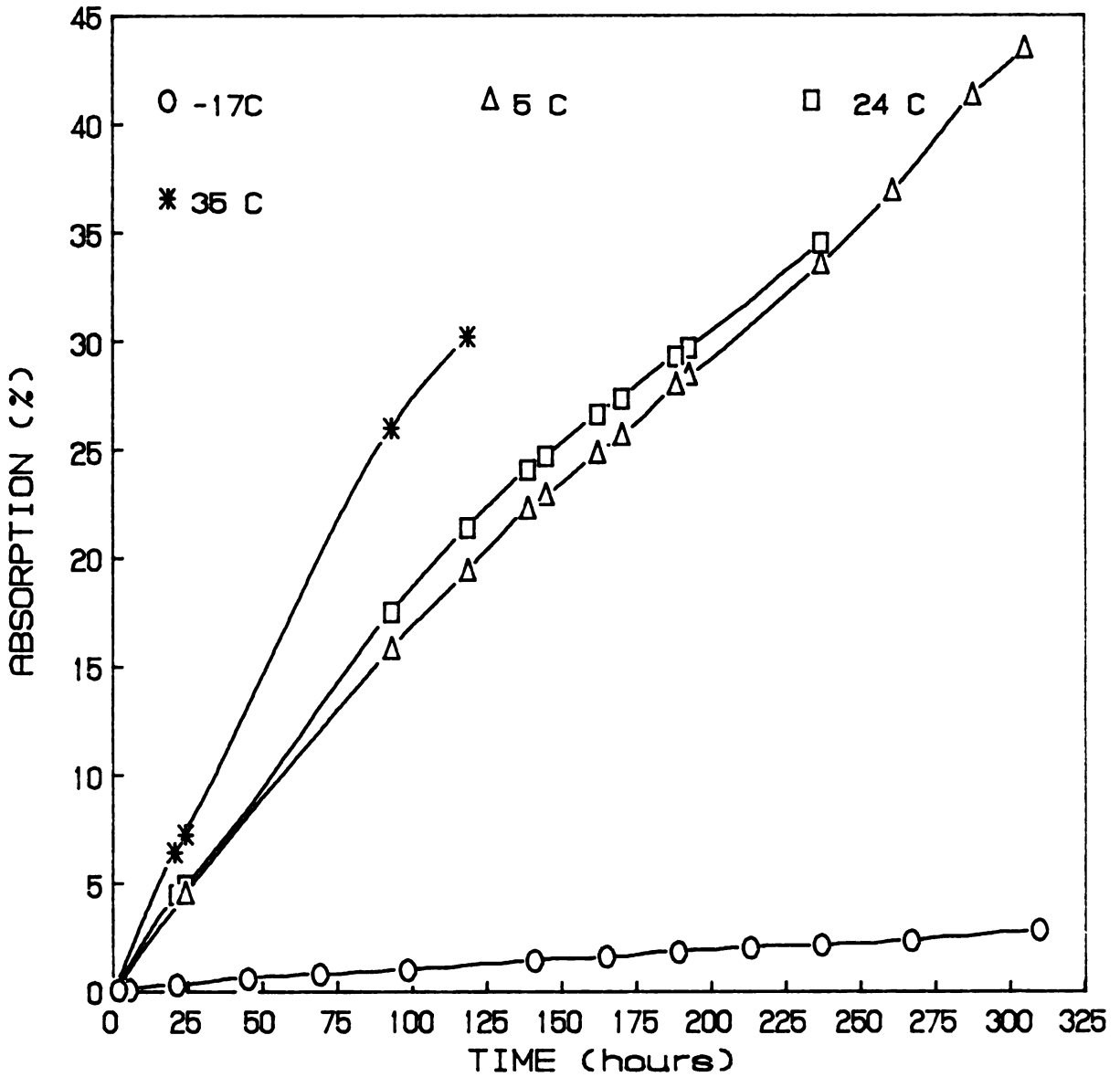


FIGURE 8. *ABSORPTION OF DIPROPYL DISULFIDE BY HIPS*

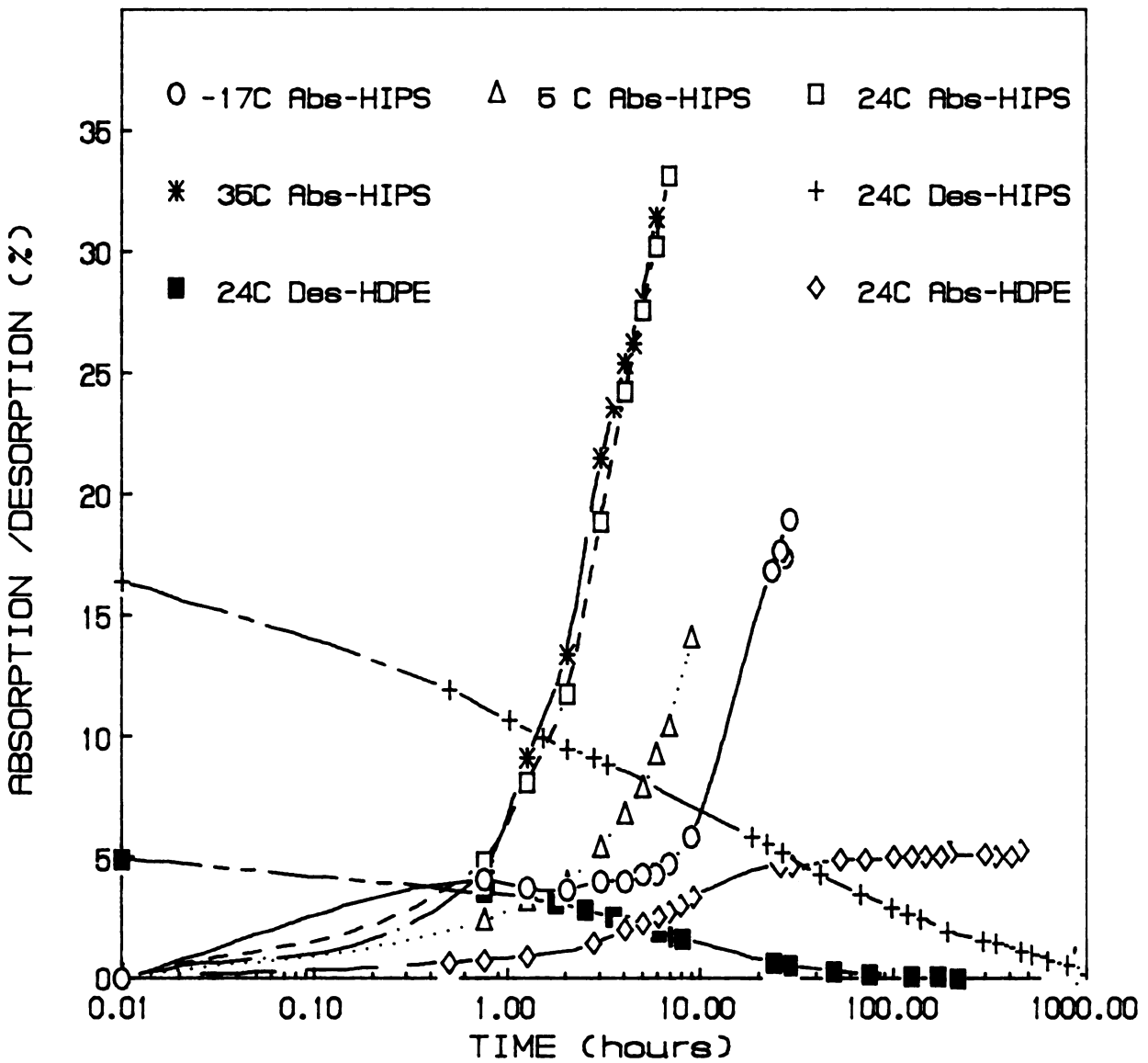


FIGURE 9. *ABSORPTION / DESORPTION OF DIMETHYL DISULFIDE BY HIPS AND HDPE*

is shown at 24°C. Absorption and desorption of dimethyl disulfide by HDPE is shown at 24°C. Maximum absorption of dimethyl disulfide by HIPS was 33.2% (wt/wt) after 7 hours at 24°C. Samples held at 35°C, 24°C, and 5°C dissolved in the penetrant solutions after 8 hours of exposure. The sample evaluated at -17°C dissolved after 28 hours of exposure to the dimethyl disulfide vapor. At 24°C the HIPS sample desorbed 99.4% of the sorbed probe compound. Only .6% of the dimethyl disulfide was retained by the polymer. In comparison, the HDPE sample absorbed a maximum of 5.4% (wt/wt) at 24°C and desorbed an equivalent amount. None of the probe compound was retained by the polymer.

In Figure 10 is shown the absorption of dimethyl disulfide by HIPS at -17°C, 5°C, 24°C, and 35°C. Polymer samples at 35°C and 24°C experienced absorption rates significantly higher than samples at 5°C and -17°C. This effect can be attributed to the increased penetrant vapor pressure at 35°C and 24°C. The polymer is exposed to more vapor molecules than those samples at 5°C and-17°C.

In Figures 11 and 12 the absorption and desorption of dipropyl disulfide and dimethyl disulfide by PP are shown. For both probe compounds, equilibrium absorption was approximately 9% (wt/wt) at all test temperatures.

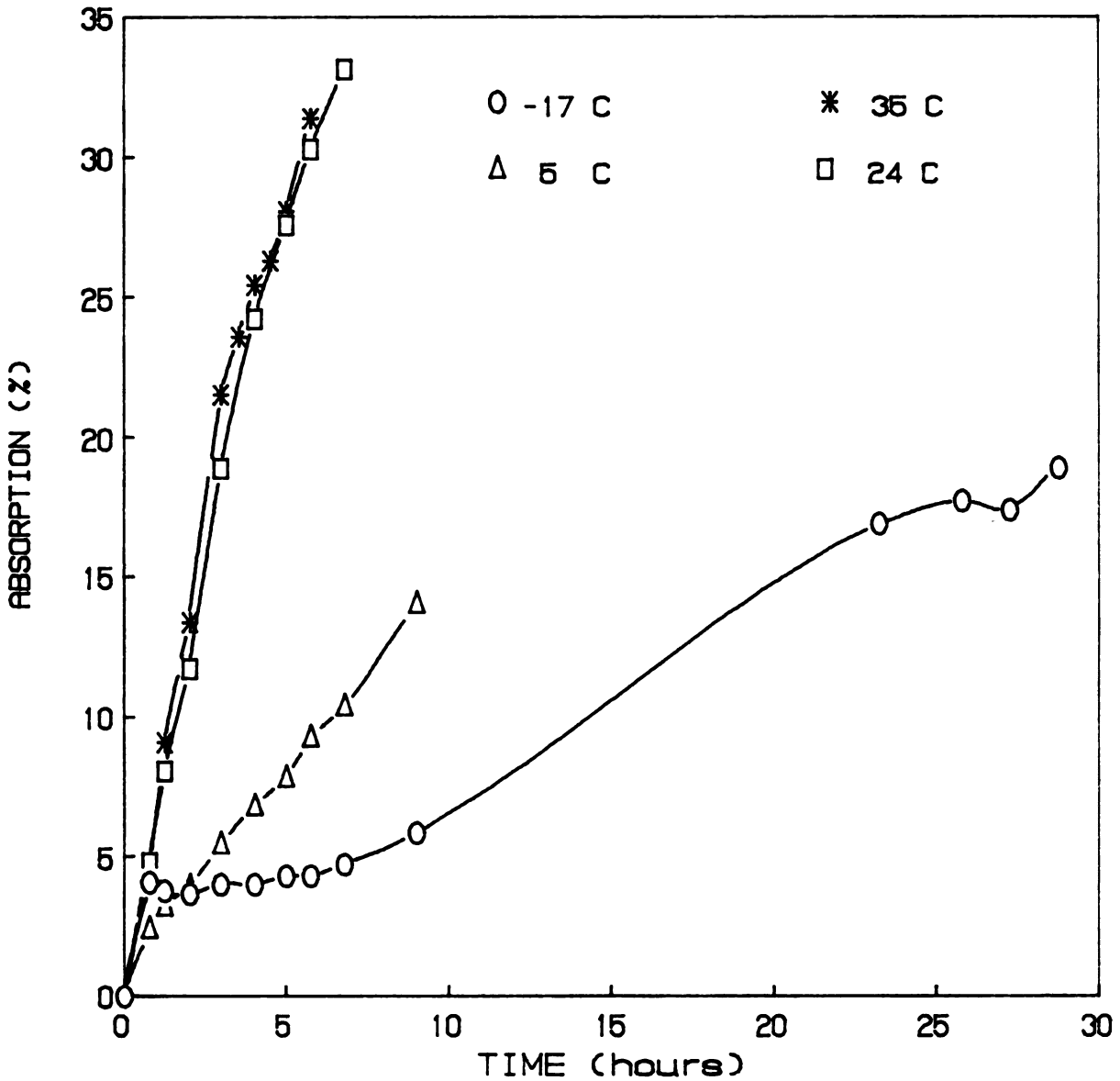


FIGURE 10. *ABSORPTION OF DIMETHYL DISULFIDE BY HIPS*

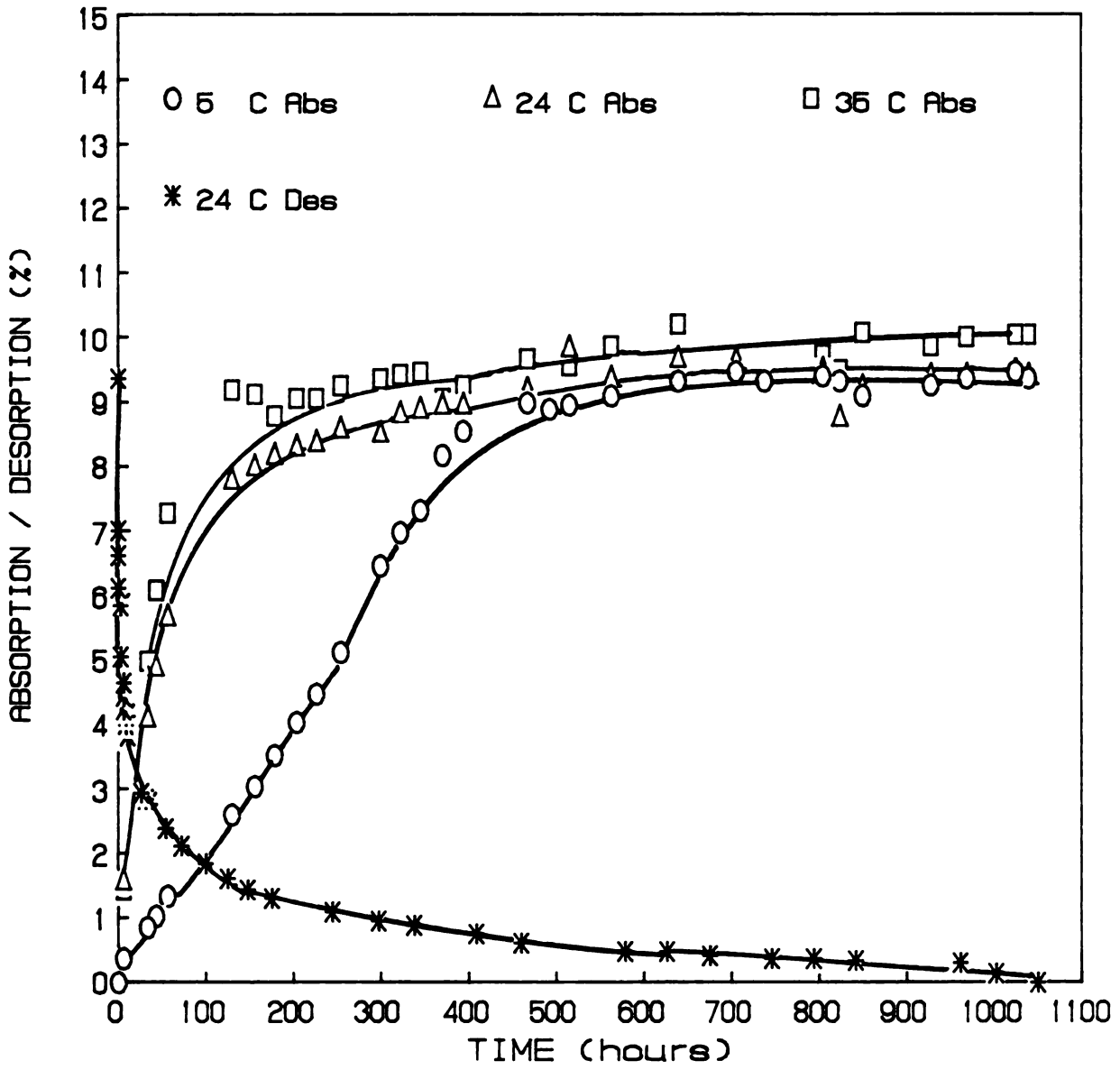


FIGURE 11. *ABSORPTION / DESORPTION OF DIPROPYL DISULFIDE BY PP*

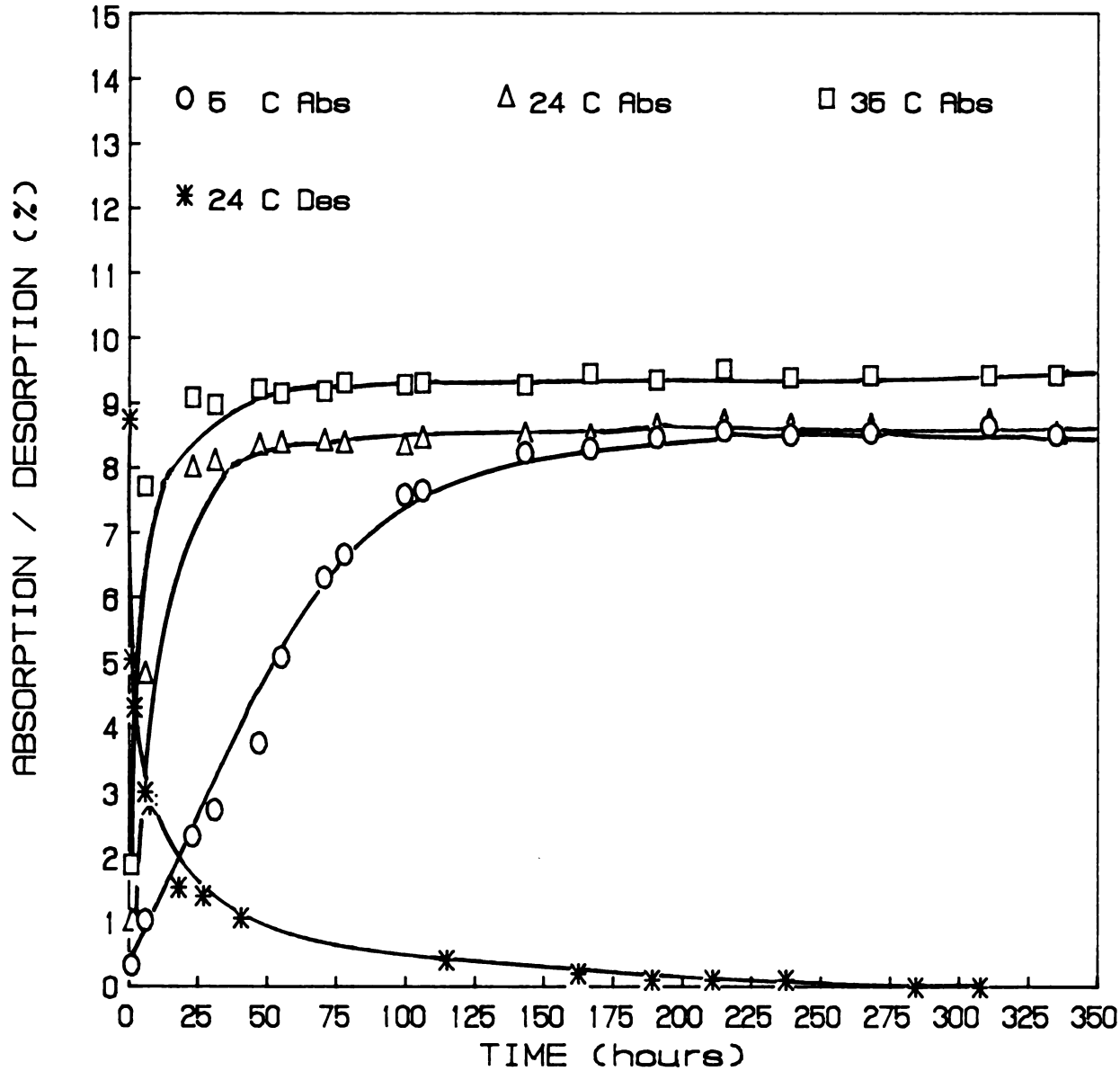


FIGURE 12. *ABSORPTION / DESORPTION OF DIMETHYL DISULFIDE BY PP*

As shown in the following table, time required for PP samples exposed to dimethyl disulfide to reach equilibrium was much shorter than that for samples exposed to dipropyl disulfide.

Table 3

Time Required to Reach Equilibrium Sorption for PP Samples Exposed to Penetrant Vapor*

Temperature	Dimethyl disulfide	Dipropyl disulfide
35°C	22 hr	130 hr
24°C	214 hr	370 hr
5°C	310 hr	465 hr

*All samples achieved equilibrium at approximately 9% absorption

Dimethyl disulfide and dipropyl disulfide were not retained by the polymer. At 24°C the PP completely desorbed both probe compounds.

The solubility of dimethyl disulfide and dipropyl disulfide in HDPE and PP is substantially lower than in HIPS. HIPS retains a significant portion of the sorbed dipropyl disulfide, while HDPE and PP desorb 100% of both probes. Equilibrium distribution of dipropyl disulfide and dimethyl disulfide between the product and container would result in much lower probe compound concentrations in HDPE and PP structures than in the HIPS. This is significant in avoiding the effects of "flavor scalping"

or loss due to sorption for a product whose quality is associated with the retention of volatile aroma constituents.

EQUILIBRIUM VAPOR PRESSURE

The equilibrium vapor pressures of dimethyl disulfide and dipropyl disulfide were determined for the pure probe and simulant systems over a range of concentrations and temperatures. Simulant systems with probe compound concentrations of 20 ppm, 100 ppm, and 1000 ppm (wt/wt) were analyzed at temperatures of $5^{o}C$, $26^{o}C$, and $35^{o}C$. These concentration levels were chosen based on estimates of the actual amount of dimethyl disulfide and dipropyl disulfide in the onion flavored sour cream (Appendix VIII, Table 15). At these concentrations equilibrium vapor pressures were used to extrapolate equilibrium vapor pressure for 80 ppm dimethyl disulfide and 10 ppm dipropyl disulfide by substitution of these values into equations 5-9. In Appendix IX, Table 16, are listed all equations used in this section. Sensitivity of GC analysis did not allow quantification at all concentration levels and temperatures. Equilibrium vapor pressures were not obtained for dipropyl disulfide 20 ppm simulant samples. Dipropyl disulfide samples at $5^{o}C$ ($278^{o}K$) and 100 ppm were also below detectable limits. In Figures 13 and 14 are the probe equilibrium vapor

pressures (expressed as ppm in the vapor phase) as a function of temperature for the simulant and pure probe systems. In Figures 15 and 16 are the probe equilibrium vapor pressures as a function of simulant probe concentration from Figures 13 and 14. The experimental data shown was derived by linear regression analysis using the least square method (Gacula and Singh, 1984). Equations describing the curves (Equations 5-9 for Figures 15 and 16) for various storage temperatures were then derived. These expressions describe the vapor phase concentration of dimethyl disulfide and dipropyl disulfide as a function of simulant probe concentration. By substituting the probe concentrations existing in the product into equations 5-9, the actual equilibrium vapor pressure of dimethyl disulfide and dipropyl disulfide in the product was determined for several temperatures (Appendix IX, Table 16).

ABSORPTION OF PROBE COMPOUNDS AS A FUNCTION OF TIME

In order to relate the behavior of the pure probe system to the actual product, it was first necessary to determine the temperature referred to as T_2. T_2 is the temperature at which the equilibrium vapor pressure (ppm) of the pure probe standard is equivalent to the

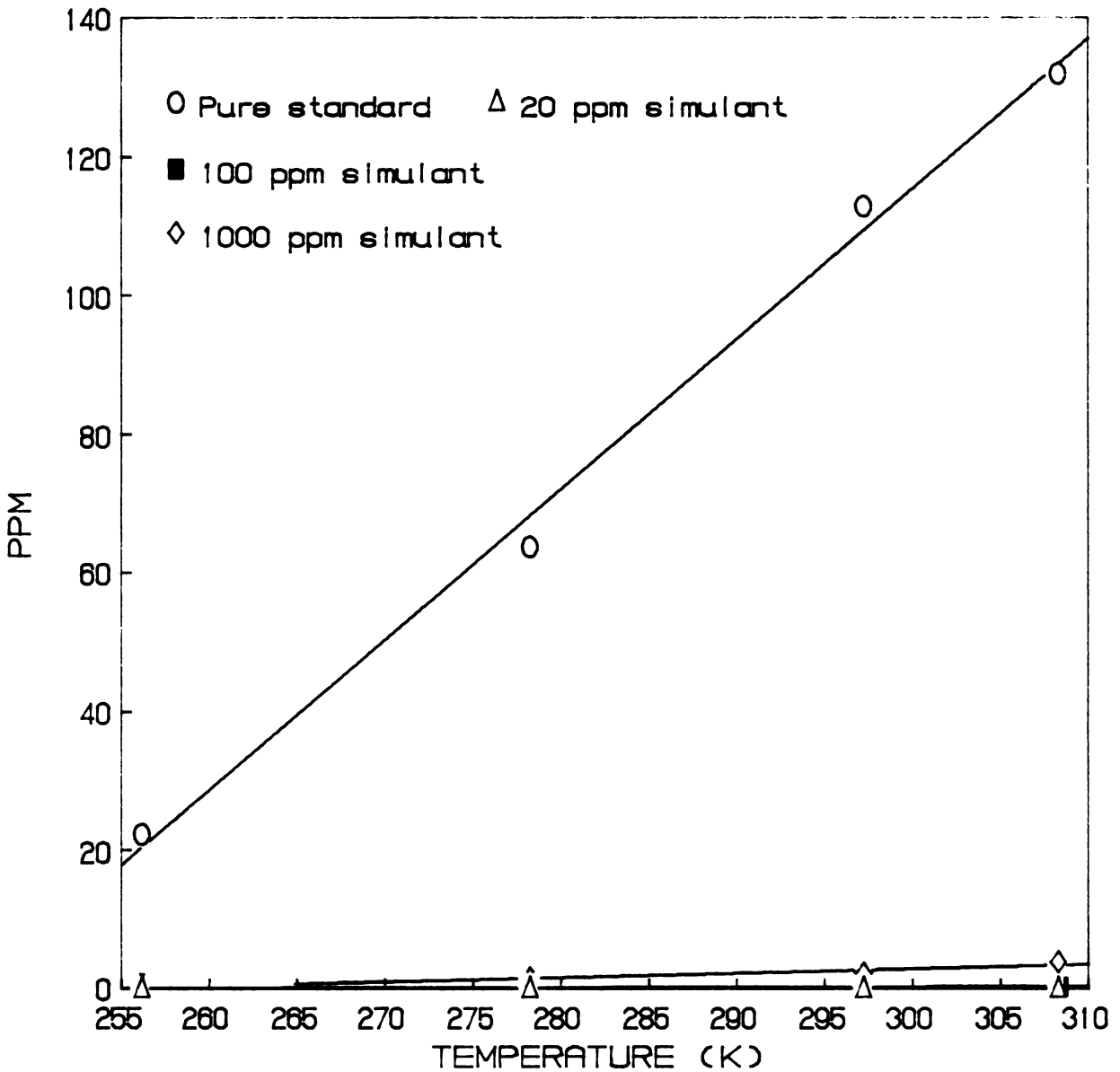


FIGURE 13. *EQUILIBRIUM VAPOR PRESSURE OF DIMETHYL DISULFIDE AS A FUNCTION OF TEMPERATURE*

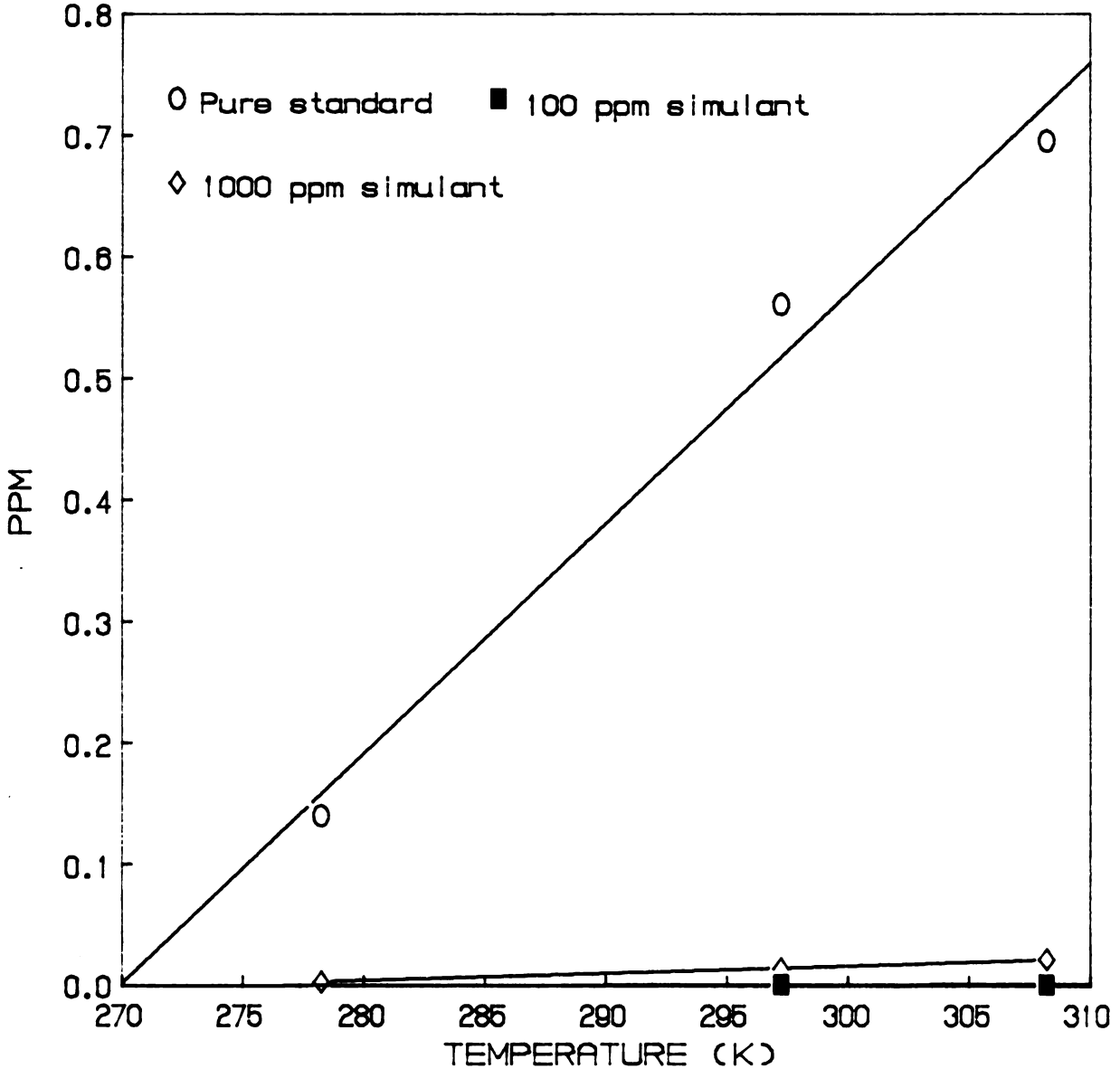


FIGURE 14. *EQUILIBRIUM VAPOR PRESSURE OF DIPROPYL DISULFIDE AS A FUNCTION OF TEMPERATURE*

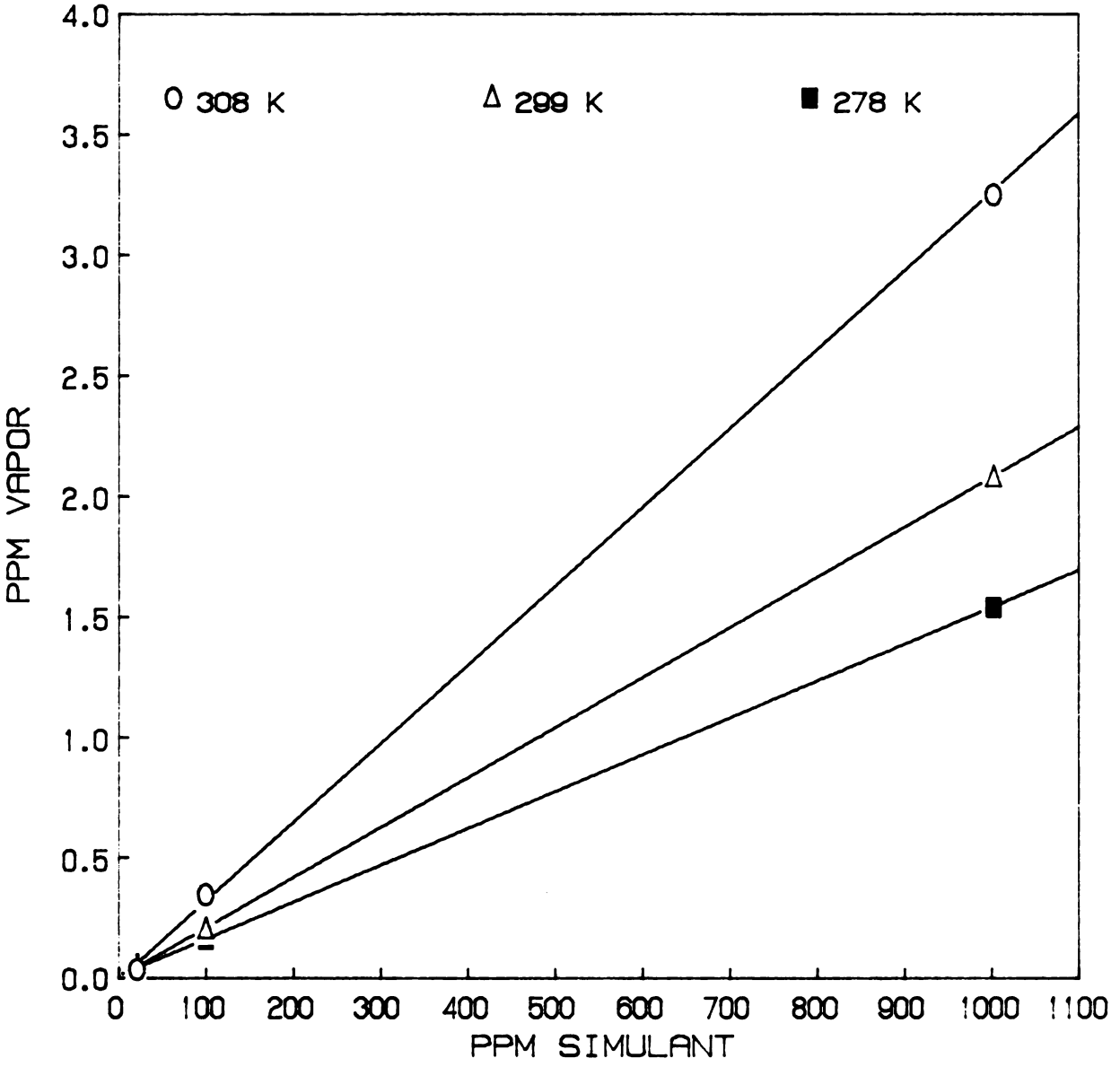


FIGURE 15. *EQUILIBRIUM VAPOR PRESSURE OF DIMETHYL DISULFIDE AS A FUNCTION OF SIMULANT PROBE CONCENTRATION*

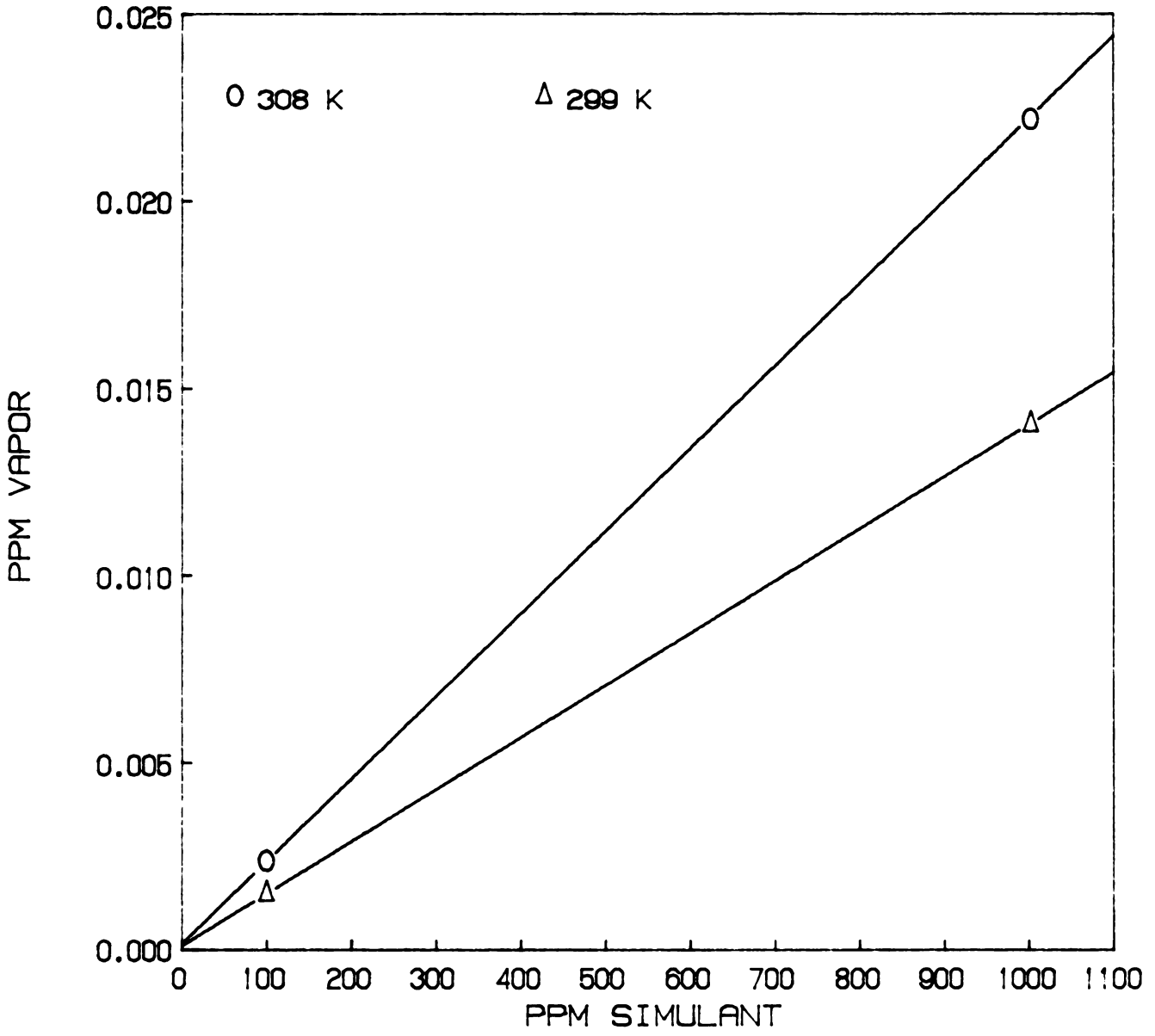


FIGURE 16. *EQUILIBRIUM VAPOR PRESSURE OF DIPROPYL DISULFIDE AS A FUNCTION OF SIMULANT PROBE CONCENTRATION*

equilibrium vapor pressure in the actual product at the normal storage temperature (T_1=5^{o}C). To determine equilibrium vapor pressure as a function of temperature, linear regression analysis was performed on results derived from equations 5-9. Equations 10 and 11 and Figures 17 and 18 describe the vapor phase concentration of probe compound in the product as a function of temperature. T_1=5^{o}C(278^{o}k) can be substituted into equations 10 and 11 to find a T_2 which represents the temperature of the pure probe that approximates behavior of the actual product. From substitution of T_1 into equations 10 and 11, results are shown which represent the actual concentration of probe vapor in the product at 5^{o}C. Equations 12 and 13 derived from Figures 13 and 14 describe equilibrium vapor pressure for the pure probe systems as a function of temperature. By substituting the concentration of probe vapor found at T_1 into equations 12 and 13 (representing the pure standard), T_2 can be determined. Results for T_2 from equations 12 and 13 are given in Appendix IX, Table 16.

In order to relate the amount of sorption occurring at T_2 to time, Figures 19 and 20 were constructed using data from sorption studies. From these results it was possible to determine percent absorption at T_2=-26.4^{o}C for dimethyl disulfide (results were extrapolated) and T_2=-3.3^{o}C for dipropyl disulfide at several time

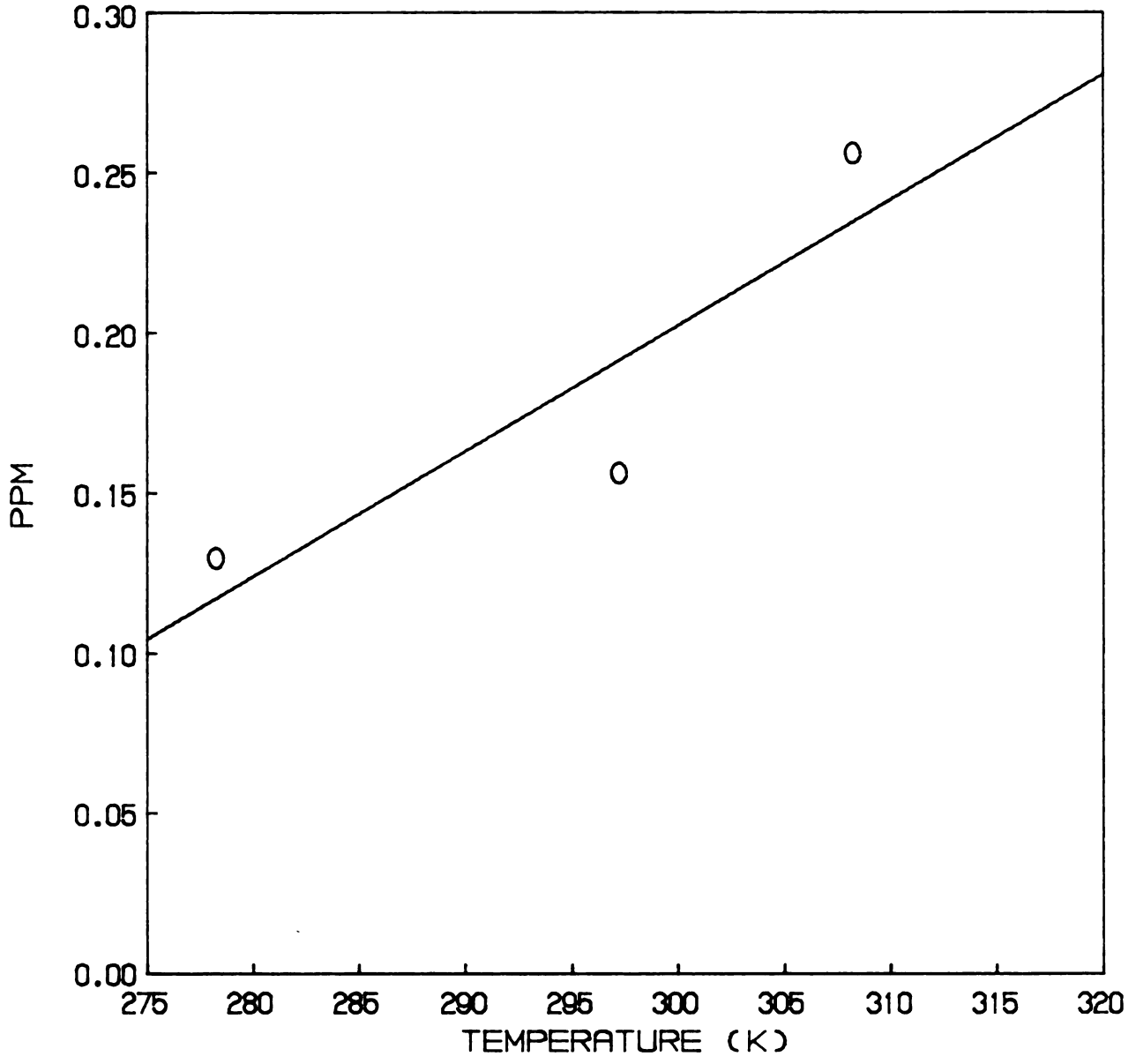


FIGURE 17. *EQUILIBRIUM VAPOR PRESSURE OF DIMETHYL DISULFIDE IN ONION FLAVORED SOUR CREAM AS A FUNCTION OF TEMPERATURE*

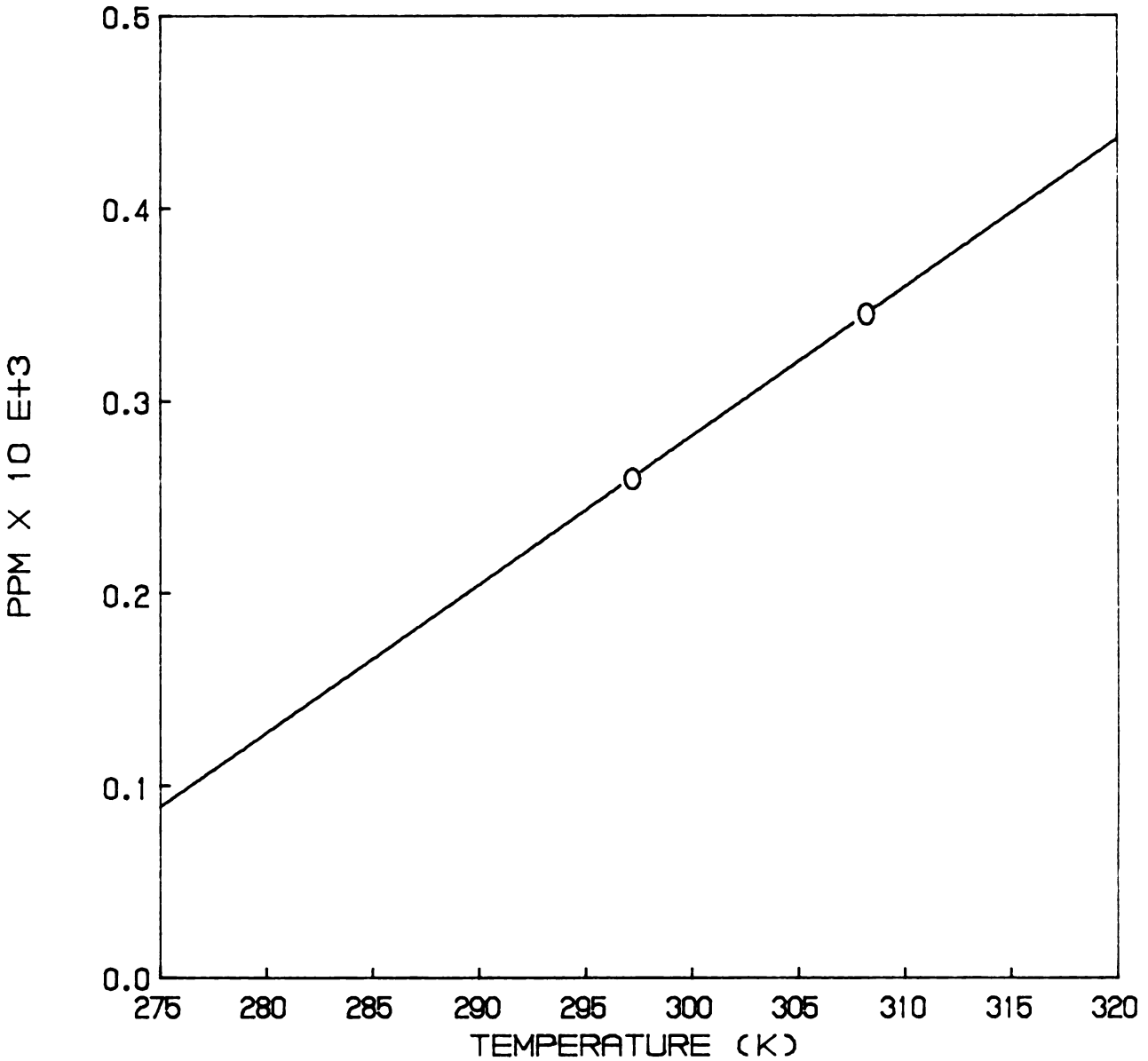


FIGURE 18. *EQUILIBRIUM VAPOR PRESSURE OF DIPROPYL DISULFIDE IN ONION FLAVORED SOUR CREAM AS A FUNCTION OF TEMPERATURE*

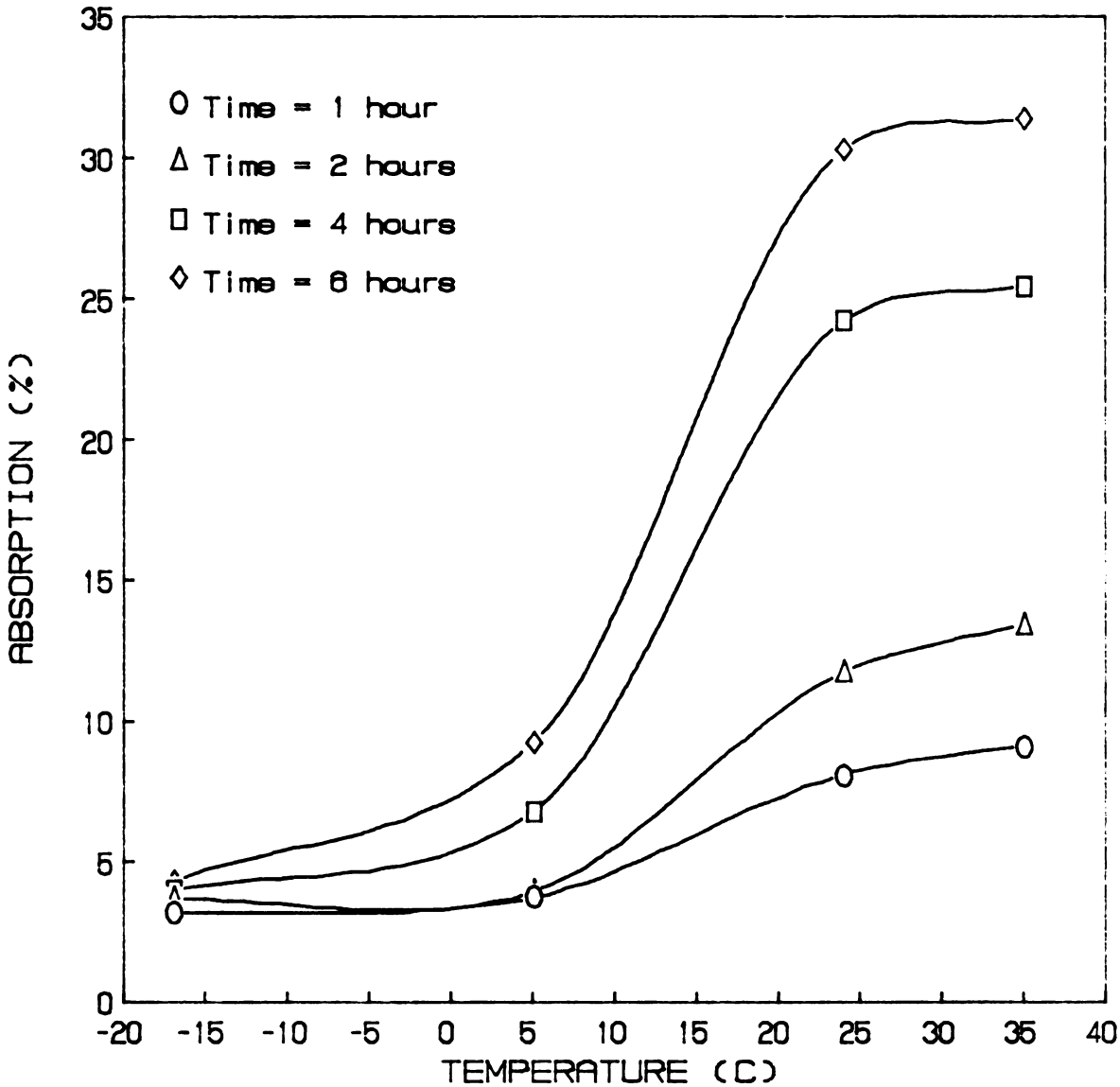


FIGURE 19. *ABSORPTION OF DIMETHYL DISULFIDE BY HIPS AS A FUNCTION OF TEMPERATURE*

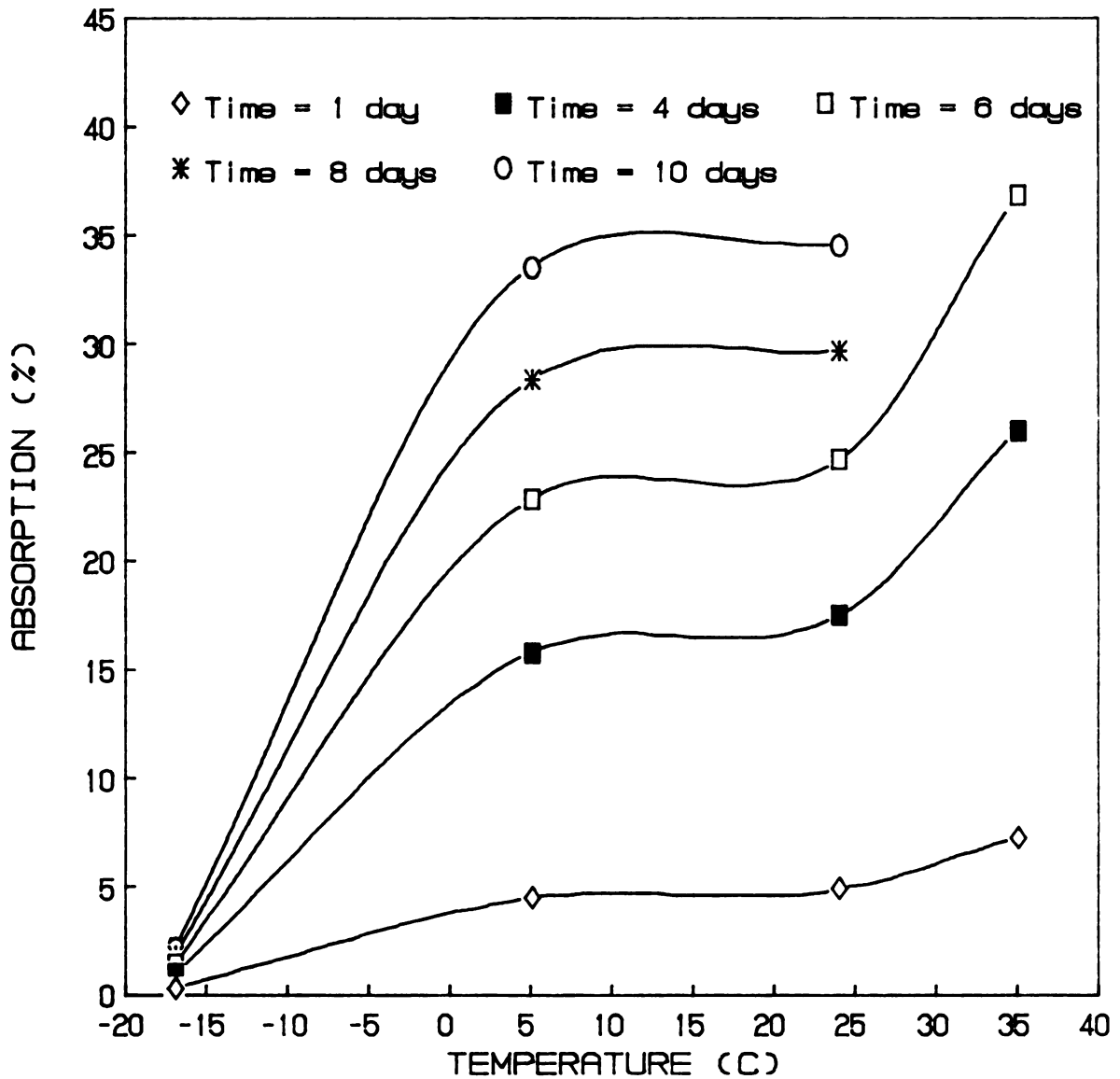


FIGURE 20. *ABSORPTION OF DIPROPYL DISULFIDE BY HIPS AS A FUNCTION OF TEMPERATURE*

intervals. Figures 21 and 22 were prepared from these data. These graphs of percent absorption vs. time for the 80 ppm dimethyl disulfide and 10 ppm dipropyl disulfide simulant systems approximate behavior of the actual product stored at $5^{o}C$.

The capacity of a container to absorb dimethyl disulfide and dipropyl disulfide is a function of the equilibrium concentration of probe in the polymer (maximum absorption). The amount of probe actually available for absorption is a function of the concentration of probe compound in the product. By using equations 1 and 2, the capacity of the container to absorb the probe and the actual amount of probe available can be determined.

$$\text{Capacity of container to absorb probe (mg)} = \frac{C_c \times C}{100} \quad (1)$$

where C_c = equilibrium concentration of probe compound in the polymer (% maximum absorption from Figures 19 and 20)

C = weight of polymer container (mg)

$$\text{Amount of probe compound available (mg)} = C_p \times P \quad (2)$$

where C_p = concentration of probe compound in the product (ppm from Table 1)

P = weight of product (kg)

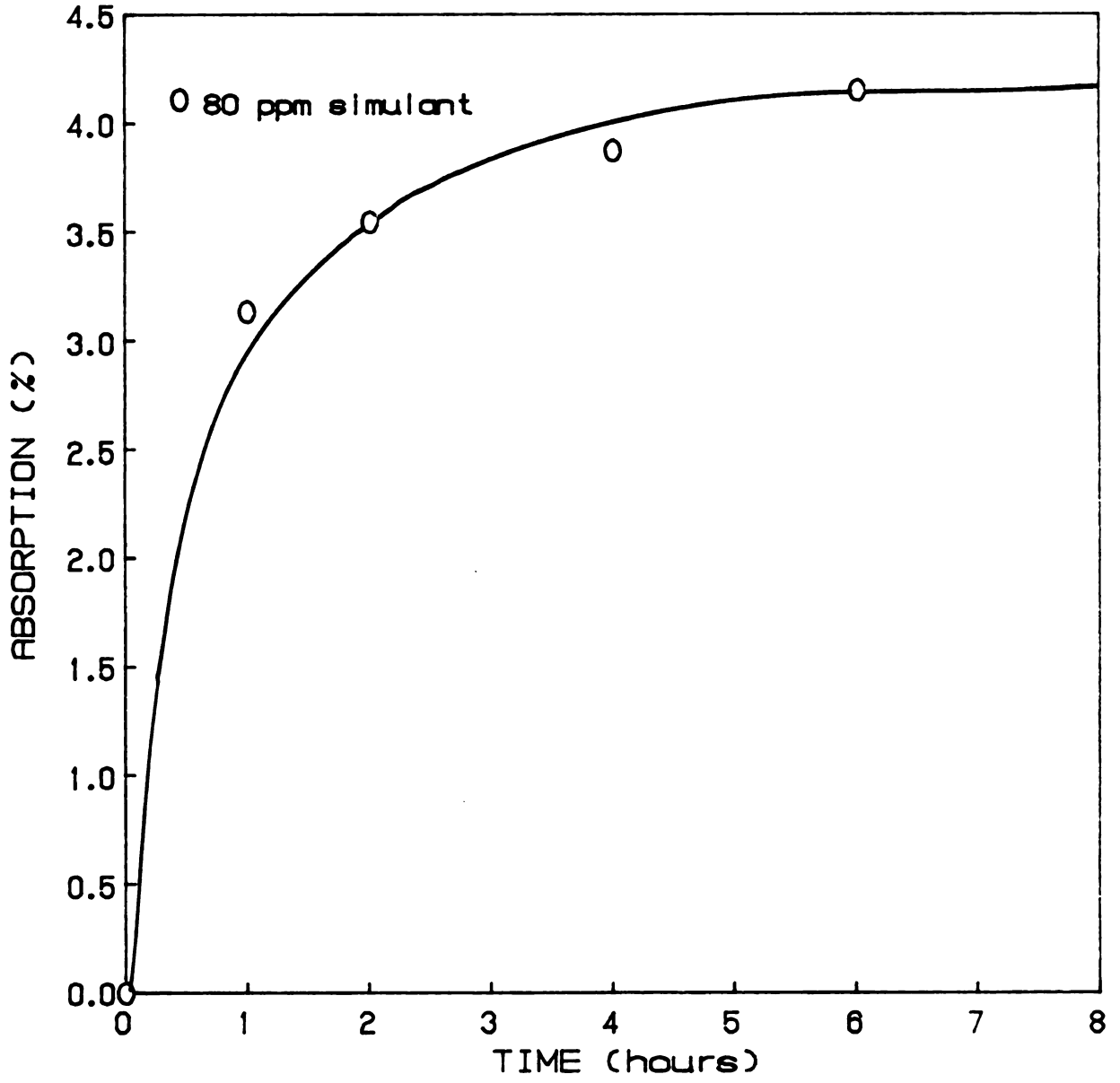


FIGURE 21. *ABSORPTION OF DIMETHYL DISULFIDE BY HIPS AS A FUNCTION OF TIME*

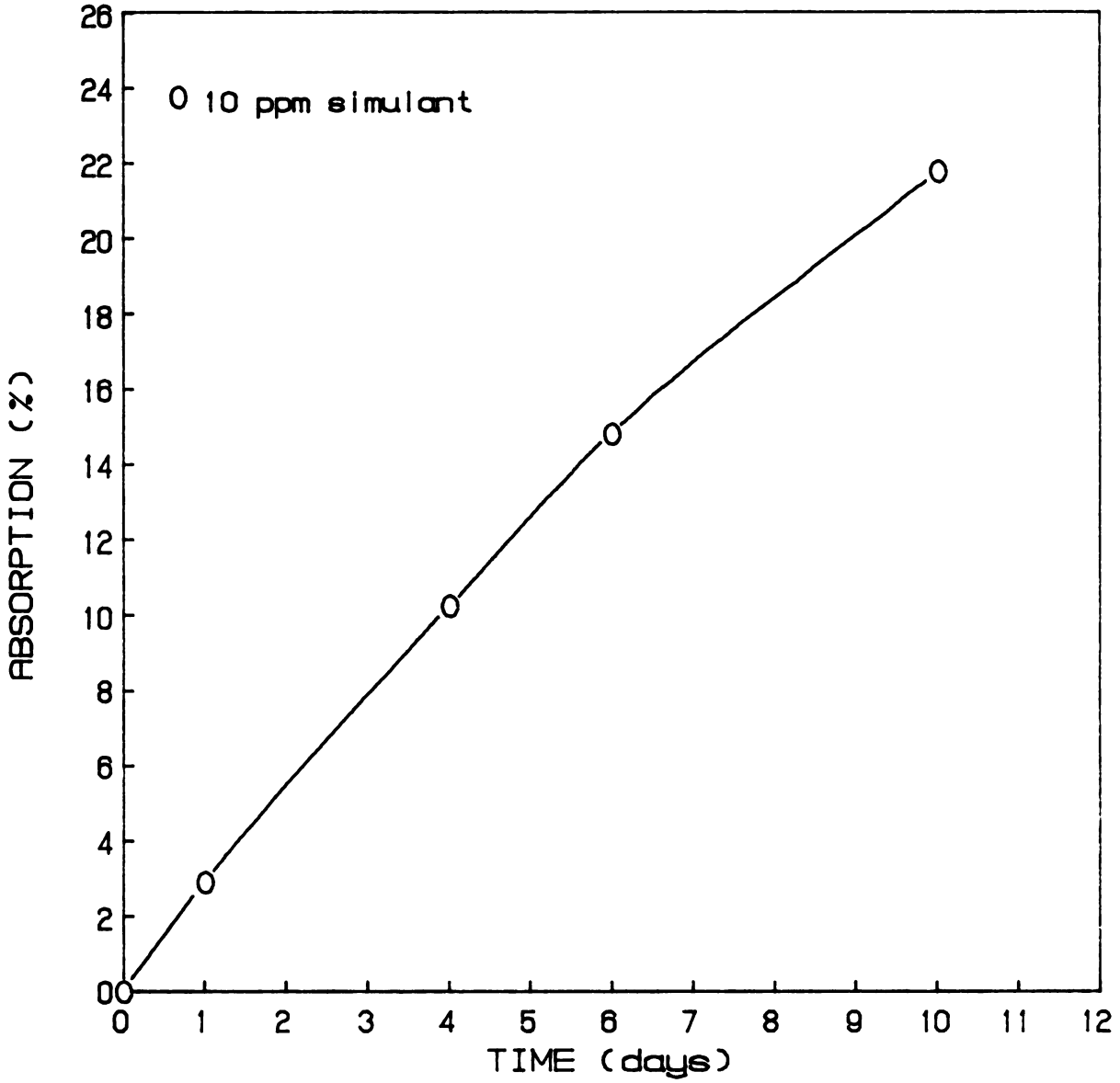


FIGURE 22. *ABSORPTION OF DIPROPYL DISULFIDE BY HIPS AS A FUNCTION OF TIME*

The capacity of the HIPS container used in this study to absorb dimethyl disulfide and the actual amount of dimethyl disulfide available in the product were determined as follows:

$$\text{HIPS Capacity to absorb } Me_2S_2 = \frac{(4.2)\ (9500mg)}{100} = 399mg$$

$$Me_2S_2 \text{ Available} = (80.1 \text{ ppm})\ (.236kg) = 18.9 \text{ mg}$$

In Table 4 are results for the three test materials and two probe compounds. In all cases the quantity of available probe is much smaller than the absorption capacity of the container. Each test container has the potential to absorb 100% of the dimethyl disulfide and dipropyl disulfide contained in the onion flavored sour cream.

Table 4

Absorption Capacity of HIPS, PP, and HDPE and Available Probe Compound in Onion Flavored Sour Cream.

	Dimethyl disulfide		Dipropyl disulfide	
Test Material	Capacity	Available	Capacity	Available
HIPS	399.0 mg	18.9 mg	2090.0 mg	2.1 mg
PP	346.9 mg	18.9 mg	1817.2 mg	2.1 mg
HDPE	558.6 mg	18.9 mg	2926.0 mg	2.1 mg

SENSORY ANALYSIS

An untrained panel of 534 participants evaluated a control sample and a sample of unflavored sour cream which had been exposed to the onion flavored product. Samples were presented in a paired-comparison/simple difference test to determine if the unflavored product had absorbed any off odors or flavors during storage. Only two panelists detected an off flavor related to onion and/or garlic in the unflavored product. Two panelists noted these flavors in the control product not exposed to the onion/garlic flavored sour cream. In Table 5, a contingency table analysis of responses for test and control samples is shown.

Table 5

Sensory Evaluation Contingency Table.

Observed (O)

	Class 1	Class 2	Grand Total
Test	2	532	534
Control	2	532	534
Total	4	1,064	1,068

Expected (E)

	Class 1	Class 2	Grand Total
Test	2	532	534
Control	2	532	534
Total	4	1,064	1,068

Results for Table 5 were derived from equation 3.

$$E_{ij} = R_i C_{j/N} \quad (3)$$

where R_i = Row total

C_j = Column total

N = Grand total

Class 1 responses are defined as panelists noting onion and/or garlic off flavors or odors. Class 2 responses are defined as panelists not noting onion and/or garlic off flavors or odors. Chi-Square was calculated from equation 4.

$$\sum_{i=1}^{2} \sum_{j=1}^{2} \left[(O_{ij}-E_{ij})^2 / E_{ij} \right] = (2-2)^2 / 2=0 \quad (4)$$

where O_{ij} = observed
E_{ij} = expected

The contingency table analysis of responses for test and control samples gave Chi-Square equal to zero. Thus, statistical analysis indicates that the results show no difference in panelists' responses to test and control samples.

The results of the sensory studies provide additional insight into the possible mechanisms of flavor loss. Solubility of flavor components in the polymer matrix appears to be the dominant mechanism. If permeation of volatile flavor compounds does occur from flavored to unflavored product, it is not at levels which adversely affect product quality or would be detected by consumers.

CONCLUSION

Aroma and flavor compounds are important constituents of many foods. The ability of a package system to prevent loss of these compounds directly influences product quality. In this study the mechanisms of flavor loss for a product/ package system were determined. The major findings are summarized.

(1) Sorption was the major mechanism responsible for flavor loss.

   a. Absorption Studies. Dimethyl disulfide and dipropyl disulfide were very soluble in HIPS.

   b. Desorption Studies. Dimethyl disulfide and dipropyl disulfide were retained by HIPS during desorption studies.

   c. Permeation Studies. No detectable amount of permeation was quantified.

   d. Sensory Analysis. Panelists could not detect off odor or flavors which could be attributed to permeation from flavored to unflavored product.

(2) Absorption of probe compounds by the package. Based on the high capacity of the container to

absorb and the small amount of probe compound available in the product, the system can act as an infinite sink. This accurately describes the HIPS, PP, and HDPE test materials.

(3) Temperature effects on sorption of probe compounds were minimal except at very low temperatures. Penetrant vapor pressure was sufficiently lowered at -17^{o}C to decrease sorption rates.

(4) Quality of the product over time will be dependent on the diffusion coefficient of flavor constituents. The rate at which these compounds come into contact with the package wall will determine the rate of flavor loss.

(5) Products stored near the onion flavored sour cream were not adversely affected by pick-up of off flavors or odors. No special storage or handling procedures are required for this product.

(6) No detectable amount of permeation was quantified.

   a. Sensory analysis panelists could not detect off odor or flavors which could be attributed to permeation from flavored to unflavored product.

Sorption may occur at a higher rate than predicted due to two factors:

(1) Maximum absorption rates for HIPS were based on measurements obtained before the polymer dissolved in the penetrant solution. If the polymer remained intact, an equilibrium sorption rate could be determined.

(2) The temperature T_2 is lower than the actual product storage temperature. The physical state of the polymer at T_2 was not taken into account when determining rate of sorption. Temperature influences sorption by affecting penetrant vapor pressures, but it can also alter the physical structure of the polymer. More sorption will occur at a higher temperature as the polymer matrix swells. For this reason a lower temperature of T_2 will lead to an underestimation of sorption.

Of the three materials tested, HIPS had the highest degree of interaction with the product. PP and HDPE absorbed and retained much less of the probe compounds than HIPS. HDPE and PP have the capacity to absorb 100% of the probe compounds; however, the rate of absorption is significantly lower than that of HIPS. Using HDPE or PP could reduce the effects of flavor scalping during the critical shelf life period.

Gaining an understanding of the mechanisms of flavor loss allows selection of packaging systems which will optimize quality and compatability. As the use of plastics in packaging increases, it becomes increasingly important to characterize interactions between products and packages. The methods used in this study can be applied to a wide variety of materials and foods. Much more accurate estimations of shelf life can be based on loss of principal flavor components, as opposed to overall quality perceptions. Accuracy of shelf life predictions could be further improved by determining the diffusion coefficients of principal flavor constituents in the product. The loss of flavor as a function of time could be quantified in this manner.

These studies show that the quality of the product can be affected by flavor scalping. Flavor loss from a package can affect surrounding products. Reducing flavor loss can improve the quality of the product itself and others in contact with it. This could have a major impact on the food packaging industry as it continues to utilize greater amounts of plastics for an ever increasing variety of foods.

APPENDICES

APPENDIX I

APPENDIX I

Table 6: Properties of High Impact Polystyrene (Chevron, 1986)

Property	*Test Method	Value	Units
Melt Flow Condition	D1238	2.7	gms/10 min
Izod Impact - 73°F	D256 (1/4" thick)	1.9	Ft-lb/in Notch
Izod Impact - 0°F	D256 (1/4" thick)	1.3	Ft-lb/in Notch
Dart Impact - 73°F	NBS PS-31-70	440	Ft-lb/in Thick
Dart Impact - 0°F	NBS PS-31-70	415	Ft-lb/in Thick
Vicant Softening Temp.	D1525	214	°F
Deflection Temp. 264 psi Unannealed	D648	185	°F
Tensile Strength - Break	D638 at 2.0 in/min	3,200	psi
Tensile Strength - Yield	D638 at 2.0 in/min	2,800	psi
Tensile Elongation - Break	D638	70	%

Table 6: continued

Property	*Test Method	Value	Units
Tensile Modulus	D638 at .05 in/min	270,000	psi
Rockwell Hardness	D785	70	L Scale
Specific Gravity	D792	1.03	

*All Test Methods refer to ASTM Standards except those noted as NBS (National Bureau of Standards).

This material complies with Food Additive Regulation 21 CFR 177.1640 for food contact.

APPENDIX II

APPENDIX II

Table 7: Approximate Composition of Fresh and Dehydrated Onion (Qureshi et al., 1968) (Farrell, 1985)

	Fresh Onion (per 100 g)	Dehydrated Onion (per 100 g)
Moisture	83.7 g	5.0 g
Protein	1.406 g	10.1 g
Fat	0.256 g	1.1 g
Fiber	0.623 g	5.7 g
Ash	0.508 g	3.2 g
Calcium	10.0 mg	363 mg
Iron	0.366 mg	3.0 mg
Magnesium	11.97 mg	122 mg
Phosphorous	28.0 mg	340 mg
Potassium	217.2 mg	943 mg
Sodium	17.2 mg	54.0 mg
Zinc	0.172 mg	2.0 mg
Ascorbic Acid	9.6 mg	15.0 mg

Table 8: Physical Characteristics of Toasted, Chopped, Dehydrated Onions (Farrell, 1985)

Characteristic	Maximum
Moisture	3.25 (Dry Basis)
Color Optical Index	90
Total Plate Count	300,000 organisms

U.S. Standard size sieve	
Maximum %	Sieve Size
2 (retained ON)	4
40 (pass through	8
90 (pass through)	12

APPENDIX III

APPENDIX III

Table 9: Specifications for 8 oz High Impact Polystyrene and Polypropylene Tubs (Land O' Lakes Inc., 1987)

Dimension	High Impact Polystyrene Tub	Polypropylene Tub
Wall thickness	.013"-.017"	.013"-.017"
Height	2.3598"-2.4222"	1.870"-1.890"
Top diameter	3.808"-3.838"	4.133"-4.157"
Overflow capacity	7.7-7.9 fl. oz	10.14 fl. oz
Piece weight	7.5-11.5 g	6.5-10.5 g

Table 10: Polypropylene and High Density Polyethylene Properties (Shell Chemical Co., 1987) (Soltex Polymer Corp., 1987)

Property	Test Method	Polypropylene	High Density Polyethylene
Density	D1505	0.903 g/cc	0.960 g/cc
Melt Flow	D1238	2.0 g/10 min	0.70 g/10 min
Tensile Yield Strength (2.0 in/min)	D638	5,000 psi	4,300 psi
Flexural Modulus	D790	200,000 psi	212,000 psi
Notched Izod Impact Strength	D256	0.6 ft-lb/in	3.4 ft-lb/in
Heat Deflection Temp. (66 psi)	D648	220°F	242°F
Vicat Softening Temp.	D1525	305°F	266°F

Both materials comply with Food Additive Regulation 21 CFR 177.1520 for contact with foods.

APPENDIX IV

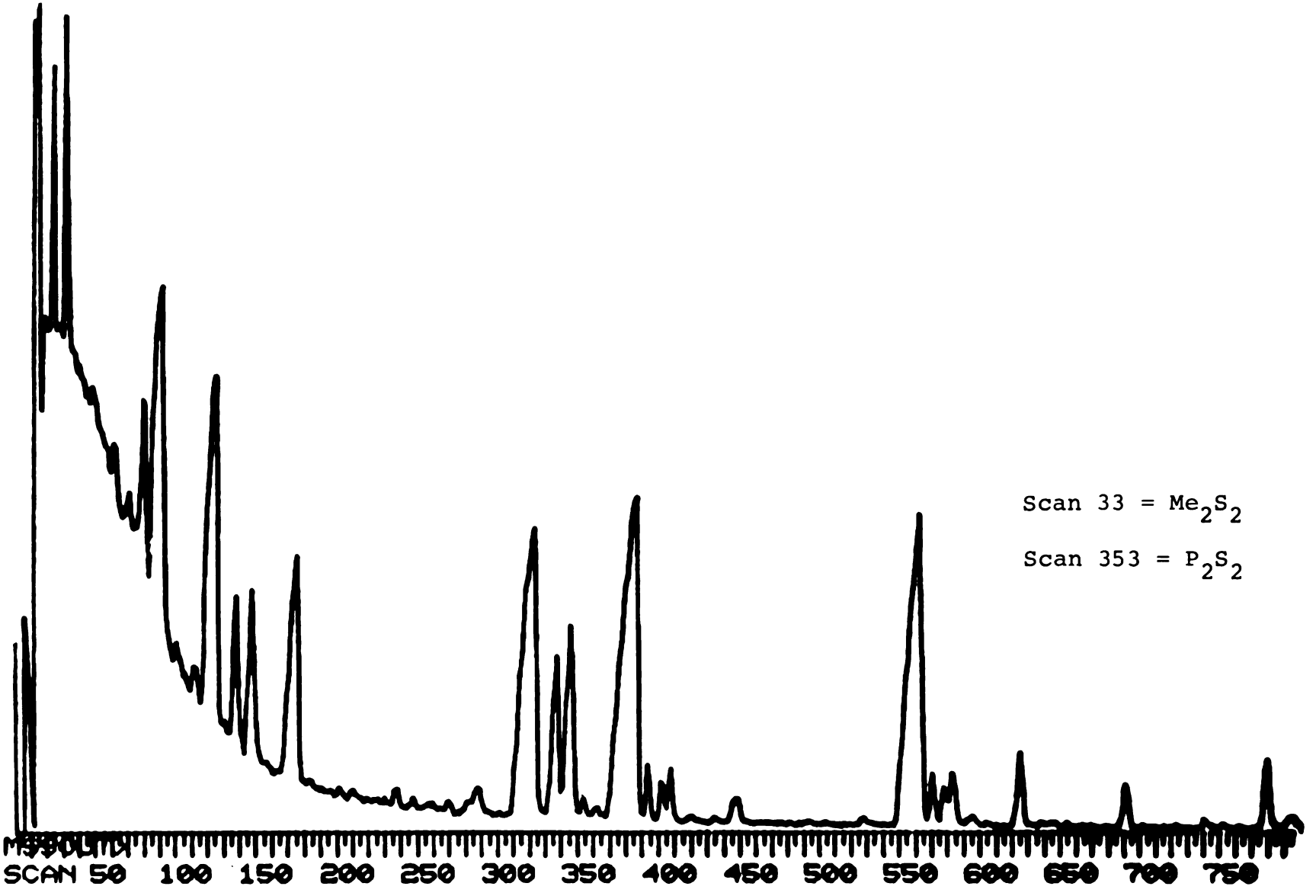


Figure 23. GC/MS Total Ion Scan of Dehydrated Onion Powder Extract

APPENDIX IV

Table 11: Probe Compound Properties

Property	Dipropyl Disulfide	Dimethyl Disulfide
Density	.960	1.057
Molecular Weight	150.30	94.19
Solubility	insoluble in H_2O	insoluble in H_2O
Boiling Range	195-196°C	107-111°C
Refractive Index	1.4967	1.526
Flash point	66°C	14°C
Chemical Formula	$(CH_3CH_2CH_2S)_2$	CH_3SSCH_3
Typical Assay (GLC)	97%	99%

APPENDIX V

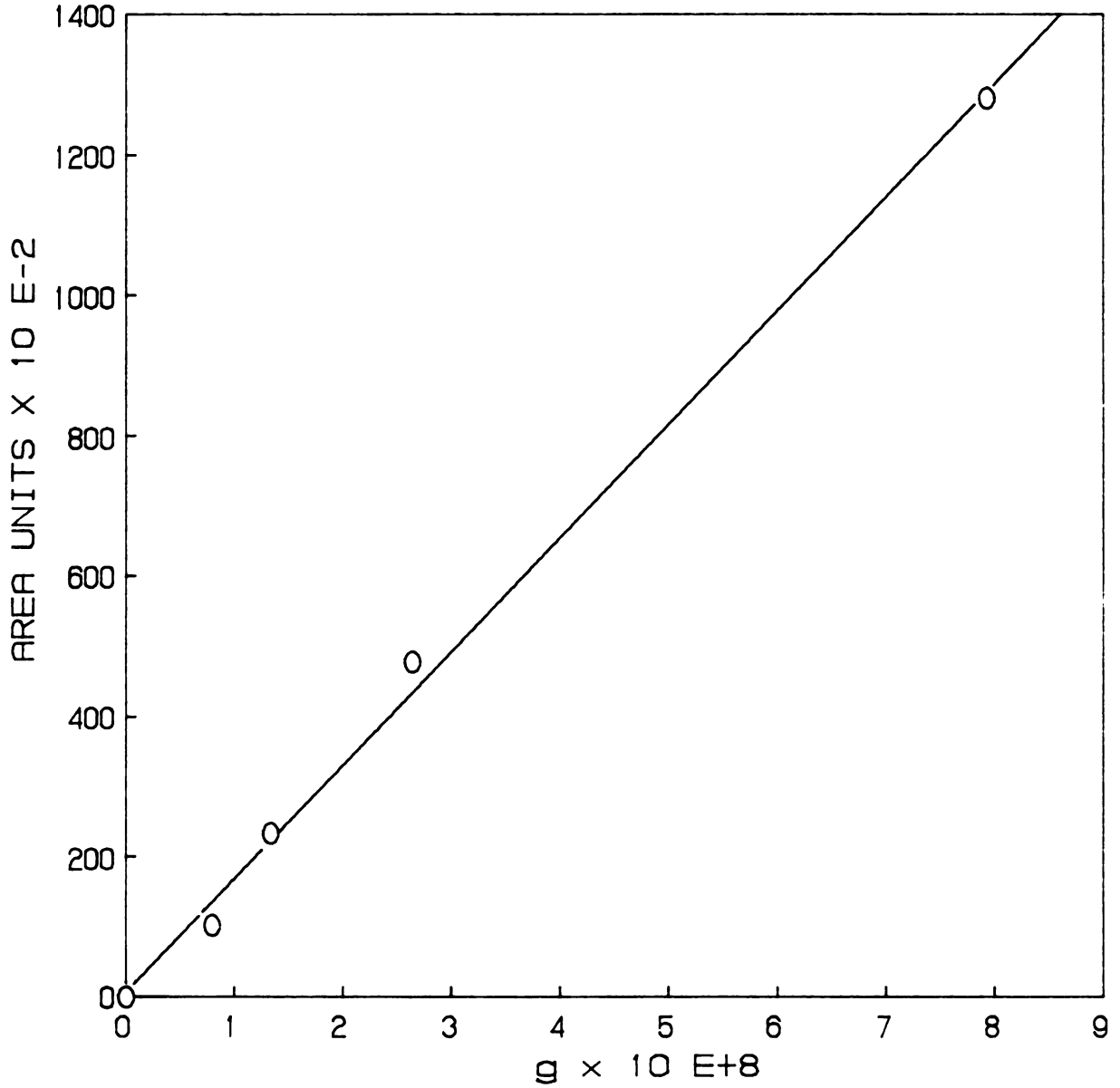


Figure 24. *STANDARD CURVE FOR DIMETHYL DISULFIDE AREA RESPONSE AS A FUNCTION OF QUANTITY*

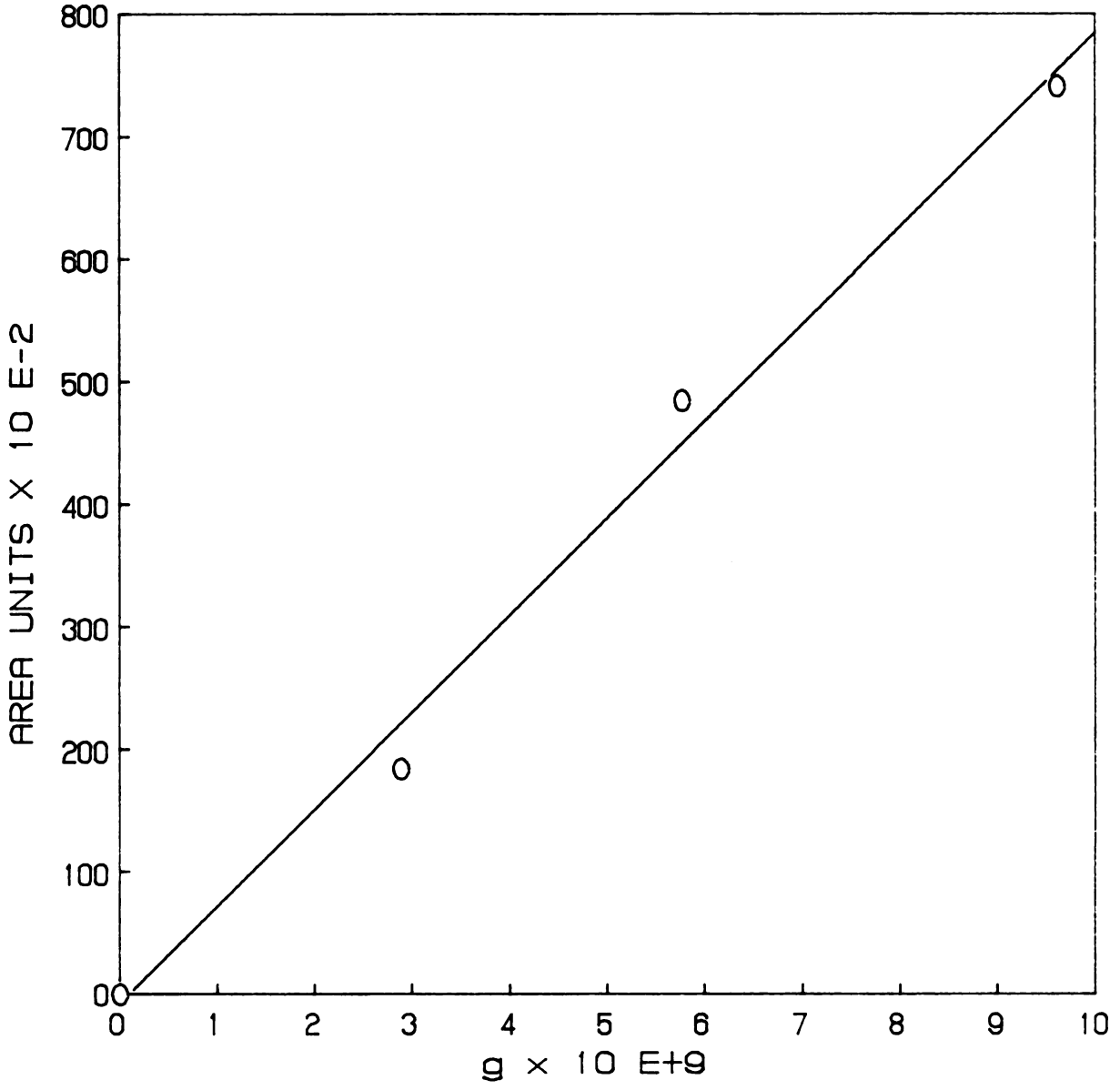


Figure 25. *STANDARD CURVE FOR DIPROPYL DISULFIDE AREA RESPONSE AS A FUNCTION OF QUANTITY*

APPENDIX VI

APPENDIX VI

CONSENT FORM FOR TASTE PANEL MEMBERS

School of Packaging
Michigan State University

Lean Cream Ingredients:

Cultured sour cream, whey protein concentrate, skim milk, lactic acid, water, food starch-modified, natural flavor, agar, potassium sorbate (a preservative), Vitamin A palmitate.

I _____ have read the above list of ingredients and find none that I know I am allergic to. I have also been informed of the nature of the research (including experimental materials and procedures) which will be used during the tasting session. I agree to serve on this taste panel, which is being conducted on this _____ day of _____ 1987. I understand that I am free to withdraw my consent and to discontinue participation in the panel at any time without penalty.

_____
Signature

_____
Date

Figure 26.

QUESTIONNAIRE

For the pair of samples, indicate whether the samples are the same or are different by placing an X in the appropriate space. If the samples are different, please describe (i.e., type of off flavor detected). Taste as much or as little of each sample as you wish in order for you to answer these questions.

SAMPLE PAIR 137 versus 264

Different _____ Not different _____

If different, please describe the difference:

_____

_____

_____

Figure 26: Cont'd.

QUESTIONNAIRE

For the pair of samples, indicate whether the samples are the same or are different by placing an X in the appropriate space. If the samples are different, please describe (i.e., type of off flavor detected). Taste as much or as little of each sample as you wish in order for you to answer these questions.

SAMPLE PAIR 538 versus 701

Different _____ Not Different _____

If different, please describe the difference:

_____

_____

_____

Figure 26: Cont'd.

APPENDIX VII

APPENDIX VII

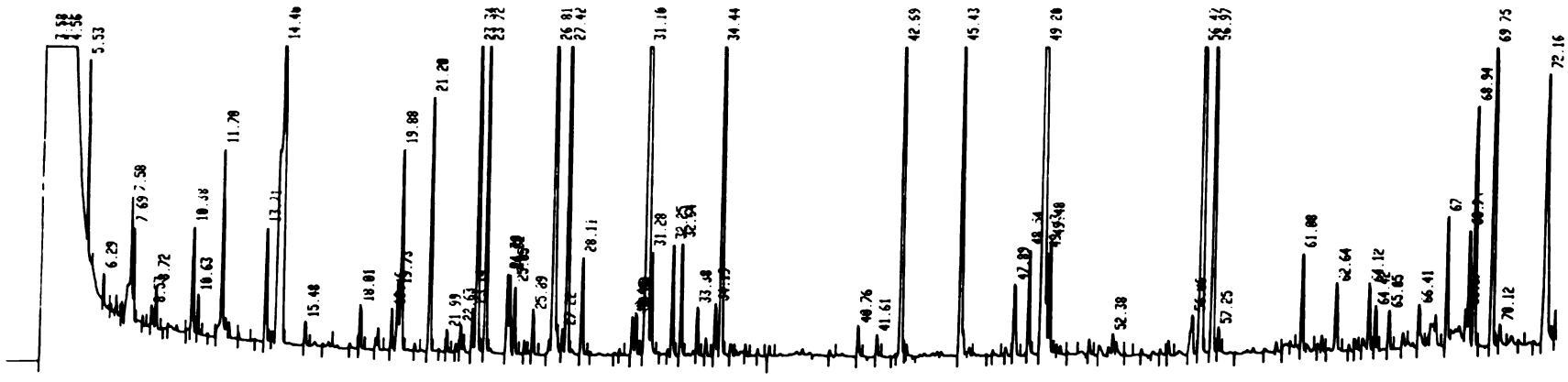


Figure 27. GC Analysis of Onion Flavored Sour Cream Extract

APPENDIX VIII

APPENDIX VIII

Table 12: Percent Recoveries for Dimethyl disulfide and Dipropyl disulfide -- Total loss (extraction and concentration)

Known Probe Compound Concentration	Grams of Probe: Before Extraction and Concentration	Grams of Probe: After Extraction and Concentration	% Total Loss
18 ul Me_2S_2 in 50 ml Solvent	3.12×10^{-3} g	5.63×10^{-4} g	82%
18 ul P_2S_2 in 50 ml Solvent	1.36 g	.56 g	58.8%

Table 13: Percent Recoveries for Dimethyl disulfide and Dipropyl disulfide--Loss due to extraction

Known Probe Compound Concentration	Grams of Probe: Before Extraction	Grams of Probe: After Extraction	% Loss due to Extraction
10 ul Me_2S_2 in 22 ml Solvent	1.035×10^{-3} g	2.74×10^{-4} g	73.5%
10 ul P_2S_2 in 22 ml Solvent	.6075 g	.352 g	42%

Table 14: Percent Recoveries for Dimethyl disulfide and Dipropyl disulfide--Loss due to concentration*

Probe	% Loss due to Concentration
Me_2S_2	8.5%
P_2S_2	16.8%

*(% total loss-% extraction loss = loss due to concentration)

Table 15: Concentration of Probe Compounds in Onion Flavored Sour Cream

Probe	Grams Probe*	Actual Grams Probe**	% Probe in Product	ppm Probe in Product
Me_2S_2	7.20×10^{-4} g	4.00×10^{-3} g	.008%	80 ppm
P_2S_2	1.83×10^{-4} g	4.48×10^{-4} g	.0009%	9 ppm

*Based on 50 g sample dehydrated onion
**Based on 50 g sample dehydrated onion--taking into account % recovery

APPENDIX IX

APPENDIX IX

Table 16: Determination of T_2*

Equation Number	Figure Number	Probe Compound	Conditions	Equation	Substitution	Results
5	15	Me_2S_2	308°K	$y=(-4.556\times10^{-3})+(3.264\times10^{-3})X$	X^1=80 ppm	y^2=.256 ppm
6	15	Me_2S_2	297°K	$y=(-2.957\times10^{-4})+(1.964\times10^{-3})X$	X^1=80 ppm	y^2=.157 ppm
7	15	Me_2S_2	278°K	$y=(2.433\times10^{-3})+(1.590\times10^{-3})X$	X^1=80 ppm	y^2=.130 ppm
8	16	P_2S_2	308°K	$y=(1.333\times10^{-4})+(2.117\times10^{-5})X$	X^1=10 ppm	$y^2=3.45\times10^{-4}$ ppm
9	16	P_2S_2	297°K	$y=(1.209\times10^{-4})+(1.393\times10^{-5})X$	X^1=10 ppm	$y^2=2.60\times10^{-4}$ ppm
10	17	Me_2S_2	80 ppm	$y=(-9.744\times10^{-1})+(3.923\times10^{-3})X$	X^3=278°K	y^4=.116 ppm
11	18	P_2S_2	10 ppm	$y=(-2.040\times10^{-3})+(7.739\times10^{-6})X$	X^3=278°K	$y^4=.112\times10^{-3}$ ppm
12	13	Me_2S_2	pure probe	$y=(-5.341\times10^{2})+(2.165)X$	y=.116 ppm	x^5=247°K/-26.4°C
13	14	P_2S_2	pure probe	$y=(-5.104)+(1.891\times10^{-2})X$	$y=.112\times10^{-3}$ ppm	x^5=270°K/-3.3°C

X^1 = Actual concentration of probe compound in product
y^2 = equilibrium vapor pressure in product at the given temperature
X^3 = T_1 = 5°C = 278°K
y^4 = equilibrium vapor pressure in product at T_1(5°C)
X^5 = T_2

*T_2 = Temperature at which the equilibrium vapor pressure of the pure probe standard is equivalent to the equilibrium vapor pressure in the actual product at normal storage temperatures (5°C).

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BIBLIOGRAPHY

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