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**US ARMY
TROOP
SUPPORT COMMAND
NATICK RD&E CENTER**

NRDEC
SCIENCE SYMPOSIUM
PROCEEDINGS

2-4 JUNE 1986
VOLUME I

UNITED STATES ARMY NATICK
RESEARCH, DEVELOPMENT AND ENGINEERING CENTER
NATICK, MASSACHUSETTS 01760-5000

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Natick RD&E Center held its first Science Symposium 2-4 June 1986. Since Natick programs emphasize efforts that will protect, sustain, shelter and resupply the soldier on the battlefield, the theme of the Symposium was, appropriately, TECHNOLOGY FOR THE SOLDIER. Twenty-four NRDEC papers, including seven 1986 Army Science Conference papers, were presented. The Symposium included papers and presenters from all five Natick research and development Directorates: Advanced Systems Concepts, Aero-Mechanical Engineering, Food Engineering, Individual Protection, and Science and Advanced Technology. It also included co-authors and presenters from several universities. The twenty-four papers represented the efforts of 59 researchers/authors. Volume I of the NRDEC SCIENCE SYMPOSIUM PROCEEDINGS has unlimited distribution and it includes papers in the following areas: Individual Protection Concepts, Chemical Biological Protection for the Soldier, Military Materials Development, and Initiatives in Rations, Food Science and Feeding Concepts. Volume II, NATICK/TR-86/051L, is authorized for distribution to DoD components only. Volume II includes papers in the following areas: Individual Protection Concepts, Chemical/Biological Protection, Military (over)

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John A. Sousa	(617) 651-4243	STRNC-TT

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83 APR edition may be used until exhausted.
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VEGETABLE OILS   ACTIVATED CARBON   MICROCLIMATE COOLING

Materials Development and Initiatives in Rations, Food Science and Feeding Concepts.

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4 June 1986

SUBJECT: Proceedings of the 1986 NRDEC Science Symposium

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1. Natick RD&E Center held its first Science Symposium 2-4 June 1986. Since Natick programs emphasize efforts that will protect, sustain, shelter and resupply the soldier on the battlefield, the theme of the Symposium was, appropriately, TECHNOLOGY FOR THE SOLDIER.

2. Twenty-four NRDEC papers, including seven 1986 Army Science Conference papers, were presented. Several of these papers will be published in technical journals. General topical areas were:

> Individual Protection Concepts
> Chemical Biological Protection for the Soldier
> Military Materials Development
> Initiatives in Rations, Food Science and Feeding Concepts
> Systems Improvements

3. The Symposium included papers and presenters from all five Natick research and development Directorates:

> Advanced Systems Concepts Directorate
> Aero-Mechanical Engineering Directorate
> Food Engineering Directorate
> Individual Protection Directorate
> Science and Advanced Technology Directorate

It also included co-authors and presenters from several universities. The 24 papers represented the outstanding efforts of 59 researchers/authors.

STRNC-T
SUBJECT: Proceedings of the 1986 NRDEC Science Symposium

4. The Science Symposium was established by our Associate Technical Director for Technology, Dr. John A. Sousa. The threefold purpose of the Symposium was:

   a. To recognize and encourage scientific and engineering talent.

   b. To demonstrate excellence in research and development.

   c. To stimulate the interchange of ideas among scientists and engineers at Natick, as well as attendees from other Army commands, universities and the private sector.

5. The Symposium was a great success. It provided a lively professional exchange among Natick researchers and external attendees. We plan to hold it on a regular basis in the future.

6. The Proceedings contained in these two unclassified volumes will be of value to attendees and others interested in Natick research and development efforts. Volume I has unlimited distribution, but Volume II is limited to DoD components. These Proceedings should be placed in technical libraries to be available as references.

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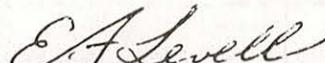
EDWARD F. LEVELL
Technical Director

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2. Oklahoma State University Faculty. 1985 University Faculty Research Fellow at NRDEC.
3. Norwegian Food Research Institute Staff. 1985 Visiting Scientist at NRDEC.

* 1986 Army Science Conference Paper

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4. St. Lawrence University Faculty. 1985 University Faculty Research Fellow at NRDEC.

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5. Norwegian Food Research Institute Staff. 1985 Visiting Scientist at NRDEC.

* 1986 Army Science Conference Paper

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6. University of Massachusetts at Amherst Faculty.
7. Framingham State College Faculty.

*   1986 Army Science Conference Paper

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* 1986 Army Science Conference Paper

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TITLE: Heat Exchanger Design for a Microclimate Cooling Unit

ALFRED L. ALLEN, DR.,* AND MARK T. HOLTZAPPLE, DR.

ABSTRACT:

A soldier encapsulated in chemical and biological (CB) protective clothing can be subjected to heat stress since his metabolic waste heat cannot be removed at a sufficiently high rate. In order for the soldier to remain in thermal equilibrium while performing his mission in CB protective clothing, supplemental cooling must be provided.

One viable approach to supplying supplemental cooling to the individual soldier is the development of a lightweight, portable microclimate cooling unit. At the Natick Research, Development and Engineering Center, a Stirling-engine-driven vapor-compression system is being constructed. The success of this approach relies not only on the engine's performance, but on proper heat exchange design as well.

The microclimate cooling unit has three principal heat exchangers: 1) evaporator; 2) condenser; and 3) waste engine heat exchanger. This paper will address the development of all three heat exchangers, which must be lightweight, of minimum size and orientation insensitive.

The evaporator consists of 1/2" iron pipe size (IPS) aluminum pipe with exterior spines to give an extended heat transfer area. The interior of the evaporator contains sintered aluminum to aid in the orientation insensitivity. Tests have shown that this evaporator has extremely high heat transfer capabilities and is orientation insensitive. The condenser is 1/8" IPS spined aluminum pipe where heat is transferred from condensing refrigerant on the interior surface to air flowing around the exterior surface. This heat exchanger has proven to be superior to traditional plate and fin type exchangers in terms of heat transfer capabilities per pound of exchanger and also in terms of power needed to supply forced air. The waste engine heat exchanger consists of the same spined pipe used in the condenser. White oil is used as the heat transfer medium. Turbulence inducers increased the inside heat transfer coefficient by a factor of four.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Research Chemical Engineer, Science and Advanced Technology Directorate, U.S. Army Natick Research, Development and Engineering Center Natick, MA 01760-5020
PAST EXPERIENCE: Research Chemical Engineer, U.S. Army Natick Research and Development Laboratories, Food Science Laboratory, Natick, MA 1973-1982
DEGREES HELD: Bachelor of Science, University of Rhode Island, 1967. Ph.D., University of Rhode Island, 1974.

HEAT EXCHANGER DESIGN FOR A
MICROCLIMATE COOLING UNIT

ALFRED L. ALLEN, DR.
MARK T. HOLTZAPPLE, DR.

INTRODUCTION

Through an extensive front-end analysis (1) it was determined
that the best approach to microclimate cooling for the individual soldier was
the development of a Stirling engine powered vapor-compression cooling unit.
Although the development of the Stirling engine (2) for microclimate cooling
represents a significant advancement in heat engine technology, this paper will
deal with the in-house development of the vapor compression system, namely heat
exchanger design.

There are three principal areas of heat exchange in the Stirling
powered cooling unit: 1) evaporator, 2) condenser, and 3) waste engine heat
exchanger. These heat exchangers must be designed to be functional,
lightweight and orientation insensitive.

EXPERIMENTAL METHOD

Evaporator Design:

The evaporator must be capable of transferring 400 to 550 watts
of heat from a glycol-water mixture to an evaporating working fluid
(e.g.,"Freon"). The glycol-water solution recirculates from a vest worn by the
soldier, where heat is picked up, to the evaporator where heat is transferred
to supply the heat of vaporization to the refrigerant. The evaporator must
perform this task regardless of its orientation. To minimize the orientation
sensitivity, it was decided to use sintered material on the internal surface
(refrigerant side) to aid in keeping the inside surface continually wet with
refrigerant, thereby ensuring that the entire heat transfer surface will be
utilized. These evaporators were sintered by Thermacore, Inc., Lancaster,
Pennsylvania. Figure 1 shows a typical sintered pattern used for evaluation.
On the external surface (water-glycol side) extended surfaces (Heatron, Inc.)
were used to create turbulence as a means of increasing the external heat
transfer coefficient.

To evaluate the various evaporator designs, each evaporator in
turn was plumbed into a highly instrumented bench scale refrigerant loop.
Temperature and pressure were measured before and after the compressor and
before the evaporator. The refrigerant flow rate was measured with Model C-6
mass flow meter from Micromotion, Boulder, CO.

EXTERNAL SPINES

FREON VAPOR

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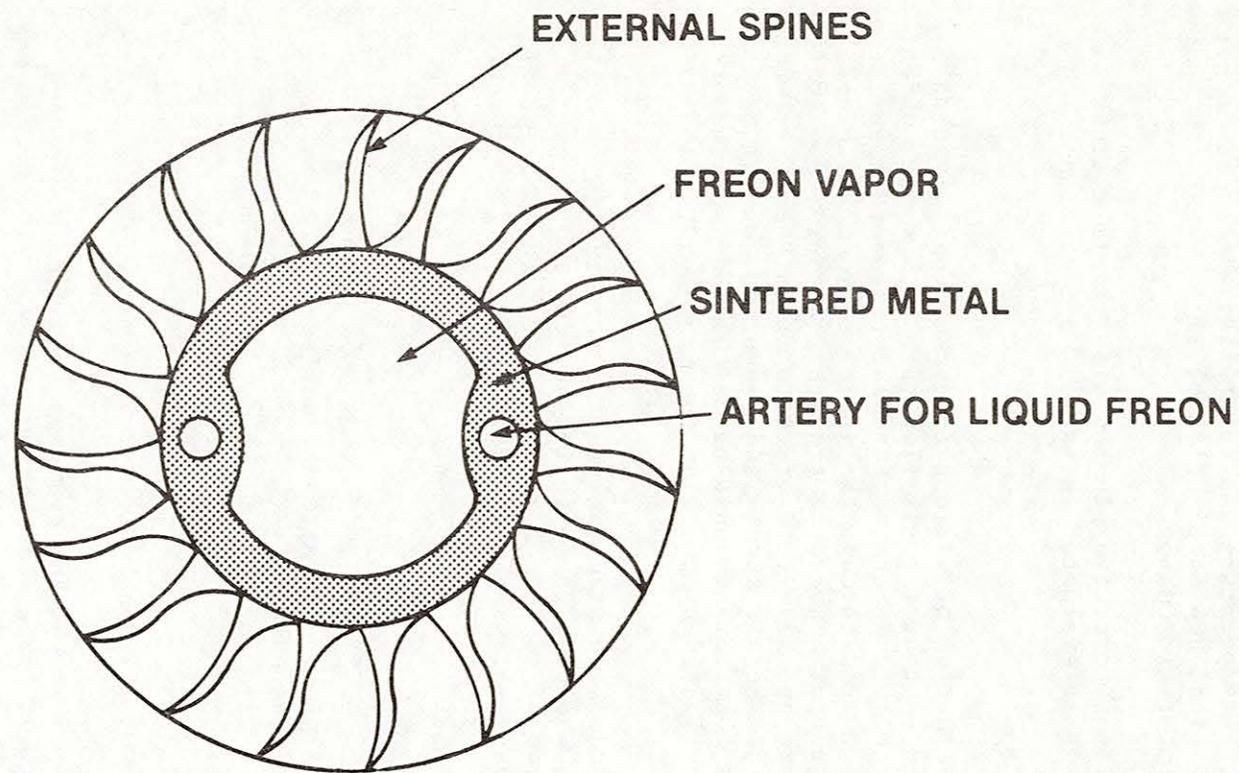
Figure 1. Cross section of evaporator.

The water flow rate was controlled with a Model 81152 Micropump (Concord, CA) and water temperature was controlled with a constant temperature bath (Model 260, Precision, GCA Corp, Chicago, Il). Water flow rates were measured with a laboratory rotometer.

The evaporators were plumbed with flexible lines so that their performance could be evaluated in various orientations.

Condenser Design:

For evaluation of various condenser configurations, a wind tunnel was constructed so that the air flow rate around the condenser could be controlled and measured. To determine the heat transfer capabilities of the condensers, water was pumped through the inside surface while air flowed around the outside. The amount of heat being transferred could be calculated by knowing the temperature and flow rate of the water stream. By measuring the air velocity profile of the air stream and measuring the air temperature, the overall heat transfer coefficient could be calculated. Different configurations were evaluated by changing the tube spacing and using different tube diameters.

The condensers were constructed from 1/8-in iron pipe size (IPS) and 1/4-in IPS aluminum pipe. The exterior surface of the pipe was chiseled giving rise to pin fins of uniform length which covered the exterior surface in a spiral manner. These heat exchangers were manufactured by Heatron, Inc., York, Pennsylvania.

Waste Engine Heat Exchanger Design:

Heatron pipes with extended surfaces were evaluated in a manner similar to the condensers.

EVALUATION

Evaporator Design:

Seven copper and one aluminum evaporators were evaluated in the bench scale refrigeration loop. Each evaporator was sintered on the interior surface. The center of each evaporator was hollow to allow the emerging vapors to escape the sintered matrix and flow to the exit end of the evaporator. Placed in the entrance to the evaporator was a disk with a hole situated at the outer edge to force the entering liquid refrigerant into the sintered matrix. The refrigerant picks up heat from the water flowing on the external surface causing a phase change in the refrigerant. The refrigerant vapor then migrates to the hollow center where it subsequently leaves the evaporator. Conditions in the evaporator were controlled by an externally referenced thermo-expansion valve. This valve essentially controls the amount of refrigerant entering the evaporator by responding to the temperature and pressure at the evaporator exit. The control valve is adjustable so that the quality (degree of superheat) of the existing refrigerant can be controlled.

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When the evaporators were run with no superheat, flooding would occur when orientation was altered during operation. It was determined that there has to be a some superheat to guarantee that the evaporator has enough capacity to prevent liquid refrigerant from exiting the evaporator under all orientations. The level of superheat required for satisfactory operation varied for each evaporator from 6 to 15° C (11 to 27° F). See Table 1.

TABLE 1. Slope and Intercept for the Wilson Plot for Evaporators

Evaporator	Superheat (F)	Intercept	Heat transfer Coefficient (BTU/hr-sqft-F)	Slope
Copper with 2 arteries	24-27	0.875	1140	0.167
Copper with 2 arteries	15-19	0.850	1180	0.186
Copper with 1 artery	12-16	1.025	980	0.184
Copper with 1 artery	12-16	1.025	980	0.131
Copper with 1 artery	~13	1.075	930	0.166
Copper with 2 arteries	15-16	0.60	1670	0.193
Copper with no sintering		3.95	277	0.287
Aluminum with 2 arteries		0.771	1300	0.149

The sintering of the evaporators not only enhanced the orientation insensitivity, but also dramatically increased the overall heat transfer coefficient of the evaporator as compared to an unsintered evaporator. Typically, the inside heat transfer coefficient varied from 1000 to 1400 Btu/hr-sqft-F for evaporators with sintered interiors. One evaporator with no sintered interior was evaluated under similar conditions. Its interior heat transfer coefficient was estimated to be around 200 Btu/hr-sqft-F.

The heat transfer coefficient was determined through the use of a Wilson (3) plot. If the reciprocal of the overall heat transfer coefficient is plotted against the water flow rate (exterior surface) raised to the -0.8 power, a straight line exists. By extrapolating to the ordinate intercept, (infinite water flow), the inside heat transfer coefficient can be determined. The heat transfer resistances of the evaporator material (thermal conductivity) and exterior resistance at infinite water flow can be neglected. Therefore the ordinate intercept represents the internal heat transfer coefficient. Figure 2 shows a typical plot. Table 1 gives the slope and intercept for the Wilson plot for each evaporator evaluated.

Condenser Design:

Aluminum pipes of two different diameters were investigated for use as a condenser: 1/4-in IPS and 1/8-in IPS. The exterior of these heat exchangers was spined by Heatron, Inc. The principal objective in designing the condenser was to minimize the weight per unit of heat transfer capacity. To reduce the amount of heat transfer area required for heat rejection, a fan will be present to move air across the condensers. A second criterion was to design for the minimum fan power per unit of heat transfer capacity. Spacing between the pipes was varied to determine both the change in heat transfer capacity and air pressure drop under different air flow rates. Selection of the best configuration is based not only on these two criteria but is also restrained by the geometry of the microclimate prototype.

As with the evaporators, the external heat transfer coefficient can be estimated by moving a known volume of air over the external surface and pumping water through the pipe interior. By measuring the entrance and exit temperature of the water and the temperature of the air stream, the amount of heat transferred can be calculated along with the overall heat transfer coefficient. A Wilson plot of the reciprocal of the overall heat transfer coefficient versus the water flow rate raised to the -0.8 power will give a straight line whose ordinate intercept represents the external heat transfer coefficient. As with the evaporators, the heat transfer resistance offered by the aluminum material is neglected. The intercept represents the heat transfer coefficient at infinite water flow. Therefore, the resistance to heat transfer on the internal surface can also be neglected when determining the exterior heat transfer coefficient. Figures 3-8 show the Wilson plots for the two different size aluminum pipes at three different pipe spacings.
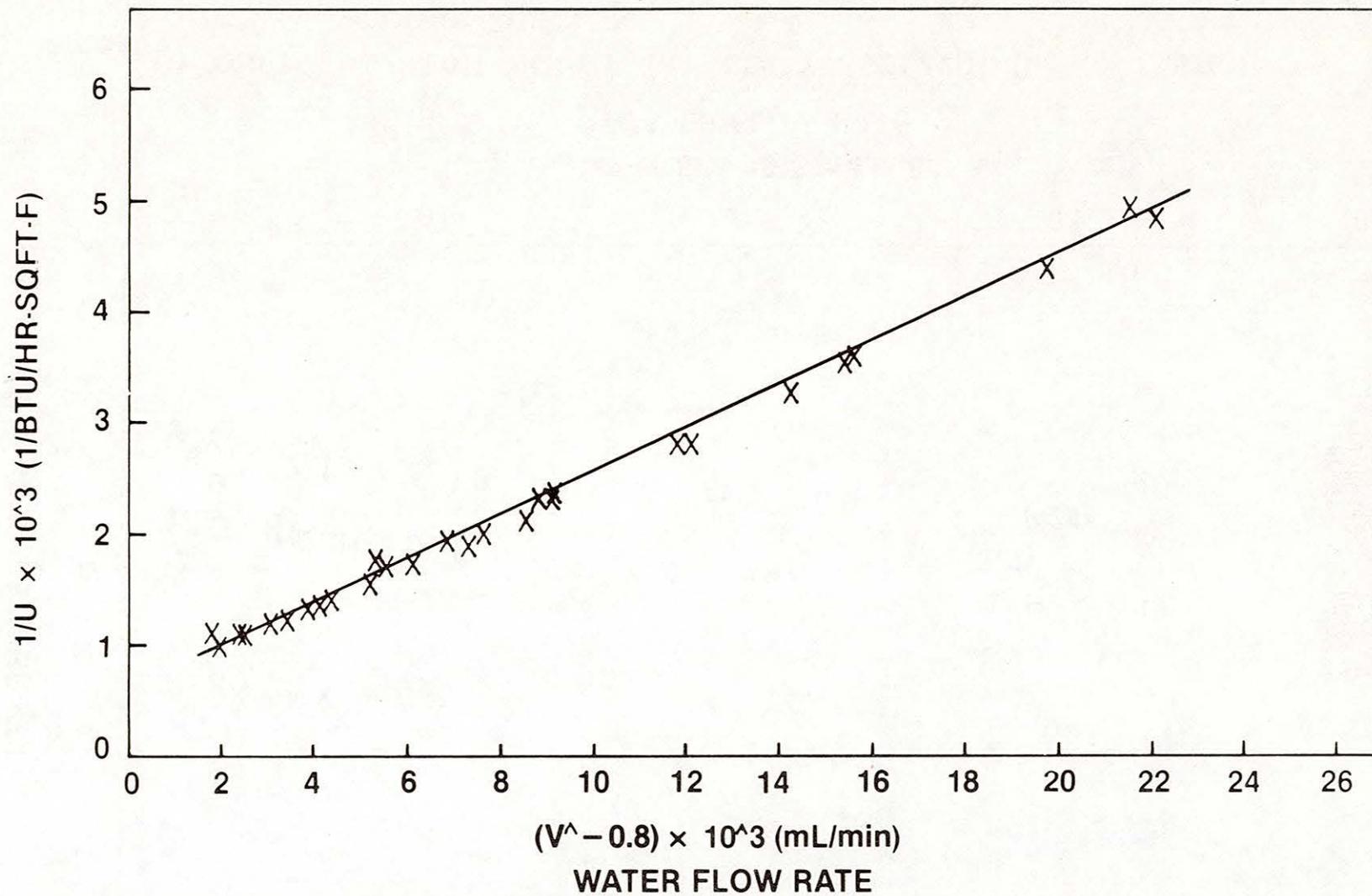
Figure 2. Wilson plot for copper evaporator.
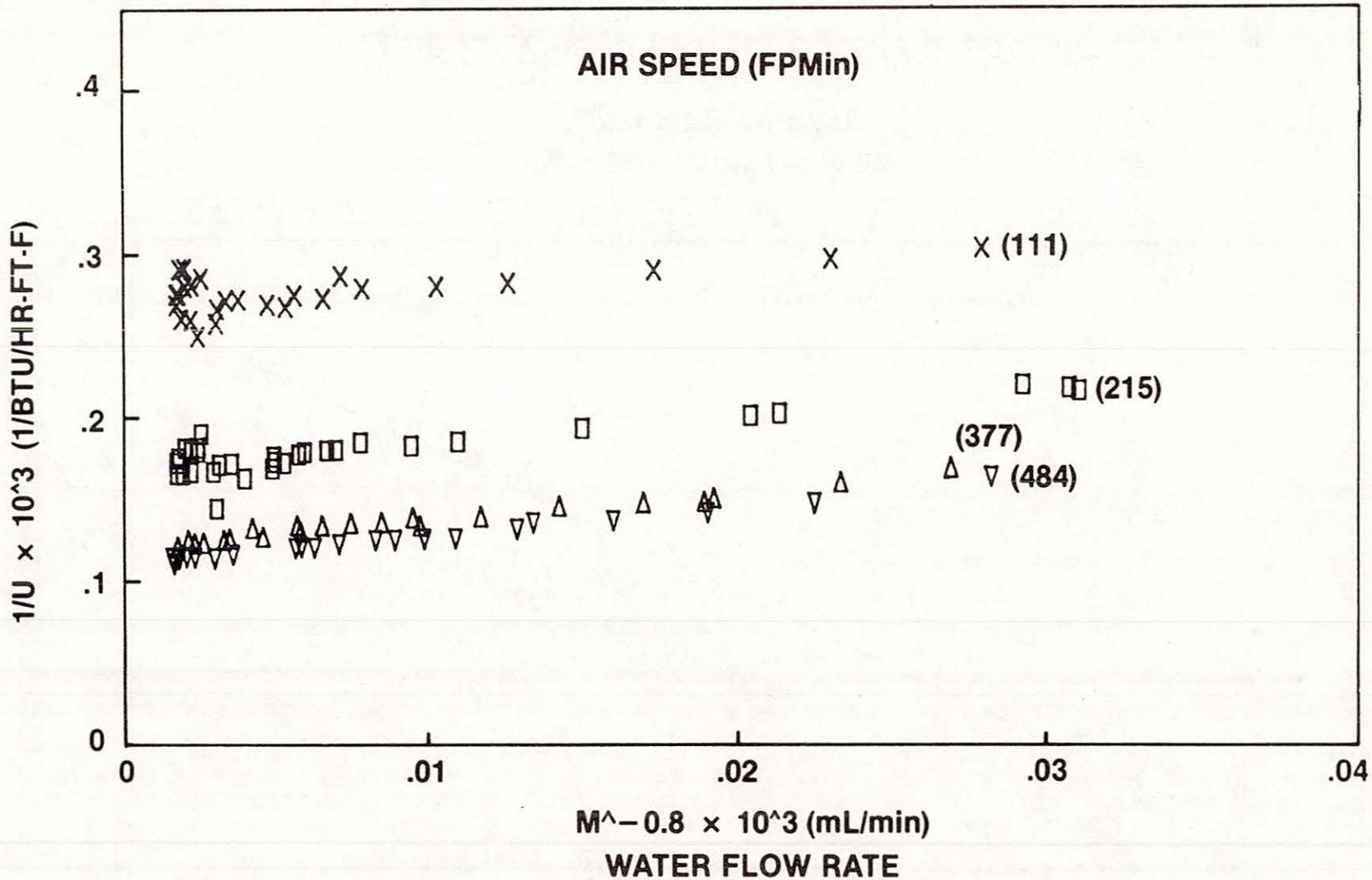
Figure 3. Wilson plot for 1/8″ condenser with 0.522″ center to center spacing.
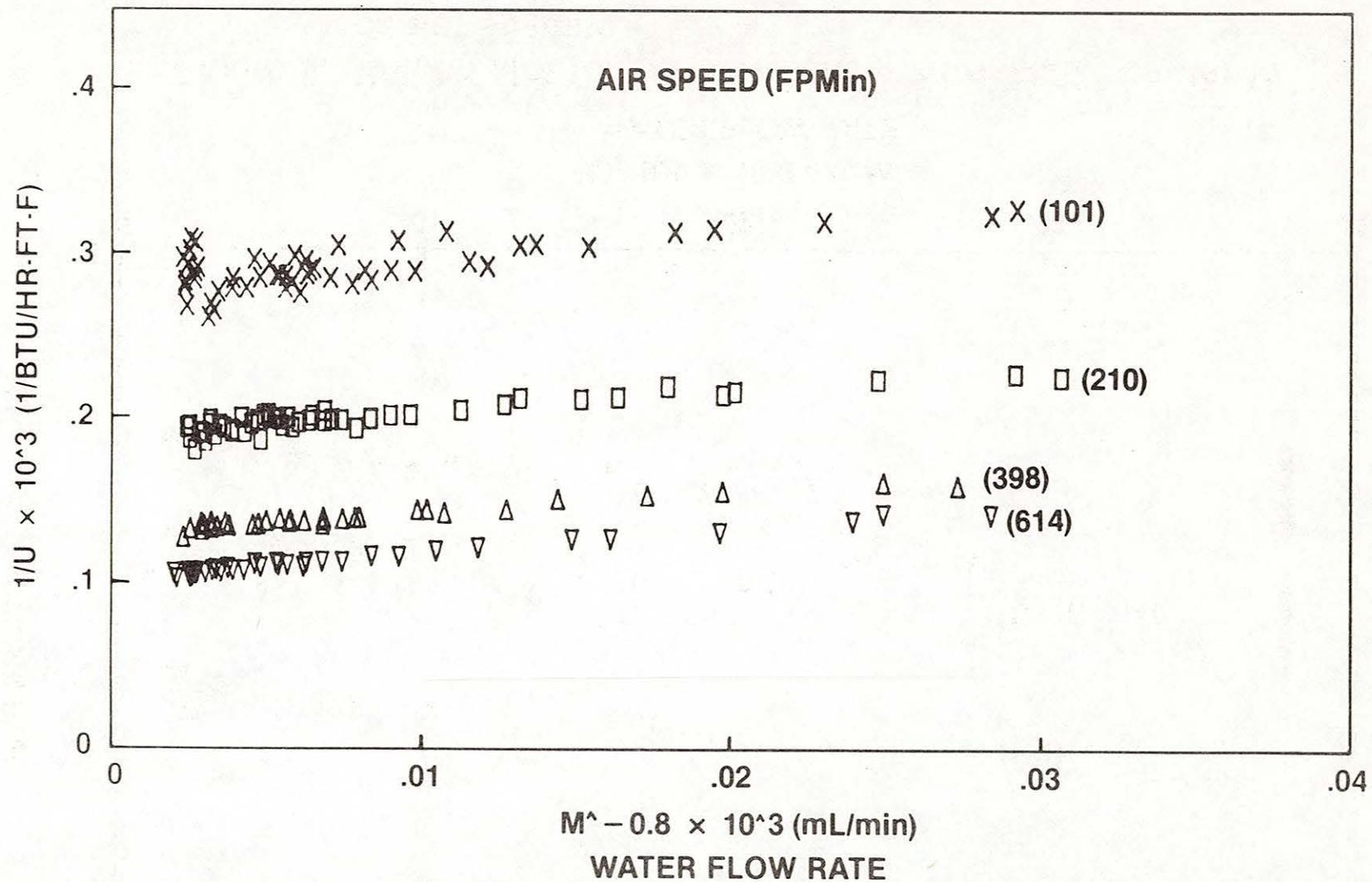
Figure 4. Wilson plot for 1/8″ condenser with 0.643″ center to center spacing.

X (108)

☐ (211)

Δ (426)

∇ (593)

+ (792)

AIR SPEED (FPMin)

1/U × 10^3 (1/BTU/HR·FT·F)

.4

.3

.2

.1

0

0   .01   .02   .03   .04

M^−0.8 × 10^3 (ml/min)

WATER FLOW RATE
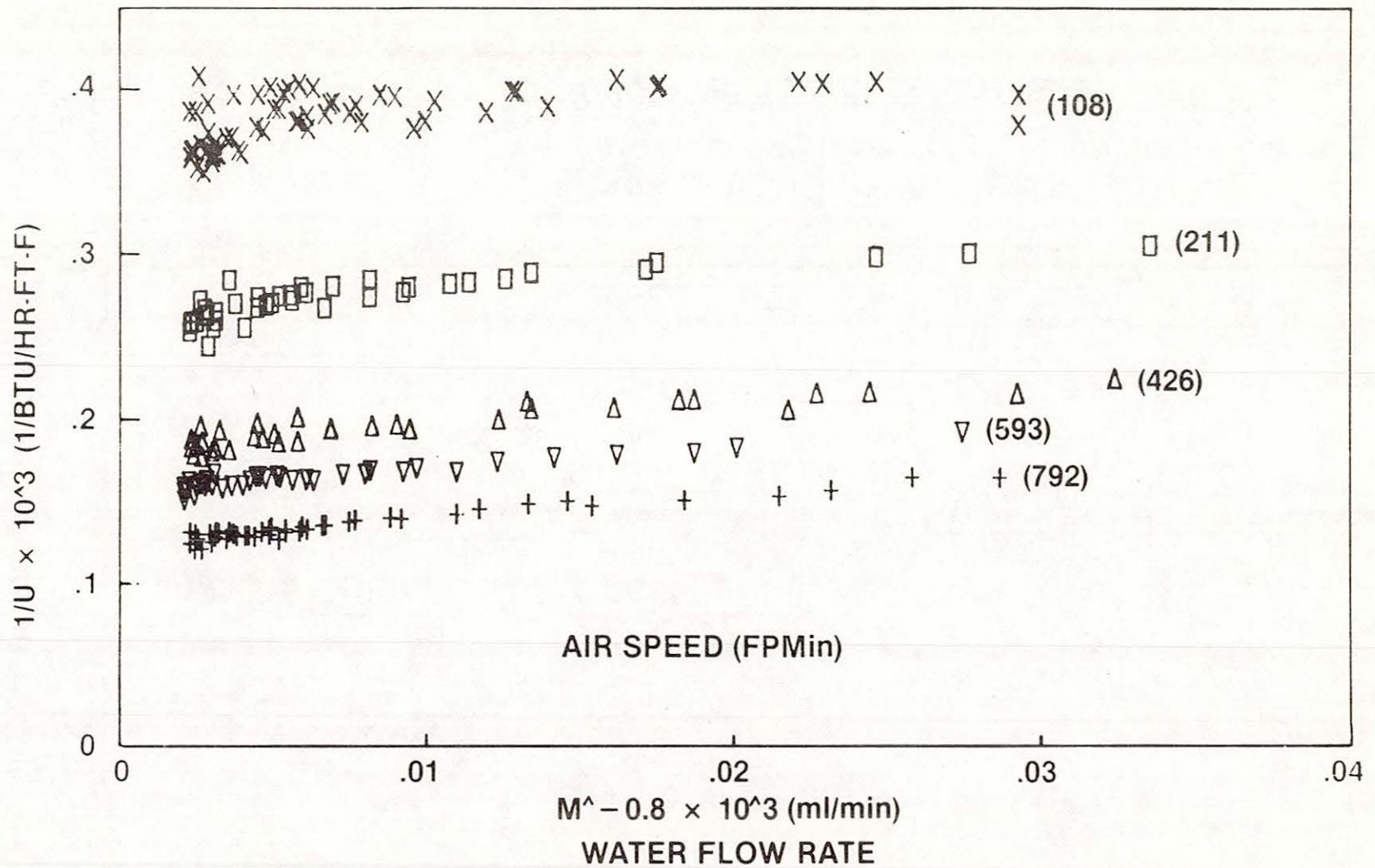
Figure 5. Wilson plot for 1/8″ condenser with 0.896″ center to center spacing.

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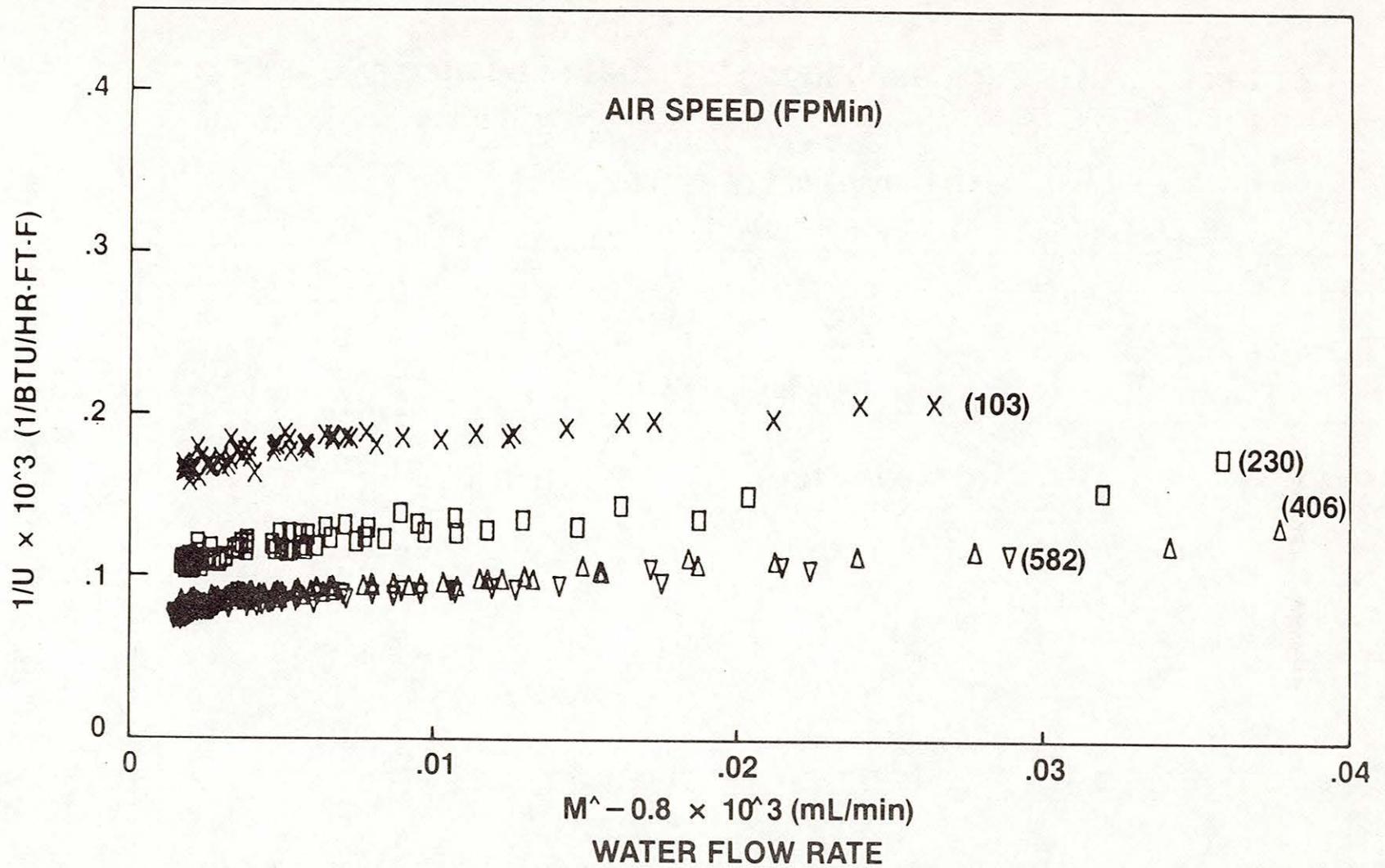
Figure 6. Wilson plot for 1/4″ condenser with 0.792″ center to center spacing.

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AIR SPEED (FPMin)

1/U × 10^3 (1/BTU/HR·FT·F)

X (105)

(206)
(421)
(585)
(724)

.4

.3

.2

.1

0

0   .01   .02   .03   .04

M^−0.8 × 10^3 (mL/min)
WATER FLOW RATE
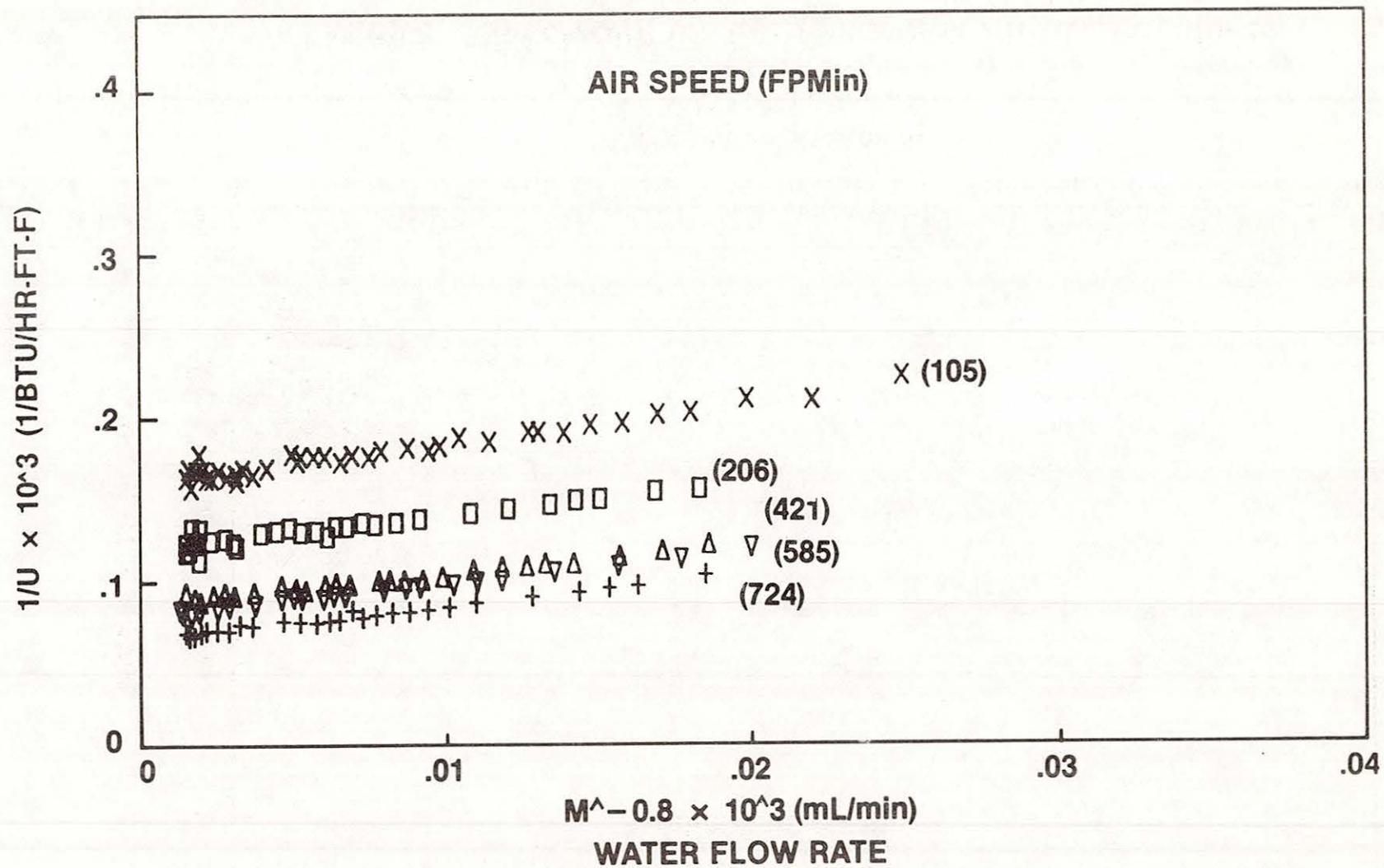
Figure 7. Wilson plot for 1/4″ condenser with 1-1/8″ center to center spacing.
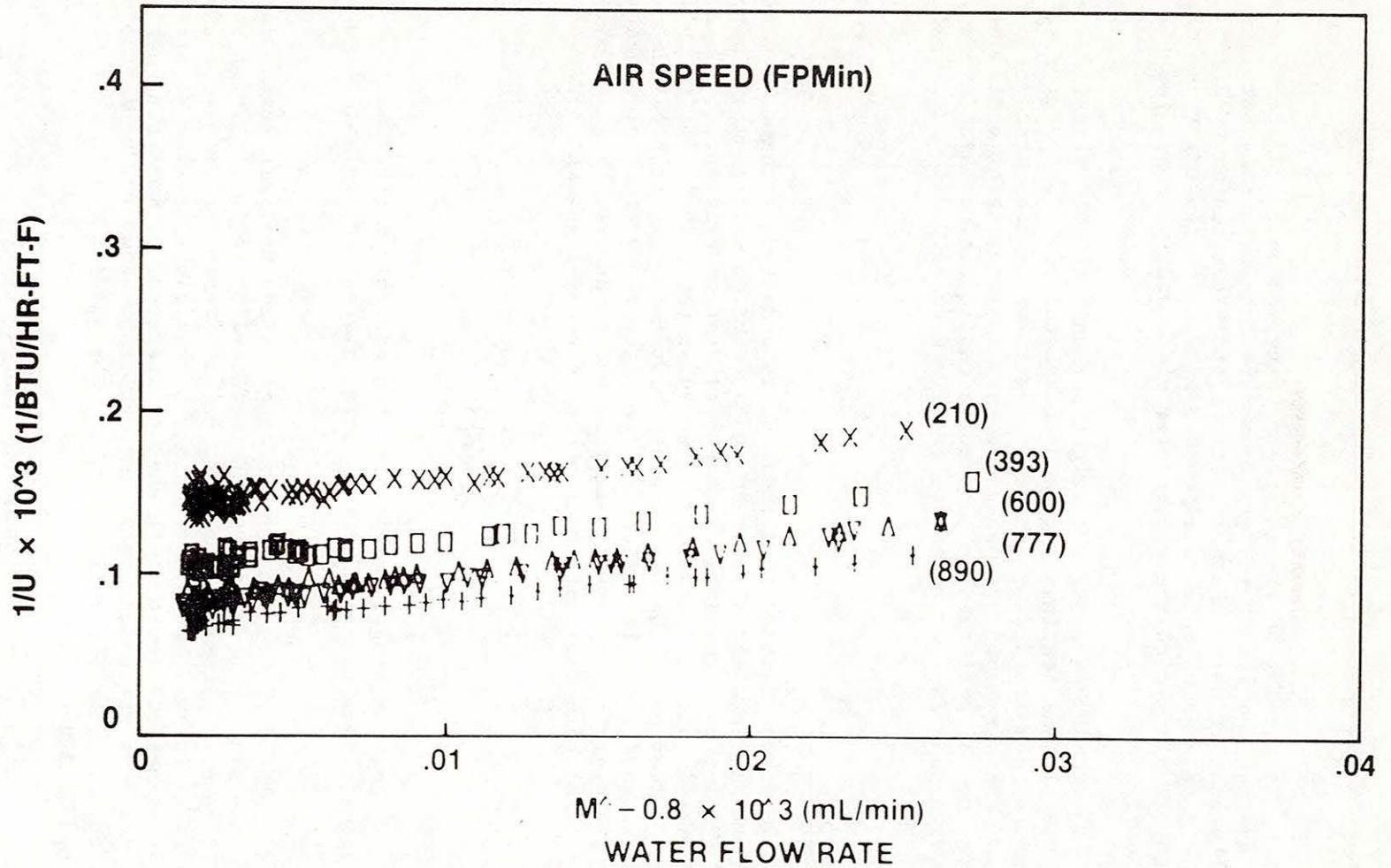
Figure 8. Wilson plot for 1/4″ condenser with 1.5″ center to center spacing.

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If the log of the intercept (exterior heat transfer coefficient) is plotted against the log of the air flow rate, the resulting straight line describes the heat transfer characteristic of that particular pipe and geometry. Figure 9 shows this relationship for one condenser. These data are shown in Table 2 along with the Wilson plot slope and intercept for all the condenser configurations.

With these data, the weight per unit of heat transfer can be determined for all the spacings and geometries studied. The power required to move air across these condenser geometries can also be determined from the air pressure drop and air flow rate measurements. An intelligent design of the condenser can now be performed by choosing a configuration which minimizes the condenser weight and fan power (noise level). Figure 10 shows the design for the condenser.

Waste Engine Heat Exchanger

It was decided that from the condenser data that the waste engine heat exchanger would also be designed from the same aluminum pipe as the condenser. To increase the internal heat transfer coefficient, turbulence inducers (aluminum wire spiral) were inserted in the interior of the aluminum pipe. Since rejection of the engine waste heat is not as critical as the condenser heat rejection, it was decided to place the waste engine heat exchanger in the air stream downstream from the condenser. Figure 10 shows the configuration for both the waste engine heat exchanger and the condenser.

CONCLUSION

Heat exchanger designs for the portable microclimate conditioning unit have to consider the entire system and the soldier who will have to carry it.

The size, for instance, for all three heat exchangers is affected by the size or power output of the Stirling engine. A high powered engine would require a smaller condenser but the waste engine heat exchanger would have to be larger. Knowledge of human physiology is also required since lowering the evaporator temperature does not necessarily mean that more heat can be removed from the soldier. If the evaporator temperature is too cold, vasoconstriction occurs around the torso of the soldier wearing the vest and heat transfer is hindered.

The design of the condenser and waste heat exchanger is also affected by how much power can be afforded to operate a fan for moving air across their surfaces and by how much fan noise is acceptable.

In the evaluation of the first Stirling-powered microclimate cooling unit, all the above factors will have to be considered so that optimal refinements can be made to produce an effective item for the soldier in a CB environment.

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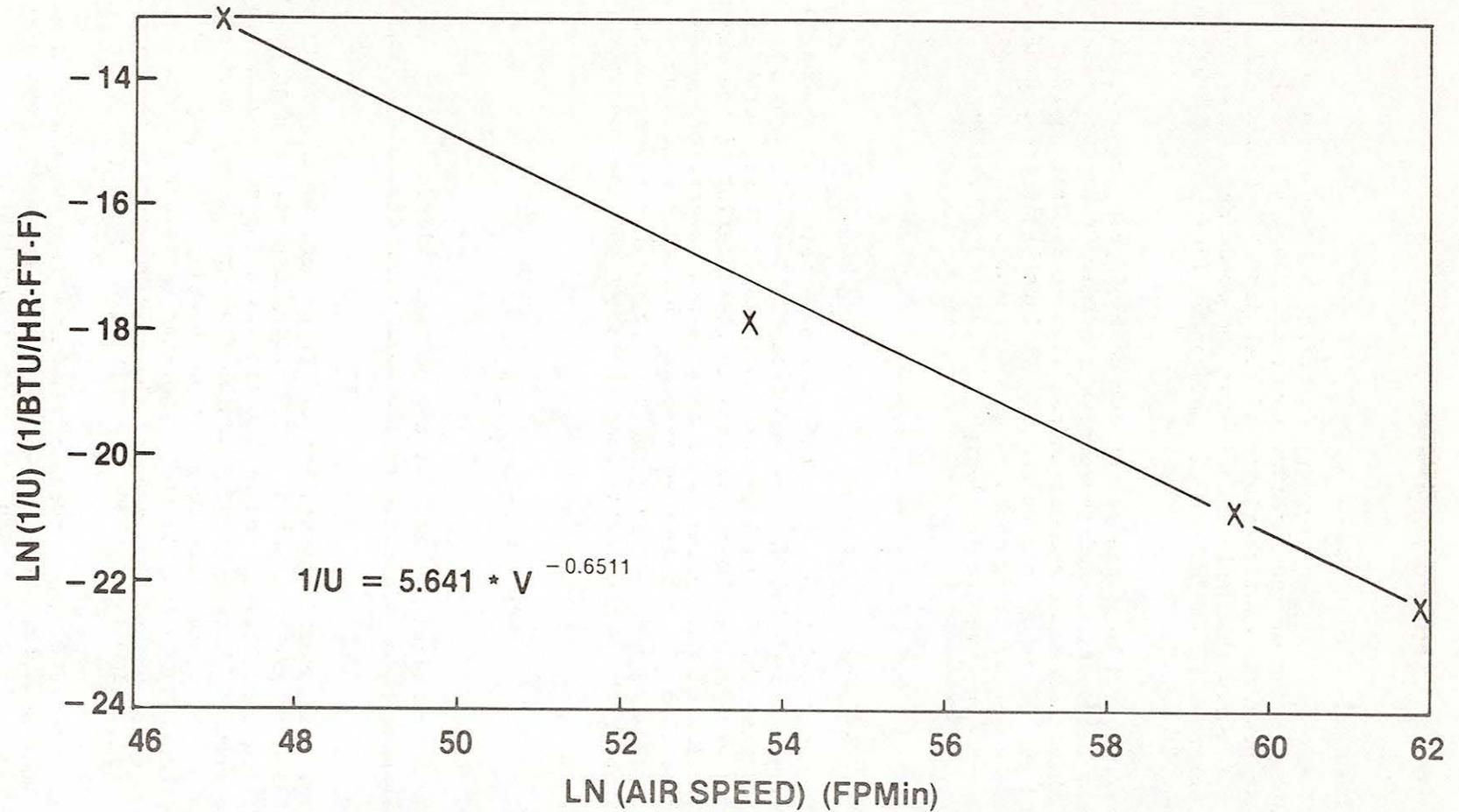
Figure 9. Log-log plot of Wilson plot intercept vs. air flow rate for 1/8" condenser with 0.522" center to center spacing.

Table 2. Wilson Plot Slope and Intercept for Condenser

1/4" HEATRON ALUMINUM TUBING

| NOMINAL AIR SPEED (FPM) | SPACING | | | | | |
| | 1 - 1/2 " | | 1 - 1/8" | | 0.792" | |
	SLOPE	INTCPT	SLOPE	INTCPT	SLOPE	INTCPT
100			2.584	0.1581	1.815	0.1610
200	1.680	0.1473	2.220	0.1173	1.969	0.1023
400	1.910	0.1084	1.959	0.0846	1.520	0.0751
600	1.850	0.0893	2.195	0.0696	1.532	0.0638
800	1.970	0.0763	2.195	0.0623		
900	1.795	0.0717				

1/8" HEATRON ALUMINUM TUBING

| NOMINAL AIR SPEED (FPM) | SPACING | | | | | |
| | 0.643" | | 0.896" | | 0.522" | |
	SLOPE	INTCPT	SLOPE	INTCPT	SLOPE	INTCPT
100	1.794	0.2851	1.375	0.3720	1.180	0.2669
200	1.512	0.1947	1.661	0.2606	1.670	0.1656
400	1.362	0.1357	1.394	0.1828	1.700	0.1191
500					1.806	0.1018
600	1.668	0.1014	1.378	0.1498		
800			1.569	0.1234		

AIR FLOW

CROSS
SECTION

CONDENSER

ENGINE
WASTE HEAT

17

← 15″ →
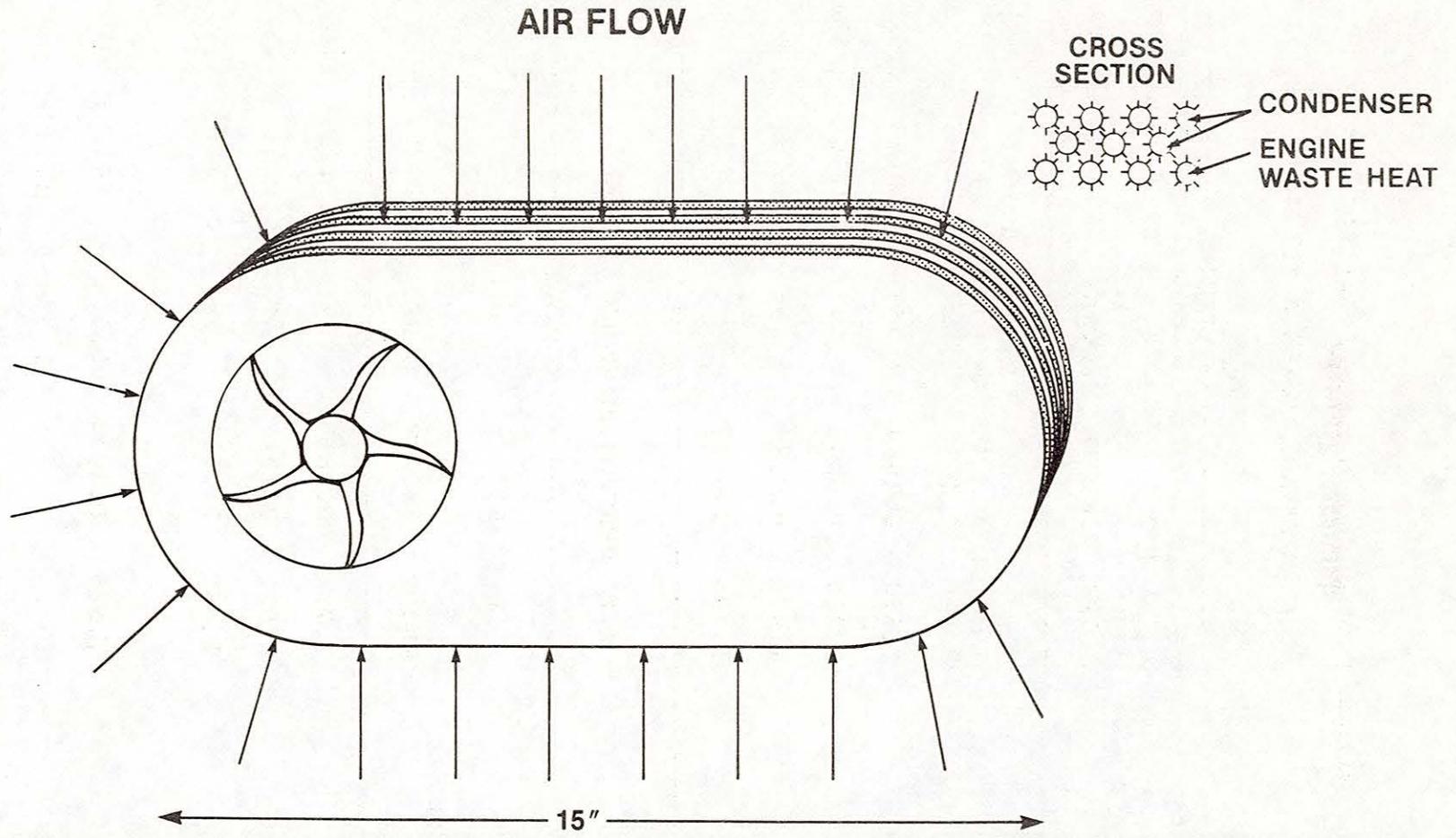
Figure 10. Condenser and waste engine heat exchange configuration.

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TITLE: The Role of Sweating on Comfort and Performance in an Encapsulation Environment: A Study of Hand Encapsulation Using Different Glove Liners

DONNA H. BRANSON, DR.,* AND LYNDA ABUSAMRA, MS.

ABSTRACT:

Although the use of a microclimate cooling vest can prolong the length of time that soldiers can perform in Mission Oriented Protective Posture (MOPP) gear without suffering serious heat stress, sweating in the extremities remains a problem in terms of comfort and performance. This study was designed to determine the effects of four types of glove liners on sweating of the hands, the perception of comfort and manual dexterity. Military subjects were studied in Battle Dress Uniform and MOPP gear in a moderate thermal environment. Significant glove liner weight differences were found with the Air Force glove exhibiting the greatest absorption of sweat. There was a tendency for subjects wearing the standard Army liner to experience the lowest sweat rate. Glove liner type had no significant effect on manual dexterity. There was a tendency for the standard Army liner to be perceived as the most snug and the Air Force liner as the least snug. Subjects frequently complained about the snug fitting Army liner. Perception of temperature and thermal comfort for the hands did not differ by glove liner. Tactile descriptors related to retention of sweat, such as clamminess, stickiness and dampness, indicated increased discomfort over the experimental session.

*BIOGRAPHY
PRESENT ASSIGNMENT: Associate Professor, Oklahoma State University, Stillwater, OK
PAST EXPERIENCE: Research in thermal response of subjects wearing functionally designed protective clothing; (Michigan State University, Federal Aviation Administration)
DEGREES HELD: Ph.D. Michigan State University, 1982; M.S. University of Rhode Island, 1976; B.A. Rosary College, 1965

THE ROLE OF SWEATING ON COMFORT AND PERFORMANCE IN AN
ENCAPSULATION ENVIRONMENT: A STUDY OF HAND ENCAPSULATION USING
DIFFERENT GLOVE LINERS

DONNA H. BRANSON, DR.
LYNDA ABUSAMRA, MS.

INTRODUCTION

Although the use of a microclimate cooling vest can prolong
the length of time that soldiers can perform in Mission Oriented
Protective Posture (MOPP) gear without suffering serious heat
stress, sweating in the extremities is a problem in terms of
performance and overall comfort (1). The purpose of the present
study was to evaluate four glove liners of different
compositions, two string-knit and two seam-stitched, with regard
to their differential effects on sweating on the hand, manual
dexterity performance, and the perception of comfort in a
moderate thermal environment. Lightweight, stretchable, knitted
cotton fabric, seam-stitched gloves are currently issued to
military troops with a pair of standard butyl rubber
chemical-biological protective gloves (2, 3). The cotton gloves
are worn under the butyl gloves "to aid in the absorption of the
moisture which accumulates within the impermeable rubber glove."
(2). Replacement of the standard Army, knitted cotton fabric,
seam-stitched glove liner is under consideration (4).

METHOD

Subjects.
Sixteen male military volunteers participated as subjects. They
ranged in age from 18 to 25 years with a mean age of 21.1
years. All subjects were enlisted Army personnel assigned on
temporary duty to the Natick Test Subject Platoon at the U.S.
Army Natick Research, Development and Engineering Center. All
subjects were informed of the nature, duration, purpose, and
benefits of the experiment, and each signed an informed consent
statement.

Handwear

The following glove liners were selected for evaluation:

1. The current standard 100% cotton, seam-stitched Army liner (3).
2. A 100% cotton seam-stitched liner adopted by the Air Force for use with the 7-mil and 14-mil CB gloves (5).
3. A 100% cotton string-knit candidate liner.
4. A 50% cotton/50% acrylic string-knit candidate liner.

Physical characteristics of the glove liners are given in Table 1. Each glove liner was worn beneath the 14-mil CB protective butyl rubber glove.

TABLE 1

Physical Characteristics of Glove Liners

	Army	Air Force	Cotton Liner	Cotton/Acryl. Liner
Fiber Content	100% Cotton	100% Cotton	100% Cotton	50% Cotton 50% Acrylic
Weight (oz/yd^2)	4.0	6.1	10.4	9.6
Thickness	0.020	0.042	0.056	0.059
Yarn Count	18/1	35/1	14/1	14/1
Fabric Structure	Plain Knit	Rib Knit	Plain Knit	Plain Knit
Wales/In.	28	36	15	15
Courses/In.	26	39	17	17
Length*	7.88	13.73	10.20	10.29

* Measured in inches from the tip of the middle finger to the lower edge when the gloves are flat and unstretched.

Experimental Design

A repeated measures Latin square design was used. Subjects were studied in pairs for the 32 sessions comprising the study. Sixteen sessions were conducted in the morning and 16 sessions in the afternoon. All glove liners were tested an equal number of times in the morning and in the afternoon. Each subject participated in four 2-hour test sessions (two morning and two afternoon) while wearing each of the glove liners. Subjects were randomly assigned to two partners for test sessions. All four glove liners were worn, in a randomized sequence, every test day.

Test Facilities/Test Apparatus

Testing was conducted in the Sensory Analysis Psychophysiology Laboratory, Science and Advanced Technology Directorate. Ambient room temperature ranged from $22.2^{\circ}C$ to $29.7^{\circ}C$ with a mean temperature of $26.1^{\circ}C$. All subjects wore battle dress uniforms (BDU) and the MOPP jacket zipped and snapped throughout each phase of the experiment.

Skin temperature was measured with a YSI 709B thermistor probe attached with adhesive tape to the palmar surface of the nondominant hand. A General Eastern System 1100 DP (Dew Point) Hygrometer was used to measure ambient room temperature and dew point of the hand from a sweat capsule attached to the skin with hypoallergenic skin glue. Skin temperature and dew point, of the nondominant hand, were continuously recorded on a Graphtec, Inc. P.O.C. Multicoder MC6624 Strip Recorder. A TRS-80 Model III computer, which was interfaced with the strip recorder, recorded skin temperature, dew point, and sweat rate every five minutes. The conversion of dew point to sweat rate was calculated using the following equation, as given in Avellini, (7):

$$SR = \frac{M \, pH_2O \, F}{ART}$$

where

SR = sweat rate
M = molecular weight of water
A = area under the sweat capsule
R = universal gas constant (62.358 mm Hg-liters/mole)
pH_2o = partial pressure of water in the sample gas leaving the capsule and is directly related to dew point
F = flow rate in liters/minute
T = temperature in degrees Kelvin of air entering the capsule.

Glove weights were taken, to the nearest 0.1g, on a Sartorius electronic prercision top-loading balance, Model 1403MP7-2, both immediately before and after each test session.

Manual Dexterity Tasks

A battery of tests was assembled as indices of manual dexterity performance (Purdue Pegboard One-hand Test, Purdue Pegboard Assembly Test, Minnesota Rate of Manipulation One-Hand Turning and Placing Test, O'Connor Finger Dexterity Test (8,9,10). These tasks were administered, in the order indicated, at the beginning and again at the end of every test session.

Perceptual Measures

Two instruments were used to measure the subject's perception of hand temperature (Fig. 1) and hand thermal comfort (Fig. 2). Perception of hand temperature was assessed in each hand using the classic ASHRAE (10) seven-point rating scale with one indicating cold and seven indicating hot. Thermal comfort was also assessed in each hand using a seven-point rating scale with one indicating extremely comfortable and seven indicating extremely uncomfortable.

For the present study, perception of wetness, fit, and tactile sensations (Fig. 3) were assessed using surveys completed by the subjects during the experiment. Definitions of the descriptors were provided to minimize use, by the subjects, of different definitions of the same descriptor. This instrument is an adaptation of those used by Hollies et al. (12) and Lofquist et al. (13). A seven-point scale was also used to assess the subject's perception of the overall comfort of the liners.

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Subject: _____   Survey Number: _____

Test Date: _____

Test Time: _____ A.M. _____ P.M.

Please circle the number which best describes your perceived temperature in your instrumented hand.

    1. COLD

    2. COOL

    3. SLIGHTLY

    4. NEUTRAL

    5. SLIGHTLY WARM

    6. WARM

    7. HOT

Please circle the number which best describes your perceived temperature for your non-instrumented hand.

    1. COLD

    2. COOL

    3. SLIGHTLY COOL

    4. NEUTRAL

    5. SLIGHTLY WARM

    6. WARM

    7. HOT

Figure 1. Hand and temperature perception survey instrument.

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Subject: _____   Survey Number: _____

Test Date: _____

Test Time: _____ A.M. _____ P.M.

Please circle the number which describes how comfortable the temperature of your <u>instrumented</u> hand feels.

    1.   EXTREMELY COMFORTABLE

    2.   MODERATELY COMFORTABLE

    3.   SLIGHTLY COMFORTABLE

    4.   NEUTRAL

    5.   SLIGHTLY UNCOMFORTABLE

    6.   MODERATELY UNCOMFORTABLE

    7.   EXTREMELY UNCOMFORTABLE

Please circle the number which describes how comfortable the temperature of you <u>other</u> hand feels.

    1.   EXTREMELY COMFORTABLE

    2.   MODERATELY COMFORTABLE

    3.   SLIGHTLY COMFORTABLE

    4.   NEUTRAL

    5.   SLIGHTLY UNCOMFORTABLE

    6.   MODERATELY UNCOMFORTABLE

    7.   EXTREMELY UNCOMFORTABLE

Figure 2. <u>Hand thermal comfort survey instrument.</u>

Subject: _____   Survey Number: _____

Test Date: _____

Test Time: _____ A.M. _____ P.M.

1. For each of the words listed below, please write the number
    which best describes how you perceive the feel of the glove
    liners you are wearing today.

    USE THE SCALE: 1=EXTREMELY, 2=MOSTLY, 3=SLIGHTLY,
                     4=NOT AL ALL
    (According to the intensity of your feeling).

    _____ SNUG   (right or close in fit)

    _____ HEAVY   (in terms of weight of the liner)

    _____ STIFF   (resistant to bending)

    _____ STICKY (moist and adheres to skin)

    _____ CLAMMY (cold, moist, clinging to touch)

    _____ DAMP   (moistness or wetness)

    _____ ROUGH   (not smooth, coarse)

    _____ SCRATCHY (irritating, itchy)

2. Keeping the above attributes in mind, please circle the number
    which best describes your perceived over-all comfort of the
    glove liners you are wearing today.

        1. EXTREMELY COMFORTABLE

        2. MODERATELY COMFORTABLE

        3. SLIGHTLY COMFORTABLE

        4. NEUTRAL

        5. SLIGHTLY UNCOMFORTABLE

        6. MODERATELY UNCOMFORTABLE

        7. EXTREMELY UNCOMFORTABLE

Figure 3. Liner comfort survey instrument.

PROCEDURE

Before testing began, a glove-fit and manual dexterity training session was held. Each subject was fitted for a pair of appropriately sized 14-mil, butyl CB protective gloves. The glove for each subject's nondominant hand was marked while the subject wore the glove to ensure a satisfactory placement of the sweat capsule. Five hand-dimension measurements were also made on the right hand of each subject while the subject was bare-handed. These measurements were used subsequently to choose each subject's standard Army liner to ensure the best fit possible. During the training sessions the directions for each task were read and the procedure demonstrated by an investigator before the subject was given four test trials. Subjects completed all of the test trials while wearing their issued CB gloves with a nontest liner.

A hole 19 mm in diameter was cut for the sweat capsule in the CB glove for the nondominant hand. The liners were similarly cut after a bead of glue was applied around the marked opening to prevent ravelling. The liners were conditioned at 20+/-2 C and 40+/-3% RH for twenty-four hours preceding the test session. Immediately prior to each test session, the liners and the CB gloves, including a paper towel sealed in a plastic bag, were weighed.

At the beginning of each test session, subjects donned, zipped, and snapped an appropriately sized MOPP jacket over their BDUs. The liners were donned and a fit evaluation of the liners was done. The sweat capsule and skin temperature thermistor probe were affixed to the palmar surface of the nondominant hand. Once the CB gloves were donned and the sweat capsule was secured, the two-hour test session began.

Subjects completed eight sets of temperature perception and thermal comfort surveys (every 15 minutes) during the test. During the time between performing the two sets of psychomotor tasks, subjects were encouraged to participate in various nonphysical, mind-challenging games, such as Trivial Pursuit and Risk.

At the end of the test session, the probes were disconnected. The butyl glove was removed and placed in its original plastic bag. The glove liner was removed and placed in its original plastic bag. The hand was wiped with paper toweling, which was then placed in the bag with the CB glove. Both bags were sealed and weighed. The CB gloves were cleaned and prepared for the next day's testing.

RESULTS

Sweat Rate and Skin Temperature.

Sweat rate among the subjects ranged from 0.52 mg/cm/min to 0.65 mg/cm/min. There was a tendency for subjects to have the lowest sweat rate while wearing the standard Army 100% cotton liner, and to experience the highest sweat rate while wearing the cotton/acrylic blend candidate liner. However, an analysis of variance indicates that there were no significant differences among the glove liners. Analysis of variance of skin temperatures indicates a main effect for time of measurement. Regardless of the glove liner worn, subjects' skin temperatures increased over time with no significant difference by glove liner.

Perceived Hand Temperature and Thermal Comfort.

ANOVA results for perceived hand temperature of the instrumented and the noninstrumented hand determined a main effect for time but not for glove liner condition. Thus, subjects rated both hands warmer over time regardless of the glove liner worn. Data on the perception of thermal comfort were similar to the temperature perception data with subjects reporting greater thermal discomfort as time progressed for all liner conditions. A main effect for time was significant. No significant differences were found by hand (instrumented vs noninstrumented) for either perceived temperature or perceived thermal comfort.

Manual Dexterity Performance.

Analysis of variance indicates that a main effect for time was found for three of the four tasks, the Minnesota, the O'Conner, and the Purdue Right-Hand tests. For these tasks, regardless of the glove liner worn, the scores obtained at the end of the test session were significantly better than the scores at the beginning of the test session. Psychomotor performance did not appear to be influenced by the type of liner worn beneath the protective glove under the moderate environmental conditions of this experiment.

Perceived Liner Comfort.

For the first descriptor, snug, a liner effect was highly significant (F = 7.8, and p <0.003). Examination of these data, which are shown in Table 2, indicates that the Air Force liner was the least snug and the standard Army liner was reported as being the most snug. Indeed, subjects frequently complained about the snug fitting Army liner. A main effect for liner was also found for the second comfort descriptor, heavy, (F = 5.07, p <0.0041, Table 2). Both of the candidate liners were perceived by the subjects as being heavier than the standard Army and Air Force liner.

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TABLE 2.

Mean Liner Comfort Votes for Snug and Heavy Descriptors
by Liner

Liner Comfort Descriptor	Army Liner	Air Force Liner	Candidate 1 Cotton Liner	Candidate 2 Cotton/Acrylic Liner
Snug	1.98	2.91	2.12	2.08
Heavy	3.61	3.61	3.37	3.27

No significant effects were found for the third comfort
descriptor, stiffness. Subjects did not find any of the liners
stiff.

A survey number main effect was found for the fourth
descriptor, stickiness, the fifth descriptor, clammy, and the
sixth descriptor, dampness. Since a liner effect was not found,
the data were collapsed over liners to determine mean scores for
each descriptor by survey number (Table 3). Subjects reported
increased stickiness, clamminess, and dampness over time
regardless of the liner worn.

TABLE 3.

Mean Liner Comfort Votes for Sticky, Clammy, Damp
Descriptors by Survey Number

Survey Number	1	2	3	4	5	6	7	8
Sticky	3.44	3.19	3.19	3.06	3.02	3.03	3.03	2.97
Clammy	3.52	3.16	3.06	2.86	2.91	2.97	2.91	2.77
Damp	3.39	2.88	2.80	2.69	2.70	2.58	2.52	2.45

Analysis of the data for the seventh descriptor, roughness, indicated a main effect for liner (F = 4.79, p <0.0056) and for survey number (F = 2.52, p <0...0193). The mean scores by liner over time are shown in Table 4. Examination of these data indicates that the Air Force liner was perceived as the least rough. There was also a trend for the two candidate glove liners to be perceived as the roughest.

TABLE 4.

Mean Liner Comfort Scores for the Descriptor Roughness
by Survey Number

| Liner | Survey Number | | | | | | | |
Condition	1	2	3	4	5	6	7	8
Army Liner	3.44	3.38	3.38	3.19	3.13	3.38	3.31	3.31
Air Force Liner	3.75	3.63	3.50	3.56	3.69	3.63	3.63	3.63
Candidate 1 Cotton Liner	3.31	3.13	2.94	3.00	3.06	3.00	3.00	3.00
Candidate 2 Cotton/Acrylic Liner	3.13	3.25	3.00	3.13	3.00	2.81	2.94	2.88

While there were no significant main effects for the eighth descriptor, scratchiness, there was a tendency for the subjects to rate the two candidate liners as being more scratchy.

An overall liner comfort score was determined by liner over time. Results of ANOVA showed that there was a main effect for survey number but not for liner. Thus subjects reported increased discomfort over time regardless of the liner worn.

Glove Weight Changes.

To determine absorption of moisture of the test glove liners, the liners were weighed immediately before each test session and at the conclusion of the session. ANOVA results indicated a significant difference in liner weight changes. Post-hoc Sheffe comparisons found that the weight difference for the Army and the 100% cotton candidate liners were significantly less than the weight change of the Air Force liner. Weight change for the Army liner was also significantly less than the weight change found for the cotton/acrylic candidate liner.

DISCUSSION

This study was designed to determine the effects of four glove liners on sweating of the hands, absorption of sweat by glove liners, manual dexterity, and the perception of comfort in a moderate thermal environment. Although there was a tendency for subjects wearing the standard Army liner to experience the lowest sweat rate, and subjects wearing the cotton/acrylic candidate liner to experience the highest sweat rate, the glove liners studied did not produce statistically significant effects on either sweat rate or manual dexterity under conditions of this experiment. The dexterity measures used are sensitive and reliable. It is possible that no glove liner being considered for use with chemical protective ensembles will have significant impact on manual dexterity.

Several comfort measures revealed significant differences among glove liners. The standard Army liners were perceived as most snug; indeed subjects frequently complained about the snug fitting Army liner. Both string-knit candidate liners were judged heavier than the standard Army and Air Force seam-stitched liners. Second, for several descriptors, comfort changed as the experimental session progressed. Specifically, the glove liners felt significantly more sticky, clammy and damp over time. These factors contributed to the significant increase in overall discomfort during the experimental session across glove liners. It is especially noteworthy that these results relate to the accumulation of sweat in glove liners.

Assessment of clothing comfort is a complex subject since clothing comfort is related to physical, psychological, and physiological factors as well as to the interactions among these factors. There is general agreement that the movements of heat, moisture, and air through both a fabric and a garment are major determinants of clothing comfort. Most agree that discomfort is caused by liquid sweat remaining on the skin (13). Hollies and Goldman (12) concluded that "comfort acceptance of garments next to the skin is in some way related to the ability of these garments to remove sweat from the skin-garment interface." DeMartino et al. (14) noted that ideal clothing, which touches the skin, should be able to transport liquid water without feeling wet. In addition to the major factors affecting moisture transport, various tactile sensations are associated with clothing comfort. Terms that have been used in the past include clingy, scratchy, soft, heavy, light, and picky (12,13,14,15). Difficulty in measurement of these subjective factors is compounded by the problem of different people assigning different meanings to these tactile sensations.

CONCLUSIONS

These results show that significant differences in clothing comfort can be measured even when objective measures of variables related to comfort, such as skin temperature and sweat rate, do not reveal differences. The present studies were conducted under moderate environmental conditions. It is expected that future studies of this sort, under more extreme thermal conditions, will reveal significant differences in a wider spectrum of comfort measures as well as sweat rate and behavioral performance.

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TITLE: A Calorically Dense Ration for the 21st Century

JACK BRIGGS, MR.,* C. PATRICK DUNNE, DR., MARYANN GRAHAM,
MS., EINAR RISVIK, MR., ARMAND CARDELLO, DR., ANN BARRETT,
MS., AND IRWIN A. TAUB, DR.

ABSTRACT:

An entirely new concept for achieving compactness and convenience in a
combat ration has been developed to meet the needs of the Army in the 21st
century. It is based on new technologies to maximize caloric density. The
ration to be used will be nutritionally sufficient to avoid performance
decrements for soldiers operating in stressful environments.

The new ration concept centers around four distinct, calorically dense
components configured into easy-to-use modules. Some components will have
caloric densities ranging as high as 7.1 kcal/cc. Multiples of a modular
unit could be used depending on total caloric needs. The technologies
developed to produce these components are based on the principle that
achieving high caloric density requires a porous matrix that can be
compressed or infused. These are referred to as "ICE" technologies
(Infusion, Compression and Extrusion).

Using compression technology, a family of dairy bars with 6.0-6.8
kcal/cc was developed. Shelf-stability has been demonstrated by holding
samples for eight weeks at 125°F and finding no objective or subjective
evidence of lipid oxidation. To obtain this stability, a novel
synergistic combination of antioxidants was used.

Using infusion of extruded matrices, a family of products of 5-6
kcal/cc was developed. This new technology involves infusing, under
vacuum, a high-melt lipoidal liquid containing dispersed particles of
protein, sugars, and flavors into different carbohydrate matrices made
using extrusion cooking from corn, rice, or wheat flours . Infusates have
been developed with yogurt, chocolate, cheese, and chicken.

The acceptance ratings of these "rich" products have been high when
field-tested as components of other new operational rations.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Project Officer, Nutritional Sustainment Module;
Food Technologist, Food Engineering Directorate
PAST EXPERIENCE: Senior Food Technologist, Carnation Co. and T.J.
Lipton, Inc.
DEGREES HELD: B.S. Biology, Ft. Lewis College, CO; M.S.
Biochemistry, Colorado State University, Ft. Collins, CO.

A CALORICALLY DENSE RATION FOR THE 21st CENTURY

JACK BRIGGS, MR., C. PATRICK DUNNE, DR., MARYANN GRAHAM, MS., EINAR
RISVIK, MR., ARMAND CARDELLO, DR., ANN BARRETT, MS., & IRWIN TAUB, DR.

INTRODUCTION

The Army 21 concept for the battlefield scenario for the years
2000-2015 is predicated on highly mobile forces equipped with lightweight,
high technology equipment being engaged in high intensity combat far
removed from traditional supply reconstitution points, perhaps for 3-5
days. Each mobile force element must be self-sustaining and continue to
operate at peak efficiency, despite considerable stress. This concept
dictates a requirement for a ration surpassing any existing ration.

Such a ration of the future should have four distinctive
characteristics:

1. It must be of the highest possible caloric density, approaching
7.1 kcal/cc; this compactness would allow a dismounted soldier to carry
easily a 3-5 day supply of food meeting the 3600-kcal daily requirement.

2. It must be nutritionally adequate to maintain physical and mental
performance under highly stressful operational conditions; it should be
supplemented with a variety of natural and/or synthetic food components to
ensure maximum caloric utilization and maximum nutritive value.

3. It must be acceptable to the consumer, despite its unfamiliar
nature, throughout the period of use, which might even exceed 5 days.

4. It must be of optimum utility, consumable on the move without any
preparation, and modular in design; for example, a 900-kcal module should
be combinable to form rations of 1800, 2700, 3600, and 4500 kcal/day to
meet specific combat scenario requirements.

The Nutritional Sustainment Module (NSM) described here meets the challenge for the Army 21 ration and represents the optimum in caloric density, in nutrient selection, in acceptance of engineered foods, and in convenience of use and handling. As seen from Fig. 1, the caloric density, taking packaging into account, has increased from the Meal Combat Individual (MCI) at 0.95 kcal/cc to the Food Packet Assault at 1.25 kcal/cc to the Ration Light Weight 30 Day (RLW-30D), currently under development, targeted at 2.25 kcal/cc. The NSM ration is targeted at an even higher caloric density of 4.75 kcal/cc. The maximum component caloric density of 7.1 kcal/cc is achieved with a composition of 60% lipid/35% carbohydrate + protein and a mass density of 1 g/cc.
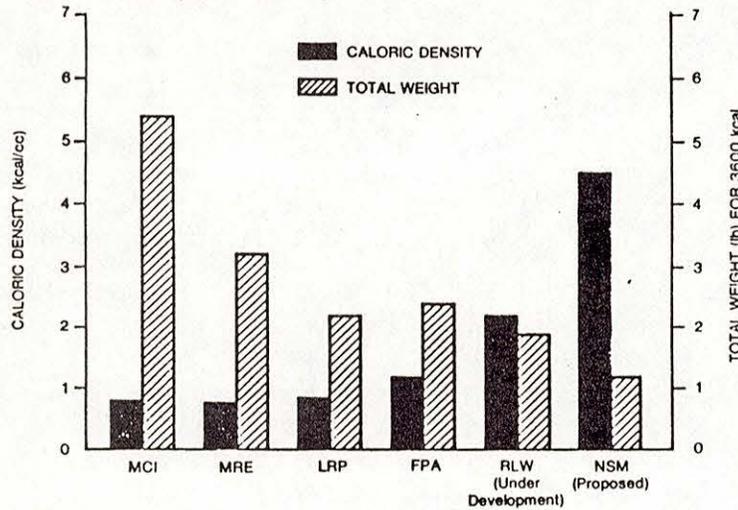
Fig. 1   EVOLUTION TOWARDS ULTIMATE WEIGHT REDUCTION
AND CALORIC DENSIFICATION

This ration has nutritional components, including sources of protein, essential minerals, and fiber, selected on the basis of currently understood physiological mechanisms. It has been engineered from a sensory perspective to optimize the consumer's preference for specific textural and flavor attributes. As currently envisaged, it is shaped and packaged to allow one to remove the components quickly from a vehicle- and uniform-compatible module that, in principle, can be combined in ways to suit almost any tactical demand for a shelf-stable, directly consumable ration.

The basis for the design and the data validating these character-istics are described with respect to caloric densification, nutrient optimization, sensory optimization, and modularization.

EXPERIMENTAL CHARACTERIZATION AND VALIDATION

Processing Techniques

Advancements in the state of the art of three different areas of food technology were needed to test the achievable limits of calorically dense ration items that have enough variety and quality in flavor and texture to be consumable by soldiers in the field.

A bench model vacuum infuser was used to force flavored and fortified melted lipids into the pores of dried foods. The process involves placing the food in a chamber, which is then evacuated and into which flows the melted lipid containing flavors, proteins, or other nutrients, upon applying atmospheric pressure to the lipid held in a reservoir.

Conventional freeze dryers and food presses were used to dehydrate and compress certain components. The drying was accomplished at low platen temperatures, under vacuum, reducing the product moisture to less than 1%. Direct compression of dry powders was also used to produce other calorie dense components. Appropriate stabilizing agents were added before compression.

A Wenger X-20 cooking extruder was used to develop a wide range of porous carbohydrate and proteinaceous matrices, which were subsequently infused with the lipid-based infusate. The principle of extrusion is to cook the flour (gelatinizing the starch and denaturing the protein) at $250\text{-}350^0\text{F}$ for a short time (1-2 min) under 500 to 1500 psi and then to release the plastic mass to atmospheric conditions through a die orifice. This sudden release of pressure causes a rapid loss of steam from the mass, which then rapidly expands into a honeycomb matrix structure. The matrix can be engineered by changing processing conditions or ingredients to provide a desired cell structure and porosity.

Characterization of Components

The porosity and structure of the extrudates are characterized using mercury intrusion porosimetry, scanning electron microscopy (SEM), pycnometry, Instron force-deformation analysis, and detailed chemical analysis of selected components. Data from these tests contribute to understanding the influence of extrusion formulas and processing parameters on cell structure, pore size and distribution, physical strength, and nutrient retention.

The viscosity of infusates, the size distribution of suspended particles, and the overall infusibility are characterized using a Brookfield viscometer, a mechanical spectrometer, light scattering analysis, and light microscopy.

Nutrient Stability

The stability of lipids with respect to the development of oxidative rancidity was monitored using a variety of chemical analyses, including: thiobarbituric acid (TBA), peroxide values (PV), and purge-trap with gas chromatography/mass spectrometry.

The stability of proteins with respect to cross-linking and loss of essential lysine was evaluated using fluorescence techniques, HPLC analysis of furosine, lysine dye-binding methods, and chromatographic separation of digests from proteins treated with pronase.

Acceptance Testing

A seven day field test was conducted at Ft. Bliss, Texas in which four different flavors (almond, mixed nut, vanilla, and orange/pineapple/coconut) of the dairy bar products were evaluated as components of another combat ration under development. It involved 47 members of the 9th Infantry Division Scouts divided into one Command & Control group, one Radio group, and six Patrol groups. Subjects ate only their assigned ration; water was not restricted. The Command & Control and Radio groups consisted of individuals in rear position tents or shelters. The Patrol groups were taken by helicopters to landing zones 2-10 kms from their individual forward positions; some remained hidden there until extraction, while others moved daily. Data were collected using three methods: a Daily Ration Log Book, a post-test questionnaire, and personal interviews. Each man carried his own Daily Ration Log Book into which he recorded the amounts of rations he consumed and his ratings of the acceptability of individual ration components.

<div align="center">

RESULTS AND DISCUSSION

Caloric Densification

</div>

Conceptual Basis

To achieve high caloric density, as many calories as possible must be packed in a minimum volume. An increased caloric density can be achieved by infusion, compression, and extrusion (ICE) technologies (Fig. 2). The principle is to obtain a porous matrix either by dehydration or extrusion and then to compress it or infuse it. Compression has been the main technology used by the military for caloric densification. The expanded, starch-rich matrix is produced by extrusion cooking. By controlling components and processing conditions, a matrix can be produced with desired nutrients and proper pore size distribution, which governs the infusibility of the matrix. Extruded matrices have been made from corn, rice, and wheat flours.
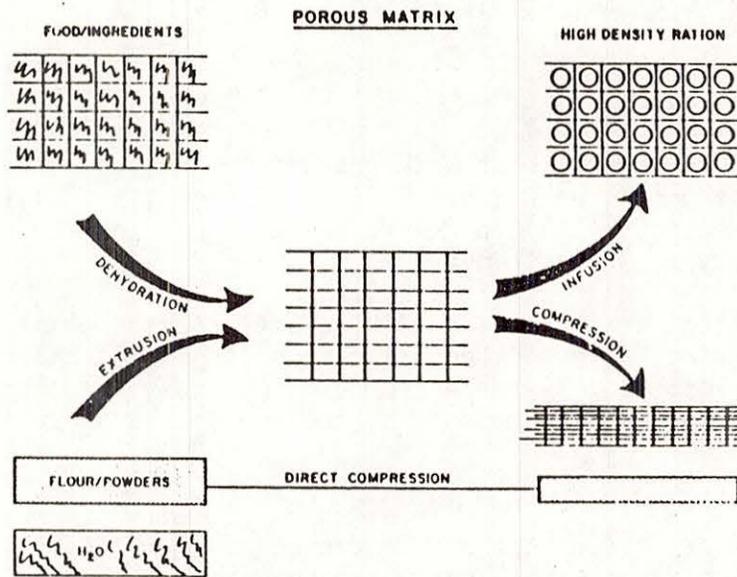
Fig. 2   Caloric Densification

Infusion has now become another major method for densification because the infusate is a fortified, flavored, high melt lipid that is formulated to contain finely ground, uniformly dispersed particulates that add nutritive and textural value to the infused extrudate. In this way a calorically dense food with either a crunchy texture or a soft, moist texture is achieved.

To put this densification concept into perspective, consider that the highest caloric food ingredients used by man are lipids at about 9 kcal/g, while proteins and carbohydrates are about 4 kcal/g (1) . Some increase in caloric density may be achieved by physically compressing them or by decreasing the non-caloric constituents. There are limits to the amount of compression possible for different food ingredients (Table 1). Pure lipid can be compressed to 0.9 g/cc, equivalent to 8.1 kcal/cc, and pure protein or carbohydrate can be compressed to 1.4 g/cc, equivalent to 5.5 kcal/cc. The target for the NSM components is 5.5 to 7.1 kcal/cc, depending on the component.

Technology Products

ICE technologies have been used to develop many calorie dense food items that fall into three basic families of components: dairy bars, infused extrudates, and compressed or infused meat bars.

A family of dairy bars (yogurt-based) has been developed containing 12-16% protein, 50-60% fat, and 20-30% carbohydrates and having a caloric density of 6.2-7.2 kcal/cc. Products such as almond, mixed nut, banana

walnut, orange/pineapple/coconut, and strawberry dairy bars have received excellent ratings (6.0-7.0 on a 9-point Hedonic scale) from technologist panels and even higher ratings when eaten in the field by soldiers (see below). These are compressed, dehydrated bars and represent the highest caloric density consumable component.

A family of infused extrudates, referred to as "carbocrisps" or "carbocrunches," has also been developed. These starch-based extrudates made from corn, rice, and wheat flours have adequate porosity and structural strength for subsequent infusion; oat bran has also been added to improve structure. The infusates used are often formulated with 50% finely ground particulates and 50% high melt vegetable oil. Such formulations have appropriate viscosity for complete filling of the voids in the extrudate. The flavored infusates, which include yogurt, chocolate, maple, cheese, nacho, yams, and even chicken flavors and solids, bring the overall caloric density of the carbocrisp up to approximately 5.5 kcal/cc.

A family of compressed or infused meat bars, referred to as "steak sticks," is under development, and certain components have already proven feasible and attractive. Most noteworthy are the compressed turkey and seafood/chowder bars and an infused turkey bar. These have about 6 kcal/cc, and are most similar to "familiar" foods.

Table 1. Compression Effects on Caloric Density

Food Ingredient	Specific Caloric Value (kcal/g)	Compressed (Crystal) Density (g/cc)	Limit Caloric Density (kcal/cc)
Protein (Soy, Casein)	4.0	1.38	5.5
Carbohydrate (Sugar, Starch)	4.0	1.55	6.2
Lipid (Fat or Oil)	9.0	0.9	8.1
Mixture - Coffee Whitener (36% fat)	5.5	1.17	6.4
Dairy Bar (60% fat)	7.2	0.95	6.8
Water	0	1.0	0

Validation of Process Effectiveness

Compression

The suitability and effectiveness of compression, with or without prior dehydration, to produce calorie dense ration components have been extensively validated. Both the dairy and meat bars can be routinely produced using freeze-drying techniques, provided that low temperatures are used to drive off moisture without causing cross-linking (or "scorching"); both dehydrated products can be compressed into cohesive bars. Certain entree and beverage bars can be produced by direct compression. The quality of the compressed bars was validated by standard sensory and instrumental tests.

Extrusion and Infusion

The effectiveness of the extrusion and infusion processes is ascertained by entirely new methods of evaluation. To ensure that the final infused extrudate has the prescribed caloric density requires that the extrudate have the desired porosity and that the infusate have the desired viscosity, surface tension, and particle size distribution. These requirements have been validated.
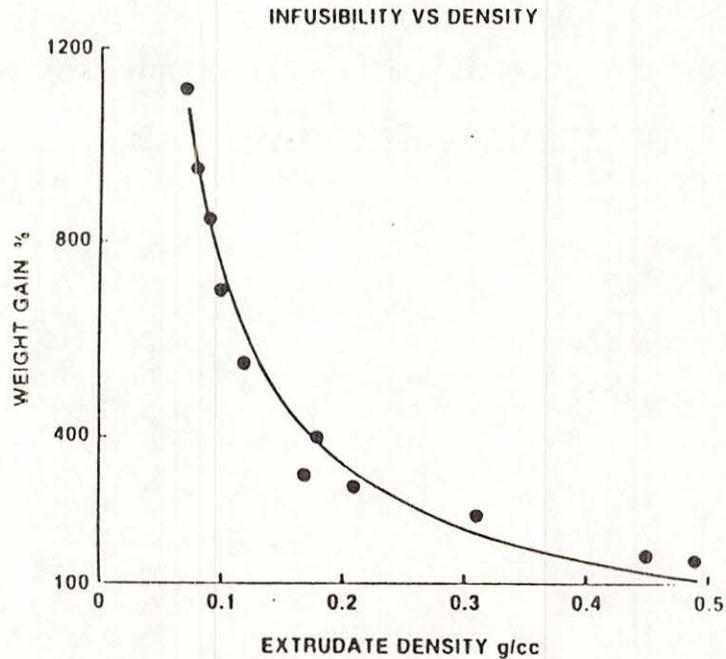

Fig. 3 Relation of Infusibility to Bulk Density

Porosity and subsequent infusibility of extruded products are largely influenced by the degree of expansion of the extruded product. Bulk density has been shown to be a reliable indicator of infusibility. Fig. 3 shows that there is an inverse relationship between the bulk density and the weight gained by pickup of the infusion fluid. Increases in weight during infusion have been as high as 12-fold for well-expanded, extruded products of low bulk density less than 0.07 g/cc. This increase corresponds to an increase in caloric density from 0.3 kcal/cc for the porous matrix to 5.6 kcal/cc for the infused product..

Viscosity of the infusion liquid is a key factor influencing infusibility. The lipid formulas often contain up to 50% by weight of suspended particles, and are thus highly viscous. This viscosity is quite temperature dependent; dairy proteins added to infusates, for example, tend to coagulate and reduce flowability at higher temperatures. As shown in Table 2, viscosity is controllable through the addition of a surfactant, such as as lecithin.

Table 2. Viscosity of Lipid-Based Infusion Formulas

Temp(^{O}F)	Shear Stress at 50 rpm (Relative values: % of full scale)		
	Milk Powder (50%)	Yogurt Powder (25%)	Yogurt Powder (25%) + 1.5% Lecithin
100	21	-	-
115	-	11	4.5
130	25	17	3.5
160	35	40	2.5

The uniform distribution of particulates in the infused extrudate depends on the ratio of the median size of suspended particles to the median size of pores in the extrudate. The particle size distribution, determined by light scattering techniques, can range from 1 to over 100 microns; the extrudate pore size distribution, determined by mercury intrusion porosimetry, can range from 10 to 150 microns in diameter. (Large cells are produced by the explosive extrusion process; the small pores in the cell walls, however, influence the migration of infusate from cell to cell.) If the particle/pore size ratio is excessively high, segregation of the particles occurs as the infusate passes into the extrudate. Such segregation is evident for normally milled sugar particles that have been dyed to discern their presence visually. If this ratio is sufficiently low, most of the suspended particles remain uniformly distributed in the lipid as it infuses throughout the extrudate. The increased uniformity of sugar particles that had been milled from 60 microns down to about 10 microns using a pneumatic system has been demonstrated. The associated data on the influence of viscosity,

extrudate density, and particle/pore size ratio on infusibility show that appropriate process control can be obtained.

Nutrient Optimization and Supplementation

Conceptual Basis

Nominal caloric value, in and of itself, is not a sufficient criterion for assuring nutritional adequacy and functional benefit to the consumer. The type of ingredients and the ability of the body to utilize them must be considered. In the case of NSM components produced by compression or by infusion of extruded starch matrices, a large portion of the calories are contributed from lipids; their utilization is crucial. The proteins selected need to be efficient sources of key amino acids, without leading to excessive excretion of nitrogenous waste, which increases water consumption. The carbohydrates should be mainly complex carbohydrates, as opposed to simple sugars. Soluble fibers such as pectin have to be included. Sufficient carbohydrates may need to be included in the form of extra supplements to overcome any potential ketone body formation arising from incomplete lipid metabolism. Essential minerals and vitamins also need to be included.

Nutrient Selection

The selection of NSM ingredients with appropriate nutrients focused initially on the compressed dairy bar component and subsequently on the infusate and extrudate for the carbocrisp component.

Whole milk yogurt was chosen as a base for the family of dairy bars (vanilla, almond, mixed nut, etc.). It has many special nutritional features including high calcium content, lactose utilization factors, and acids to stabilize the product. The milk fats have a high level of easily metabolized, medium chain length fatty acids. Sunflower oil was also chosen to provide the essential nutrient, linoleic acid. Lactalbumin was chosen as a protein supplement, and various nutmeats were chosen because they enhanced the calories, the micronutrient content and, incidentally, the textural variety. Pectin was selected as a source of added soluble fiber. It is multifunctional; it provides some caloric value and has the ability to function as a slow release agent for calories from sugars (2).

The amount of fatty infusate in the carbocrisp and the types of fat making up the infusate were selected, on the basis of current knowledge, to optimize caloric utilization. Since the infused extrudate is about 80% by weight infusate, the ratio of carbohydrate to lipid was adjusted by selection of the particulates suspended in the infusion lipid; morever, the composition was selected to avoid ketosis. Refinement of this knowledge is in process. Since the infusate must be liquid for infusion

and solid for consumption, the type of fatty acids making up the oil are relatively long in chain length and high in degree of saturation - - properties that are acceptable but not ideal with respect to digestibility and metabolic utilization. Based on recent reports, the dietary oat bran being included in the extrudate for added structure may reduce blood cholesterol (3) and might compensate partially for effects of the high fat content.

Stability Validation

Crucial to the success of such calorically dense components is the stability of the lipids. Avoiding oxidation of the unsaturated fatty acids requires antioxidants that can be completely effective when used at levels permitted by regulation. Consequently, a novel, synergistic combination of vitamin E, ascorbyl palmitate, and BHA is employed. The first two also serve as additional sources of essential micronutrients.
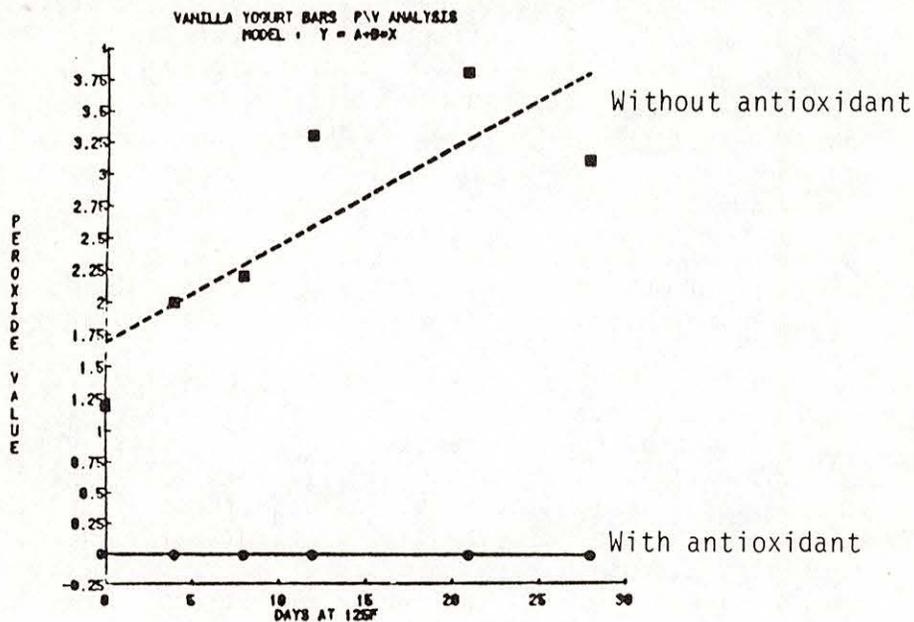
Fig. 4 Formation of Peroxide During Storage

The stability of these high calorie ration components was proven by holding several of the dairy bars at 125°F for up to eight weeks. Some samples were formulated with antioxidants and packed either under air or under vacuum; some were formulated without any antioxidants and similarly packed. There were little or no sensory differences noted in samples with antioxidants when examined by both trained and consumer panels. Most importantly, there were no detectable changes in TBA or peroxide values in samples with antioxidants, whereas these indicators of rancidity rose

extensively in samples without antioxidants (see Fig. 4). Analysis by the
purge-trap technique using gas chromatography coupled to a mass
spectrometer revealed no fat oxidation by-products, such as pentane and
hexanal, throughout the shelf-life test. Analysis of the antioxidants as
a function of time in storage revealed that ascorbyl palmitate decreased
most rapidly followed by vitamin E, indicating that these antioxidant
vitamins continued their protective function throughout the duration of
this heat stress test. This breakthrough in extending the shelf stability
of high fat products opens a new frontier for further enhancing caloric
densities, up to limits imposed by consumer acceptance.

Sensory Engineering and Acceptance Optimization

Conceptual Basis

Critical to the acceptance of a new and unfamiliar ration epitomized
by the NSM is the optimization of the sensory quality within the
constraints imposed by ingredient, nutritional, and functional
requirements. The high fat content in the NSM, the possible complete
reliance on the ration for many days, and the demand for convenient
handling and compact storage emphasize the need to build into the
components and into the overall ration those features that promote
acceptance in a field setting. Consequently, appropriate strategies were
pursued to ascertain and validate what these positive attributes should
and could be.

Attribute Identification

To obtain an indication of the probable acceptance of two NSM
components, the compressed dairy bar and the nacho cheese flavored carbo-
crunch, the sensory characteristics and overall ratings for these bars
were compared in a laboratory setting against those for eight somewhat
comparable commercial food bars. The almond dairy bar rated as high on
the 9-point scale as the Planter's peanut bar and the Carnation breakfast
bar; however, the carbocrunch scored 2 points lower.

In order to ascertain which attributes contributed to acceptance or
non-acceptance, it was necessary to know to what extent the bars that were
liked were similar, to what extent the bars that were disliked were
similar, and how the sensory variables related to one another. Using the
multivariate statistical approach of partial least-squares regression
(PLS) to analyze the data gives the two-factor space shown in Fig. 5,
where the numbers shown represent the mean acceptance scores for each
bar. Scores over 6.0 cluster tightly along a diagonal area bounded by the
granola cluster and the almond dairy bar. Factor t_1 in this type of
representation is primarily a texture dimension with grainy, hard, dense,
chewy, and cohesive products on the left, porous and crunchy products just

to the right of the centroid, and oily, mouth-coating, and mouth-drying products to the far right; factor t_2 is primarily a flavor dimension, with sweet, nutty, and dairy flavors at the bottom, fruity and sour/bitter flavors near the centroid, and heavy, meaty, and salty flavors near the top. Based on this analysis, it appears that the nacho carbocrunch had too much of the oily and mouth-coating properties to be higher in acceptance.

SCORES OF FOOD BARS
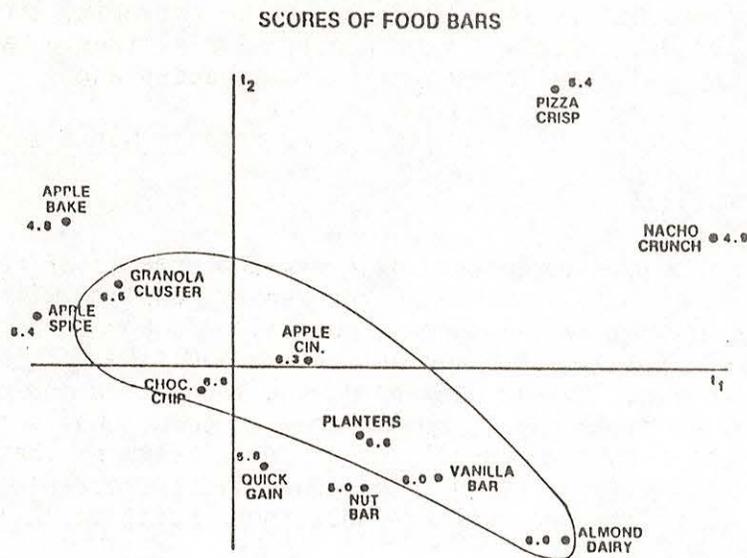
Fig. 5   Relation of Acceptance to Product Characteristics

Validation of Field Acceptance

To obtain a validation of the acceptance of an NSM component in the field, a test of several dairy bars was conducted at Ft. Bliss using three groups of soldiers (see Acceptance Testing). Proper assessment of these components (used in conjunction with other Ration Light Weight 30-Day components) required that the evaluators be made familiar with the ration and use it under realistic field conditions and that the acceptance data be collected over a prolonged period of consumption. The data obtained, as shown in Table 3 for each of the four flavors of dairy bar, indicate that not only are they rated high, but that they are rated higher by the isolated Patrol groups than by the Command and Control/Radio groups. Moreover, for the almond dairy bar, both sets of ratings are higher than those obtained in the laboratory setting. These data are consistent with the notion that acceptance of an operational ration will increase as one moves more toward the situation and conditions under which the ration is designed to be used.

Table 3. Acceptance Ratings of Dairy Bars at Borderstar Field Test

Dairy Bar	Command & Radio Groups (n=14)	Field Patrol Group (n=14)
Orange/Pineapple/ Coconut	7.08	8.31
Mixed Nut	7.23	8.21
Almond	7.14	8.36
Vanilla	6.42	7.92

Ratings are on a 9-point Hedonic scale, with the highest rating 9 = excellent; 8 = very good; 7 = good.

The data also demonstrate, as shown in Fig. 6, that the high acceptance is maintained even over an extended period of consumption. There is no indication of the well-known monotony effect, whereby acceptance declines with continued use of the same or comparable item.

BORDERSTAR FIELD TEST DATA
ON YOGURT BARS
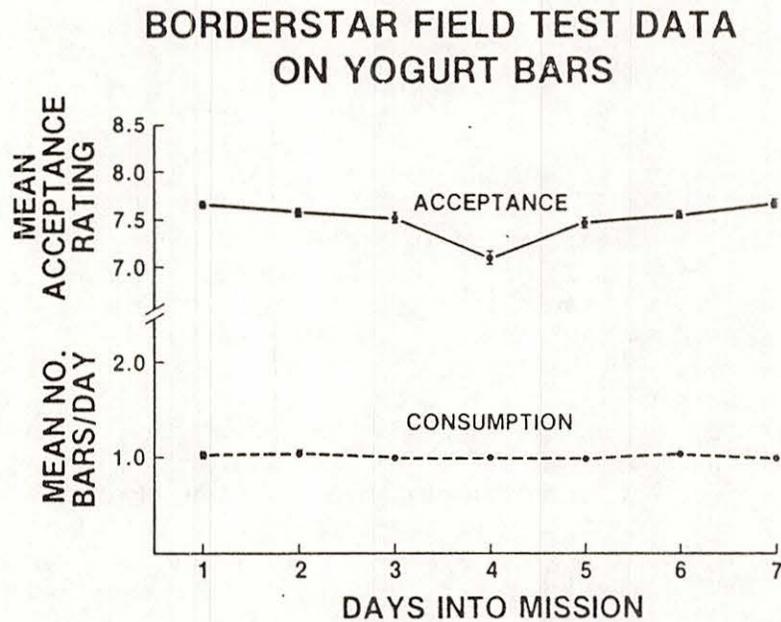
Fig. 6 Effect of Extended Consumption

Modularization

Conceptual Basis

The need to minimize space requirements and to maximize ease-of-use can be met, in principle, by engineering the components into a shape that can be compactly stacked, by designing protective packaging for these components that can be readily unwrapped, by standardizing the packaged components into a modular unit that can be combined into multiples of a daily ration, and by configuring the collection of modules into a stowable unit that interfaces with protective clothing or a troop carrying vehicle. The more compact the shape, the lower is the ratio of package volume to component volume and the less compromised is the overall caloric density of the packaged component. The more readily unwrappable, the more convenient it is for a soldier to eat on the move, even with one hand. The more uniform in size and shape are the modules, the simpler it is to combine them for different tactical situations and climatic conditions. The more system-compatible the configuration, the more effective is the subsistence support provided.
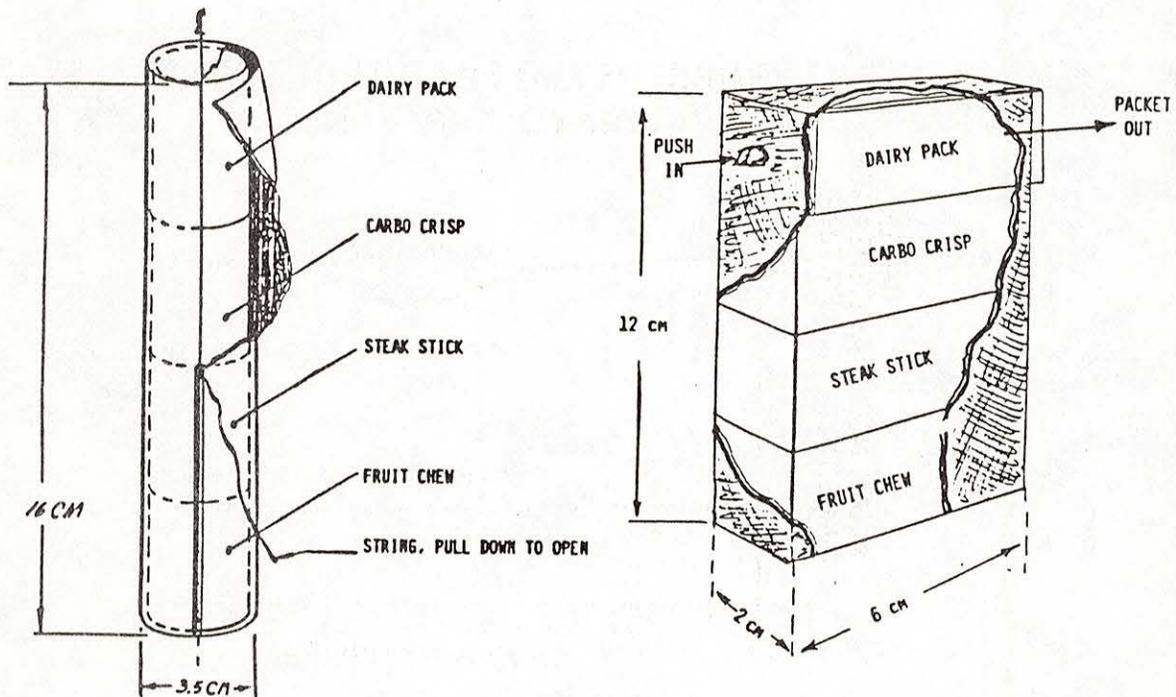
Fig. 7 Proposed Modular Package Configurations

Technical Possibilities

The NSM, as currently envisaged and demonstrated in the laboratory, exceeds in compactness and convenience any currently available ration. Two of several designs considered are shown in Fig. 7. In each case, there is a stacked arrangement of four basic components: dairy bar, carbocrisp, steak stick, and fruit chew. Each set forms a module that is about 900 kcal, so that four would be used for normal environments and five for the arctic. The cylindrical unit is shown with a "pull down" string, but other "pull up" sleeve arrangements are possibilities for easy unwrapping. The rectangular unit is shown with a component "ejector" device, but other pull up arrangements would work as well. In both cases, other combinations and configurations have been explored to make them stowable in special pockets that could be built into a soldier's uniform, either around the sleeves of the outer garment or around the pants' legs. The final choice of shape and configuration will be made on the basis of data on relative logistical advantage and soldier preference.

CONCLUSION

The development of the NSM, as the solution to the problem presented for subsisting in the battlefield of the future, represents a major evolutionary advance in operational rations. Most of the major criteria relating to caloric density, nutritional optimization, acceptance of an unfamiliar food, and convenient modularization have been satisfied, at least in the laboratory. The eventual adaptation of these components into modules that can be combined for tactic-specific use and that can be interfaced with protective systems is fairly certain. There are other criteria for such a ration, not discussed here, that need to be addressed. The most challenging among these criteria is the supplementation of the components with ingredients that ensure the maintenance and even enhancement of performance, despite the stressful conditions envisaged. Meeting this challenge will be the goal of the second generation NSM.

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TITLE: A Method for Spectral and Spatial Analyses of Natural
Terrain for Camouflage Effectiveness

W.J. Cardozo*

ABSTRACT:

The Terrain Analysis System (TAS) was developed to satisfy the need for
a scientific method for objectively determining a camouflage pattern and
coloration based on natural terrain reflectance data. A video camera and
recorder, with narrow bandpass filters are used to obtain the video
imagery of a scene. The system includes a minicomputer with digitizing
boards. The system software is used to digitize the scene and calculate
reflectance data and color coordinates (CIELAB*) for every picture element
(pixel) in the scene. A statistical analysis is performed upon the
completed CIELAB* files and a displayable domain file of five domains or
less is created. The domain file can be displayed on a color monitor or a
plot can be produced on the system's pen plotter.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Project Officer for Terrain Analysis System

PAST EXPERIENCE: Lab Chemist, Roma Chemical, Fall River, MA;
Plant Chemist, Arnold Print Works, Adams, MA; Manager of Process
Development, Cranston Print Works, Cranston, RI

DEGREES HELD: Bachelor of Science in Mathematics and Bachelor
of Science in Textile Chemistry, Southeastern Massachusetts University

A METHOD FOR SPECTRAL AND SPATIAL ANALYSES OF NATURAL TERRAIN
FOR CAMOUFLAGE EFFECTIVENESS

W.J. CARDOZO

INTRODUCTION

The four-color Woodland pattern and the six-color desert pattern are currently the Army's two standard camouflage patterns. The only current means of evaluating camouflage effectiveness is via detectability studies of the proposed patterns and colors. This involves contracting for the printing of the camouflage fabrics, construction of uniforms, and completion of the detectability field study. This approach is costly and time consuming, and the results determine only which of the items tested was best under the given test conditions. Clearly, an objective means of evaluating camouflage development is required. Such a technique should allow one to determine the coloration, size, and shape of the pattern required for a given terrain. These objectives were carefully defined in a contract released by Natick Research, Development, and Engineering Center (NRDEC) and the Terrain Analysis System (TAS) is the end result of the completed contract.

The Terrain Analysis System (TAS) has four major functions. They are: the acquisition of terrain reflectance images, calculation of reflectance data and CIELAB* files, statistical analysis of data, and the graphical display of results. The best way to explain the TAS is to follow the required procedures, beginning with the acquisition of terrain reflectance images.

MATERIAL AND METHOD

The equipment includes the following (See Figure 1):

1. DEC PDP 11/23 Minicomputer with dual RL02 disk drives and the RSX 11M Plus operating system.

2. JVC 3/4" Video cassette recorder.

3. FORA Digital time base corrector.

4. MTI-Dage Model 65 Video camera with SIT tube.

5. Image processing hardware from Image Processing Technology Inc.

6. B&W and RGB video monitors.

7. Hewlett-Packard graphics plotter.

8. DEC VT-102 terminal and keyboard.

9. DEC Letterwriter 100.

SIT Camera and Filter Wheel

B&W Monitor

Hard Copy Terminal.

3/4" U-matic Video Cassette Recorder

Digital Time Base Corrector

DTAS System Cabinet

14" RGB Color Monitor

CRT Input Terminal
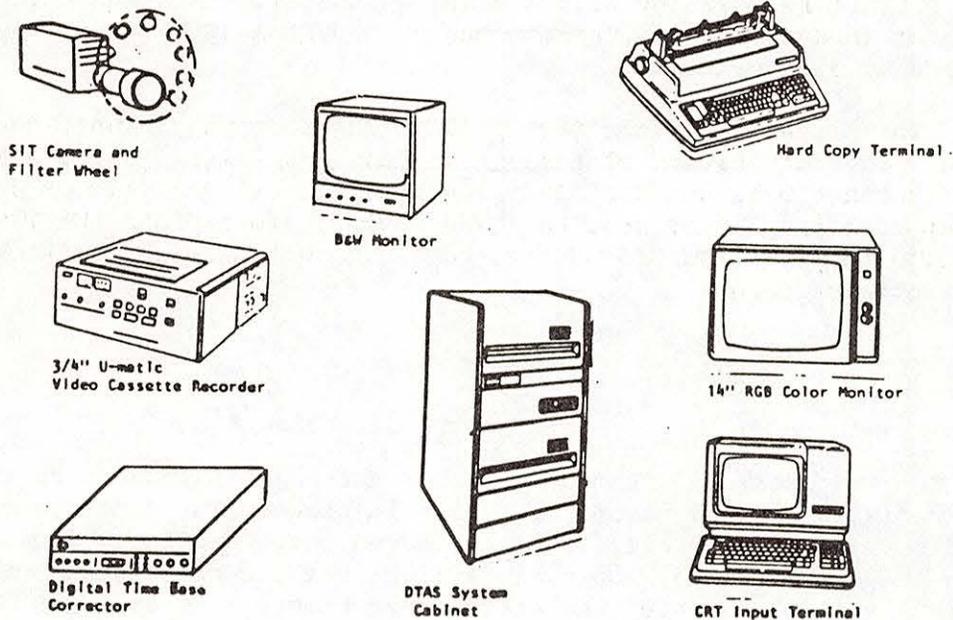
Figure 1.   Equipment for Terrain Analysis (1).

Acquisition of Terrain Data

The equipment used for data acquisition is portable, which allows the user to collect images at remote locations. Obtaining an image requires the use of the video camera, two tripods, narrow bandpass filters, shade box, rangefinder, video cassette recorder with remote control, black and white monitor, batteries, neutral gray card, and the target board. (See Figure 2.)
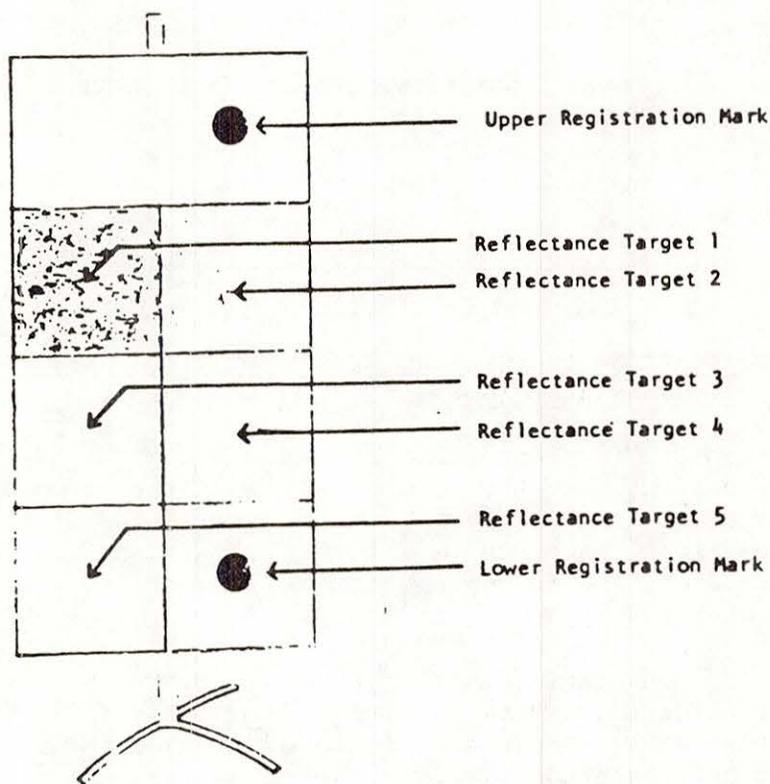
Figure 2. Target board (2).

The video camera with the shadebox attached is focused on the scene desired with the 460 nanometer filter in place. The function of the shadebox is to allow only light reflected perpendicularly from the scene into the camera lense. Natural daylight has the greatest amount of energy available at 460 nanometers. (See Figure 3.) By adjusting the camera settings at this wavelength, the user is assured that all the images recorded at other wavelengths will not exceed the current dynamic range of the camera.

54
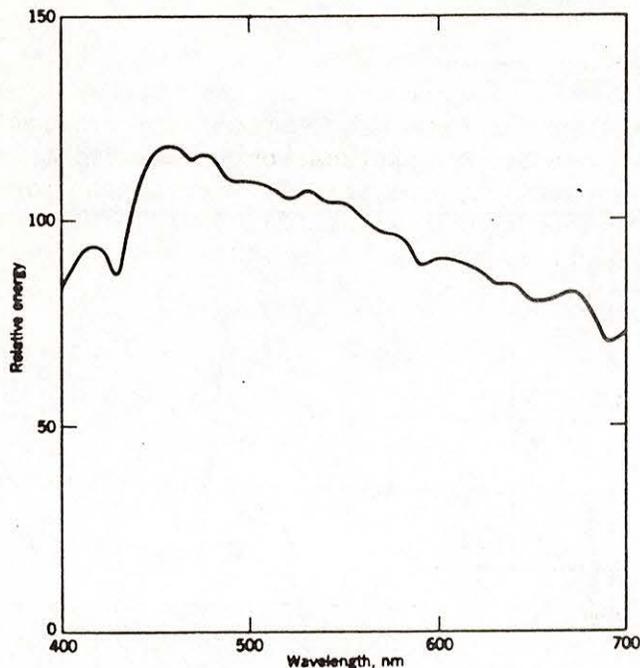
Figure 3.   The relative energy distribution at each wavelength, for
            typical daylight (3).

The target board is placed into the scene such that it subtends
approximately one third of the vertical image of the scene. The aperture
and gain controls on the camera are adjusted until the five distinct gray
shades of the target board can be observed on the monitor. Once the gray
shades are achieved, the settings are held constant and the image
recording can begin.

With the 460 nanometer filter still in place, the neutral gray card
is held in front of the camera so that it completely fills the monitor
screen. Approximately 30 seconds of this image is recorded and will be
used later to calibrate the camera.

The scene is recorded from 400-700 nanometers at 20 nanometer
intervals using the appropriate narrow bandpass filters. The wavelengths
from 400-700 nanometers represent the visual range of the electromagnetic
spectrum. The spectral reflectance curve is approximated by calculating
the reflectance at the 16 different wavelengths, which correspond to the
peak transmission of the narrow bandpass filters. (See Figure 4.) The
image is recorded for at least 15 seconds at each of the 16 different
wavelengths. One must be extremely careful not to move the camera

throughout the recording session. The calculation of the spectral reflectance curves depends upon the superimposition of picture elements (pixels) for each of the images. By viewing the monitor during recording, one can determine if an image is acceptable, or should be retaped.

3 CAVITY FILTER
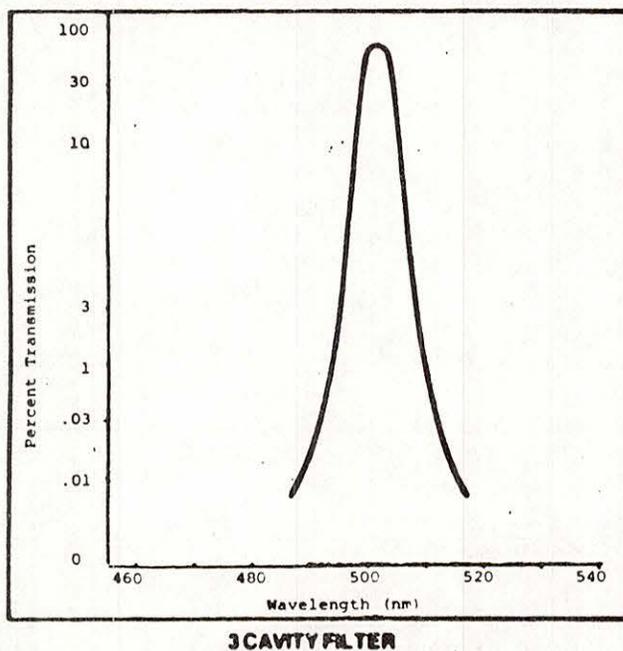
Figure 4. Example of the transmission curve of a narrow bandpass filter with maximum transmission at 500nm.

After the recording session is complete, the distances from the camera to scene, and camera to target board must be noted. A description of the scene and lighting conditions is written. This completes the acquisition of terrain data.

Reflectance Data and CIELAB* File Calculations

The TAS is then used to convert the recorded video data to reflectance files and CIELAB* files stored on the RL02 disks. A CIELAB* file contains the three uniform color space coordinates for each pixel from the original scene. The dimensions are L*, a*, and b*. The formulas used for calculating these coordinates are found in Table 1. A file name, distances to the scene and target board, and the distance between reference points on the target board are entered. These distance values are used to calculate the dimensions of the picture element displayed on the color monitor.

Digitized images are obtained by routing the video output signal from the video cassette recorder through the time base corrector. This corrected signal is sent to the black and white (B&W) monitor and to the digitizing boards of the computer. When the image displayed on the B&W monitor represents the desired image for digitizing, the user signals the computer via the keyboard to begin digitizing. The digitizing hardware obtains 256 video frames from the time base corrector, calculates an average image, and displays the final gray-scale image on the Red, Green, Blue (RGB) monitor. This frame-grabbing process takes approximately fifteen seconds, which accounts for the recording times during data acquisition.

The first image to be digitized can be any one of the scene images recorded at the different wavelengths. The digitized image is used to provide a set of nine reference points to the computer. The keyboard is used to control a crosshair cursor on the color monitor. The cursor is moved to the points requested by the computer terminal, and the position confirmed by keyboard signal. The nine points to be located and marked are: the two reference points of the target board, the center of the five gray-scale targets, the upper lefthand corner of the scene, and the lower righthand corner of the scene.

Recorded imagery of the neutral gray card is digitized next. The shade of the card is a highly uniform gray and the image resulting from the 256 video frame average is the basis for creating a camera calibration file to be used when the scene is digitized at the various wavelengths. The center horizontal line is used to compute the average signal of the gray card image. A calibration factor for each pixel is then calculated and stored in the file. This file is used to adjust the results of the scenes as they are digitized.

The digitizing of the scene at each of the different wavelengths is begun after the successful creation of the calibration file. The only input required prior to digitizing is the name of the file and the wavelength of the recorded image. The user has the option of accepting or rejecting the digitized image. If the image is approved, the reflectance values for each pixel in the scene are calculated and stored as a wavelength file on the disk. This process is continued until all of the scenes have been saved as reflectance files, or rejected.

The reflectance values of each pixel in a scene at a given wavelength are calculated by reference to the five standard targets which range progressively from white to gray to black. The actual reflectance values for these targets at 20 nanometer intervals from 400-700 nanometers are

permanently stored as data statements in the Fortran code. These values were determined by reading samples of the target shades on the Diano Match-Scan spectrophotometer under D-65 monochromatic illumination, and supplying this information to the contractor. The location of the center of the five targets was determined previously. The signal which produces every pixel on the color monitor is stored in the image processing boards. Therefore, it follows that the actual reflectance of the target versus the signal level is known. The reflectance values for each pixel in the scene is calculated by interpolating or extrapolating as necessary. (See Figure 5.)
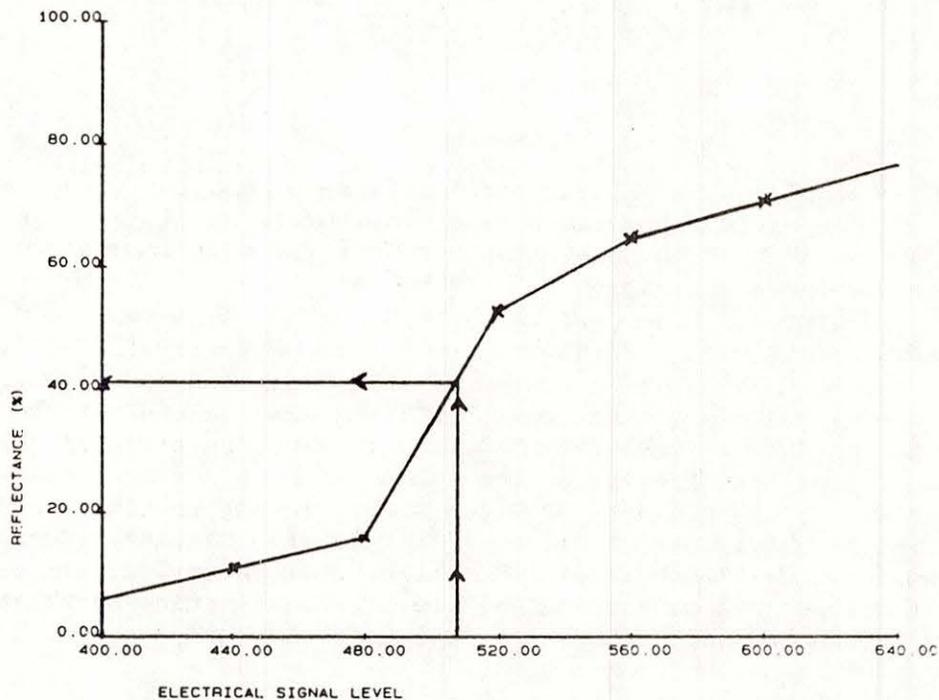
Figure 5. Calculation of a pixel's percent reflectance.

A final large reflectance file is created by combining all the wavelength reflectance files for the scene. If a wavelength reflectance file is missing, the reflectances are calculated by interpolating between the nearest higher and lower wavelength files, or by extrapolating if the missing file is not between two files.

Finally a CIELAB* file is created. The CIE X,Y,Z tristimulus values for each pixel are calculated first. These require the use of the scene reflectance file, an illuminant file, and the stored standard observer tristimulus values. The L*,a*,b* values are calculated from the X,Y,Z values and are stored in the Lab* file (4). It is these CIELAB* values which are used for the domain clustering process. The formulas for

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calculating the X,Y,Z values and the L*,a*,b* values are as follows:

TABLE 1.   Equations for Calculation of CIELAB* Coordinates

$$k = 100/\Sigma S(i)\bar{y}(i)$$

$$X_o = k\Sigma S(i)\bar{x}(i) \qquad\qquad X = k\Sigma R(i)S(i)\bar{x}(i)$$
$$Y_o = k\Sigma S(i)\bar{y}(i) \qquad\qquad Y = k\Sigma R(i)S(i)\bar{y}(i)$$
$$Z_o = k\Sigma S(i)\bar{z}(i) \qquad\qquad Z = k\Sigma R(i)S(i)\bar{z}(i)$$

$$L* = 116(Y/Y_w)^{\frac{1}{3}} - 16$$
$$a* = 500[(X/X_w)^{\frac{1}{3}} - (Y/Y_w)^{\frac{1}{3}}]$$
$$b* = 200[(Y/Y_w)^{\frac{1}{3}} - (Z/Z_w)^{\frac{1}{3}}]$$

i = wavelength
R = reflectance
S = spectral radiance
$\bar{x},\bar{y},\bar{z}$ = standard observer spectral tristimulus values
X_w,Y_w,Z_w = tristimulus values of the referance white
X,Y,Z = calculated tristimulus values
$L*,a*,b*$ = color coordinates of 3-D Cielab* uniform color space

Statistical Analysis of Data

There are several functions which can be performed on the CIELAB*
file. The most significant process is the clustering program. This
program will determine the statistically optimal values for the colors
and shape of a camouflage pattern which is representative of the original
scene. The clustering process goes through three distinct stages. They
are a histograming routine, a Euclidean clustering routine, followed by
an optimization technique. Prior to running the CIELAB* clustering
program, the user may change any of nine input values, or accept the
default values. The parameters and their corresponding defaults are
listed below:

Clustering Menu

Name of the Cielab file to use as input	DL1:SCN010.LAB
NFIN (Number of final domains, 1-5)	5
INTERV (Initial histogram cell size)	3
INCR (Histogram cell size increment)	2
ITHRSH (Minimum number of pixels to be a domain)	10
NSWTCH (# of domains to switch to Euclidean clustering)	20

Name of the file to save results (Blank means do not save)

Number of optimization cycles and variance multiple   5   4

     The final number of domains represents the number of colors to which one wishes the data to be reduced. The histograming process begins by dividing the color space into cubes whose dimensions are equal to the initial histogram cell size. Every pixel in the CIELAB* file is assigned to the cube which bounds the pixel's L*,a*,b* coordinates. When all the pixels are assigned, a count is made of the number of pixels per cell. Each cell is considered to be a domain if the number of pixels per cell is greater than the value entered for ITHRSH. If the number of domains is greater than NSWTCH, the size of the cube is increased by INCR, and the whole process is repeated. When the number of allowable domains is less than or equal to NSWTCH, then the histograming process is complete, and the Euclidean clustering begins. The average L*, a*, b* values and the variance for each domain are also calculated during each cycle of the histogram process. (See Table 2 and Figure 6.)

TABLE 2. Output Report from one Cycle of Histograming Routine.

```
NDOM   16

ICELL   NUMBER   CENTL    CENTA    CENTB    VAR
  1      1631     63.18   -35.25    44.39   0.1748889160E+02
  2      1443     63.63   -40.10    43.91   0.5885742187E+01
  3       664     50.57    55.63    31.25   0.7572204590E+01
  4      1120     32.00    23.10   -33.70   0.2430493164E+02
  5       846     31.74    24.04   -40.88   0.9439819336E+01
  6      1145     94.04    -6.78    86.86   0.2308593750E+01
  7      2689     56.56   -35.04    41.86   0.1482409668E+02
  8       659     54.45   -33.80    35.65   0.1890856934E+02
  9      4353     44.53    56.19    34.16   0.1973754883E+02
 10       775     90.23    -8.66    89.50   0.2713769531E+02
 11      1614     90.34    -3.42    90.40   0.2227050781E+02
 12       550     24.56    30.06   -41.96   0.1519067383E+02
 13       672     23.66    25.10   -40.60   0.9419433594E+01
 14      4456     90.38    -3.16    96.69   0.6832031250E+01
 15      1535     24.18    22.68   -35.02   0.1846838379E+02
 16       499     43.64    54.56    40.42   0.1538195801E+02

TOTAL NUMBER OF PIXELS ASSIGNED TO DOMAINS = 24651.


MEAN L =   54.86      MEAN A =    7.82      MEAN B =   27.68

TRACE OF SW =   14.70      TRACE OF SB = 4354.78      BETA 4 =   296.28      BETA 5 =   64007.34

NUMBER OF OCCUPIED CELLS =   332
```
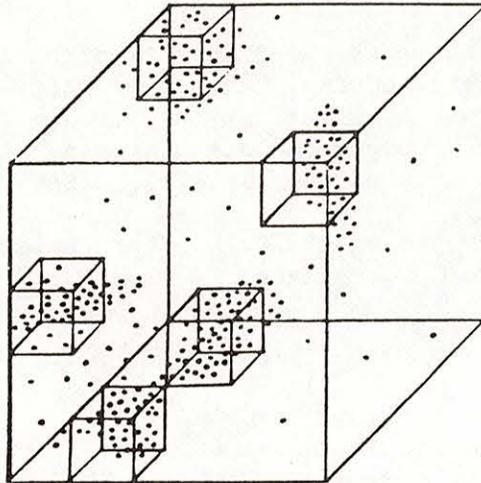
Figure 6.   Histograming Domains in Color Space (5).

In the Euclidean clustering, the distance between all possible pairs of domain centroidal values is calculated, and the two domains which are closest are used to produce a new domain centroidal L*, a*, b* value.   A weighted means procedure is used to calculate this new domain centroid, and the total number of domains is reduced by one.   This cycle is repeated until the number of domains is equal to the final number of domains previously chosen by the user.   (See Figure 7.)
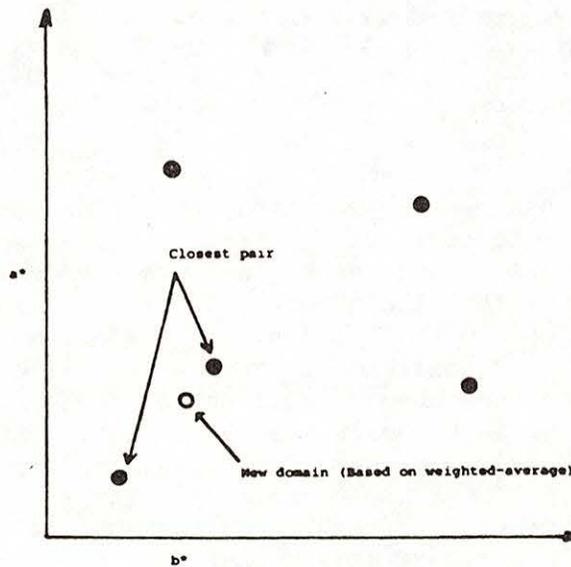
Figure 7.   Domain Reduction by Euclidean Clustering.

The final process is an optimization routine. The histograming algorithm is a fast routine, but a poor initial choice of parameters by the user could result in unacceptable domain coordinates. The default values used by the program do not guarantee accurate domain centroids, but in general, give good results (6). (See Figure 8 and Table 3.)

TABLE 3. Spectrophotometric Color Coordinates of Woodland Pattern Versus TAS Domain Centroid Coordinates.

|		L*	a*	b*	▲L*	▲a*	▲b*	▲E*
Black	Spectro.	16.95	1.14	-2.28				
	Optim.	19.67	-0.46	0.89	-2.72	1.60	-3.17	4.47
	Proper	18.10	0.33	-0.01	-1.15	-0.81	-2.27	2.67
	Improper	24.98	2.95	9.57	-8.03	-1.81	-11.85	14.43
Brown	Spectro.	26.46	3.15	9.06				
	Optim.	25.64	3.30	9.69	0.82	-0.15	-0.63	1.04
	Proper	24.79	3.10	9.20	1.67	0.05	-0.14	1.68
	Improper	25.08	3.93	9.88	1.38	-0.78	-0.82	1.78
Green	Spectro.	31.67	-6.54	10.05				
	Optim.	30.97	-7.87	11.58	0.70	1.33	-1.53	2.14
	Proper	31.51	-8.05	12.10	0.16	1.51	-2.05	2.55
	Improper	26.11	2.97	10.90	5.56	9.51	-0.85	11.05
Light Green	Spectro.	42.22	-1.70	14.47				
	Optim.	40.93	-3.26	16.16	1.29	1.56	-1.69	2.64
	Proper	41.17	-3.93	15.66	1.05	2.23	-1.19	2.74
	Improper	31.99	-10.06	12.00	10.23	8.36	2.47	13.44

For these reasons, an optimization subroutine was neccessary. The first pass of OPTIM (the optimizing subroutine) is used to determine the smallest distance between each pixel and the domain centroids. If this distance is less than the chosen multiple of the variance, then that pixel is assigned to that domain. If the distance is greater, the pixel is eliminated from this and all further cycles of OPTIM. When all of the pixels have been assigned or eliminated, new centroidal values,average, and variance for each domain are determined. The optimizing routine will run until the maximum number of cycles (user input) is reached, or no changes in domain assignment are made. The resulting domain file is used for graphical display of results on the RGB monitor, plotter, or the printer. Table 4 illustrates output from one cycle of the clustering subroutine.
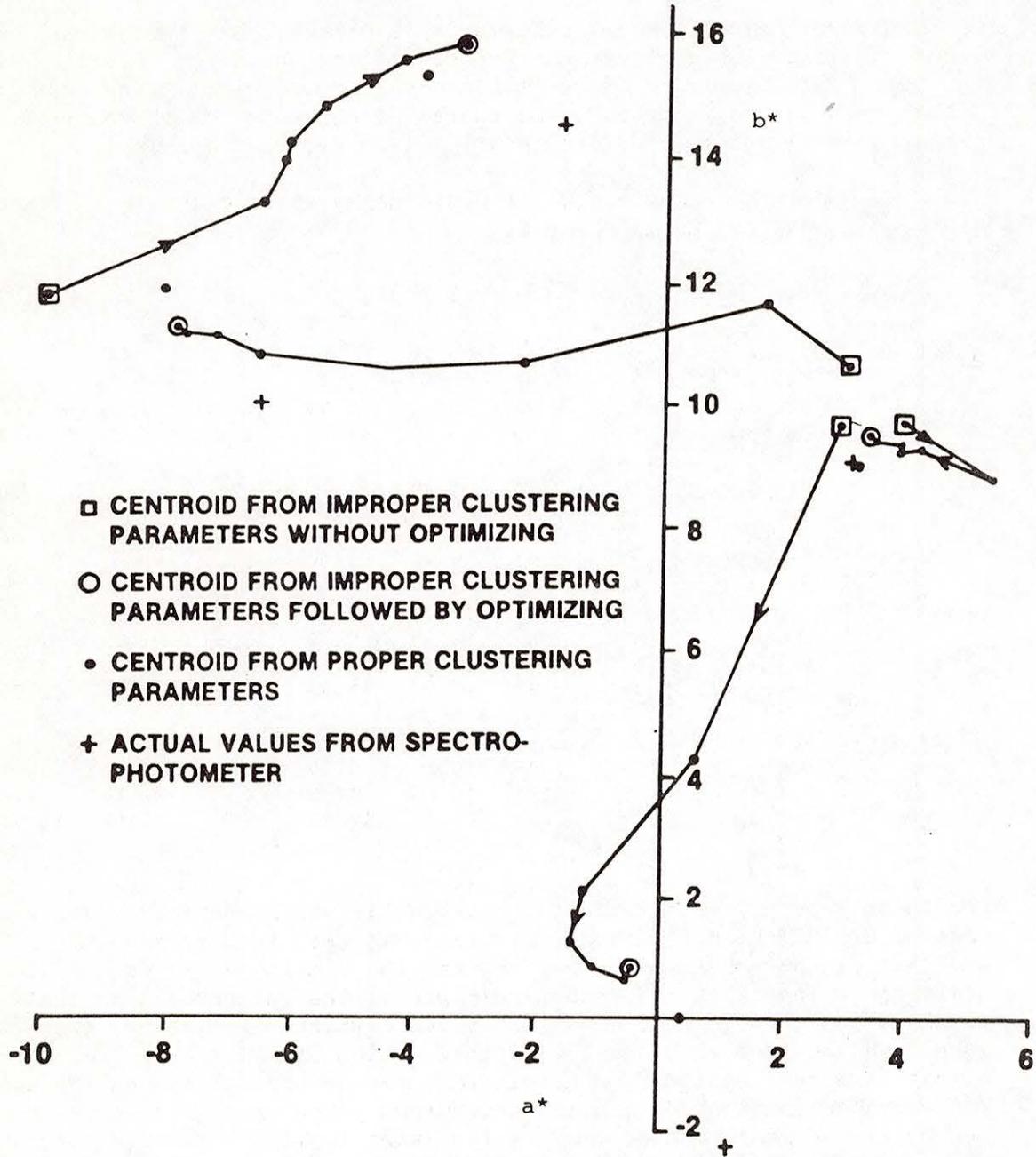
Figure 8.   Migration of domain centroids

CENTROID FROM IMPROPER CLUSTERING
PARAMETERS WITHOUT OPTIMIZING

CENTROID FROM IMPROPER CLUSTERING
PARAMETERS FOLLOWED BY OPTIMIZING

CENTROID FROM PROPER CLUSTERING
PARAMETERS

ACTUAL VALUES FROM SPECTRO-
PHOTOMETER

TABLE 4. Output Report from one Cycle of Optimization Routine

```
NDOM    4

ICELL   NUMBER   CENTL     CENTA     CENTB     VAR
  1     5995     45.05     55.73     34.02     0.2972436523E+02
  2     6254     27.70     25.13    -36.86     0.5502587891E+02
  3     8212     90.89     -4.33     93.55     0.2945800781E+02
  4     6953     59.70    -36.02     42.60     0.3895715332E+02

TOTAL NUMBER OF PIXELS ASSIGNED TO DOMAINS = 27414.


MEAN L =  55.84      MEAN A =  10.12      MEAN B =  33.33

TRACE OF SW =  38.29      TRACE OF SB = 5145.13      BETA 4 =  134.37      BETA 5 =  197014.00


T TEST COMPARISON BETWEEN DOMAINS.

            1            2            3            4            5            6            7

2 0.6747E+03
3 0.1041E+04   0.1329E+04
4 0.9079E+03   0.8770E+03   0.7054E+03

RATIO OF BETWEEN/WITHIN DOMAIN VARIANCES:

.1731E+03     0.9350E+02   0.1747E+03   0.1321E+03

NUMBER OF DOMAIN CHANGES =      0
DISTANCE FROM CENTROID   DOMAIN 1   DOMAIN 2   DOMAIN 3   DOMAIN 4   DOMAIN 5

   0.00 -   0.49          2          4          4          6          0
   0.50 -   0.99         11          5         22         76          0
   1.00 -   1.49         34         35         90        164          0
   1.50 -   1.99        118         58        382        187          0
   2.00 -   2.49        259         95        726        232          0
   2.50 -   2.99        483        141        628        259          0
   3.00 -   3.49        592        179        591        334          0
   3.50 -   3.99        657        257        664        389          0
   4.00 -   4.49        491        297        732        553          0
   4.50 -   4.99        427        386        818        598          0
   5.00 -   5.49        475        448        700        588          0
   5.50 -   5.99        556        519        603        565          0
   6.00 -   6.49        506        517        453        547          0
   6.50 -   6.99        358        506        335        504          0
   7.00 -   7.49        276        435        250        502          0
   7.50 -   7.99        199        383        243        314          0
   8.00 -   8.49        159        362        253        197          0
   8.50 -   8.99        126        313        206        187          0
   9.00 -   9.49        129        246        153        159          0
   9.50 -   9.99        109        218        130        149          0
  10.00 -  10.49         25        170         94        135          0
  10.50 -  10.99          3        151         73         90          0
  11.00 -  11.49          0        115         62         94          0
  11.50 -  11.99          0        123          0         69          0
  12.00 -  12.49          0        116          0         48          0
  12.50 -  12.99          0        100          0          7          0
  13.00 -  13.49          0         48          0          0          0
  13.50 -  13.99          0         20          0          0          0
  14.00 -  14.49          0          7          0          0          0
```

Domain Assignment

The domain assignment program is used to create a displayable file as a result of L*, a*, b* values entered by the user. The shortest distance between the L*, a*, b* domain values and every pixel is determined. Each pixel is assigned to the domain to which it is closest. (See Figure 9.)

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This routine is usually run using the domain centroidal values from the clustering algorithm to "clean up" the image, since many pixels may not have been assigned to any of the valid domains.
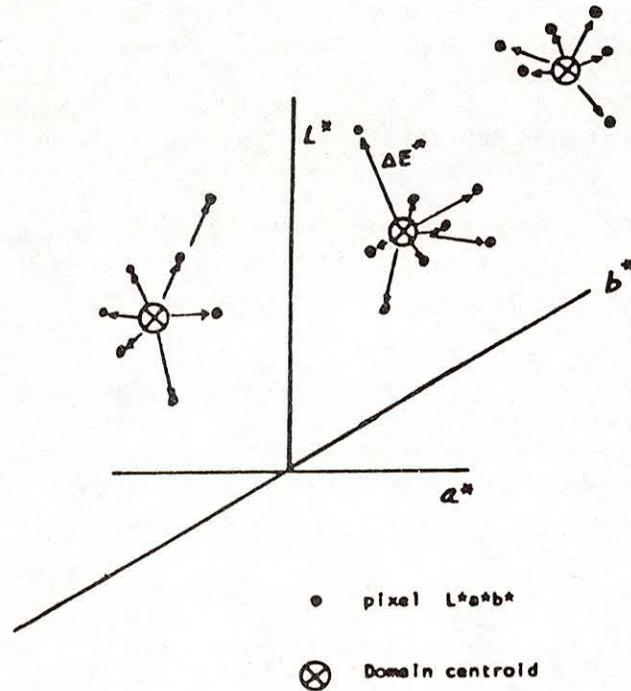

Figure 9. Domain Assignment Routine.

Since the user has control over the number of domains (from 1-5) and the corresponding L*, a*, b* values, this program can also be used to experiment with the effect of various L*, a*, b* coordinates on displayable domain files.

RANGE and SEGMNT Programs

The two remaining programs which make use of the CIELAB* files are SEGMNT and RANGE. SEGMNT allows the user to choose a rectangular section of any CIELAB* file and create a new CIELAB* file, which is a subset of the original file. The original scene is displayed as a gray-scale image. The operator chooses the upper lefthand corner and lower righthand coordinates of the rectangular segment desired by using a crosshair cursor. The domain assignment program or the clustering routine could now be used on this new file.

The RANGE program approximates viewing the scene at an integral multiple of the original distance at which the scene was recorded. For a given value of N, an NxN square of pixel L*, a*, b* values is averaged. This value is stored in a CIELAB* range-filtered file. The process begins in the upper left-hand corner of the scene and continues, moving from left to right by a factor of N until the horizontal row is complete. Then the process returns to the left side, moves down by a factor of N, and does that row. (See Figures 10 and 11.) These cycles continue until a new CIELAB* file of size Z_1 x Z_2 is created. For an original file size of X x Y it follows that Z_1 = (X-X mod (N))/N and Z_2 = (Y-Y mod (N))/N. This range filtered file may now be operated upon by the clustering or domain assignment programs.

Any original CIELAB* file may be segmented or range filtered, or segmented and range filtered, or vice versa. A segmented file can not be resegmented nor can a range filtered file be refiltered.

The remaining routines of the TAS are all utility programs which produce reports, plots, and displays, or calculate data for displays. They involve the following:

1. Display a domain file image on the color monitor
2. Interactively change the red, green, and blue components of any domain displayed
3. Create or modify an illuminant file
4. Print the header information associated with a particular file
5. Calculate the RGB values and print report
6. Draw outlines of domains on the plotter
7. Plot the reflectance curves of pixels closest to domain centroids

The function of the above utilities is reasonably apparent. The report generated by the calculation of RGB values gives a lot of information and an example is shown in Table 5.

Current Work

The TAS has been used to analyze approximately 15 scenes to date. The results seem reasonable; however, the accuracy of the resultant L*, a*, b* values has been questioned. The complete analysis of a scene is a lengthy process so in order to justify this time, the TAS is currently being tested under several different controlled conditions. Particular emphasis is being placed on the accuracy of the pixel reflectance data at
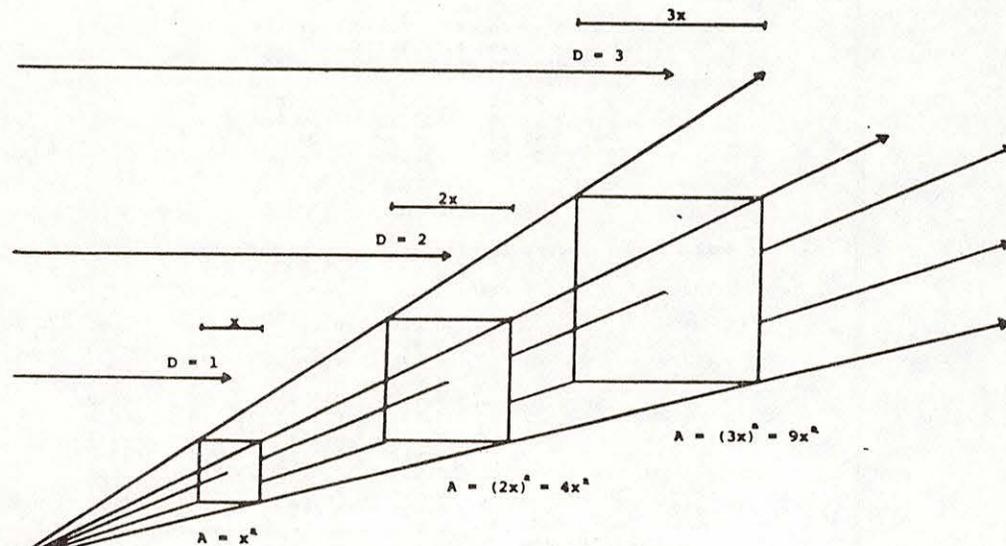
As the distance increases by a factor of N, where N = 1,2,3,4.....
the area increases by a factor of N^2.

Figure 10.   Increase in area as a function of increasing distance.

An object of area $A = x^2$ which at distance D, covers the full
field of view, will have an image resolution of 500x500 pixels.
This is the full field resolution of the system for any distance.
At distance MD (where M = 2,3,4,...) the same object will
cover $x^2/(Mx)^2 = 1/M^2$ of the field of view, and will have a resolution
of 500/M by 500/M pixels. Range filtering at distance MD requires
the translation of $(500)^2$ pixels to $(500/M)^2$ pixels, or M^2 pixels to 1.
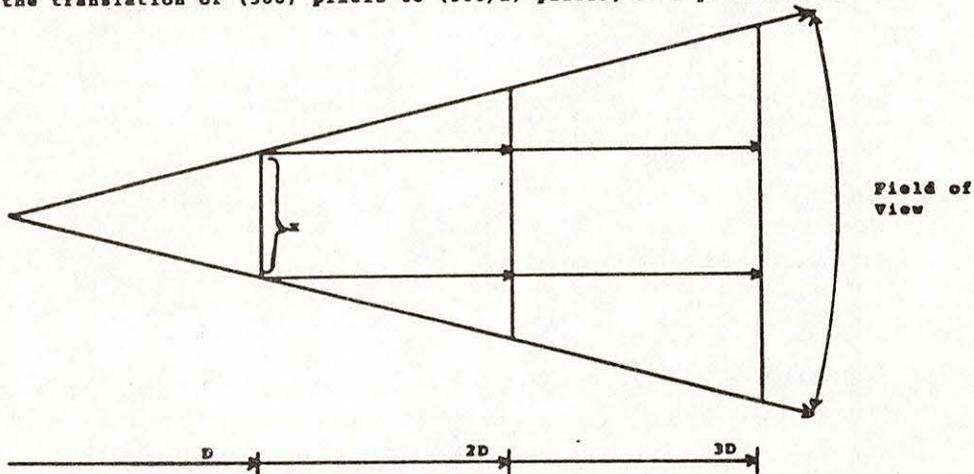
Figure 11.   Effect of range filtering on scene resolution.

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TABLE 5. RGB Output Report

```
CIELAB file used as input:   BL1:WCN111.LAB
DOMAIN file used as input:   BL1:SCN111.DOM
DATA BASE file used as input: BL1:WCN111.DAT
Domain number    La      aA       ba
       1         45.05   55.73    34.02
       2         27.70   25.13   -36.86
       3         90.89   -4.33    93.55
       4         59.70  -36.02    42.60
```

Reflectance spectra of closest pixels to centroids

Wavelength	Domain: 1	2	3	4	5
380	0.069	0.134	0.093	0.097	
400	0.057	0.152	0.084	0.084	
420	0.046	0.170	0.076	0.072	
440	0.051	0.216	0.074	0.074	
460	0.043	0.199	0.074	0.069	
480	0.040	0.107	0.074	0.078	
500	0.056	0.056	0.210	0.191	
520	0.067	0.049	0.724	0.405	
540	0.053	0.044	0.841	0.382	
560	0.054	0.040	0.922	0.313	
580	0.085	0.042	0.801	0.244	
600	0.263	0.076	0.968	0.177	
620	0.554	0.047	1.000	0.161	
640	0.820	0.030	1.000	0.150	
660	1.000	0.045	1.000	0.152	
680	1.000	0.031	1.000	0.169	
700	1.000	0.000	1.000	0.187	

```
MAMILL = BLO:ILLUM.D65        STANDARD EQUAL ENERGY TRI-STIMULUS VALUES
SPECTRAL IRRADIANCE VALUES    FOR BIGX   FOR BIGY   FOR BIGZ
       50.00000               0.0014     0.0000     0.0065
       82.80000               0.0143     0.0004     0.0679
       93.50000               0.1344     0.0040     0.6456
      104.90000               0.3483     0.0230     1.7471
      117.80000               0.2908     0.0600     1.6692
      115.90000               0.0956     0.1390     0.8130
      109.40000               0.0049     0.3230     0.2720
      104.90000               0.0633     0.7100     0.0782
      104.40000               0.2904     0.9540     0.0203
      100.00000               0.5945     0.9950     0.0039
       95.70000               0.9163     0.8700     0.0017
       90.00000               1.0622     0.6310     0.0008
       87.60000               0.8544     0.3810     0.0002
       83.70000               0.4479     0.1750     0.0000
       80.20000               0.1649     0.0620     0.0000
       76.30000               0.0468     0.0170     0.0000
       71.60000               0.0114     0.0041     0.0000
```

THE BIGX,BIGY,BIGZ VALUES

	1	DOMAIN 2	3	4
BIGX	2.63800	0.78397	7.69507	1.97315
BIGY	1.55485	0.56307	8.29840	2.93965
BIGZ	0.53880	2.04322	1.09269	0.98657

XYZ TO RGB TRANSFORMATION MATRIX

```
   X        Y        Z
 2.750   -1.149   -0.426
-1.119    2.026   -0.333
 0.138   -0.333    1.104
```

CALIBRATION FACTOR =   22.84721756

	DOMAIN 1	2	3	4	5
R	120.	15.	255.	37.	0.
G	0.	-10.	179.	78.	0.
B	10.	50.	-11.	9.	0.

Domain Number	Pixel Row	Column	Distance to Nearest Pixel
1	122	103	0.417E+00
2	77	45	0.106E+00
3	111	83	0.181E+00
4	135	74	0.144E+00

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each wavelength, since this is the initial data from which many of the results are determined. An example of one of these tests is in Figure 12. A review of recent data indicates that the difference between TAS-generated values and those obtained on a spectrophotometer are not that large. Initial results implicate the data acquisition process as the source of any errors. This should be easily solved by establishing a more stringent calibration routine.

The strengths of the TAS are in objectively determining the real color coordinates for a given number of domains of any natural terrain. The size and shape of the pattern for a given distance are also objectively determined. Comparison of the woodland or desert camouflage patterns with natural terrains will be continued following completion of the above tests. Funds have been approved (fiscal 87) to use the TAS as an aid in designing the pattern shapes and coloration of an urban camouflage fabric.

Future TAS Work

A Request for Proposal (RFP) was recently released by the Natick Research, Development and Engineering Center which would extend the usefulness of the TAS into three distinct areas.

The first phase would extend the range of the data acquisition into the infrared, from 700 nanometers to 900 nanometers. The clustering algorithm will be able to produce display files of up to five domains using both the three dye, false color infrared film technique or photocathode spectral sensitivity data for the Starlight Scope, a passive image intensifying device.

The domain clustering process of the second phase will be applicable to video-recorded imagery from a starlight scope or thermal imager. Additionally, we will be able to outline any area on the monitor and get statistical information such as average, minumum, and maximum brightness, number of pixels at a given brightness level, etc. These brightness values will have a direct relationship to the image used. As an example, the average brightness of a given outlined area of a thermal image will relate to a known temperature.

The final phase will allow the user to overlay any domain file image onto a scene displayed on the RGB monitor. The simulation of calculated contrast and the effects of increasing observation distance are required. This phase may be very difficult to achieve, but if successful will allow the effectiveness of a camouflage pattern of a given scene to be numerically defined.
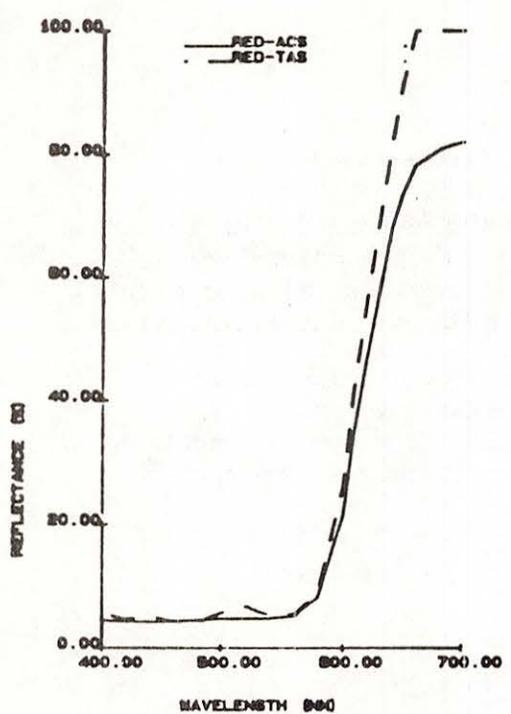
a. Reflectance curves of red domain centroid
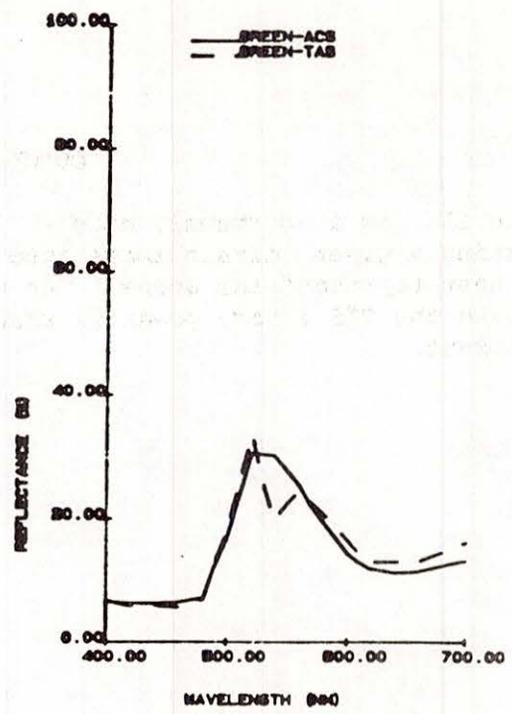
b. Reflectance curves of green domain centroid
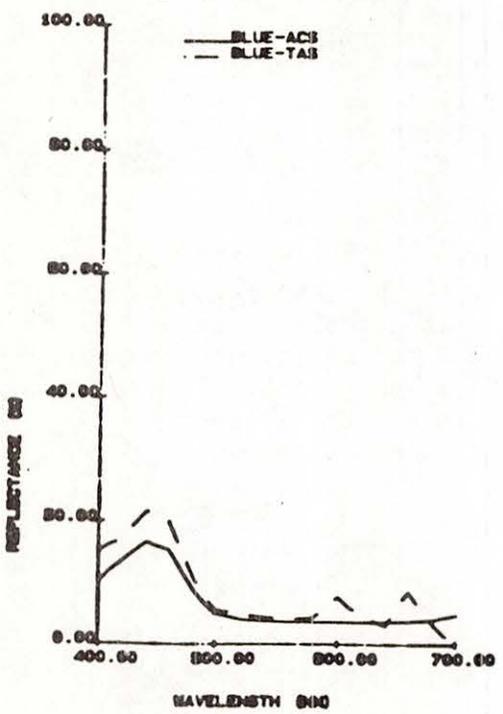
c. Reflectance curves of blue domain centroid
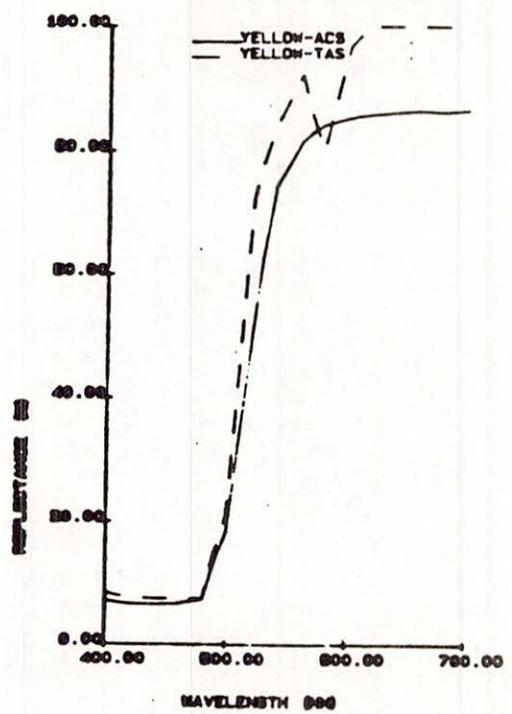
d. Reflectance curves of yellow domain centroid

Figure 12. Spectrophotometric reflectance curves versus TAS generated reflectance curves.

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CONCLUSION

The TAS, as it currently exists, is an effective tool for objectively converting a given terrain image into a pattern of five colors (or less) which best represent the scene. The proposed extensions, if successful, will make the TAS a very powerful research tool for effective camouflage development.

CARDOZO

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TITLE: Synthesis and Evaluation of Reactive Polymers for Chemical Protection

JOHN H. CORNELL, DR.,* JOHN CULLEN, MR., GRETCHEN C. RICHARD, MRS., JOHN T. STAPLER, MR., AND FRANK H. BISSETT, DR.

ABSTRACT:

One of the goals of the Army chemical defense program is the development of systems based upon materials or polymers that can neutralize phosphorus-containing neurotoxins. These materials could then be incorporated into chemical protective clothing and other combat equipment items to provide a self-de-contamination capability. It has now been quantitatively shown that agents, in particular G-agents, can be detoxified by a hydrolysis reaction (i.e., reaction with water to produce nontoxic compounds) that is effected or catalyzed by modified polymers.

For these polymers, novel monomeric models that contain some of the more reactive groups were synthesized in good yield. Then the catalytic effect of these compounds on the hydrolysis of bis(p-nitrophenyl)methyl-phosphonate, a G-agent surrogate, was evaluated by a spectrophotometric method.

The results indicated that polymeric systems containing these reactive groups should be effective for detoxification of phosphate-based neurotoxins. In addition, the synthetic approaches employed in this work suggest methods for synthesis of polymers, or attachment of reactive groups to pre-existing synthetic or natural polymers.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Chemistry Branch, Physical Sciences Division, Science and Advanced Technology Directorate, U.S. Army Natick Research, Development and Engineering Center, Natick, MA 01760.
PAST EXPERIENCE: Research Chemist, Nitrogen Division, Allied Chemical and Dye, Hopewell, VA., Research Chemist, Monsanto Research Corp., Everett, MA.
DEGREES HELD: B.S., Harvard University, 1948; M.S., Stanford University, 1950; Ph.D., Stanford University, 1952.

SYNTHESIS AND EVALUATION OF REACTIVE
POLYMERS FOR CHEMICAL PROTECTION

JOHN H. CORNELL, DR., JOHN CULLEN, MR., GRETCHEN
C. RICHARD, MRS., JOHN T. STAPLER, MR., AND
FRANK H. BISSETT, DR.

One of the goals of the Army's chemical defense program
is the development of a detoxification system based on
materials or polymers that can be effectively used to
counteract the toxic effects of chemical warfare agents.
These materials could then be incorporated into chemical
protective clothing and other combat equipment items to
provide a self-decontamination capability. Many of these
agents are phosphorus-containing neurotoxins with the general
structure 1.

$$
\begin{array}{c}
Y \\
\| \\
R - P - X \\
| \\
O\,R'
\end{array}
\quad (1)
$$
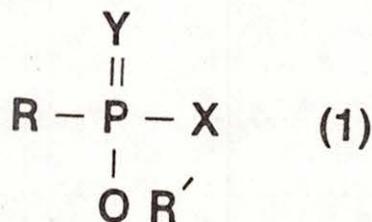
(For example, for soman R=methyl; R'=pinacolyl; Y=O; X=F.)

Such molecules can be detoxified by hydrolysis, e.g.,
conversion of X to OH. Physiologically, these agents exert
their effects by acting as inhibitors of the enzyme
acetylcholinesterase (1). The active site of
acetylcholinesterase is known to contain a histidine residue
whose imidazole ring is involved in substrate binding and may
act as a general acid-base catalyst and a serine whose
hydroxyl group functions as a nucleophile.

There have been efforts to develop a chemical system that will act catalytically to hydrolyze phosphonates of generalized structure 1. At Natick, such systems are being tested on a synthetic analog of 1, bis-p-nitrophenyl methylphosphonate (2), structure 2, hydrolysis of which can be easily monitored spectrophotometrically by the appearance of the nitrophenolate ion.

$$O_2N-\langle \bigcirc \rangle - O - \overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle CH_3}{|}}{P}} - O - \langle \bigcirc \rangle - NO_2 \qquad (2)$$
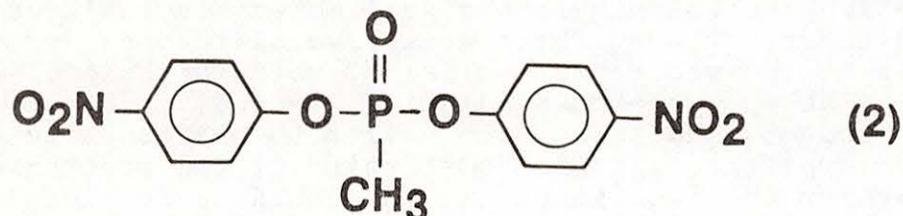
A number of different organic functional groups have been shown to increase the rate of hydrolysis of structure 2 above and similar phosphonate esters. Among these are hydroxy and imidazole groups, which are to be expected based on the analogy to acetylcholinesterase. Other nucleophilic functional groups such as oximes (3), hydroxamates (4), thiols (5), and iodosobenzoates (6) have been shown to promote ester and phosphate ester hydrolysis.

In addition, enhancements of rates of hydrolysis have been observed with mixed micelles of small molecules containing one of the above functional groups and a surfactant, and also with polymers in which hydrophilic side chains have been covalently attached to a hydrophobic backbone (triphase catalysis) (7).

In the present work the effect on the hydrolysis of agent surrogates by combining groups such as hydroxamate and hydrophilic moieties such as ethoxy in a monomeric catalytic molecule has been evaluated.

In addition, the synthetic approaches employed in this work suggest methods for synthesis of polymers, or attachment of these groups to pre-existing synthetic or natural polymers, to provide polymeric materials for general application in self-detoxifying clothing and other combat items.

One ultimate goal of this research is to prepare a synthetic or natural polymer that has been chain-extended with polyethylene glycol (PEG), which can in turn be function-

alized so as to attach a nucleophile at the end of the PEG
chain. The functionalized polymers can be expected to be
efficient catalysts for the hydrolysis of phosphate esters and
will be tested with compound 2.

It was decided to begin by preparing monomeric analogs of
these in which the polyethylene glycol moiety is replaced with
a 2-methoxyethoxy group. There were several reasons for this
choice: first, the starting material, 2-methoxyethanol, is a
readily available, well-known material; secondly, the
monomeric products should be much easier to characterize using
physical and spectroscopic methods; thirdly, the synthetic
methodology for the functionalizations could be developed more
easily for the monomeric systems; and, finally, the monomers
themselves may be effective catalysts for hydrolysis and can
be so tested. Even if the monomers are not especially
effective catalysts themselves, they may be useful in telling
us which particular functionalized polymers to concentrate
future synthetic efforts upon.

Initially, it was decided to prepare monomeric oximes and
hydroxamates because they should be synthetically very
accessible and are known to be effective catalysts for the
hydrolysis of organophosphate esters. In embarking upon this
synthetic effort care was taken to choose reactions and
reaction conditions that should be readily transferable to the
polymeric system. In fact, after the proper reaction
conditions have been worked out, the reactions may be simpler
with the polymeric systems since working up the reaction in
these cases should consist only of washing the polymer with
the appropriate solvent or reagent.

Synthesis of 3-(2-Methoxyethoxy)propanaldoxime

The aldoxime was prepared from 2-methoxyethanol as shown
in the scheme below (structures 3 and 4):

$$CH_3O \diagup OH + CH_2 = CH - \overset{\overset{\textstyle O}{\|}}{CH} \xrightarrow{Et_3N} CH_3O \diagup O \diagup \overset{\overset{\textstyle O}{\|}}{C} H$$

(3)

$$(3)\xrightarrow[\text{NA}_2\text{CO}_3]{\text{NH}_2\text{OH·HCl}} \quad CH_3O \frown O \frown \overset{\displaystyle N-OH}{\underset{\displaystyle H}{C}}$$

(4)
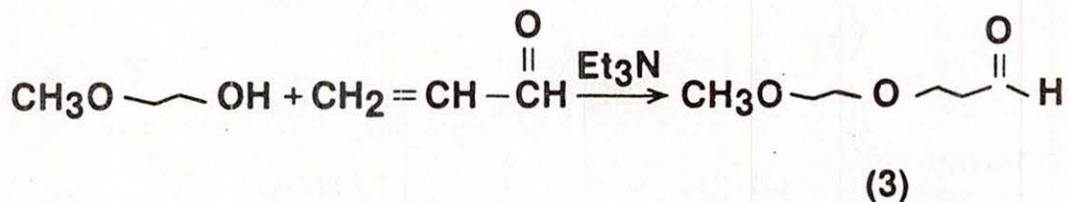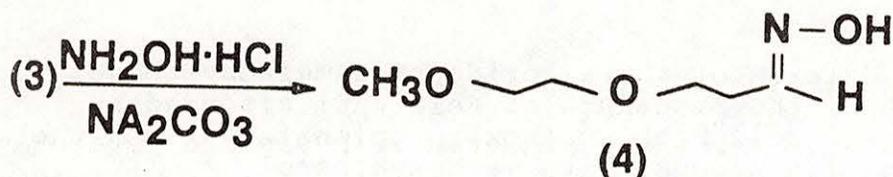
Michael addition of methoxyethanol to acrolein with triethylamine as a catalyst gave 3-(2-methoxyethoxy)propanal 3 in low yield (8). After purification by vacuum distillation aldehyde 3 was characterized by the carbonyl stretch at 1720 cm^{-1} in its infrared (IR) spectrum and the absorption at 9.79 due to the aldehyde proton in the proton magnetic resonance (PMR) spectrum. The aldehyde was converted into the aldoxime 4 by treatment with hydroxylamine hydrochloride and sodium carbonate in aqueous solution (9). The formation of compound 4 could be seen in the IR spectrum of the product by the disappearance of the carbonyl peak and the presence of an OH stretch at 3100-3600 cm^{-1} and a C=N stretch at 1650 cm^{-1}. The PMR spectrum of compound 4 revealed that it is actually an approximately 1.1 mixture of the <u>syn</u> and <u>anti</u> stereoisomers. A sample purified by vacuum distillation gave a satisfactory elemental analysis.

Synthesis of Potassium 3-(2-Methoxyethoxy)propiohydroxamate

The hydroxamic acid was prepared as its potassium salt as shown in the scheme below (structures 5, 6 and 7).

$$CH_3O \frown OH + CH_2{=}CH-\overset{\displaystyle O}{\overset{\|}{C}}OCH_3 \xrightarrow[\text{2) HOAC}]{\text{1) Na}}$$

$$CH_3O \frown O \frown \overset{\displaystyle O}{\overset{\|}{C}} OCH_3 + \text{BYPRODUCT}$$

(5)   (6)

$$\xrightarrow[\text{KOH/CH}_3\text{OH}]{\text{NH}_2\text{OH · HCl}} \quad CH_3O \frown O \frown \overset{\displaystyle O}{\overset{\|}{C}} NHO^{\ominus} K^{\oplus}$$

(7)

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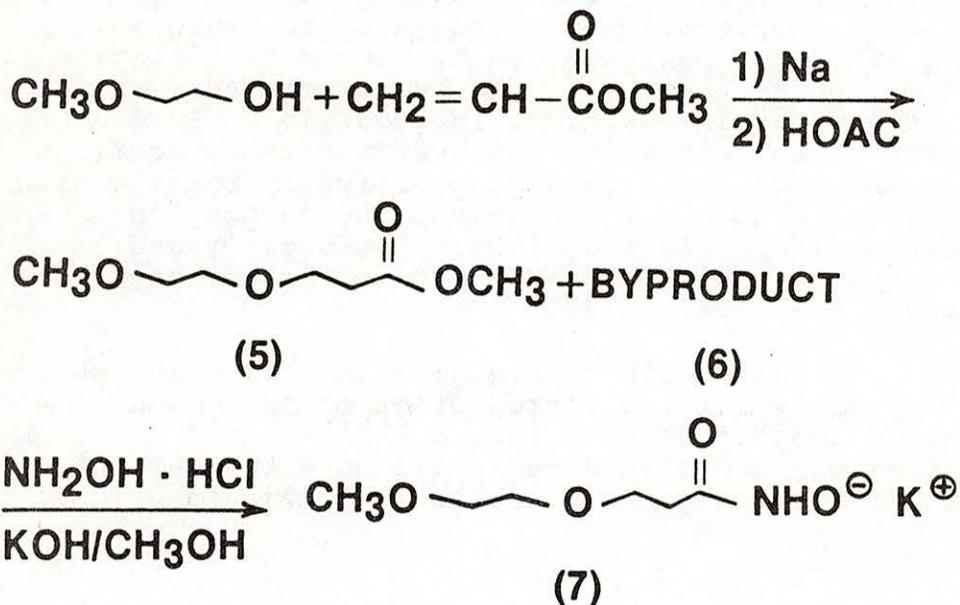
Michael addition of the alkoxide of 2-methoxyethanol to methylacrylate by the procedure of Feit (10) afforded a mixture of methyl 3-(2-methoxyethoxy)propionate, 5, and the transesterification product with methoxyethanol, 2-methoxyethyl 3-(2-methoxyethoxy) propionate, 6, in low yield. The ratio of compound 5 to 6 could be determined by integration of the PMR spectrum. Three different runs gave very similar results and the product distilled in a narrow (2^0C) temperature range.

It was concluded that the product was an azeotropic mixture of the two esters consisting of 72% compound 5 and 28% compound 6. They could not be separated by thin layer chromatography (TLC). The mixture of azeotropes was used directly in the next step since both esters react to form the same hydroxamic acid.

Conversion of the esters to the hydroxamic acid proved to be more difficult than was originally anticipated. In practice the reaction could not be carried out in aqueous solution since the product was too water soluble and could not be extracted. In addition, the esters proved to be rather unreactive toward NH_2OH. Ethyl benzoate can be converted to benzohydroxamic acid by brief treatment with NH_2OH at or below room temperature (11), although treatment of esters 5 and 6 with hydroxylamine at room temperature for extended periods afforded only recovered starting material. When the reaction was done in refluxing methanol for 18 hours, conversion of the esters was completed as indicated by TLC. Acidification of the reaction mixture gave the hydroxamic acid, but on attempted purification by vacuum distillation it appeared to decompose. Finally, the hydroxamic acid was isolated as the potassium salt, 7, in good yield. Evidence for the conversion of the esters to the hydroxamate is confirmed in several ways; compound 7 gives a positive hydroxamic acid test when treated with $FeCl_3$ solution; the carbonyl band in the IR spectrum is shifted from 1725 to 1660 cm^{-1}; and in the PMR spectrum the CH_2 group adjacent to the carbonyl is shifted upfield from 2.61 to 2.38 .

The synthetic methodology developed in this research project should allow for the introduction of oxime and hydroxamic acid functionalities into a PEG-extended polystyrene resin. These structures all have two carbons between the terminal oxygen and the nucleophilic functional

group. It might be useful to prepare analogs with only one intervening carbon. In fact, 2-(2-methoxyethoxy)acetic acid (12) has been prepared in low yield from methoxyethanol and ethyl bromoacetate.

The procedure was adapted from the synthesis by Royer (12) of carboxymethyl-polyethylene glycol. It would appear that a better synthesis would be the reaction of the alkoxide salt of methoxyethanol with chloroacetic acid (13). Reaction of this product with thionyl chloride should give the analogous acid chloride, which should react quite readily with hydroxylamine to give a hydroxamic acid or with hydrazine to give a hydrazide, a functional group which might be expected to be a nucleophilic catalyst.

Another promising area for future research would be the functionalization of alkyl polyethylene glycols such as the Brij compounds. These nonionic surfactants have the generalized structure

$$CH_3(CH_2)_n(OCH_2CH_2)_mOH \quad (8)$$
where: $n=11-17$ and $m=4-23$.
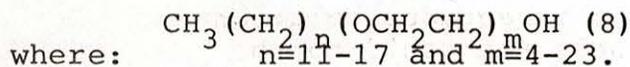
These compounds would appear to be ideal substrates for the synthesis of functionalized surfactants which would be expected to form micelles in which the nucleophilic catalyst is covalently bound. The Brij compounds could be tested for hydrolytic activity as well as oxime and hydroxamate functionalized Brij compounds, which might be prepared using the methodology developed for the small monomeric compounds.

Evaluation of Reactive Compounds

The catalytic activity of the reactive compounds was evaluated by their effect on the rate of hydrolysis of an agent surrogate, bis(p-nitrophenyl) methylphosphonate shown below:
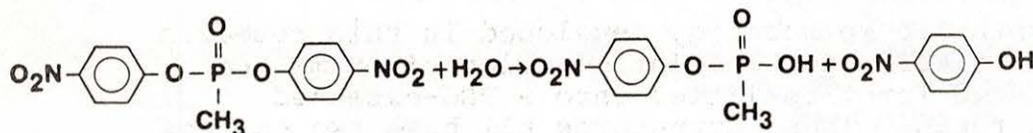
The reaction was buffered to pH 7.0 with bis(2-hydroxyethyl) imino tris(hydroxymethylmethane), "Bis-tris"(0.05 molar). Under these conditions the p-nitrophenol produced is converted to the ionic form whose concentration can be followed spectrophotometrically.

These determinations were carried out using a Gilford Model 2400S spectrometer which allows scanning of four temperature controlled samples (cuvettes) simultaneously at a fixed wavelength of 410 nanometers (the absorption maximum of the p-nitrophenolate ion). The output for each sample consisted of a chart showing absorption as a function of reaction time.

If a first order reaction is assumed, then reaction rates and half-lives can be derived from these data (14).

A typical run involved the use of cuvettes as follows:

CUVETTES	CONTENTS	PURPOSE
1.	Bis tris + BPNMP	Reference
2.	Bis tris/BPNMP + Sample a	Evaluation of a
3.	Bis tris/BPNMP + Sample b	Evaluation of b
4.	Bis tris + PNP	Reference

The first cuvette indicated the rate of the uncatalyzed surrogate hydrolysis, while the fourth cuvette served as an end-of-reaction indicator.

In addition to compounds 4 and 7 that were synthesized for this work, the following commercially available compounds were evaluated for catalytic activity by the foregoing procedure: Imidazole, 4-hydroxymethyl imidazole, tris (hydroxymethyl)aminomethane, and histamine. The above compounds were found to be inactive. The synthesized compounds that were also evaluated comprised 3-(2-methoxyethoxy)propanaldoxime, compound 4, methyl 3-(2-methoxyethoxy) propionate/2-methoxyethyl 3-(2-methoxyethoxy)propionate, compounds 5 and 6, , methoxyethyloxyacetohydroxamic acid, compound 7 (as the potassium salt) and 2-methoxyethoxypropionic acid.

All of these compounds were evaluated by the foregoing method. Only one, compound 7, gave evidence of significant catalytic activity. It produced a reaction rate approximately 4X greater than that of the uncatalyzed reaction (Fig. 1, Table 1).

FIGURE 1

### EFFECT OF CATALYST ON SURROGATE HYDROLYSIS

CORNELL, CULLEN, RICHARD, STAPLER, AND BISSETT
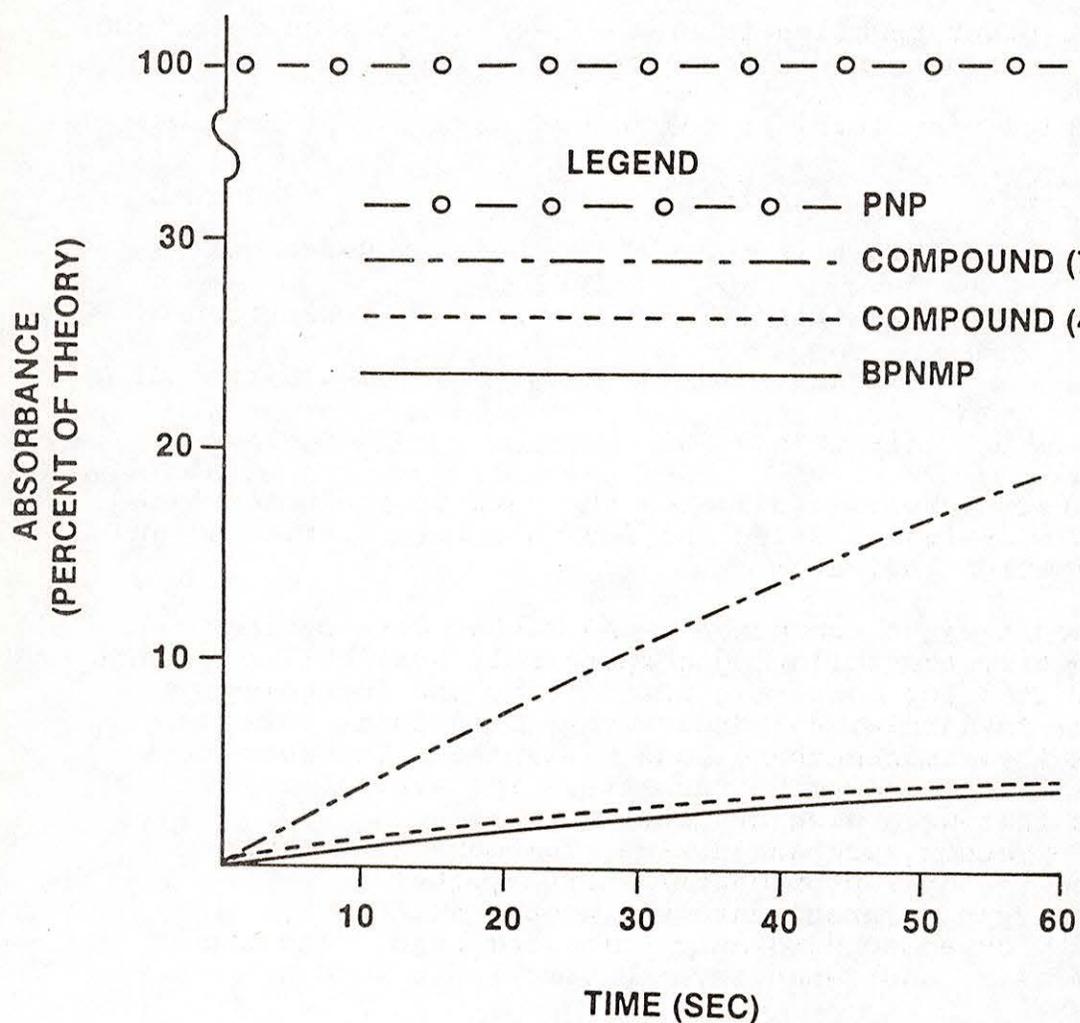
TABLE 1

EFFECT OF CATALYST ON SURROGATE HYDROLYSIS

CUVETTE NO.	CONTENTS	REACTION RATE $kX10^{-5}$ (%/Mol-Sec)	HALF LIFE $t_{1/2}$ (Sec.)
1.	Bis-tris + BPNMP (Reference)	3.13	22128
2.	Bis-tris + BPNMP + 4	3.13	22128
3.	Bis-tris + BPNMP + 7	12.61	5497

In summary, it was found that reactive groups such as hydroxamate and hydrophilic moieties such as ethoxy would be most effective for detoxification. When incorporated into the polymer model the rate of hydrolysis of the surrogate was increased up to a factor of four times. This demonstrated the feasibility of imparting detoxifying capabilities to polymeric systems by incorporating these functionalities in their structures and thus providing polymeric materials for general application in self-detoxifying clothing and combat items.

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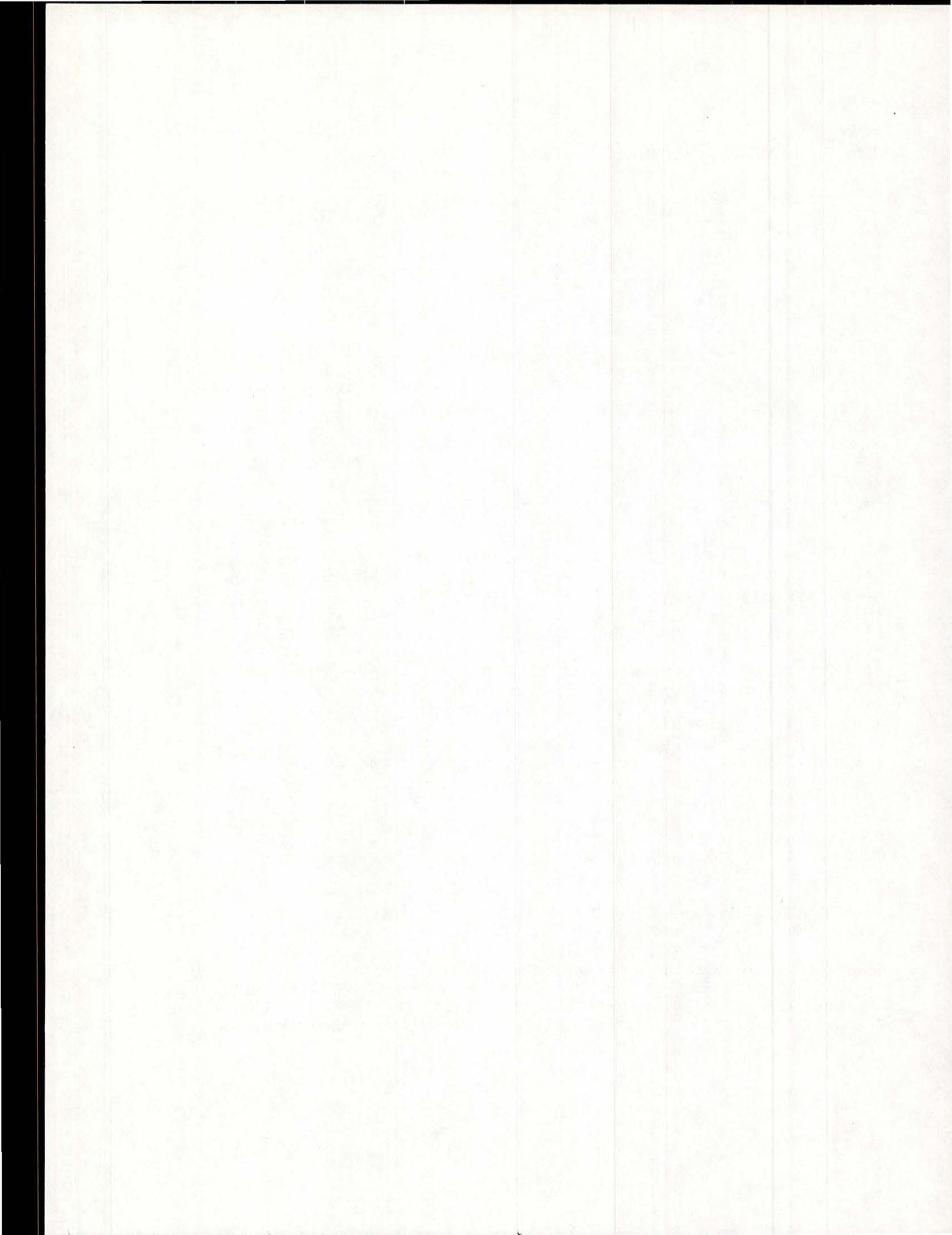
TITLE: The Interdependency of Food and Fluid Intake:
Scientific and Military Perspectives

DIANNE B. ENGELL, DR.*

ABSTRACT:

Numerous studies have shown that food and fluid
consumption are interdependent in nonhuman species. However,
there is a paucity of information on the relationship between
fluid intake, food preference, and consumption in humans.
Because of this dearth in the human literature, a series of
studies were designed to investigate this relationship in
humans in order to understand the role of fluid intake in the
acceptability and consumption of rations by soldiers in the
field. A study to determine the temporal and quantitative
relationship between fluid and food intake will be presented.

Twenty male military subjects participated in a repeated
measures design investigation. During both phases, food
intake was ad-libitum at specific mealtimes. However, fluid
intake was ad-libitum during one phase, while during the other
phase fluid intake was limited. The following observations
were made during this study: (1) approximately 70% of all
24-hour fluid intake occurred at mealtime even when fluid was
available at all times; (2) when fluid availability was
limited, subjects voluntarily reduced their food intake by
about 37%; (3) food acceptability, as measured by hedonic
ratings, was not significantly affected when fluid
availability was limited even though ration intake was
significantly reduced; (4) the intensity of thirst sensations
(e.g., having dry mouth and throat, having difficulty
swallowing) were significantly and negatively correlated with
food intake. These findings are discussed with emphasis on
combat ration development and field feeding systems.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Research Psychologist, U.S. Army
Natick Research, Development, and Engineering Center
PAST EXPERIENCE: Teaching Fellow/Research Fellow, Clark
University, Worcester, Massachusetts, 1978-1982.
DEGREES HELD: Bachelor of Science, Simmons College,
Boston, MA 1977.   Master of Arts, Clark University,
Worcester, MA, 1981. Ph.D., Clark University, Worcester, MA,
1985.

THE INTERPENDENCY OF FOOD AND FLUID INTAKE: SCIENTIFIC AND MILITARY PERSPECTIVES

DIANNE B. ENGELL, DR.

INTRODUCTION

In temperate environments when food and water are easily accessible, there is a close relationship between feeding and drinking in nonhuman species (1,2,3,4). For example, approximately 70% of total 24-hr water intake is ingested just before, during, or immediately following meals (1,2,5). In addition, a significant positive correlation has been found between the amount of water ingested with a meal and the size of the meal (1,2). Furthermore, in the rat, the ratio of meal associated drinking to the size of the meal is greater on a high protein diet than on a high carbohydrate diet (1). Thus, there is a temporal, quantitative, and qualitative relationship between eating and drinking under ad-libitum conditions in mammals.

The interdependency of food and water intake has also been demonstrated in many species under conditions of deprivation or restriction. Animals voluntarily reduce food intake when water intake is restricted (2,6,7,8), and they usually limit water intake when food intake is restricted (6,9,10). However, this relationship between food and water intake is variable. An increase in ambient temperature, for example, can result in decreased food intake and increased water intake (11), and food deprivation may result in an increase in water intake (12).

Although considerable data exist that demonstrate the interdependency of food and water intake in nonhuman species, there is a paucity of information on this relationship in humans. Some of the existing data are anecdotal, some are contradictory, and some have been collected from poorly designed studies (e.g., see 13). Because of this dearth of information, a series of studies was designed to investigate this relationship in humans in order to understand the factors that promote the acceptability and consumption of rations by soldiers in the field. The purpose of the study presented

here was to determine the quantitative and temporal
relationship between food and fluid intake and to assess the
effects of fluid restriction on food acceptability and intake.

METHOD

Subjects

Twenty male subjects volunteered to participate in this
experiment. Subjects had a mean (+SE) age of 23 (+0.3) years,
body weight of 81.7 (+3.9)Kg, and height of 178 (+2.6)cm.
Following a briefing on the design of the experiment, each
subject gave his written consent by signing a Volunteer
Participation Agreement.

Protocol

Each subject participated twice: on one occasion he was
in the control ad-libitum fluid intake (ALF) group, on another
he was in the restricted fluid intake (RF) group. The
sessions were counterbalanced so that half of the subjects
were in the control group for their first trial, and half were
in the control group for their second trial. During the ALF
and RF trials, food intake was ad-libitum at scheduled
mealtimes. During the RF trial, fluid intake was restricted
to about 250 ml at mealtimes; during the ALF trial, fluid
intake was ad-libitum. During each session half of the
subjects participated in the control (ALF) group and half
participated in the RF group. Each session was approximately
48 hours and included five consecutive meals.

During the 7 days preceding the experiment, nude body
weights for each subject were obtained using an electronic
balance (+10g) each morning after voiding and before breakfast
to determine each subject's baseline weight. During the
study, body weights were recorded three times daily to ensure
that moderate dehydration in subjects was avoided.

Subjects ate all of their meals and slept at the
Environmental Testing Facility. Dinner was served on day one;
breakfast, lunch, and dinner were served on day two; breakfast
was served on day three. Between meals, subjects could select
from various activities including moderate exercises such as
bicycling, jogging, weight lifting and sedentary activities
such as reading, watching television and playing cards. Each
subject kept an activity log during his first phase, and he
duplicated his activity on his second phase.

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All the foods and beverages consumed by all subjects were measured on an electronic balance (+1.0g). All meals were at scheduled times: breakfast, 0800; lunch, 1200; dinner, 1700. No other food was available to subjects during the sessions. Subjects in both groups were allowed to eat as much as they wanted at meal time. Hedonic ratings of all food items were collected using a nine-point hedonic scale (14). When in the control group, subjects were allowed to drink beverages during and between meals, including overnight. When in the RF group, each subject was given about 250ml of beverage to drink with his meals; no other fluid was allowed.

Meals consisted of mostly prepackaged and prepared foods supplemented with some fresh foods. Menus were served in random order. On the average, each meal (excluding beverages) contained approximately 12% protein, 37% carbohydrate, 15% fat, 35% moisture and 1% salt. Carbohydrates contributed about 45% of the total calories, and fat and protein contributed approximately 41% and 14%, respectively.

Prior to each meal during each session, subjects filled out a "Thirst & Hunger Sensation Scale" (THSS). The THSS is a booklet containing several category scales arranged in a random order. Each thirst or hunger sensation, paired with a scale marked "not at all" at one end and "severe" at the other, appears on a separate page of paper in the booklet. "Not at all" appears on the right end of the scale on some pages, and on others it appears on the left. It was thought that the procedures of using separate pages for each sensation and scale pair, random order of sensations, and random position of "not at all" and "severe" on each scale would reduce possible order effects. Similar scales have been used successfully in investigations of thirst (e.g., 15, 16) and hunger.

RESULTS

Temporal Association Between Eating and Drinking

The data show that when fluid was ad-libitum, 70.6% (+2.8%) of 24-hour fluid intake was consumed at mealtime. The pattern of 24-hour fluid intake is shown in figure 1. On the average, significantly more fluid was drunk during meals than between meal periods (t = 7.57, p<.001). Approximately 653 ml (+108) were consumed during each mealtime, and about 304 ml (+216) were ingested between meals, including the overnight period.

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Fluid deficits that accrued between meals were made up at
meal times even though fluids were easily accessible between
meals. Body water was clearly lost between meals due to
sweating, exercise, and metabolic needs. While in the RF
group, the final average percent body weight lost was 2.3%
($\pm$0.21). The range of percent body weight losses was from 0.2
to 3.7% when in the RF group.
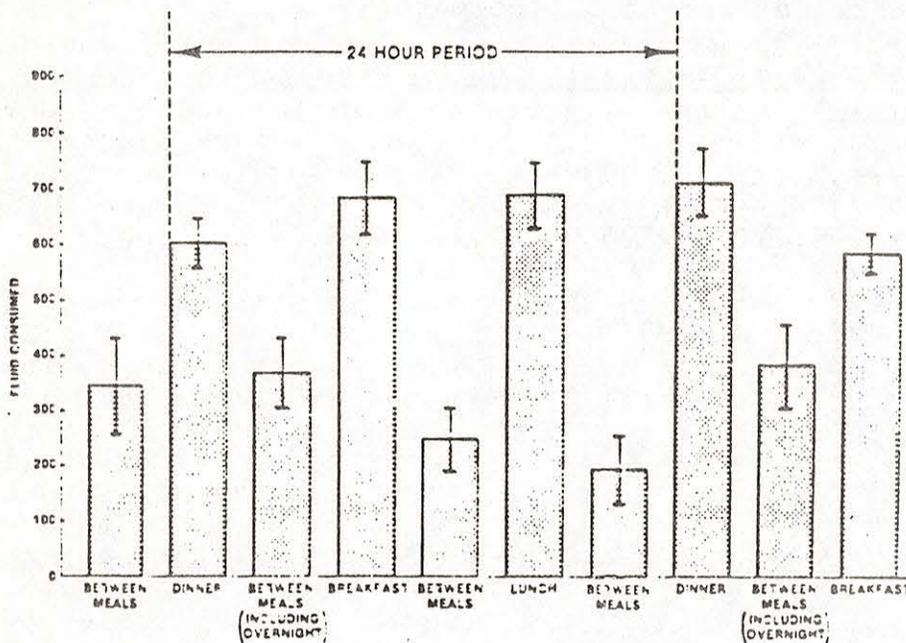
Figure 1. Pattern of fluid intake for 48 hours including five
consecutive meals.*

* One 24-hour period is indicated. Mean intake (g$\pm$SE) is
shown for 20 male subjects.

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Quantitative Relationships Between Food and Water Intake

A Pearson Product-Moment correlation between food consumed and fluid ingested at all five meal times was calculated and was not statistically significant. However, for two of the five mealtimes, there was a significant positive correlation between food and fluid intake: for meal 3 (a lunch), r = +0.44, p<.03; for meal 5 (a breakfast), r = +0.57, p<.01. There is nothing peculiar about these two meals or mealtimes. The food and fluid intake data for each mealtime represent intake data from three groups of subjects eating three different but comparable meals.

Effect of Fluid Restriction on Voluntary Food Intake and Acceptability

Those subjects who were in the restricted fluid intake group voluntarily restricted their food intake. This finding supports the oft-quoted generalization that the restriction of one commodity leads to the voluntary restriction of the other. See Table 1 below for a comparison of food intake in control and RF groups.

TABLE 1. Comparison of Food Intake by Control and Fluid Restricted Subjects.

INTAKE PER MEAL (mean ± SE)	CONTROL CONDITION	RESTRICTED FLUID CONDITION	t VALUE (Matched pairs)	PROBABILITY
CALORIES (Kcal)	1114(±116)	702(±86)	8.18	p < .001
PROTEIN (g)	47(±7)	30(±5)	4.84	p < .001
CARBOHYDRATE (g)	130(±11)	79(±9)	4.85	P < .001
FAT (g)	50(±6)	32(±5)	5.33	P < .001

Intake of carbohydrate, protein, and fat were each restricted by approximately 39%, 36%, and 35%, respectively. However, because most foods served were composites of carbohydrate, protein and fat, it is not accurate to state that subjects restricted their intake of nutrient types to the same extent. Table 2 shows how control and RF food intake data compare to the Joint Service Regulation, AR 40-25, Nutrition Allowances, Standards, and Education (17).

TABLE 2. Comparison of Daily Recommended Intake and Daily Intake During Control and Restricted Fluid (RF) Condition.*

	DAILY RECOMMENDED RATION	CONTROL CONDITION MEAN INTAKE (+SE)	RF CONDITION MEAN INTAKE (+SE)
Calories (kcal)	2800-3600	3343 (+348)	2106 (+258)
Protein (g)	100	141 (+21)	91 (+15)
Carbohydrate (g)	400	390 (+33)	238 (+27)
Fat (g)	not to exceed 160	150 (+18)	97 (+15)

*Daily recommended intake figures from Joint Service Regulation AR 40-25, Nutrition Allowances, Standards, and Education.

There was no difference between RF and ALF groups in hedonic ratings for the meals as a whole or for individual food items. When in the RF group, subjects rated the food (mean + SE) 6.9 (+ 0.9) on a 9 point scale; when in the control group, they rated the food 7.1 (+ 0.9).

Although there was a significant difference between control and RF groups in a pre-meal thirst ratings (t = 7.78, p<.001), there was no significant difference in pre-meal hunger ratings (t = 0.67, NS). Pearson Product-Moment Correlations were calculated between food intake and scores on "I feel thirsty" and "I feel hungry" scales. There were no significant correlations between "I feel hungry" and food intake for subjects during either control or RF conditions. However, there was a significant and negative correlation between the intensity of the sensation "I feel thirsty" and the amount of food ingested (r = -0.47, p<.02). That is, as the intensity of thirst sensations increases, the amount of food consumed decreases. A significant correlation (p<.01) between a general feeling of thirst and a loss of appetite was expressed by approximately 30% of the subjects.

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DISCUSSION

When food was served at three specific times and fluid intake was <u>ad-libitum</u> during a 24-hour period, approximately 70% of all fluid intake occured at meal times. Although fluid deficits accrued between meals and fluid was always easily accessible, most of the total fluid consumed during a 24-hour period occured at meal times. This pattern is remarkably similar to that observed in nonhumans. In nonhuman species, 70% of all fluid intake occurs at mealtimes (1,2,5). However, in a study of food and water intake in men in a desert environment, Adolph and Wills (13) found that only 50% of total fluid intake was ingested with meals by men in the desert. This value is lower than the one that we found, probably because more fluid is consumed between meals when ambient temperatures are high. The effect of climatic conditions on the interdependency of food and fluid intake was not addressed in this study.

There are several explanations for the close temporal relationship between eating and drinking. None of the explanations are mutually exclusive. It is possible that "meal associated drinking" occurs for lubrication to facilitate chewing and/or swallowing. Kissileff (5,18) found that when salivation is experimentally reduced in rats either by salivarectomy or pharmacologically, drinking is attenuated if water is infused orally but not if it is infused gastrically. These results suggest that prandial drinking occurs primarily for lubrication. It is quite possible that eating food can induce drinking because drinking reduces adversive sensations evoked by dry or spicy food.

An alternative but compatable explanation for the close temporal association between food and fluid intake is an ecological one. In the control condition fluid was available to subjects at all times. Although beverages were easily accessible between meals (they were stored in a refrigerator in a centrally located room), subjects had to make more of an effort to obtain a beverage between meals than during meals when beverages were served to subjects. The "between meals fluids" may have been relatively more difficult to obtain than those served with meals, and thus less may have been consumed between meals than during meals due to ecological factors. Some authors (e.g., 19,20,21) have argued that water intake depends on both the state of the body fluids and the "availability of water", which is partially perceptual. Logan (20) has addressed this issue in an experiment in which rats had to bar-press for water on either "easy terms" or "hard terms". "Easy terms" was defined as a relatively large quantity of water for a relatively small number of presses or a light bar; "hard terms" was defined as a relatively small amount of water for a relatively larger number of presses or a

heavily-weighted bar. Logan found that "hard term" rats had an asymptotic 24-hour water intake of 15 ml, and "soft term" rats one of 23 ml. The conclusion that "accessibility" significantly affects intake was also made by Marwine and Collier in their study (21).

Another explanation for the close temporal relationship between food and fluid intake is that "meal-associated drinking" is related to actual physiological states. Eating may cause cellular dehydration by increasing osmolality in the digestive tract (22), or eating may cause extracellular dehydration by causing secretions of isotontonic digestive juices into the stomach. Thus, eating may elicit drinking via cellular or extracellular thirst stimuli via the sodium-osomotic-vasopressin pathway or the renin-angiotensin system, respectively. Deaux, Sato, & Kakolewski (23) found that drinking was preceded by a rise in osmolality when rats were fed discrete meals. Blair-West and Brook (24) found that eating resulted in an immediate rise in plasma renin activity and a reduction in plasma volume in sheep. Kraly has suggested that eating may elicit drinking via vagally medicated mechanisms involving histamine, insulin, and serotonin (25), and Houpt (26) has suggested that gastric acid plays a significant role in "meal-associated drinking".

The question of whether "meal-associated drinking" occurs as a consequence of physiological changes induced by eating or is related to anticipatory physiological needs has been addressed by Fitzsimons (27). Fitzsimons has argued that the sight, taste, or smell of food or the presence of food in the stomach could be associated with a specific metabolic need and thus serve as a conditioned stimulus to drinking. Fitzsimons and LeMagnen (1) found that when a diet rich in carbohydrates was changed to a diet that was high in protein, rats increased their water intake. At first this additional intake was not well synchronized with mealtimes. However, after a few days the additional water was ingested with meals, reestablishing a close temporal relationship between eating and drinking, and a positive and significant correlation between food and water intake. Fitzsimons and LeMagnen (1) proposed that rats learned to "anticipate" the future requirements of water before the need arose. Although this study is frequently mentioned, there have been no successful replications nor similar research efforts. Rowland (28), for example, investigated the effect of salt levels in the diet and found that most of the additional drinking associated with high salt diets occurred between meals, and there was no trend to increase "meal-associated anticipatory drinking".

The close temporal relationship between food and water intake has important military application. Fluids should be abundant at mealtimes so that soldiers can drink copiously and thus restore fluids lost between mealtimes. Because the high level of meal-associated drinking observed in our experiment may be due to ecological issues, such as relative accessiblity of fluid during and between meals, it may be important for the military to have fluids easily accessible between meals to enhance between meal drinking.

A significant correlation between the size of the meal and the amount of fluid consumed was found during only two meals in the present study, and the overall correlation between meal size and amount of drinking for all five meals was not significant. Although a significant correlation has found between amount of water ingested with a meal and the size of the meal in nonhuman species (e.g.,1,2), an insignificant correlation was also found in humans by Adolph (29). There are three reasons for finding significance in nonhuman species and not in humans: (1) nonhuman subjects are usually given dry pellets or powdered laboratory chow to eat, and human subjects are given food with moisture (for example, the foods in our study contained about 35% moisture); (2) nonhuman studies are usually run for many days more than human studies (Nomile and Barraco's study of pigeons, for example, was a 28-day study - few facilities could run such a long-term study with healthy human subjects); (3) there may be species differences that may reflect adaptation to ecological niches.

When fluid intake was restricted, subjects voluntarily restricted their food intake. On the average, when beverage intake was restricted, subjects ate only about 63% of what their food intake had been when beverage intake was ad-libitum. Bolles (7) found that in rats food intake was reduced to 62% of normal when water intake was limited. Other investigators have found similar levels of voluntary restriction of food intake during water deprivation (30) (31).

When on a fluid restricted regimen, subjects ate significantly less than the daily recommended standard for caloric, protein, and carbohydrate intake (17). The accumulation of nutritional deficits over a period of days may have deleterious effects on health and performance of soldiers in the field. The voluntary restriction of food intake that occurs as a consequence of water restriction could be a serious military problem during a long operation. Quantitative degradation of performance during a relatively short period remains to be assessed.

Intake of carbohydrate, protein, and fat were restricted to about the same extent in our experiment. However, because the foods served were composites of nutrients it is not accurate to state that individuals selectively restricted nutrient types to the same extent from a variety of foods that were especially high in particular nutrients. It would be interesting to see if fluid restricted individuals differentially restrict the intake of protein foods that have a high water demand. Some may hypothesize that protein foods might be consumed less than carbohydrate or fat because the relatively high water demands of protein may be "anticipated".

Food acceptability as measured by hedonic ratings was essentially identical in RF and ALF groups but food intake was significantly different in the two groups. This finding addresses the utility of using acceptance testing in the laboratory to predict intake in the field. While acceptability testing is sometimes a good predictor of consumption (32), it is important to note that there are several factors in addition to acceptability that affect food intake. Factors such as temperature, level of exertion, ease of food prepartation and social setting, for example, have been shown to affect human food intake. It is now clear that fluid availability also has an important effect on food intake in humans.

In conclusion, this study demonstrates that there is a quantitative and temporal relationship between food and fluid intake in humans. Approximately 70% of all 24-hour fluid intake was consumed at mealtimes when fluid intake and scheduled food intake were ad-libitum. However, when fluid intake was restricted, subjects voluntarily restricted their food intake. While food acceptability as measured by hedonic ratings was not affected by fluid restriction and thus was not a good predictor of food intake, ratings of thirst were significantly correlated with the reduction of food intake. Although several explanations for the interaction between food and fluid intake were proposed, additional studies that include continuous monitoring of systemic measures are critical to elucidate the mechanisms underlying the relationship between food and fluid intake in humans.

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TITLE: An Objective Computerized Color Measurement System

B.E. FITZGERALD, MS.,* T.R. COMMERFORD, MS. & A.O. RAMSLEY, MR.

ABSTRACT:

An instrumental objective color measurement system has been under development at the US Army Natick Research, Development and Engineering Center to provide a quantifiable means to evaluate dyed and printed textiles for shade acceptability. The system was developed in four stages. Phases I and II included the evaluation of commercially available color measurement/data processing instruments, the development of a system-wide calibration procedure, and the derivation of a color difference equation based on acceptability. In early stages of Phase III, a two-unit prototype system was purchased and installed. Later, three additional satellite units were purchased. Correlation studies were performed to determine the inter- and intra-instrument agreement after the initial purchase, and again when the system was expanded. Data from both studies indicate adequate repeatability and correlation. Phase IV has begun. Satellite units have been installed at industry sites for a system-wide preoperational trial to determine the correlation of visual and instrumental acceptability decisions and inter-instrumental decisions on production samples. Upon successful completion of Phase IV, instrumental shade evaluation will be implemented into the Government's quality assurance program.

*BIOGRAPHY:
  PRESENT ASSIGNMENT: Project Officer for the Instrumental Color Measurement System
  PAST EXPERIENCE: Student Trainee in Textile Technology, US Army Natick Research, Development and Engineering Center
  DEGREES HELD: Bachelor of Science, Framingham State College, Framingham, MA, 1984

AN OBJECTIVE COMPUTERIZED COLOR MEASUREMENT SYSTEM

B.E. FITZGERALD, MS., T.R. COMMERFORD, MS. AND
A.O. RAMSLEY, MR.

INTRODUCTION

Throughout its history, the textile industry has evaluated shade visually for want of a quantifiable method of determining an accurate shade match. Industry has long sought methods to control color, and produce consistent results from lot to lot. Today, color instrumentation has begun to aid the eye in making color matches and decisions.

If this need for consistent results is true for the commercial market, it is far more imperative for goods targeted as end items for military use. The US Army Natick Research, Development and Engineering Center (NRDEC) has developed an objective color measurement system to be used in evaluating textiles purchased by the Department of Defense (DOD). The project outlined in this paper is in its final phase and is expected to be beneficial to both the DOD and commmercial industry.

Background

The textiles used in producing military end items require a uniformity that is consistent not only within a lot, but from lot to lot. Today there are more than 500 standard fabrics used by the military to clothe and equip the soldier and to meet his/her needs in all possible situations, both on and off the battlefield.

The challenge of producing consistent results is compounded by several factors. One, is the procurement and manufacturing process for military garments. Normally, one type of fabric may be produced by several different sources. These goods are then shipped to Government warehouses before reshipment as Government Furnished Material (GFM) to garment manufacturers, who may assemble only one element of the uniform (i.e., only jackets or trousers). The most desirable achievement is to have a soldier wearing a complete uniform that appears to have been cut from the same lot. The procurement procedure, as structured, strains this achievement by mixing lots, fabric producers, and garment manufacturers.

The development of camouflage protective clothing is the second factor contributing to nonachievement of uniformity. Several camouflage patterns and colors have been developed as countersurveillance measures to protect the soldier. Disruptively patterned camouflage for a four

color Woodland and a six color Desert print requires shade control of multiple colors per fabric. This, together with specified spectral reflectance factors in the visible/near-infrared wavelength region (600 to 860 nanometers), compounds the problem of acceptability. Lack of tight control over shade only defeats the intended purpose of the camouflage uniform.

Visual shade evaluation is still the standard method of determining shade acceptability for Government contracts. The inspection process takes place in a standardized shade booth under standardized light sources that simulate either daylight or incandescent light. Included in all military specifications for textiles is a statement that says when the sample is judged against standard and tolerance samples under simulated daylight illumination, the sample shall match the standard; and when viewed under incandescent lamplight the sample shall be a good match to the standard. This is where problems arise. Though the human eye is extremely sensitive in its ability to detect small color differences, each person sees and interprets color stimuli differently.

It is understandable that conflicts may arise when a difference between two observers with normal color vision is taken into consideration. Though consistent determinations can be achieved when a large panel of observers is used, this is both impractical and economically infeasible. Tremendous losses are often incurred by both the Government and contractors when such conflicts occur. These include loss of production time, loss of profit on rejected goods, acceptance of substandard goods, and involvement in costly and lengthy litigation processes required to settle these disputes. With more than $500 million dollars expended annually in procuring textiles for military use, it is clear that the need exists for an objective method of determining shade acceptability.

Recent advances in technology for optical measuring instruments and computers now provide an opportunity to develop such an objective color measurement system for use in the procurement of goods for Government use. The benefits should be fourfold: better quality goods, savings in time and money, and fewer contractual disputes.

The plan to develop an objective instrumental color measurement system at NRDEC began in 1977.(1) Four distinct phases were outlined. Phase I involved surveying the commercial market to determine what instruments were available and suitable for the projected needs. Several instruments were evaluated and it was determined that all were suitable with some optical and computational modifications. The system was designed in Phase II. Further modifications were identified, a fail-safe calibration procedure was provided, and a color difference equation based on acceptability was developed so that pass/fail judgements could be determined. Phase III included the assembly of a

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two-unit system as a result of the competitive bid process. Correlation studies were performed to ensure that the two units were in agreement before proceeding to the next step. A short trial study was conducted on procurement samples. Shade tolerances were developed for three shades of the Woodland camouflage printed Nyco Twill battledress uniform fabric. Once these two steps had been completed successfully, the system was expanded to include three satellite units destined to be placed in contractors' facilities during Phase IV. But first, correlation studies were again performed system-wide to determine the repeatability and the degree of reliability among the five units in the system.

Currently, Phase IV is in its initial stages. The satellite units have been located at industry sites for a system-wide trial study of production samples. This phase, which is the last step prior to implementation of the system, will determine the degree of accuracy in inter- and intra-instrumental acceptability judgements and agreement between visual and instrumental evaluations.

PHASE I. SURVEY OF COMMERCIAL EQUIPMENT

The first goal of the program was to determine which commercially available instruments would satisfy NRDEC's requirements. While color measurement instrumentation has been available for more than 45 years, it is only the most recent technological advancements in the computer and optics industries that have allowed instrumentation to become sufficiently accurate, efficient, and economically feasible for a program of this type. The second goal of this phase was to determine what modifications, either optical or computational, would be necessary.

A contract was awarded to the Rensselaer Color Measurement Laboratory to assess the comparative performance of color measurement instruments commercially available. The three spectrophotometers selected for the study were the Macbeth MS-2000, Diano Match-Scan, and the Hunter D54P-5. The Macbeth MS-2000 is an abridged double beam spectrophotometer. The MS-2000 differs from the other instruments in that its light source is a xenon flash tube. The Hunter D54P-5 is a single-beam scanning spectrophotometer and the Diano Match-Scan is a double-beam spectrophotometer. Both the Hunter D54P-5 and the Match-Scan use a quartz-halogen tungsten filament lamp as the light source. Each of the three instruments utilize integrating-sphere geometry, diffuse polychromatic illumination and near-normal sample viewing. All of these instruments simulate the Commission International de l'Eclairage (CIE) standard illuminant D_{65} by an optical filtering of the light source. While the Hunter D54P-5 uses a rotating interference wedge monochromator, a grating type monochromator is incorporated into the design of the Diano Match-Scan and the MS-2000. The Match-Scan and MS-2000 use fixed grating, and single-pass monochromators, respectively. Each instrument utilizes a different

type of detector. The Match-Scan uses a photomultiplier tube, the MS-2000 an array of 17 silicon- photodiodes, and the Hunter D54P-5 a single silicon-photodiode.

NRDEC's goal to develop an objective color measurement system was aided by the National Research Council (NRC) which established the Committee on Color Measurement to advise and guide NRDEC. With input from the NRC Committee, criteria were developed to evaluate each of the commercial instruments. This list is comprised of requirements that will meet the long-term goals of this research. They are to:

1. be as sensitive as the eye in detecting small color differences;

2. produce repeatable and more consistent data than the eye;

3. be adaptable to a wide variety of surface textures and sample sizes;

4. use CIE standardized illuminant and observer data, and include specular component of reflection in the measurement;

5. provide system-wide calibration and automatic computation of colorimetric and acceptability data;

6. be sufficiently reliable, fast, inexpensive, simple to operate, and rugged for practical use in an industrial environment.

Dr. Fred Billmeyer and Ms. Paula Alessi, Rensselear Color Measurement Laboratory conducted the experiments for Phase I.(2) The analysis of instrumental stability and repeatability was determined by measuring a variety of specimens including calibrated standards, textile color difference sets, porcelain-enamel tiles, color-difference sets, and miscellaneous tiles with a variety of surface textures. Measurements of calibrated standards determined the accuracy of the measurements. These included the National Bureau of Standards (NBS) Standard Reference Materials 2101-2105, a set of transmitting filters, and British Ceramic Research Association (BCRA) reflectance tiles, calibrated at the Hemmendinger Color Laboratory.

The short-term accuracy of the instruments was evaluated based on measurements of the NBS SRM 2101-2105 filters, BCRA tiles, a variety of highly fluorescent samples and 16 sets of textile samples. These textile samples supplied by NRDEC represent sets of standard military shades and eight tolerance samples for each standard.

The long-term performance of the instruments was assessd by measuring a set of 10 Cararra glass tiles. In addition to short- and

long-term repeatability, the sensitivity to several other parameters was tested. Precision was evaluated by measuring the NRDEC porcelain tiles and textile samples. The combination of glossy Cararra glass and matte surfaced textile samples measured the effectiveness of rejecting the specular component. The photometric scales were evaluated using Johnson grey tiles. Selected textile samples were measured to determine sensitivity to weave orientation. Within piece and point-to-point variation was determined by measuring the color difference between the center and four corners of the textile and BCRA tiles.

The Rensselear study concluded that any of the three instruments performed with adequate accuracy to meet the needs of this project. The repeatability of each instrument was found to be better than 0.10 CIELAB* color difference units. Measured color differences are normally much larger than 0.10 CIELAB* unit, therefore, each of the instruments performed well. While the performance of the instruments was excellent and each was statistically the same, modifications were necessary before any one of the instruments could meet the requirements of this project. These modifications were identified as changes to the optics, to the computer software, and to the instrument itself.

PHASE II. DESIGN OF SYSTEM

The design of the system evolved in Phase II as the modifications suggested by Rensselear, the NRC Committee, and further in-house study at NRDEC were considered and discussed with the instrument manufacturers. The most significant optical modification involved extending each instrument's capability to measure into the near-infrared (near-IR) portion of the electromagnetic spectrum. This decision was made in light of camouflage fabrics that had just been developed and required careful control of spectral reflectance properties in the near-IR. For two of the three instruments, the Diano Match-Scan and the Hunter D54P-5, only minor modifications were needed to meet this requirement. For the Macbeth MS-2000, a significant and somewhat costly redesign was required. A short time later Macbeth developed a new and separate instrument capable of measuring near-IR reflectance.

Two of the instruments exhibited some polarization of the beam. The Diano Match-Scan demonstrated sensitivity to fabric orientation. It was found that the instrument had not been fitted with a retardation plate to eliminate the polarizing effect. This was easily corrected. The MS-2000 also demonstrated some polarization, but the deviations were found to be within allowed tolerances.

It was determined that additional software would be required. The initial models studied were stand-alone versions in which the microprocessors had burned-in memory. Such limited capability would not allow the flexibility of user-written programs needed to perform

analyses of correlation data. Also, the acceptability equation developed in Phase III is determined individually for each shade studied. Constants for the equation differ from shade to shade; thus, access to the software to store or to alter data is essential. Other changes needed beyond the initial capabilities were automatic averaging of multiple readings and replacement of illuminant and observer data with the 1964 CIE recommendations for illuminant D_{65} and A, and the 10° observer. It was also desirable to achieve simplicity of operation, so that a technician with only moderate training could operate the instrument with ease.

One of the major accomplishments of Phase II was the development of a system-wide, automatic calibration procedure. A fail-safe calibration method is necessary to ensure accurate and repeatable performance on a day-to-day basis among all units in the system. A contract was awarded to Clemson University to develop the procedure, with Dr. Frederick Simon and Ms. Judith Lubar performing this contractual effort.(3) The procedure contained provisions for the calibration of both the wavelength and photometric scales.

Verification of the system's performance is checked by computing tristimulus values for durable samples and comparing these with known values. Once programmed into the system, the instrument will not operate if the calibration procedure has been by-passed, or the values obtained are not within acceptable tolerances.

The Clemson Study selected standards that included a white opal glass, a yellow filter, and a grey porcelain tile. These were measured to set both the 100 percent line and set the photometric linearity of the instrument in the visible spectrum. The yellow filter determined the low and high regions of the scale and the grey tile checked the middle of the range. The stored values are compared with the daily measurements of these samples to ensure accurate performance. Also, a pair of tan polyester gelcoat plaques of known color difference were used as a measure of repeatability for both spectral reflectance and color difference. The instrument selected by the procurement process was purchased with a procedure similar to the one outlined in the Clemson study. However, it uses a black trap and three porcelain-enamel tiles (white, grey, and green) to set the 0 and 100 percent reflectance lines and to determine the linearity of the photometric scale.

The final step in designing the objective color measurement system was to develop a color difference equation to determine tolerance limits for each color. This quantification of acceptable tolerance ranges in various regions of color space was done under contract by Dr. Eugene Allen and Mr. Barry Yuhas of Lehigh University.(4) A new method of determining acceptability was needed because existing color difference formulas are based on visual perceptibility and do not consider bias,

which is an integral part of visual pass/fail evaluations in the textile industry.

Allen and Yuhas developed the numerical acceptability criteria using the following procedures. Three shades were studied: tan, olive green and dark blue. From colorimetric data on 200-300 procurement samples of each shade, 12 pairs were selected, which represented four color difference levels of samples differing only in hue, chroma, or lightness. Plus and minus directions in color space were obtained by reversing the sample pairs, for a total of 24 pairs. The sample pair with the smallest color difference was expected to pass in the majority of the acceptability judgements. Correspondingly, the pair with the largest color differences were expected to fail most of the time. The remaining two color difference levels were selected close to the just-acceptable color difference tolerance.

The samples were shown to a panel of 6 observers, representing both Government and industry, 10 times in random order, for a total of 240 determinations per observer. Each observer was asked to make a pass/fail judgement as to the acceptability of the match. The method of logistics functions was then applied to the acceptance data to determine the color difference accepted 50 percent of the time.

The Lehigh study came to several conclusions. The acceptability thresholds were defined by ellipsoids in CIELAB* space. The size and shape of each ellipsoid is defined by three constants, with a fourth constant required to define the orientation of the ellipse in the chromaticity plane. The ellipse orientation of the olive green and tan shades was in the direction of an iso-hue line. The ratio of lightness, chroma, and hue axes were 3:2:1. The blue shade was oriented along an iso-chroma line. The ratios for this shade were 1.6:1.4:1.0. No significant differences were found in the acceptability decisions made by observers from Government and industry. However, observer knowledge of the end use of the fabric did affect the judgement. The dark blue shade used in dress uniform fabric had the smallest ellipsoid. Finally, because tolerance differences are expected to vary in various regions in color space, and depending on the importance of the color match, tolerances should be determined for each individual shade.

PHASE III. ASSEMBLY OF A PROTOTYPE SYSTEM

Phases I and II provided the groundwork to define the system requirements needed to purchase a prototype system in Phase III. Through a competitive bid procurement process, Applied Color Systems (ACS) was awarded the contract for the purchase of two Spectro-Sensor instruments. The spectrophotometer which is the center of the system is a Hunter D53IR, which is basically the same as the D54P-5 studied in Phase I, with the additional capability to measure into the near-IR.

The spectrophotometer is interfaced to a Digital Equipment Corporation microcomputer or microprocessor. The master unit located at NRDEC is an RSX-11M multiuser system, PDP 11/23 with RL02 (hard disk) drives. The other instrument was placed at the Defense Personnel Support Center (DPSC) and is an RT-11 single user system, PDP 11/03 with RX02 (floppy disk) disk drives.

The only differences between the two systems are memory capacity and software capability. The NRDEC system has 124K of memory and extensive software capabilities needed for analysis of correlation data. The DPSC unit has 32K of memory. The systems are linked by a modem interface for data transmission from DPSC to NRDEC. Both systems have software packages written by ACS specifically for the color measurement program, which contain programs for measurement, acceptability testing, file maintenance, and data transmission and reception.

The systems were installed in early of 1983. Shortly thereafter, a period of initial testing was performed to determine the reliability, repeatability, and the degree of correlation between the NRDEC and DPSC systems.(5) The two units essentially perform as one, and it was important to determine that they read samples accurately and continue to do so over time.

Short-term and long-term studies were performed on a variety of samples to determine the inter- and intra-instrument reliability and correlation in both the visible (400-700 nm) and near-IR (600-900 nm) regions of the electromagnetic spectrum. These samples included 15 porcelain-enamel tiles, 20 textile swatches, and a polyester gelcoat color difference pair. The five sets of porcelain tiles represent standard shades (two tan, two green, one blue), consisting of a standard sample with full and thin limit tolerances. The two textile sets (tan and green) each contained 10 Nyco twill swatches.

The data from these samples were further studied to determine the repeatability of the instruments in the near-infrared portion of the electromagnetic spectrum. The polyester gelcoat plaques were used to determine the accuracy in measuring the color difference for a pair with known values. The mean color difference from the mean (MCDM) for each set of measurements was used to evaluate each instrument's performance. Inter-instrument agreement was determined by calculating the color difference between the means for the two instruments on a given sample.

All measurements were made under D_{65} with the specular component included on large area view mode. Tristimulus value calculations were determined for D_{65} and the $10°$ 1964 CIE supplementary standard observer. All the color difference calculations were based on the 1976 CIE L* a* b* (CIELAB*) space.

The test was divided into two portions. Short-term studies were performed over 10 consecutive days. Long-term studies of the samples were measured over 10 weeks. The color difference pair was measured 10 times over 3 weeks. Once the studies were completed at NRDEC, the samples were shipped to DPSC and the experiments repeated.

The results indicated that the two instruments performed well individually and comparatively on short- and long-term bases. The instruments exhibited MCDM's of 0.14 CIELAB* units or less. The average MCDM's were 0.10 or less, ranging from 0.04 to 0.09. The average color difference between means for the two instruments ranges from 0.06-0.12. The largest color difference noted was 0.18 CIELAB* units. Since these values are much smaller than those differences normally found between acceptability tolerances and standard samples, the instrument's performance will serve the purposes and goals of the Government program.

An operational trial was conducted to further test the feasibility of implementing the instrumental shade program as standard procedure.(6) Using the Allen and Yuhas method, shade tolerances were established for three of the four shades printed on the Woodland pattern, Nyco Twill Battledress uniform fabric.

Samples submitted to DPSC by contractors were visually evaluated for acceptability under standard lighting conditions using standard and tolerance limit samples. The samples were then measured on the DPSC system, using D_{65} and the 1964 CIE 10° supplementary observer. The cceptability data were stored and transmitted to the data bank at NRDEC. The samples were then mailed to NRDEC for testing. Approximately 1000 samples were tested in all.

The instrumental evaluations were excellent with the pass/fail judgements in agreement 90 percent of the time. The visual/instrumental agreement was good. Approximately 80 percent of the time the pass/fail decision was in agreement. The nature of the visual and instrumental methods contribute to this degree of correlation. The visual process is subjective. Only one observer was used to evaluate the samples, whereas the acceptability tolerances are based on multiple decisions of a panel of observers. The shades evaluated are part of a complex four color pattern that may influence the visual decision, when the sample shade is judged within a field of four colors. Some of the split decision judgements were made on samples that were close to the border of acceptability. This is an area where the visual observer is expected to experience some difficulty in making a decision. Finally, the visual tolerance samples and the instrumental tolerances are not exactly equivalent, and this may lead to some inconsistencies.

These initial test studies found the color measurement system to be performing well, and so the final step in Phase III could proceed. Three additional satellite instruments to be used in the Phase IV

industry trial were purchased and installed at NRDEC in 1985. The units are RT-11 single user systems, equivalent to the DPSC unit. Verification studies were needed to ensure that the instruments purchased initially were still operating properly, and that the three new instruments correlated on an inter- and intra-instrument basis. The correlation studies performed earlier in Phase III were repeated, with a few minor modifications.

The same samples included in the previous study were measured, as well as an additional shade set of the porcelain-enamel tiles and a set of four BCRA tiles. A gelcoat polyester color difference pair similar to the pair previously used was substituted. The total number of samples measured was 44.

Once again short-term studies were conducted over 10 days and long-term studies conducted over 10 weeks. The gelcoat pair were measured 10 times over 6 weeks. The same testing parameters were used. All measurements were made under simulated daylight illumination. The colorimetric data were calculated for D_{65} and the 1964 CIE 10° standard supplementary observer. Once the testing had been completed at NRDEC, the samples were shipped to DPSC for measurement. The measurements were repeated at DPSC and the data transmitted to the NRDEC data bank for correlation analyses.

The data collected was then assessed to determine the accuracy, reliability, and repeatability of the instruments on an inter- and intra-instrument basis for the two time periods studied. The average MCDM's and color difference in CIELAB* units (ΔE*) between the short- and long-term values for each instrument were used to determine the degree of repeatability for the individual instruments. The accuracy, reliability, and repeatability among the five instruments were determined by calculating the ΔE* for sample pairs of textiles and porcelain-enamel tiles.

In general, the results of the analysis indicate that the instruments perform well individually, and as a system. The purpose of these studies is not only to determine if the instruments agree, but to identify any problem areas requiring adjustments in order to maintain the necessary degree of accuracy. The findings of these tests indicated there are a few areas that require attention. These will be discussed in the results. Two of the satellites required adjustments to the lamp voltage during the studies when erratic readings were observed.

The average MCDM's for four of the five instruments (NRDEC, A, C and D) were 0.09 or less for both the short- and long-term studies. (See Table 1.) The range for the individual sample measurements on these four instruments was 0.11 for the short-term, and 0.16 for the long-term. The fifth instrument (B) had average MCDM's of 0.12 or less

TABLE 1. Comparison of Average MCDM[a] Values for Short- and Long-Term.

	Porcelain (enamel) Tiles			BCRA Tiles			Green Textiles			Tan Textiles		
	SHORT	LONG	$\Delta E*$ [b]	SHORT	LONG	$\Delta E*$	SHORT	LONG	$\Delta E*$	SHORT	LONG	$\Delta E*$
NRDEC	0.04	0.04	0.06	0.05	0.05	0.04	0.06	0.06	0.08	0.03	0.04	0.04
	±0.01	±0.02	±0.04	±0.02	±0.02	±0.03	±0.01	±0.01	±0.03	±0.03	±0.01	±0.02
A	0.05	0.04	0.07	0.06	0.08	0.04	0.06	0.05	0.06	0.05	0.06	0.05
	±0.01	±0.01	±0.03	±0.01	±0.06	±0.03	±0.01	±0.01	±0.03	±0.03	±0.01	±0.02
B	0.06	0.10	0.05	0.08	0.15	0.09	0.12	0.17	0.12	0.04	0.06	0.05
	±0.02	±0.03	±0.03	±0.05	±0.09	±0.07	±0.01	±0.02	±0.06	±0.02	±0.02	±0.02
C	0.04	0.05	0.07	0.06	0.09	0.07	0.07	0.06	0.06	0.05	0.06	0.05
	±0.02	±0.02	±0.03	±0.01	±0.05	±0.02	±0.02	±0.00	±0.03	±0.01	±0.01	±0.01
D	0.03	0.04	0.05	0.04	0.04	0.05	0.06	0.06	0.06	0.03	0.04	0.04
	±0.01	±0.02	±0.03	±0.02	±0.01	±0.01	±0.01	±0.01	±0.04	±0.01	±0.01	±0.02

[a]Mean color difference (in CIELAB* units) from a mean.

[b]Color difference in CIELAB* units.

for the short-term data and 0.17 or less for the long-term study. The short-term MCDM range for individual samples was 0.13. The long-term MCDM range was 0.23.

Another indication of the repeatability of the individual instruments is the value of the CIELAB* color difference, ΔE^*, between the values for the short- and long-term measurements. The average ΔE^* values for all groups of samples were less than 0.12. Most of the ΔE^* values ranged between 0.04 and 0.08 CIELAB* units. Instrument B had the largest average ΔE^*, 0.12, which was the average for the green textile samples. Overall, the individual instruments read the samples consistently. Instrument B does demonstrate some instability as exhibited by values of ΔE^* being slightly higher than 0.10 CIELAB* units.

The measurement of the BCRA tiles was included in this study as a test of the accuracy of the wavelength scale. The four tiles of the set were grey, deep pink, bright yellow, and cyan, representing different areas of color space. The intensity of three of the colors produces definitive spectral reflectance curves with sharp rises in reflectance within a short wavelength range. All of the instruments had average MCDM's of 0.08 or less for the group of BCRA tiles in the short-term study. The range of MCDM averages for the individual tiles was 0.12. For 50 percent of the measurements, long-term data indicated a drift from the short-term results, especially for the bright yellow and deep pink tiles. The average long-term MCDM's for the three instruments (NRDEC, A and D) were below 0.09. For instruments B and C the average MCDM's were 0.27 and 0.16, respectively. The ΔE^* values between the short- and long-term data were 0.09 or less, with the individual sample range falling between 0.01 and 0.16 CIELAB* units. While these values are not indicative of serious problems, they are beyond the 0.10 CIELAB* value that is considered the optimum. Provisions will be made to identify the cause of any erratic readings and make adjustments.

The intra-instrument analysis showed that as a system, the master and satellite units perform very well. To demonstrate this, the color difference in CIELAB* units was calculated for a matched color difference pair (tan gelcoat pair), paired textile swatches and porcelain-enamel tiles. The tiles were paired as standard sample against full tolerance sample and standard sample against thin tolerance sample. The color differences of the 23 pairs ranged from approximately 0.25 to 1.95 CIELAB* units.

The results were quite good. The tan pair data illustrates the precision of the instruments in measuring color differences. (See Table 2.) All five instruments read the color difference between 1.91 and 1.92, when measured 10 times over a 6-week period. More extensive studies measured the textile and porcelain-enamel tile pairs for the

TABLE 2.   CIELAB Color Differences for Tan Color Difference Pair.

Observance	NRDEC	A	B	C	D
1	1.91	1.92	1.93	1.89	1.94
2	1.92	1.92	1.91	1.91	1.89
3	1.91	1.93	1.88	1.90	1.90
4	1.92	1.94	1.91	1.91	1.90
5	1.92	1.91	1.91	1.90	1.90
6	1.96	1.92	1.91	1.89	1.92
7	1.94	1.92	1.94	1.92	1.90
8	1.90	1.92	1.91	1.91	1.90
9	1.92	1.91	1.92	1.91	1.91
10	1.94	1.90	1.93	1.92	1.91
Average	1.92	1.92	1.92	1.91	1.91
	±0.02	±0.01	±0.02	±0.01	±0.01

short- and long-term intervals. The data indicates that the instruments as a group consistently read the color differences for the pairs at close intervals in color space over both time periods. Instrument B read the color differences the same as the other four instruments for most of the samples. Data for two of the green textile pairs had to be disregarded. Clearly, an error was made in the measurement of the samples. The differences between instrument B and the rest of the instruments are far too large to attribute to instrumental error.

PHASE IV. INDUSTRY TRIAL

The fourth and final phase in developing the color measurement system involves placing the instruments at contractors' sites for a pre-operational trial of the system. These studies will be similar to the earlier trial study, but will be more extensive, lasting 6 months.

DPSC designated industry sites which would be likely candidates to participate in the industry trial. The instruments placed in contractors' facilities will be used by the Government Quality Assurance Representatives (QAR) to measure procurement samples for acceptability determinations. The testing done in this phase will be only for research purposes; procurement contracts will not be affected by the instrumental pass/fail decisions. The three industry sites selected were Bradford Dyeing Associates, Bradford, RI; Duro Textile Printers, Fall River, MA; and J.P. Stevens and Co., Inc., Wallace, SC..

The instruments were installed at each site in March 1986. The QAR's were trained in the system's operation, measurement and basic maintenance procedures. Minor difficulties have been experienced in reinstalling one of the systems. A disk drive was damaged in transition. Once the equipment has been repaired Phase IV will proceed at this site. The QAR's at two sites have begun to measure production samples of Woodland camouflage printed, 100 percent cotton poplin ripstop, and Quarpel-treated Nyco Twill battledress uniform fabrics. Measurement data is being stored and will be transmitted to a data bank at NRDEC for analysis.

After the samples are measured at the contractor's site, they will be forwarded to DPSC for visual evaluation of the shade and instrumental acceptability determinations on the Light Green 354, Dark Green 355, and Brown 356 shades of the Woodland camouflage pattern. The DPSC data will also be transmitted to NRDEC and the samples will be forwarded for measurement. Once the visual data and the instrumental data from DPSC, NRDEC, and the three satellite units have been compiled, they will be analyzed to determine the degree of correlation between the visual and instrumental acceptability decisions, and the inter-instrumental acceptability decisions.

Phase IV will come to a close in early 1987. Pending the outcome of the pre-operational trial, the system will be ready to initiate the instrumental measurement for shade acceptability into the quality assurance program. The immediate concerns for ensuring a smooth transition from a research and development effort to routine quality assurance include issues, such as further expansion of the system and the method of inspection. Once instrumental measurement becomes part of the quality assurance program, DPSC will be the center for analysis of data and, therefore, will require an upgrade of the DPSC unit. At the present time, that instrument has the capability to transmit but not to receive data. Also, it has not been determined whether the samples will be evaluated on a 100 percent instrumental or combination visual/instrumental basis.

The development of the objective color measurement system has been a positive step towards improving the quality of textiles used in procuring end items for military use, as well as a tool to save valuable time and financial resources. Technology in the optical and computer fields continues to change and improve at an incredible rate. This will only result in future improvements to the objective method of evaluating shade acceptability, as well as an increase in savings.

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TITLE: Soldier Oriented Research in Combat Ration Development: The
         Effects of Prolonged Feeding the Meal, Ready-To-Eat Operational
         Ration

         EDWARD HIRSCH, DR.,* RICHARD D. POPPER, DR., BARBARA JEZIOR, MS.,
         AND HERBERT L. MEISELMAN, DR.

ABSTRACT:

Current military scenarios call for troops to subsist on operational
rations as their sole source of food for extended periods of time. Two
studies were conducted in which the effects of prolonged subsistence on the
current operational ration, the Meal, Ready-To-Eat (MRE), were evaluated.

The first study was conducted in a laboratory setting with student
volunteers at the Massachusetts Institute of Technology. One group was
fed the MRE as their only food for 45 days and a control group was pro-
vided with 3,600 calories of freshly prepared food served in three meals.
In the second study, two combat support companies from the 2nd Brigade of the
25th Infantry Division were fed either the MRE or an A ration breakfast,
and MRE lunch, and an A ration dinner. The field study lasted 34 days.

The student volunteers found the MRE to be highly acceptable, con-
sumed 3,134 calories per day, and maintained their body weight over the 45-
day study. Measures of exercise endurance, mood, cognitive performance,
and psychomotor performance failed to reveal any differences between the
two dietary groups of the first study.

In the field test, the MRE food items were highly rated by the troops,
but caloric intake only averaged 2,253 calories per day compared to 2,956
for the control group. The major consequences of the low food intakes
were weight loss and some vitamin and mineral intakes that were below
recommended levels. The other measures did not reveal any major differences
between the two companies.

The relatively low food intake of the MRE group in the field test is
discussed in relation to several factors including: small portion sizes
of entree items, absence of typical breakfast foods, limited variety of
beverages, and environmental constraints on food intake.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Chief, Human Engineering Branch, Behavioral
Sciences Division, Science & Advanced Technology Directorate
    PAST EXPERIENCE: Research Psychologist, NRDEC; Associate Professor
of Psychology, Mount Holyoke College
    DEGREES HELD: B.A. Psychology, Brooklyn College; M.A. Psychology,
Temple University; Ph.D. Physiological Psychology, Rutgers University.

SOLDIER ORIENTED RESEARCH IN COMBAT RATION DEVELOPMENT: THE
EFFECTS OF PROLONGED FEEDING THE MEAL, READY-TO-EAT OPERATIONAL RATION

EDWARD HIRSCH, DR., RICHARD D. POPPER, DR.,
BARBARA JEZIOR, MS., & HERBERT L. MEISELMAN, DR.

INTRODUCTION

Current military scenarios call for troops to subsist on operational
rations for extended periods of time. It is currently not known whether
this can be accomplished without compromising troop effectiveness.
Current policy on duration of use of combat rations is contained in TB
MED 141 (1971), IB 8-250 (1974), and TM 8-501 (1961), which advise that the
Meal Combat Individual (MCI) ration should not be used as the sole source
of food for more than 10 consecutive days. Considerable savings in cost
and personnel can be achieved if this policy was modified to allow feeding
of only operational rations for longer periods of time. The present
experiments were conducted to evaluate the effects of prolonged subsistence
on the Meal, Ready-To-Eat (MRE) operational ration.

The MRE ration is formulated to meet the nutritional requirements of
young adult males. It is composed of 30 food items, 2 beverages, a
cream substitute, assorted candies, condiments, and a gravy base. These
components are divided into 12 menus with repetition of some items other
than entrees across the 12 menus. The components are contained in a
flexible retort pouch and can be eaten hot or cold. Seven of the food
items are meant to be rehydrated, but they can be eaten without adding
water. Three MRE pouches provide 3,600 calories and meet the known
requirements for all nutrients. There are reports indicating that the
MRE ration is acceptable to troops over a 7-day period (1) and that it is
preferred to the MCI (2).

The limited number of foods in the 12 meals, in conjunction with the fact that on the average, each meal will be repeated every 4 days, raises the possibility that food monotony will develop when this ration is fed as the sole food source over an extended period of time. Some investigators have found that both food intake and food acceptability decline when limited menus are offered (3, 4, 5, 6). In addition to food monotony, it is possible that some components of the MRE are not sufficiently palatable to the soldier and will not be consumed. The rejection of some components of the ration may lead to inadequate energy intake, consumption of a nutritionally imbalanced diet, or inadequate vitamin and mineral intakes due to the patterns of diet fortification and food selection.

Given the nutritional quality of the MRE and the possibility of food monotony developing, the acceptability and the consumption of the MRE were regarded as the primary measures in these experiments. Accordingly, the most frequent and intensive measurements focused on these variables. In addition, a series of measures were taken to assess any possible harmful consequences of consuming this diet, or of not eating sufficient amounts of it, or of choosing foods from the ration in such a manner that inadequate amounts of specific vitamins or minerals were consumed. These secondary measures included: mood, morale, cognitive performance, psychomotor performance, physical symptoms, body weight, body fat, and nutritional status as indexed by the circulating levels of selected blood constituents. In addition, water intake and body fluid status were measured to provide a basis for evaluating whether thirst and/or dehydration contributed to or caused inadequate food intake if this outcome developed.

Although this research effort is ultimately concerned with the effects of extended feeding on the MRE by the soldier engaged in combat, we thought it prudent to conduct our first study under controlled laboratory conditions. This ration had never been tested for more than 10 days as a sole food source, and if problems developed, they are more easily detected and remedied in the laboratory. In addition, the methods employed to evaluate performance were new and might require revision prior to a large-scale field test.

LABORATORY STUDY

Method

The laboratory study took place at the Massachusetts Institute of Technology in collaboration with Dr. Nevin Scrimshaw's group in the

Department of Nutrition and Food Sciences. The experimental group of
16 student volunteers was fed the MRE as their sole source of food
for 45 days. The control group was fed three meals of freshly prepared
food each day that provided 3,600 calories. These meals were provided in
a 12-day menu cycle that was repeated over the course of the study. The
students in both groups were free to go about their usual schedules with
the provision that they eat breakfast, lunch, and dinner between the
following hours: breakfast 0700-0900, lunch 1130-1330 and dinner 1700-1900
in a common dining room. The dining room contained a series of small tables
and chairs and could accommodate up to 40 people. Plates, glasses, and
silverware were on the table prior to each meal. A microwave oven was
available for heating components of the MRE and hot and cold water were
available for preparing beverages or rehydrating components of the MRE.
The control group was served their meal on a plate whose components were
preweighed.

Daily measures of food intake, fluid intake, and body weight were
taken on each subject. Food intake was measured directly from plate
waste. In addition to these measures food acceptability, mood, physical
symptoms, cognitive and psychomotor performance, physical work capacity,
body fluid status, and nutritional status were also measured on a regular
periodic basis for all subjects.

Results

Table 1. shows the changes in body weight in the two groups of
volunteers who participated in the laboratory study. It is apparent that

TABLE 1. Body Weight Changes in Student Volunteers Fed the MRE or
Freshly Prepared Food for 45 Days.

	Body Weight (LB)					
	Baseline		Day 22		Day 44	
	X	SD	X	SD	X	SD
MRE	157.6	18.2	156.7	17.7	156.1	17.2
Control	160.3	19.8	161.6	19.2	161.9	19.3

body weight changes were minimal in both groups. The control group gained
1.6 pounds and the MRE group lost 1.5 pounds during this 45-day study.
The group differences in body weight at the end of the study were not
statistically reliable, but the pattern of change over time was
significantly different as revealed by the interaction term in the
repeated measures analysis of variance.

Table 2. shows that the group fed freshly prepared food consumed about 300 calories more per day than the group fed only the MRE. This

TABLE 2. Daily Caloric Intake of Student Volunteers Fed the MRE Ration or Freshly Prepared Food for 45 Days.

Daily Caloric Intake (KCAL)

	X	SD
MRE	3143	498
Control	3465	462

difference in intake was statistically reliable ($p < 0.01$), but the small changes in body weight shown in Table 1 and measures of mental performance, physical work capacity, and nutritional status (7) indicate that these small differences in intake were not functionally significant. From the perspective of a monotony-variety dimension, there was, however, a decline in food intake of about 200 calories a day from the first week of this study to the last week in the MRE group. This observation suggests that food repetition was a factor contributing to the lower level of food intake in the MRE group.

To examine the issue of food monotony more closely, the acceptability ratings of each of the foods in the MRE were analyzed over the 7 weeks of the study. Only 1 food out of the 32 consumed frequently enough to be included in this type of analysis showed a significant decline in acceptability. It appears that either monotony did not underlie this decline in consumption over time, or that food acceptability is not a good predictor of consumption, particularly when the acceptability measures are only based on the foods that participants chose to eat. We think the latter is the case, but even after taking that factor into account the data still illustrates that people were not showing lowered acceptability of the MRE components they were choosing to eat. The absence of lowered acceptability in conjunction with the very small decline in food consumption over the 45 days of this test clearly suggests that food monotony is not a major factor in limiting consumption when the MRE is fed as the sole source of food under laboratory conditions.

FIELD STUDY

A major consideration in designing this experiment was that the MRE is designed to be used by troops engaged in combat. For this reason the test modelled as closely as possible the manner in which troops actually eat in the field. This consideration led us to allow the troops to trade items within the MRE menu, and it also led to the decision to provide the troops with hot sauce for their rations. Hot sauce is widely used by troops in the field, and by providing it to them we hoped to prevent any other foods from being smuggled into the field. The actual availability of outside sources of food in the field was strictly controlled. The design of the field test was coordinated closely with the command group of the participating troops so as not to interfere with the actual training mission of the field exercise, and the testing schedule was set up around the training requirement.

Method

Design. Two combat support companies from the 2nd Brigade of the 25th Infantry Division participated in the test. The experimental company subsisted for 34 days on the MRE as their sole source of food. The control company ate both the MRE and freshly prepared A ration meals, specifically a hot A ration breakfast, an MRE lunch, and a hot A ration dinner. The MRE company was issued three MRE meals at the beginning of each day and was free to consume the components during the course of the day as time permitted. The control company was fed its hot breakfast and dinner meals at scheduled times. The actual times for the control company varied from day to day. On some days the troops were fed the hot meals in the area of a mess tent, whereas on other days the hot meal was brought in insulated food containers to the location in which the troops were training. On the days that the control company was training in the general vicinity of the mess tent, beverages including coffee, fruit juice and milk were available at nonmeal times. The control company was given its MRE meal after breakfast and was free to consume it during the remainder of the day. In all other ways the two companies were equivalent and were tested in the same manner and at the same frequency.

Test Subjects. All troops from both companies participated in the test, including the NCO's and the officers. Within each company a subsample

of 30 men volunteered to undergo more intensive testing (urine and blood analyses, food and water intake, cognitive and psychomotor performance testing). The daily level of physical activity of a typical soldier in a combat support company is best characterized as moderate. The majority of troops in a combat support company spend their day in a vehicle and typically do not engage in extended running or movement on foot.

Test Site. Baseline testing took place at Schofield Barracks, Oahu, where the 25th Infantry Division is stationed. The field test took place at the Pohakuloa Training Area (PTA), Hawaii during August/September 1983. The elevation at PTA is approximately 6,000 feet. The terrain is rugged, dry and dusty except for heavy morning mist at elevations higher than base camp. The climate is warm (70-85°F) during the day and cool at night (40-60°F). The site is remote from towns, thereby minimizing the availability of outside sources of food. All subjects remained in the field exercise area except for the three mornings when the volunteers in each company came to the base camp. On these mornings physiological and psychological data were collected.

Procedure. Ten days prior to the start of the field test the following data were gathered from all men in both companies: (1) food preferences (9-point hedonic scale); (2) U.S. Surgeon General's Environmental Symptoms Questionnaire of 67 items; (3) Profile of Mood States (POMS); (4) Leadership Evaluation and Analysis Program Interaction Inventory (Adjunct Numbers 1, 2); and (5) body weight. These measures, with the exception of body weight, were repeated three times during the field test at approximately equal intervals (T_1 = days 11/12, T_2 = days 23/24 and T_3 = days 33/34) with the two companies tested on successive days. In addition, on these same days, the volunteers within each company underwent additional testing and on these individuals the following measures were taken: (6) body weight; (7) skinfold thickness at several points; (8) nutritional status as indexed by blood levels of Vitamin C, retinol, pyridoxal phosphate, folate, total protein, and plasma albumin; (9) body fluid status (urine volume, urine osmolality, hematocrit, and hemoglobin); (10) cognitive tests (Sternberg Memory Scanning Task, Baddeley Grammatical Reasoning, Wechsler Digit Span, Digit Symbol Substitution Task, Simple Mental Addition, Mental Addition with Coding); and (11) psychomotor tests (Ball-pipe Test, Atari video game, and Spoke Test). Height was also measured in the volunteers prior to the study so that percent body fat could be computed from the height, weight, and skinfold thickness measures using the standard AMEDD procedure.

Food intake, water intake, and food acceptability were measured in the 30 volunteers in each company during four test periods. The four test periods consisted of day 8-9-10 (Period A), 15-16-17 (Period B), 21-22-23 (Period C) and 31-32 (Period D). Food acceptability data were also collected from another 15-30 men in each company at each meal on the days that consumption and acceptability data were collected from the volunteers. Table 3. shows the test schedule for both the entire group and for the 30 volunteers who were studied more intensively.

TABLE 3. Testing Schedule for Prolonged Feeding of Meal, Ready-To-Eat (MRE) Rations.

Measures	Frequency	When	Sample
Food-Related Measures			
a. Food Preference	4X	Baseline, T_1, T_2, T_3	100%
b. Food Acceptability	11 days	Periods A,B,C,D	100%
c. Food and Water Consumption	11 days	Periods A,B,C,D	
Nutritional Status			
a. Body Weight	4X	Baseline, T_1, T_2, T_3	Volunteers
	2X	Baseline, T_3	Non-Volunteers
b. Anthropometric (Height, Skinfold Thickness)	2X	Baseline, T_3	Volunteers
c. Body Fluid Status	4X	Baseline, T_1, T_2, T_3	Volunteers
d. Blood Constituents	4X	Baseline, T_1, T_2, T_3	Volunteers
Clinical Symptoms			
a. Symptoms Checklist	4X	Baseline, T_1, T_2, T_3	100%
b. Weekly Availability of Physician			
Psychological Tests			
a. Cognitive & Psycho-motor Performance	4X	Baseline, T_1, T_2, T_3	Volunteers
b. Mood	4X	Baseline, T_1, T_2, T_3	100%
c. Morale & Perceptions of Leadership	4X	Baseline, T_1, T_2, T_3	100%

RESULTS

The MRE items that were consumed were very well received by the troops in both companies with average acceptability scores of 7.05 for the MRE group and 6.48 for the control group on a 9-point hedonic scale. The MRE group also rated the MRE higher than the control group rated comparable hot A ration meals. There was no indication of a decline in the acceptability of the MRE over the 34 days of the field test. The MRE was rated higher for lunch and dinner than it was for breakfast.

Although these high ratings indicate that the items consumed by an individual were highly acceptable to him, an examination of the consumption data for each of the food classes reveals that, of the items distributed, the following percentages were actually eaten by the troops: entrees - 68%, starch items - 60%, spreads - 47%, fruits - 51%, desserts - 50%, beverages - 27% and condiments and candies - 26%.

The final questionnaire about the MRE was consistent with the acceptability data. It revealed that the troops were generally satisfied with the ration's taste, appearance, variety, and ease of preparation. Their ratings of the amount of food it provided were in the neutral range and more detailed questions indicated that they felt that the portion sizes of some components were too small. Responses to the questionnaire also revealed four potential areas in which the ration could be improved: (1) the troops indicated that the entree and the dehydrated fruit portion sizes were too small; (2) the MRE group indicated that they liked the ration better for lunch and dinner than for breakfast; (3) the troops overwhelmingly indicated that they wanted more variety in the beverages that were included in the ration, and (4) the MRE group indicated that they did not consume the ration at designated meal times.

Despite its high acceptability and the troops' satisfaction with the ration, the MRE was not consumed in sufficient quantity. Table 4. shows daily caloric intake, which averaged 2,253 calories for the MRE group and 2,956 for the control group. Both values are considerably below the

TABLE 4. Daily Caloric Intake in Troops Fed Either the MRE or an A Ration Breakfast, an MRE Lunch, and an A Ration Dinner.

Daily Caloric Intake (KCAL)

	X	SD
MRE	2253	616
Control	2956	497

the recommended level of 3,600 calories for operational rations. The MRE group showed a decline in daily caloric intake over the course of the field test, whereas daily caloric intake tended to remain stable in the control group.

The low food intake did not appear to be due to dissatisfaction with the sensory properties of the ration (taste, smell, appearance) or to thirst-induced anorexia. Water intake of the MRE group was somewhat lower than that of the control group (2,678 mL/day vs. 3,128 mL/day), but was not low enough to produce increased reports of thirst or significant changes in the monitored indices of body fluid status (urine osmolality, hemotocrit and hemoglobin). Rather, the low food intake in the MRE group appears to result from several factors including: loss of appetite, absence of scheduled meals, small portion size of highly rated and consumed entree items, lack of breakfast items in the ration, and the limited variety of beverages in the ration.

The major consequences of the low food intakes were body weight loss (Figure 1.) and some vitamin and mineral intakes that were below
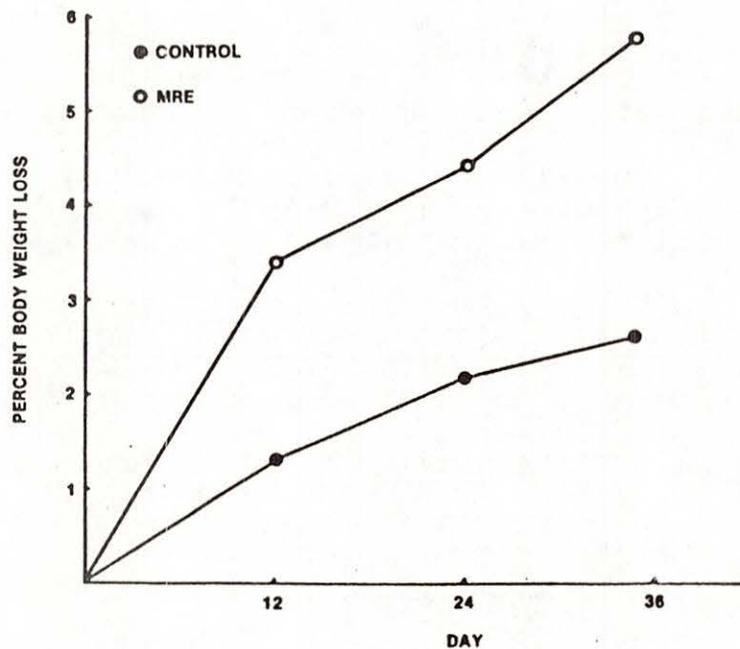
Figure 1. Percent body weight loss in MRE and control group.

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recommended levels. The majority of troops in both companies lost weight during the 34-day field test (69 of 71 in the MRE company and 57 of 68 in the control company), but the men in the MRE company lost significantly more weight than those in the control company (8.2 pounds vs. 4.6 pounds). Figures 2. and 3. show that both groups had intakes of niacin and magnesium that were below the recommended levels, and the MRE group had intakes of riboflavin, calcium, and iron that were below recommended levels.
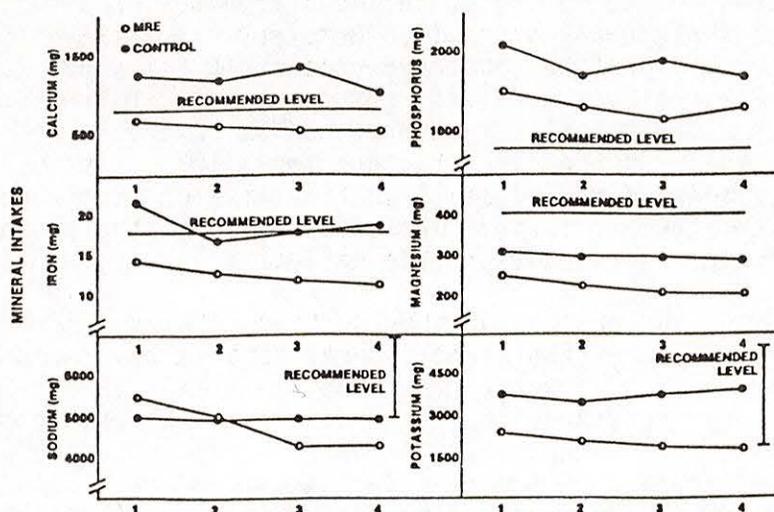
Figure 2.   Mean daily mineral intakes for MRE group and control group.
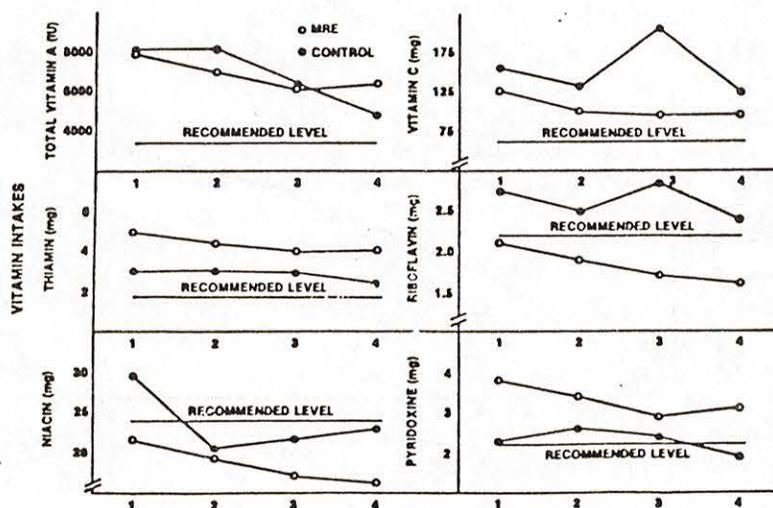
Figure 3.   Mean daily vitamin intakes for MRE group and control group.

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The other measures that were taken to evaluate any effects of prolonged subsistence on the MRE or any possible effects of nutritional deficiencies that developed did not reveal any major differences between the two companies. The questionnaire data on the incidence of physical symptoms showed that the two groups showed similar profiles of complaints and discomforts during the field test; but, of the 67 possible symptoms on the questionnaire, the 2 symptoms reported at the highest frequency were "I feel good" and "I feel alert." There were, however, two important food-related symptoms that were reported at a higher frequency by the MRE group. The MRE company reported that they had lost their appetite and that they experienced gas pressure more frequently than the control group. The MRE company did not differ from the control company on any of the six mood scales and both companies showed an improvement, which might be a test artifact. In a similar manner, the two companies did not differ from one another on measures of morale and perceptions of leadership, which were positive and stable over the four data collection periods.

The performance of the troops in the two companies did not differ on a test battery of cognitive and psychomotor tasks. The test battery measured hand-eye coordination, speed of gross arm movements, accuracy and speed of aiming at stationary and moving targets, reaction time, memory scanning rate, short term memory capacity, speed and accuracy of coding digits into symbols, grammatical reasoning, and the speed and accuracy of arithmetic problem solving. Within the MRE company, the performance of the individuals who lost the most weight (greater than 7% body weight loss) did not differ from the performance of those who lost the least amount of weight during the field test.

Despite the low levels of food intake, nutritional status as indexed by measures of hemoglobin, hematocrit, plasma albumin, plasma total protein, serum Vitamin C, serum folate, plasma pyridoxal phosphate, serum retinol, and serum zinc did not reveal significant differences between the two companies or values that were outside the normal range. Plasma albumin and total protein were consistent with adequate protein status. Values for serum Vitamin C were normal throughout the field trial. Values for retinol were at the upper range of normal levels. Serum folate values fell during the field test in both companies, but not below normal limits. Plasma pyridoxal phosphate concentrations remained unchanged during the field test in the control company, but rose above normal levels in the MRE company. Serum zinc remained within normal limits in both companies. Thus, the data on selected blood constituents indicate nutritional status was not compromised by subsistence on the MRE for 34 days.

CONCLUSION

From the perspective of the logistician, the major finding of these two studies is that the MRE can be fed as the sole source of food for extended periods of time without compromising health or performance. This finding is tempered by the fact that in the field study troops fed solely the MRE lost more weight and showed some vitamin and mineral intakes below recommended levels relative to the control group fed two hot meals. It is possible that more refined measures, or a lengthier test, would have revealed decrements in troop effectiveness. Nonetheless, these data call for a careful reexamination of policy in regard to the length of time operational rations can be fed as the sole source of subsistence.

The relatively low levels of food intake in the field study is less than optimal and raises the question of how the ration or the manner in which it is fed can be modified to improve consumption. Several observations address this issue.

First, one of the most striking aspects of these two studies is the very different levels of food intake that occurred when the MRE was fed as the sole source of food in two very different environments. In a laboratory setting energy intake was almost 1,000 calories higher per day than it was in the field.

Little systematic attention has been directed toward evaluating the influence of the eating environment on food acceptance and consumption in humans. In fact, most of the work on this dimension of intake stemmed from Schachter's (1971) provocative hypothesis about the differential role of internal and external stimuli on food intake in obese and normal weight humans. Although there are some inconsistencies in this work, generally the feeding behavior of both overweight and normal weight individuals are affected by environmental cues (8, 9), with the obese subjects intake influenced more strongly (10, 11). From the perspective of trying to assess the influence of a field environment on food intake, one general theme has clearly emerged. Anything that makes food less accessible (12), more costly (13), more difficult to obtain (14), or less salient (15, 16) leads to a reduction in food intake. All these factors are operative in a field environment and may have any important bearing on how much food is consumed by an individual fed operational rations. They are not, however, aspects of ration development that have received serious attention.

In our laboratory study, meals were only available during specified 2-hour time blocks. Hot and cold water were provided for preparing beverages and rehydration ration components. Meals were eaten in a pleasant dining room, off plates with cutlery. A microwave oven was available for heating ration components. The participants were not dirty, nor was the environment. In sum, it was easy and pleasant to consume the ration in this environment. The convenience and pleasantness of the laboratory environment stands in sharp contrast to the field setting. We have not yet begun to isolate the variables that encourage higher consumption in the laboratory, but the obvious differences in these two eating environments suggest that modifications to the way in which the operational ration is fed may contribute more to improving intake under field conditions that changes in the specific food items or their sensory attributes.

Additional insight into the factors that contribute to the relatively low levels of MRE consumption in the field was gained by the troops' responses to a final questionnaire and observations of their eating patterns during this study. The troops indicated that the portion sizes of the highly rated and highly consumed entrees were too small. The ration was also more acceptable to troops for lunch and dinner than it was for breakfast, and on the final questionnaire they indicated that they wanted breakfast items. In addition, the troops overwhelmingly indicated that they wanted more variety in the beverages that were included in the ration. We are currently testing a modified version of the MRE, which incorporates these three changes, to determine if ration acceptance and consumption are improved.

We also observed that most of the MRE company did not eat in a pattern that could be described as "three meals a day." Rather, they tended to snack or eat light meals during the day and only took the trouble to prepare a full meal late in the afternoon or evening. This pattern is in sharp contrast to both the laboratory study, where three defined meals a day were available, and to the control group in the field study, where a hot prepared breakfast and dinner meals were provided. The absence of scheduled meals may also contribute to the relatively low consumption of this ration under field conditions. As yet, we have not been successful in convincing field commanders to allow us to test the effects of scheduled meals on ration consumption. Their very reluctance on this issue may be conveying the message that no matter how successful the ration developer is in producing an appetizing, nutritious product, the nature of the battle-field may constrain food intake and make weight loss an inevitable consequence of feeding operational rations for extended time periods. Alternatively, it is equally clear that whatever can be done to make feeding more convenient in a field environment is likely to improve consumption.

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TITLE: Safeguarding the Nutritonal Adequacy of Nutritional Sustainment Modules: Kinetics of Quality Loss in Compressed Model Systems Due to Maillard Reaction

K. ANANTH NARAYAN, DR.* AND RAY E. ANDREOTTI

ABSTRACT

The kinetics of degradation of the essential amino acid lysine have been determined in compressed lysine-glucose-cellulose models exposed to expected and accelerated storage test temperature extremes. The compressed models were stressed at 40, 50 and 60 C at a water activity of 0.23 for various periods. Six different parameters (color, fluorescence, reducing capacity, furosine, glucose and lysine) were employed to follow the course of the reaction. The t 1/2 values estimated from first order plots for lysine degradation in these models were 400, 13 and 1.6 hours at 40, 50 and 60 C, respectively. Arrhenius plots relating zero, first and second order reaction rate constants with the temperature have yielded high activation energies of 42, 45 and 39 kcal/mole, respectively, with corresponding Q_{10}s of 7.1, 8.4 and 6.4, which are indicative of large temperature dependence of lysine degradation in these compressed models. There was poor correlation of fluorescence and of color increase with lysine loss. Both furosine and reducing capacity correlated highly with lysine loss, even with pooled data at all three temperatures, and demonstrated the usefulness of these indicators at variable time-temperature storage conditions.

*BIOGRAPHY
PRESENT ASSIGNMENT: Research Biochemist, Biological Sciences Div., Science & Adv. Technology Directorate, Natick RD&E Center, Natick, MA.
PAST EXPERIENCE: Research Fellow, Dept. of Applied Science, Osmania University, Hyderabad, India, 1951-1954. Research Assoc., Department of Chemistry, Washington State College, Pullman, WA, 1957-1962. Assistant Professor, Department of Food Science, University of Illiniois, Urbana, IL, 1962-1971.
DEGREES HELD: Bachelor of Science, University of Madras, Madras, India, 1949. Master of Science, Osmania University, Hyderabad, India, 1951. Doctor of Philosophy, University of Illinois, Urbana, IL, 1957.

SAFEGUARDING THE NUTRITIONAL ADEQUACY OF NUTRITIONAL SUSTAINMENT
MODULES: KINETICS OF QUALITY LOSS IN COMPRESSED MODEL SYSTEMS
DUE TO MAILLARD REACTION

K. ANANTH NARAYAN AND RAY E. ANDREOTTI

INTRODUCTION

The lightweight Nutritional Sustainment Modules (NSMs) under develop-
ment for the Army 21 require unprecedented nutritional density, balance of
essential components and stability under extreme environments in order for
the soldier to maintain optimum physical and mental performance in combat.
Biochemical research at the U. S. Army Natick Research, Development &
Engineering Center is, therefore, concerned with means of protecting the
amino acid and protein qualities of candidate NSMs engineered by the tech-
nologies of Infusion, Compression and Extrusion (ICE).

While it is recognized that protein quality losses occur during both
processing and storage of foods through the well known Maillard reaction
(Fig. 1), the quantitative aspects of the protein-reducing sugar
interactive decline in lysine availability are subject to interpretation
depending upon the methodology employed (Mauron, 1981, Hurrell and
Carpenter, 1981). For example, the guanidation and the sodium borohydride
reduction methods underestimate the available lysine because the
guanidation reaction does not go to completion and because the reduction
method determines Schiff bases (Fig. 1) to be unavailable. The
trinitrobenzene sulfonic acid and the dye binding methods are reported to
overestimate the extent of lysine availability in stored or processed
foods (Mauron, 1981) due to the reactivity of the Amadori compound (Fig.
1) with these reagents. The fluorodinitrobenzene method is also
considered far from ideal because of the reactivity of Amadori product
with this reagent and also because of the effect of degradation products
of starch in many food systems upon dinitrophenyl lysine. A critical
discussion of many of the commonly used methods and their limitations has
also been made by Friedman (1982).

In combat rations under development, the use of ICE technologies to
produce highly engineered, calorically dense foods may result in nutri-
tional damage to protein quality due to protein-reducing sugar interac-
tions. The reducing sugar need not be part of the formulation but can
arise from breakdown of starch in the extruder, or from enzymatic or acid
catalyzed hydrolysis during prolonged storage at high ambient temperature
in the normal, slightly acidic environment of most foods. The Amadori
compound formed in the Maillard reaction is not hydrolyzed by proteolytic
enzymes and, therefore, lysine which has reacted with reducing sugar is
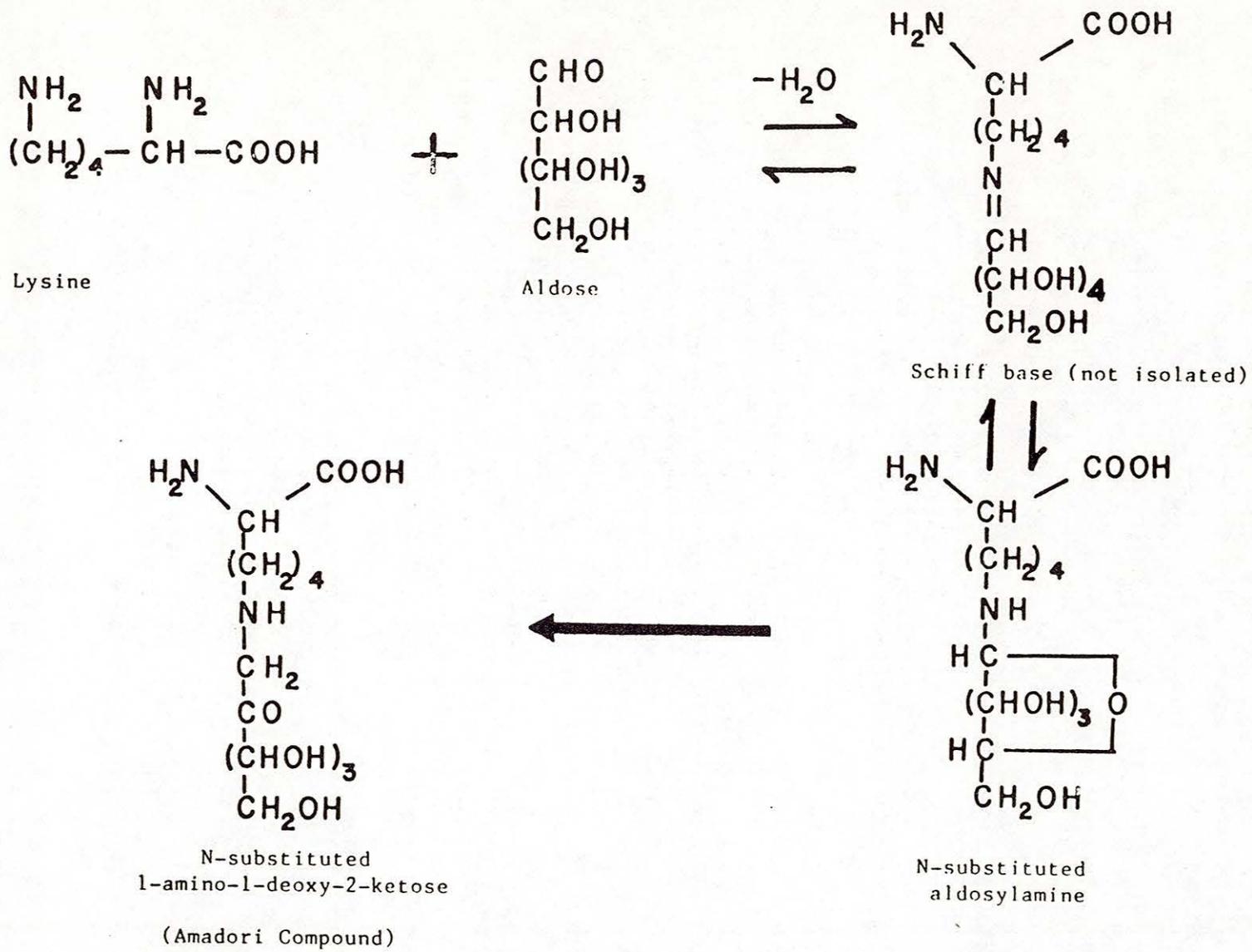
Figure 1.   Simplified scheme for the initial phase of the Maillard reaction.

biologically unavailable. Furthermore, adjacent amino acids around the blocked lysine in protein may not be digested by proteases, thereby compounding the problem of protein biavailability.

While there have been several studies on protein- and amino acid-reducing sugar models, as well as on actual food systems, most studies have been confined to one temperature or subjected to high processing temperatures (Eichner, 1975; Gumbmann, Friedman and Smith, 1983; Labuza, 1982; Labuza and Saltmarch, 1981; Wolf, Thompson and Reineccius, 1977; Warren and Labuza, 1977). Furthermore, in the previous studies determining the activation energy, lysine was often determined by indirect methods, such as by fluorodinitrobenzene or trinitrobenzene sulfonic acid or by bioassay methods. The food systems reported have been invariably tested at high water activities, high temperatures or over prolonged periods of storage (1 to 2 years), which may involve cyclical changes in temperature (Schnickels, Warmbier and Labuza, 1976; Carpenter, Morgan, Lea and Parr, 1962; Labuza, 1982). Correlations between indicators and directly determined lysine in a simple model system are not available. Additionally, the activation energies for lysine loss in foods as well as in model food systems reported in the literature vary over a wide range of 10-38 kcal/mole (Labuza and Saltmarch, 1981).

In the present investigation, compressed lysine-glucose-cellulose models were incubated at 40, 50 and 60 C at a low water activity of 0.23. The low water activity was selected to simulate the environment in compressed military foods. Unreacted lysine in the model was determined by separating it from Amadori products by ion-exchange column chromatography. Data were obtained on the rates of glucose and lysine degradation as well as on the development of reducing components, furosine (Fig. 2) released upon acid hydrolysis, fluorescence and color changes, in order to a) better understand the quantitative aspects of this complex reaction, b) assess the validity of some of the common protein quality indicators, and c) obtain data on activation energy and Q_{10} for lysine loss in a simple, compressed dry model system at low a_w and accelerated storage test temperature extremes.

<div align="center">MATERIALS AND METHODS</div>

Sample Preparation

Separate solutions of lysine, free base (Sigma Chemical Co, St. Louis, MO) and anhydrous glucose (certified reagent from Fisher Scientific Co.) in highly purified deionized Milli Q water (Millipore) were prepared. Ten mL of each solution containing 5.4 and 12.2 mmoles of lysine and glucose, respectively, were pipetted together into several freeze drying flasks and mixed well. A dispersion of 14.2 g of cellulose in Milli Q water was added to each flask, rapidly mixed and shell frozen immediately in a dry ice-ethanol bath. The flasks were freeze-dried in a manifold-type freeze
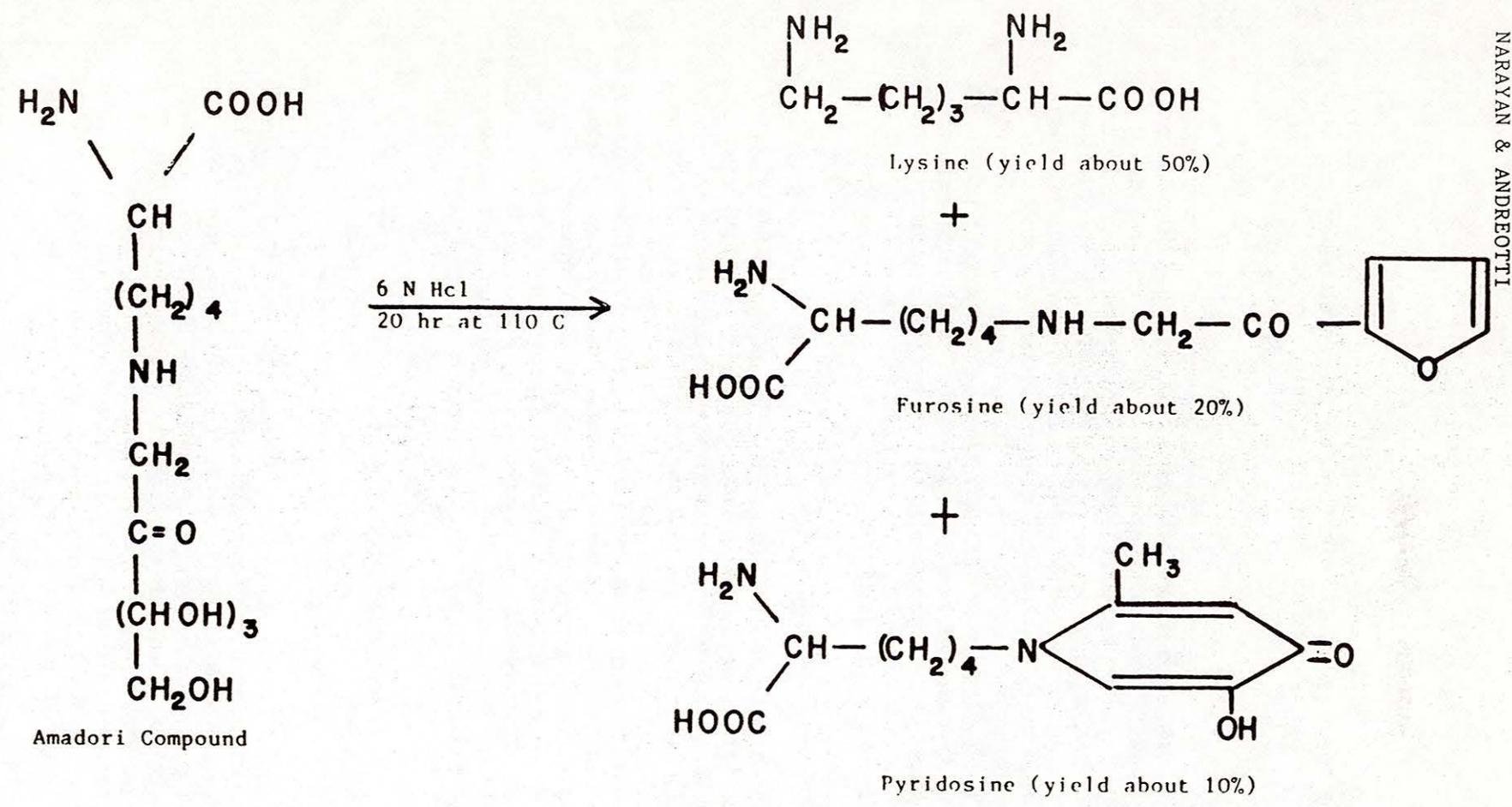
Figure 2. Formation of furosine from Amadori compound by acid hydrolysis.

dryer. The dried powders were quickly blended in a closed Mason jar in a laboratory blender. The powder was compressed into 2 g disks (4 mm thick, 25 mm diameter) using an Instron Universal Testing Instrument at 5500 psi.

Incubation

The compressed disks were incubated at 40, 50 and 60 C in separate 1/2-pint Mason jars over a saturated solution of potassium acetate to provide a water activity (a_w) of 0.23. In our experience, this is a more precise, simple and convenient procedure than the conventional dessicator method. There is far less head space, which promotes faster equilibration. Each sample can be withdrawn at a precise time without affecting the temperature or water activity of the other samples. At high temperature ranges (over 80 C), the Mason jar provides a tighter seal than the greased dessicator although there may be some possibility of decomposition of either the rubber gasket or the coating on the cap. Samples were withdrawn at periodic intervals, 0, 1, 3, 6, 12, 24, 48, 96, 144 hours, with the actual withdrawals varying with the temperature of incubation.

Analyses

Extraction. All disks were extracted with 20 mL of 0.05 M phosphate buffer, pH 5.5. The disks were ground to a fine powder before extraction. The extracts were filtered through a double layer of Whatman glass fiber paper and the volume made up to 25 mL with the same buffer.

Lysine. A Waters cation-exchange column (Amino acid analysis column) maintained at 62 C for HPLC (Millipore/Waters Associates, Milford, MA) and Waters HPLC equipment were employed to separate the lysine from three other components, which are presumably ε-fructose-lysine, α-fructose-lysine and α-ε-di-fructose-lysine components. The detection of lysine and other components was by post-column reaction with ninhydrin at 120 C. The mobile phase used was Pickering buffer, pH 7.4, 1 M Na^+ at a flow rate of 0.5 mL/min.

Glucose. A Waters carbohydrate column was used to assay for glucose in a Waters HPLC equipment. The mobile phase was 80% acetonitrile/20% water at a flow rate of 2 mL/min. The detection was by a refractive index detector.

Furosine. The sample extract was hydrolyzed with 6N HCl. Usually 0.5 mL of conc HCl (12N) was added to 0.5 mL of extract in teflon-lined screw tubes, flushed with nitrogen, capped and heated at 110 C for 20 hours. The hydrolysate was diluted with 4 mL of Milli Q water and filtered through glass wool packed into pasteur disposable pipets, rinsed thoroughly and the volume made to 10 mL. An aliquot (usually 4 mL) was evaporated in a flask to dryness at 40 C in a roto-evaporator. Milli Q water (4 mL) was added to the flask and evaporated again, and the process repeated two

more times to ensure complete removal of the acid. After the final evaporation, Milli Q water was added, mixed well and made to a suitable volume and filtered through a Milex filter type HV (Millipore/Waters Associates, Milford, MA). Samples were then analyzed in a Waters HPLC equipment for furosine with a Waters µ Bondapak C18 column by the method of Chiang (1983). The buffer used was 0.5% sodium acetate, (Fisher Scientific Co), pH 4.3 at a flow rate of 1 mL/min. The detection was by UV absorbance at 280 nm. The identity of the furosine was solely based upon the retention time of a furosine standard kindly provided by Dr. Finot.

Reducing capacity. A modification of the procedure of Crowe, Jenness and Coulter (1948) was employed to determine the reduction of potassium ferricyanide by the sample at pH 6.6 and the subsequent formation of blue ferri-ferrocyanide color by reaction with ferric chloride. The modification consisted essentially of scaling down the volumes of sample and reagents used in order to make the assay less cumbersome. In the case of protein-free models, there was also no need to go through the filtration step after addition of trichloroacetic acid.

Color. The absorbance at 410 nm was recorded in a Bausch and Lomb Model 710 Spectrophotometer (Bausch and Lomb, Boston, MA) with extract diluted appropriately to the optimum absorbance range.

Fluorescence. Serial dilutions of extracts were prepared and their fluorescence intensities were recorded in a Perkin Elmer-Hitachi Fluorescence Spectrophotometer (Perkin Elmer, Norwalk, CT) after manual optimization of excitation (λ_x) and emission (λ_m) wavelengths for each sample. (The λ_x and λ_m varied from 340–360 to 425–434, respectively. Serial dilution was necessary to ensure absence of quenching effects. Intensities recorded were based upon a quinine sulfate standard run along with each sample.

Normalization of values. Where applicable, values have been normalized to one mg of lysine per mL of extract at 0 hour. This permits comparison between experiments conducted at different temperatures, time periods or under slightly different conditions.

Kinetic data. It is recognized that the straight-forward application of the chemical kinetic theory, developed for reactions in solutions, to solid systems at low a_w is questionable. The kinetic theory is appropriate for homogenous systems (Frost and Pearson, 1953). In solid systems at low a_w, particularly in highly compressed systems, there may be zonal effects (areas where reaction occurs and where it proceeds slowly due to substrate limitation). At a water activity of 0.23, there is approximately a monomolecular layer of water (Eichner, 1975) in the lysine-glucose-Avicel system at a_w of 0.23 which introduces high diffusional resistance to the mobility of the reactants. Further, since this is a multistage

reaction, there could be selective inhibition spots. However, in the food area, the kinetic theory has been widely applied (Labuza, 1982; Labuza and Saltmarch, 1981; Wolf, Thompson and Reineccius, 1977) and has provided very useful information on shelf life. The shelf life and t 1/2 values can be obtained for a single temperature from the plot of the concentration (zero order) or the logarithm of the concentration (1st order) against time. If it is necessary to predict the stability at different temperatures, it is necessary to obtain:

$$Q_{10} = \frac{\text{shelf life at T}}{\text{shelf life at (T+10)}} = \frac{\text{rate at (T + 10)}}{\text{rate at T}} \qquad [1]$$

where T is the temperature (^{O}C). It is also obtained from E_a, the activation energy:

$$\log Q_{10} = \frac{2.19\ E_a}{T(T+10)}. \qquad [2]$$

The activation energy is obtained from a semilog plot of the rate constant against $1/T^O$K.

$$E_a = -\text{slope} \times 2.303 \times R \qquad [3]$$
where R = gas constant

$$\text{and slope} = \frac{\log K_n - \log k_m}{(1/T_2 - 1/T_1)} \qquad [4]$$

where k_n and k_m are the rate constants at temperatures (^{O}K) of T_2 and T_1. Labuza has suggested on the basis of prior work that most reactions in food follow either zero or first order kinetics (Labuza, 1982).

Rate constants. The rate constants for the first order reaction were obtained at 40, 50, and 60 C from the slopes of the semilog plots of concentration vs time:

$$\text{first order rate constant, } k_1 = \frac{-\ 2.303\ (\log C_o - \log C_f)}{t_o - t_f} \qquad [5]$$

where C_o and C_f are initial and final concentrations at times t_o and t_f.

Since the present data exhibited marked deviation from a straight line, it was necessary to select the best least squares fit. This is explained further under RESULTS.

Rate constants for the second order reaction were obtained from plots of the second order function (see below) against time:

second order reaction constant, $k_2 = \dfrac{2.303}{t(a-b)} \log \dfrac{b(a-x)}{a(b-x)}$ [6]

The second order function = $\log \dfrac{b(a-x)}{a(b-x)}$ [7]

where a = initial number of moles of glucose

      b = initial number of moles of lysine

   (a-x) = unused moles of glucose

and (b-x) = unused moles of lysine

     at t = reaction time

Here also, a straight line was not obtained. Therefore, the best linear regression fit explained under RESULTS was selected.

For the zero order rate constants, only the linear portion (see RESULTS) of the concentration vs time curves was used:

zero order rate constant, $k_o = -\dfrac{(C_o - C_f)}{(t_o - t_f)}$ [8]

where C_o and C_f are the initial and final concentration at times t_o and t_f.

The best linear regression fit explained under RESULTS was used to determine the rate constants. It is recognized that the present data

follow first order kinetics more closely than zero order kinetics. However, data were also obtained upon the assumption of zero order kinetics as explained under RESULTS.

Arrhenius plots. To determine the temperature dependence of the rate constants, the log of the rate constants was plotted against $1/T^oK$. In these plots, the log (reaction constants/2.303) is plotted against the reciprocal of the time. Since a log function is used, any constant is cancelled out in the calculation of the slope to derive E_a.

Half-times. The half-times in the case of first-order kinetics were calculated from the rate constants by the following equation:

$$t_{1/2} = \frac{0.693}{k_1} \tag{9}$$

where $t_{1/2}$ = half-life and K_1 = the first order rate constant.

Approximated estimates of successive half-times were either obtained from Fig. 3 or from linear transformation of data ([log (log C)] vs time or log C vs log t plots).

The order of the reaction can be computed from successive half-times (Frost and Pearson, 1953):

$$n = 1 + \frac{\log [(t_2/t_1) - 1]}{\log [1/(1-y)]} \tag{10}$$

where y = fraction of the decrease in concentration, which is equal to 1/2, in this case

and t_1 = first half-time

and t_2 = second half-time.

RESULTS AND DISCUSSION

Kinetics of Lysine-Glucose Degradation

Rates of lysine degradation. The rate of loss of lysine in the compressed models at 40, 50 and 60 C at a water activity of 0.23 shown in Fig. 3, illustrates the large temperature dependence of the reaction. At 40 C, the rate of lysine loss is modest compared to the rapid rates at 50 C and 60 C. At 40 and 50 C, the reaction appears to approximately
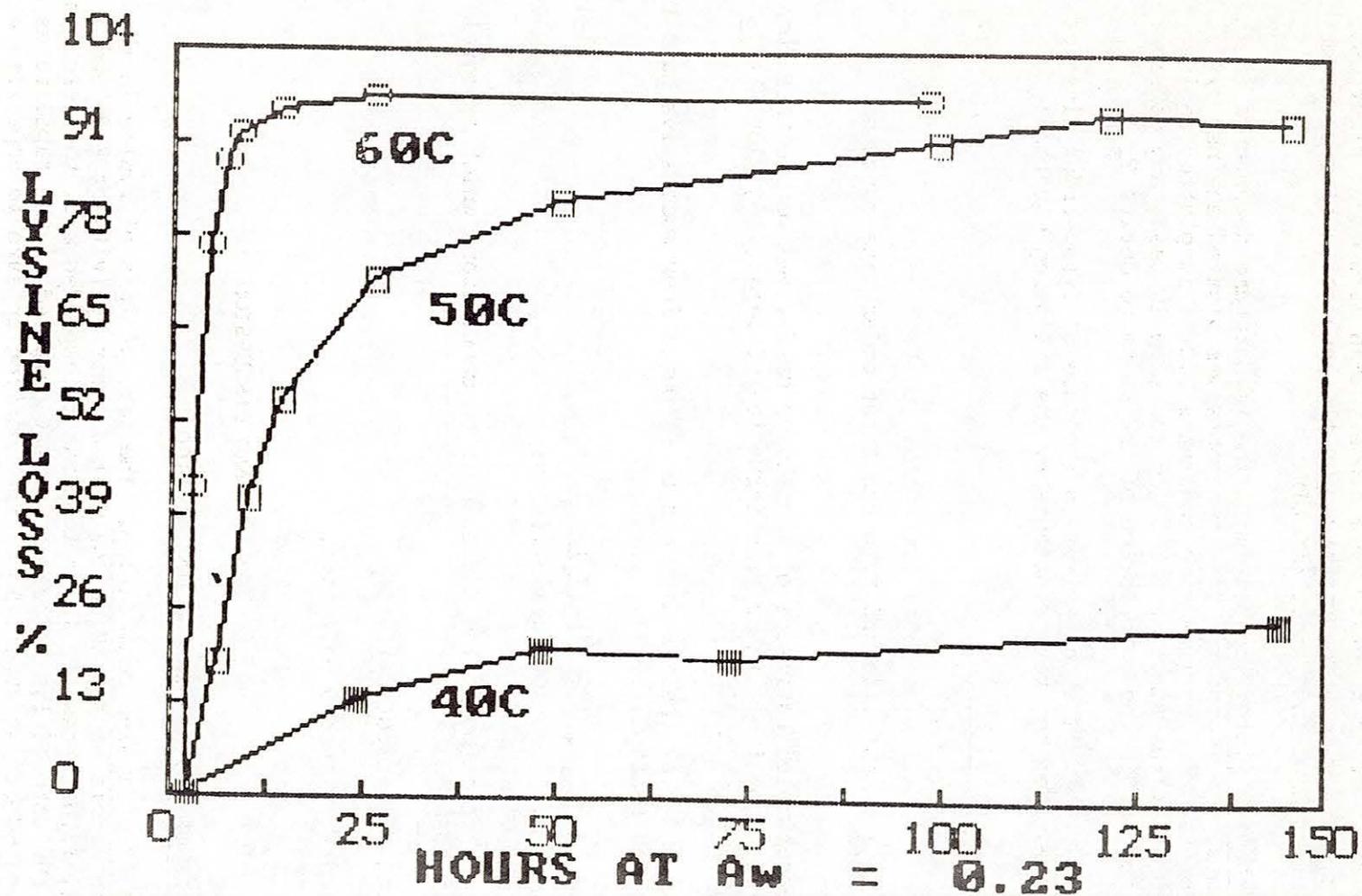
Figure 3. Rates of losses (%) of lysine in the lysine-glucose-cellulose model at 40, 50 and 60 C and a_w 0.23.

follow first order kinetics (Fig. 4). The leveling off seen after the
rapid increase in lysine loss at 60 C is clearly explainable on the basis
of total loss of lysine in the reaction. The initial mole ratio of
glucose to lysine of about 2.3 obviously promoted the near total loss of
lysine. At 50 C, the initial fast rate (Fig. 3) is followed by a slower
rate before there is near total loss in lysine which is typical of a first
order reaction. The 10 C differential between the 50 C and 60 C reactions
is clearly responsible for these differences and may be partly due to a
high diffusional resistance as a result of a tightly bound monomolecular
water layer (Eichner, 1975). This high resistance at 50 C may impede the
mobility of reactants. The curve for 40 C appears to support this
explanation.

From the nutritional standpoint, however, the damage to lysine is con-
siderable even at 40 C which is merely 104 F, a high but expected ambient
temperature, and as much as 25% is lost in 144 hours. These data are in
agreement with that of Eichner (1975) who observed a decrease of about 30%
in free amino groups at 40 C in 70 hr and an a_w of 0.23 in a lysine-
glucose-Avicel model. In the present study at 50 and 60 C, there was over
50 and 90% lysine loss, respectively, in 12 hours. While there are data
in the literature at different water activities with amino acid-carbohy-
drate models, information is lacking on either compressed or uncompressed
lysine-glucose-cellulose models at 50 and 60 C. The moisture content of
the compressed models was 2.5% as determined by prolonged dessication over
phosphorous pentoxide.

The first order plot shown in Fig. 4 suggests that the 40 C curve is
reasonably linear while that of 50 C shows definite curvature. The 60 C
curve has two distinct phases, an initial rapid phase of near complete
exhaustion of lysine followed by a second phase where there appears to be
very limited reaction. This curve is similar to that of Wolf, Thompson
and Reineccius (1977), except that, in their experiment with soy protein-
glucose model at 110 C, the levelling off took place at 50% lysine loss,
and also that they observed a middle phase of lysine recovery. The
increase in lysine observed by them may perhaps be related to the use of
the fluorodinitrobenzene procedure for determining lysine loss. Biophasic
first order plots have also been observed by Warren and Labuza (1977) with
a casein-glucose model at 35 C.

The $t_{1/2}$ values and k_1 values estimated with all or part of the
data points are shown in Table 1. At 40 C, the estimated first half-time
with all five data points is 400 hr and the estimate appears reasonable,
even though 50% of the lysine was not lost at this temperature within the
reaction period. Warren and Labuza, using a casein-glucose-propylene
glycol system at 35 C and an a_w of 0.3 estimated a half-time of 336-552
hr depending upon the lysine assay method used (1977). The $t_{1/2}$ values
at 50 C reported in Table 1 varies from 11 to 34 hr depending upon the
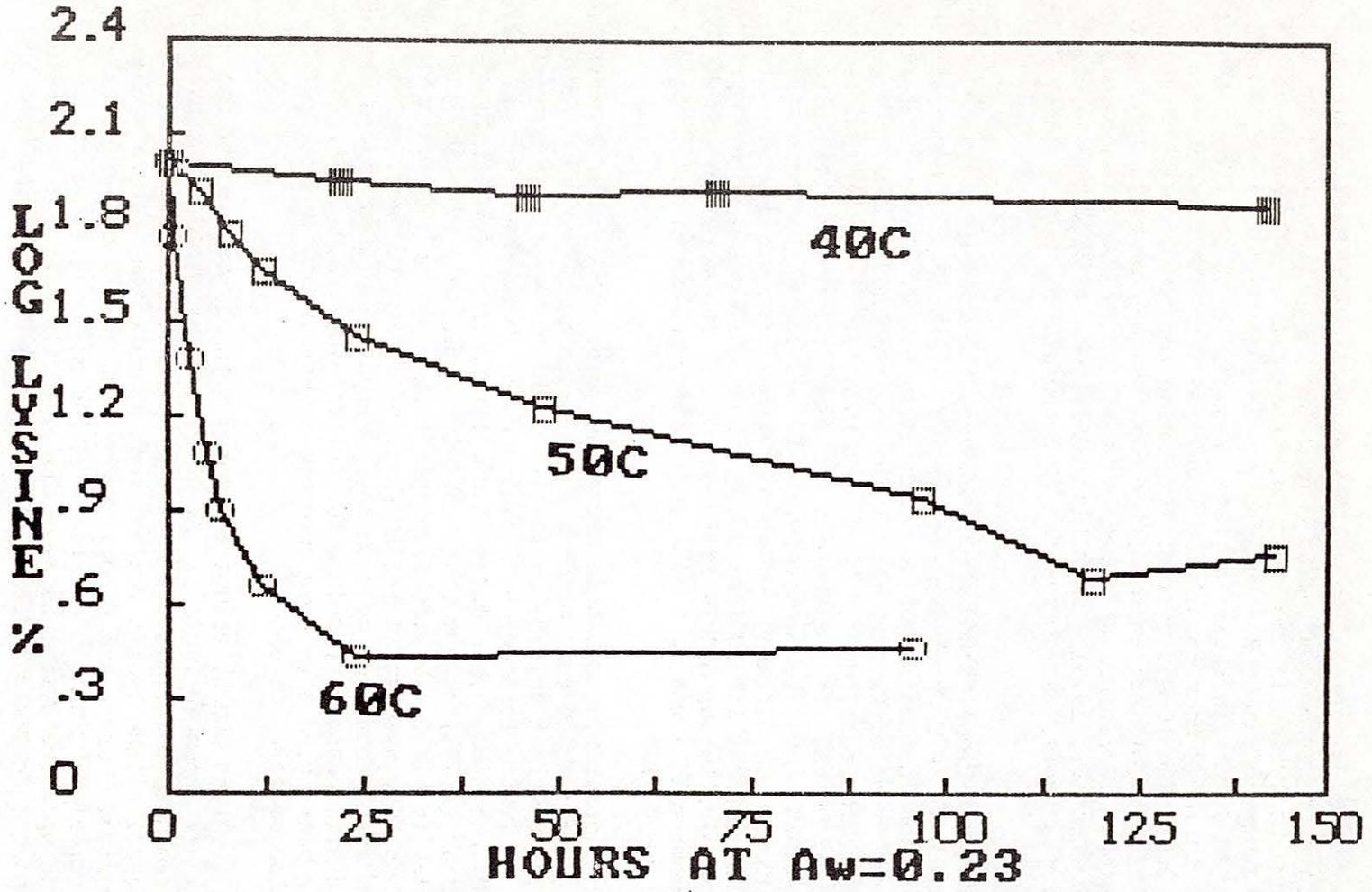
Figure 4. Semilog plots of lysine concentration (100–lysine loss %) vs time of data shown in Fig. 3.

selected time span of the experiment and is to be compared with the $t_{1/2}$
of 10 hr estimated from Fig. 3. Similarly at 60 C, the $t_{1/2}$ values
range from 1.5 to 27 hr depending upon the time span selected and are to
be compared with the observed value of 1.2 hr. The computed regression
coefficients decrease as the time span of the experiment is increased. As
mentioned earlier, while very high temperatures have been often used in
the literature (Labuza, 1981), extended storage temperature extremes such
as 50 and 60 C have not received much attention.

Rates of formation of reducing components. The rate of formation of
reducing components which arise from Amadori compounds (Fig. 1) and other
carbonyl products (Fig. 5) appears to be similar to the lysine kinetic
data, but there are major differences. The temperature effect is less
striking with reducing components, compared with lysine (Fig. 3). At 40
C, there seems to be a lag in the detection of these components. There is
also a linear increase from 46 to 142 hours, which was less noticable in
Fig. 3. At 50 C, there is a steady increase in the rate, which parallels
the observation at 50 C in Fig. 3. The formation of substantial amounts
of reducing intermediates in these reactions is noteworthy because of
their well known powerful antioxidant properties (Eichner, 1975). The
semilog plots for all temperatures indicate an initial linear phase
followed by a second phase of stabilization (Fig. 6). All the data points
do not fit a straight line. In this respect the reducing capacity is more
like other indicators used by Warren and Labuza (1977), in a food model at
35 C and an a_w of 0.3.

Rates of formation of amadori compounds. The rate of release of furo-
sine upon acid hydrolysis (Fig. 2) should be proportional to the initial
formation of Amadori compounds and to the degradation of lysine. The
reaction rates at the three temperatures (Fig. 7) are similar to data on
reducing components (Fig. 5) except for the leveling at 40 C after 46
hours. There is a definite tendency for the rate to decrease during the
later stages (Fig. 7) at 50 C and 60 C, whereas this is not so pronounced
in Fig. 5. The semilog of furosine area units vs time (Fig. 8) also exhi-
bited a biphasic nonlinear relationship similar to that seen with reducing
capacity.

Rates of formation of fluorescent compounds. It is immediately appar-
ent (Fig. 9) that the temperature plays a profound role in the production
of fluorescent compounds, much more so than in the case of reducing compon-
ents or other Amadori degradation compounds. The rate at 40 C relative to
60 C is very slow while that of 50 C is only a little more rapid. The
rates at 40 C and 50 C may be considered to be approximately linear until
to the final period and, indeed, we have linear regression coefficients of
r=0.90 and 0.99 respectively for these curves, which is indicative of zero
order reactions. The corresponding value for 60 C is 0.91 and is mislead-
ing because there are obviously two different rates. The semilog plots
(Fig. 10) are once again biphasic in nature.
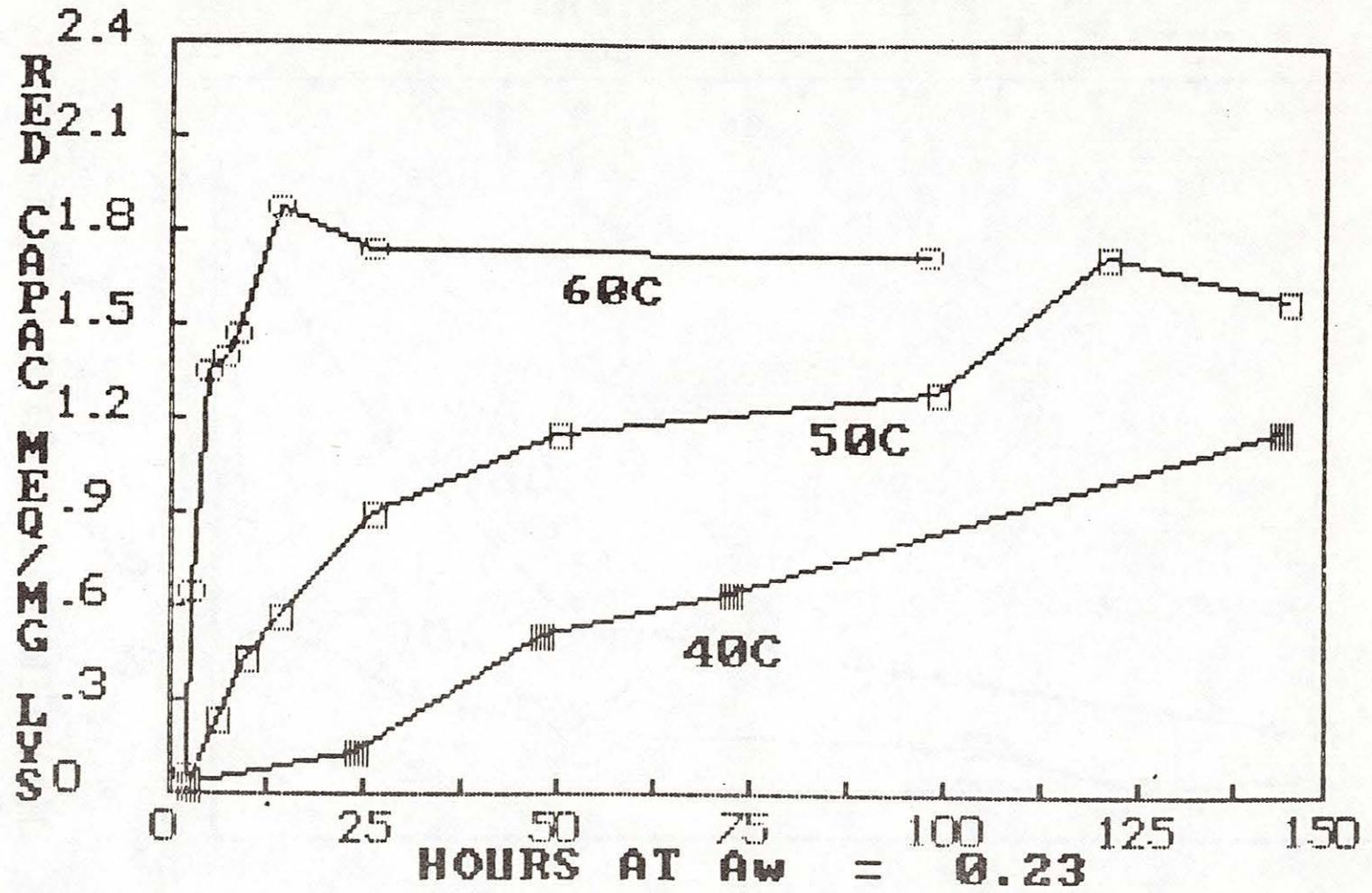
Figure 5.   Plots of reducing capacity computed as $[10^{-2}]$ milliequivalents/mg lysine vs time in the lysine-glucose-cellulose model at 40, 50 and 60 C and a_w 0.23.
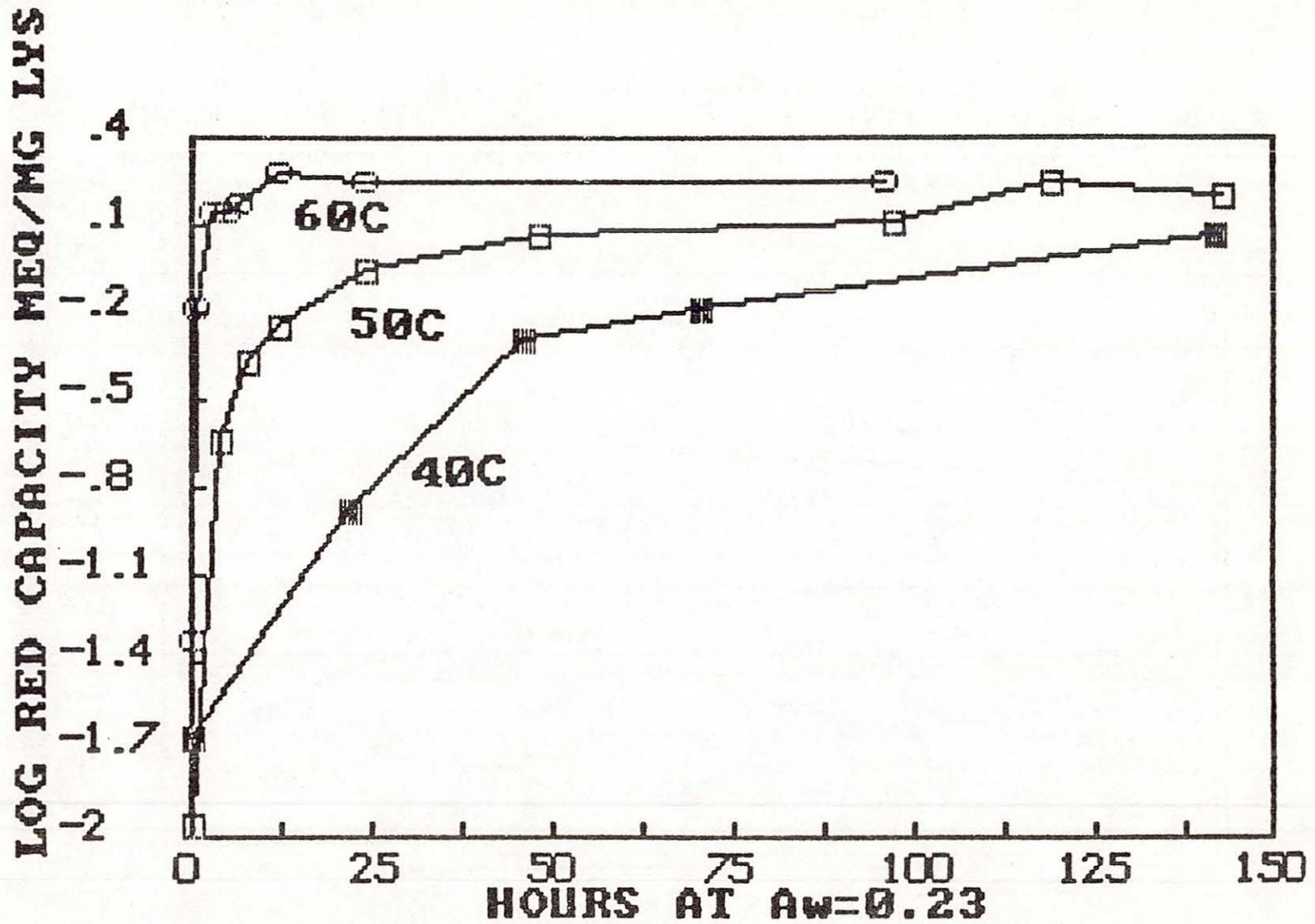
Figure 6. Semilog plots of reducing capacity vs time of data shown in Fig. 5.
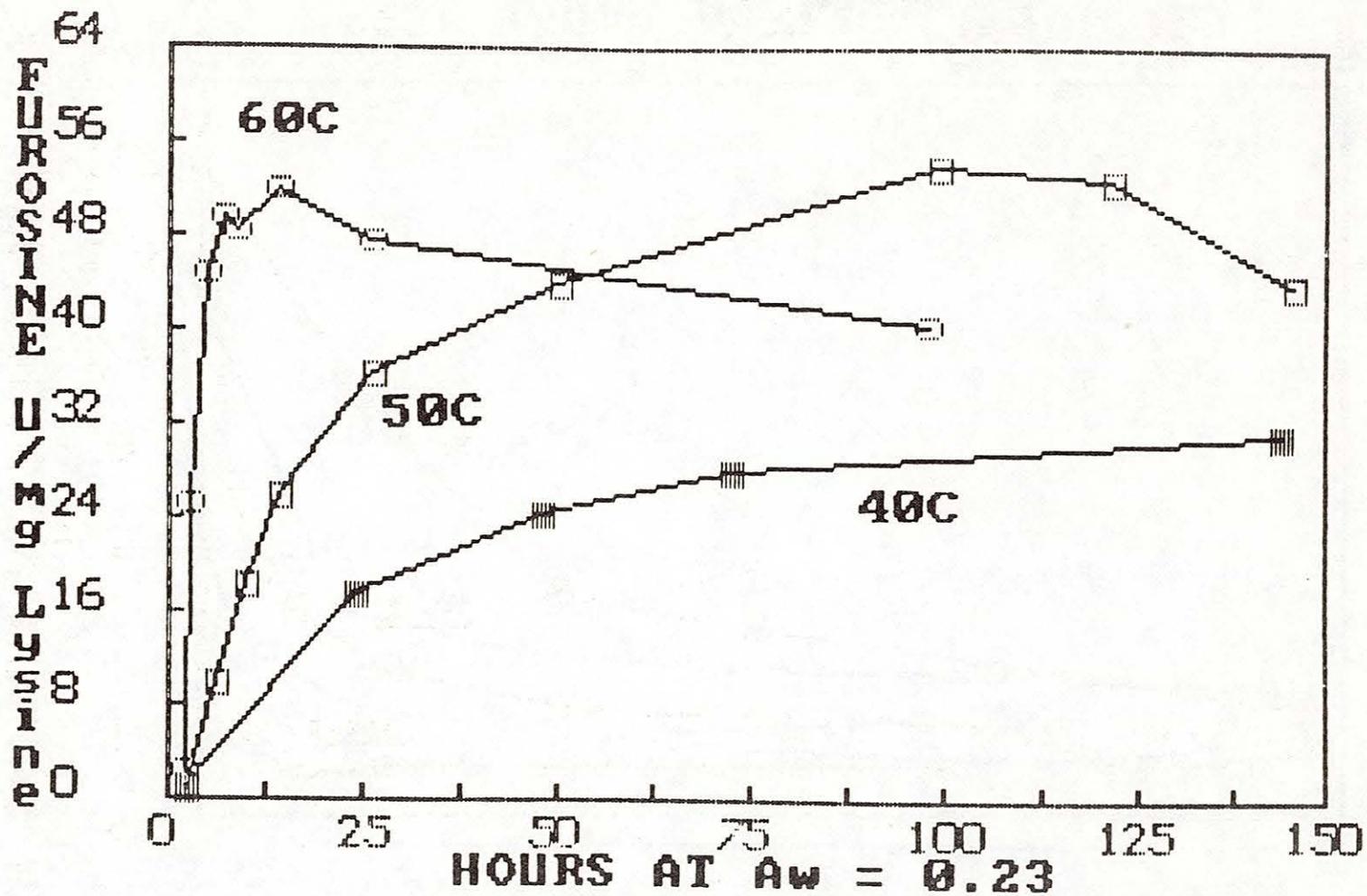
Figure 7. Rates of formation of Amadori compounds as assessed indirectly by $[10^7]$ area units of furosine/mg lysine in the lysine-glucose-cellulose model at 40, 50 and 60 C and a_w 0.23.
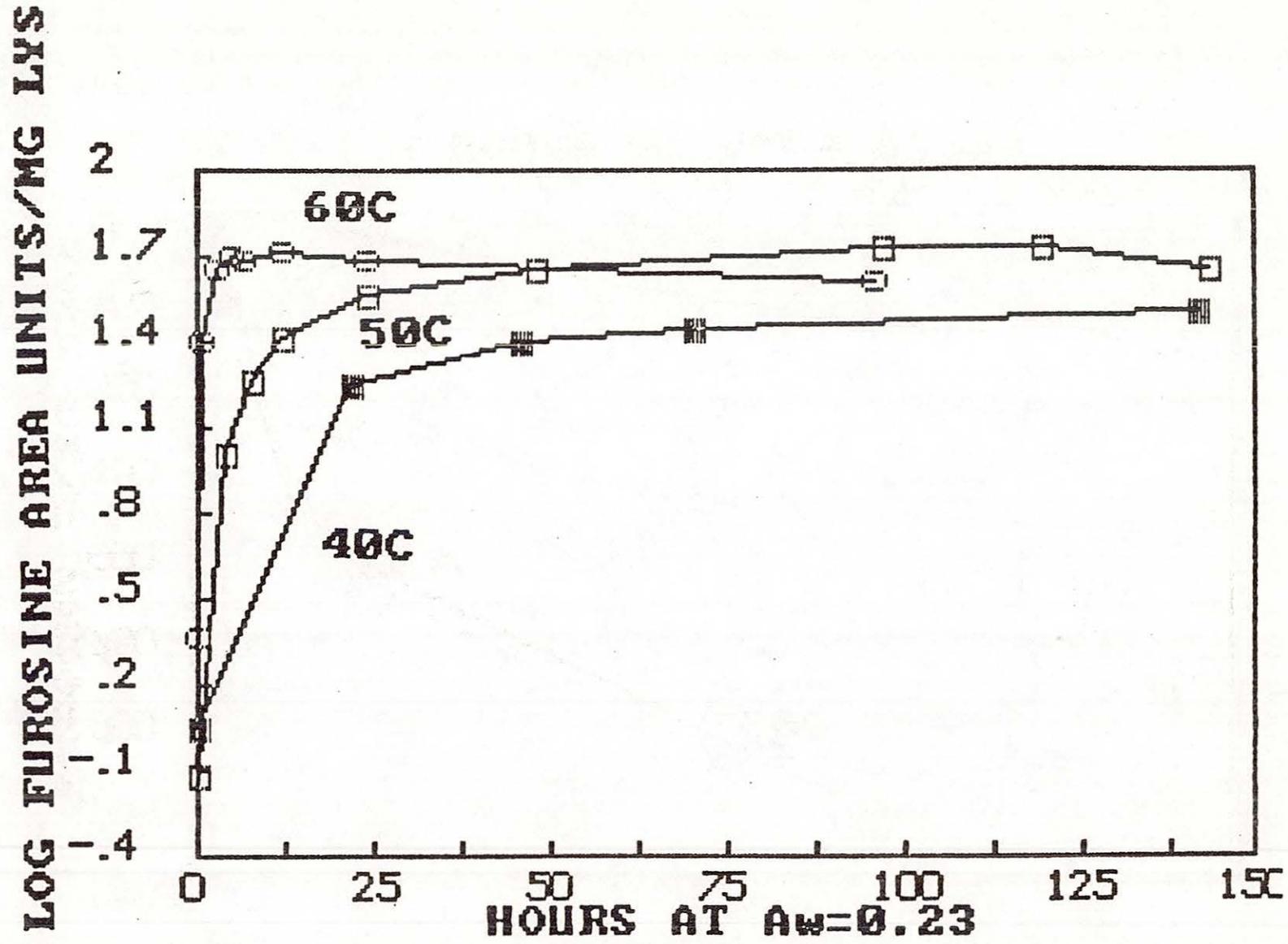
Figure 8. Semilog plots of furosine vs time of data shown in Fig. 7.
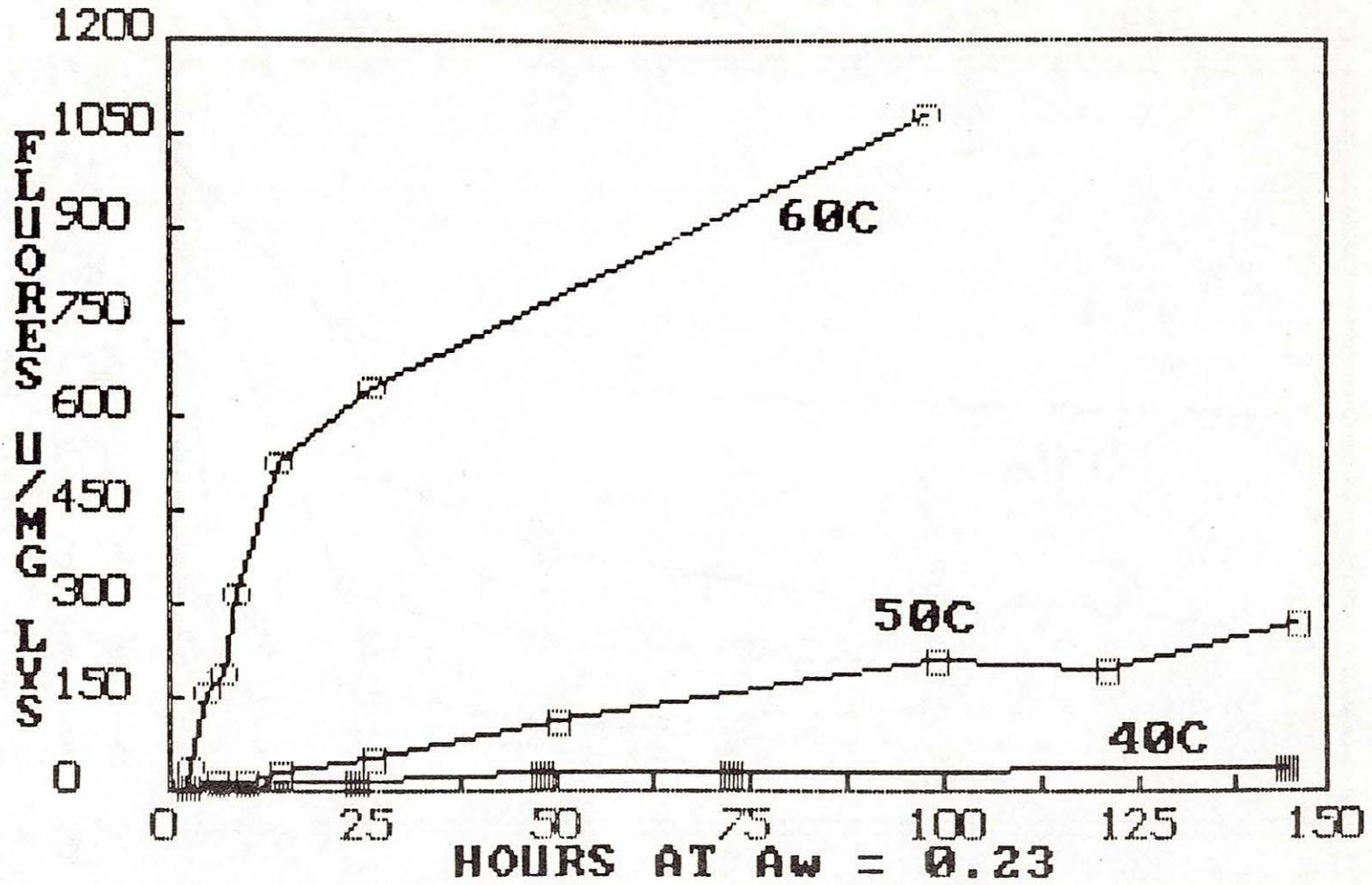
Figure 9. Rates of formation of fluorescent compounds reported as arbitrary units normalized to quinine sulfate standard/mg lysine in the lysine-glucose-cellulose model at 40, 50 and 60 C and a_w 0.23.
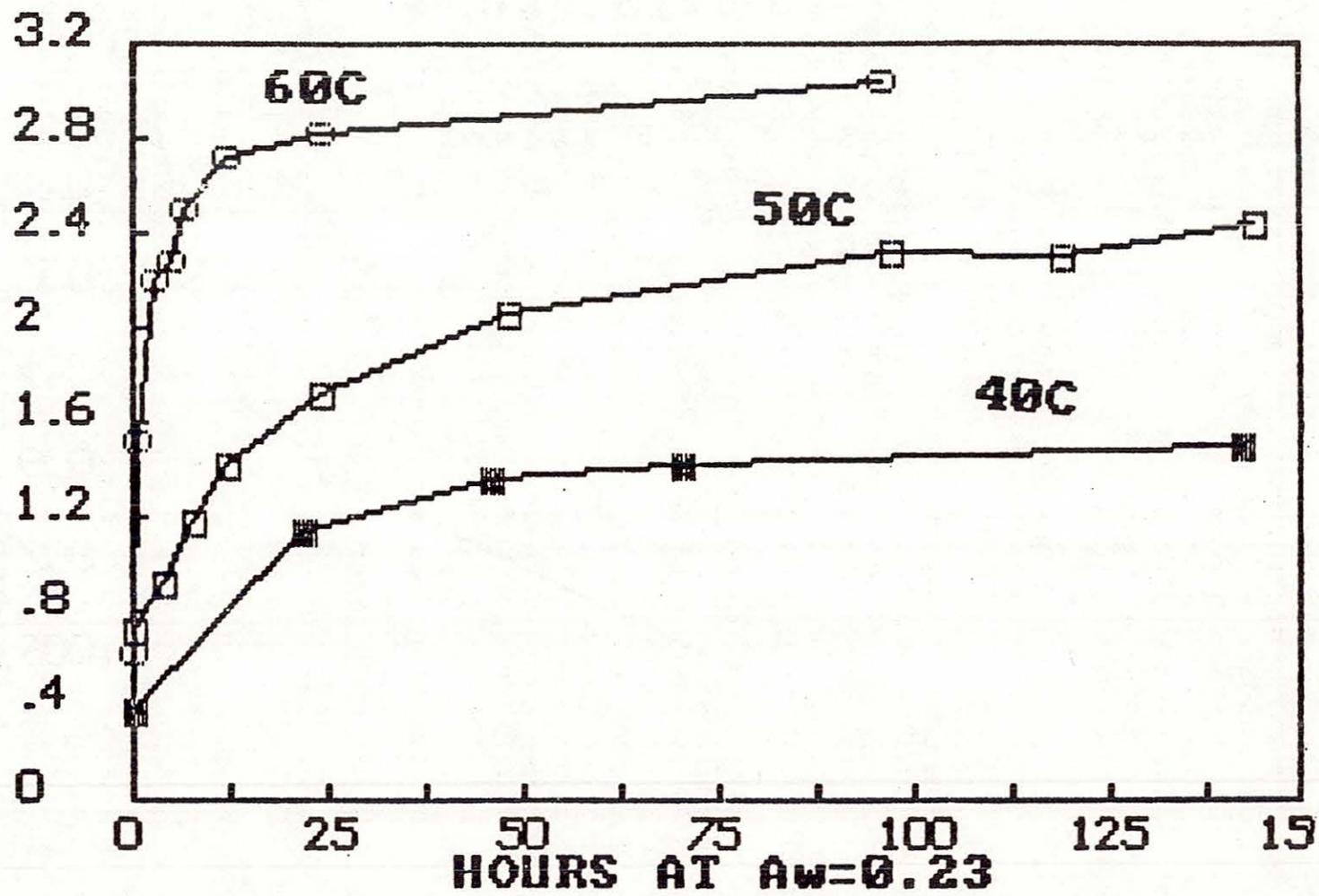
Figure 10. Semilog plots of fluorescence vs time of data shown in Fig. 9.

Both the appearance of fluorescence and color are generally associated with cross-linking reactions in foods either due to protein-reducing sugar or to oxidized lipid-protein reactions (Mauron, 1981; Porter, Black, Drolet and Kapsalis, 1983). The absence of significant fluorescence and color (see below) at the lower temperatures (40 and 50 C) suggests that cross-linking reactions leading to the formation of fluorophores and chromophores are not taking place to any great degree at 40 and 50 C. This is not surprising because of the initial phase of the Maillard reaction (Fig. 1) does not produce colored compounds or those that exhibit fluorescence.

Rates of formation of colored compounds. The color vs time plot (Fig. 11) shows even more exaggerated dependence on temperature compared with the previous Fig. 9. The rate at 40 C is exceedingly slow and that at 50 C is slow, compared with the rapid rate at 60 C. While there appeared to be no reduction in the rate of formation at 60 C of fluorescent compounds (Fig. 9), the rate of formation of the colored compounds decreased past 24 hours. The semilog plot of color vs time indicates a fairly linear relationship at 40 and 50 C, in contrast to those seen for the other indicators, such as fluorescence and furosine. However, at 60 C, a biphasic relationship was once again seen (Fig. 12).

Rates of glucose degradation. The rates of glucose degradation (Fig. 13) is similar to that of lysine degradation (Fig. 3). The initial rate of glucose loss at 50 C is less than the rate of lysine loss at 50 C due to the use of the mole ratio of 2.3 for glucose to lysine. Furthermore, the rate at 50 C for glucose is much less than that at 60 C, when compared with the corresponding rates for lysine. In addition to the temperature effect on the rate of the reaction, the diffusional resistance discussed earlier under lysine would also be operative here at 50 C by the same mechanism to retard glucose degradation from reaching the level seen at 60 C. The level of 73% loss at 50 C in 144 hours was reached in 12 hours at 60 C. The semilog plot of glucose vs time (Fig. 14) at 50 C was fairly linear but that at 60 C was curvilinear.

Correlations between Lysine and Other Indicators

Lysine and glucose. A good linear correlation (r=0.976) between lysine loss and glucose loss was obtained (Fig. 15) at 50 C when lysine losses were below 90%. With all data points taken into consideration the correlation was still quite good (r=0.955), but there was more scatter around the regression line. The mole ratio of glucose to lysine loss increased rapidly within 3 hr to 1.0 and then gradually to 1.3 at 50 C (Fig. 16). However, at 60 C, the mole ratio rose rapidly to 1.8 in the first 12 hr and then more gradually to 2.1. The deviations of glucose to lysine mole ratio from 1.0 at 50 C may be responsible for the increased scatter seen in the lysine to glucose correlation at lysine losses approaching 100%.
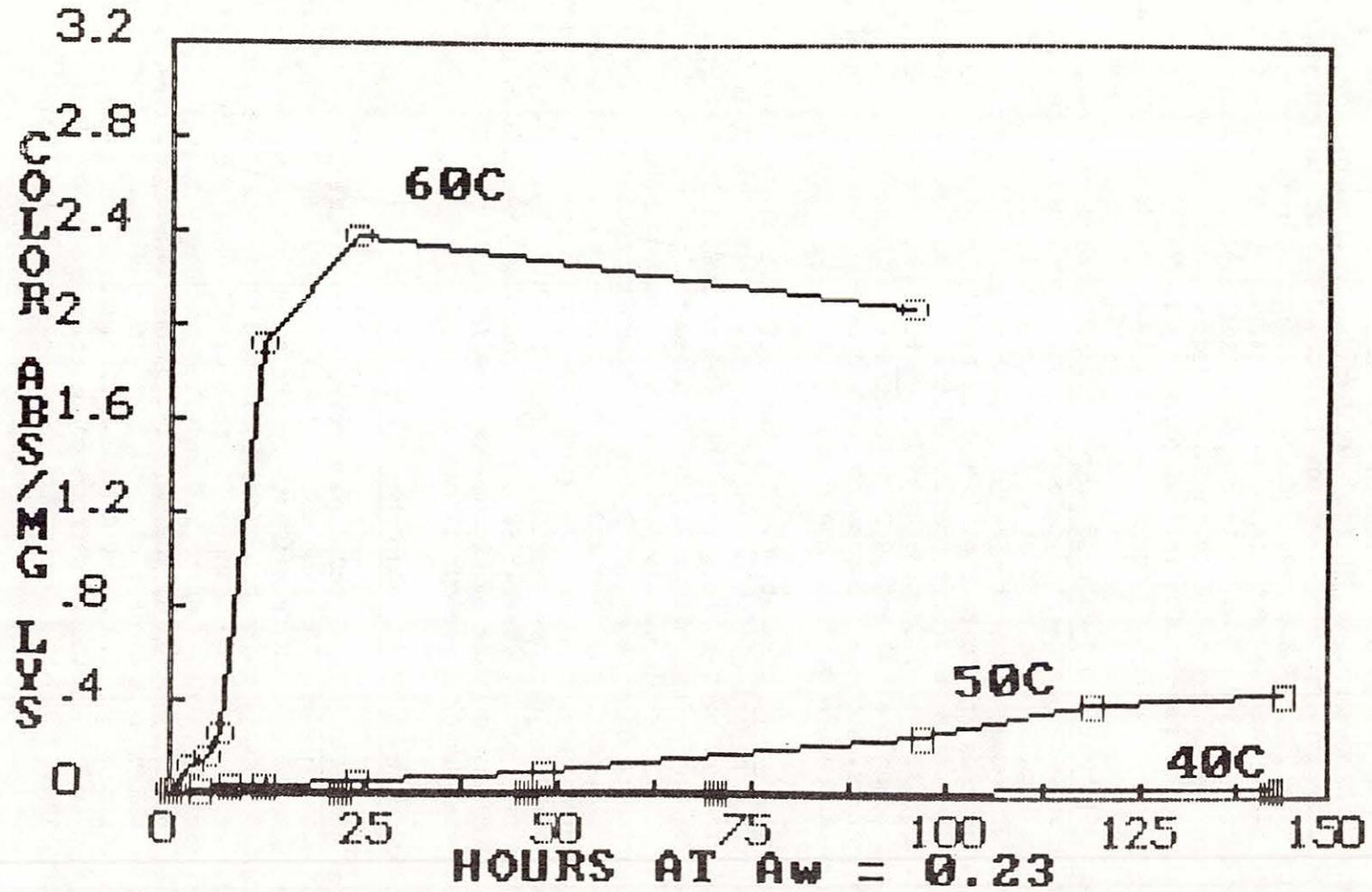
Figure 11. Rates of formation of colored pigments computed as absorbance at 410 nm/mg lysine in the lysine-glucose-cellulose model at 40, 50 and 60 C and a$_w$ 0.23.
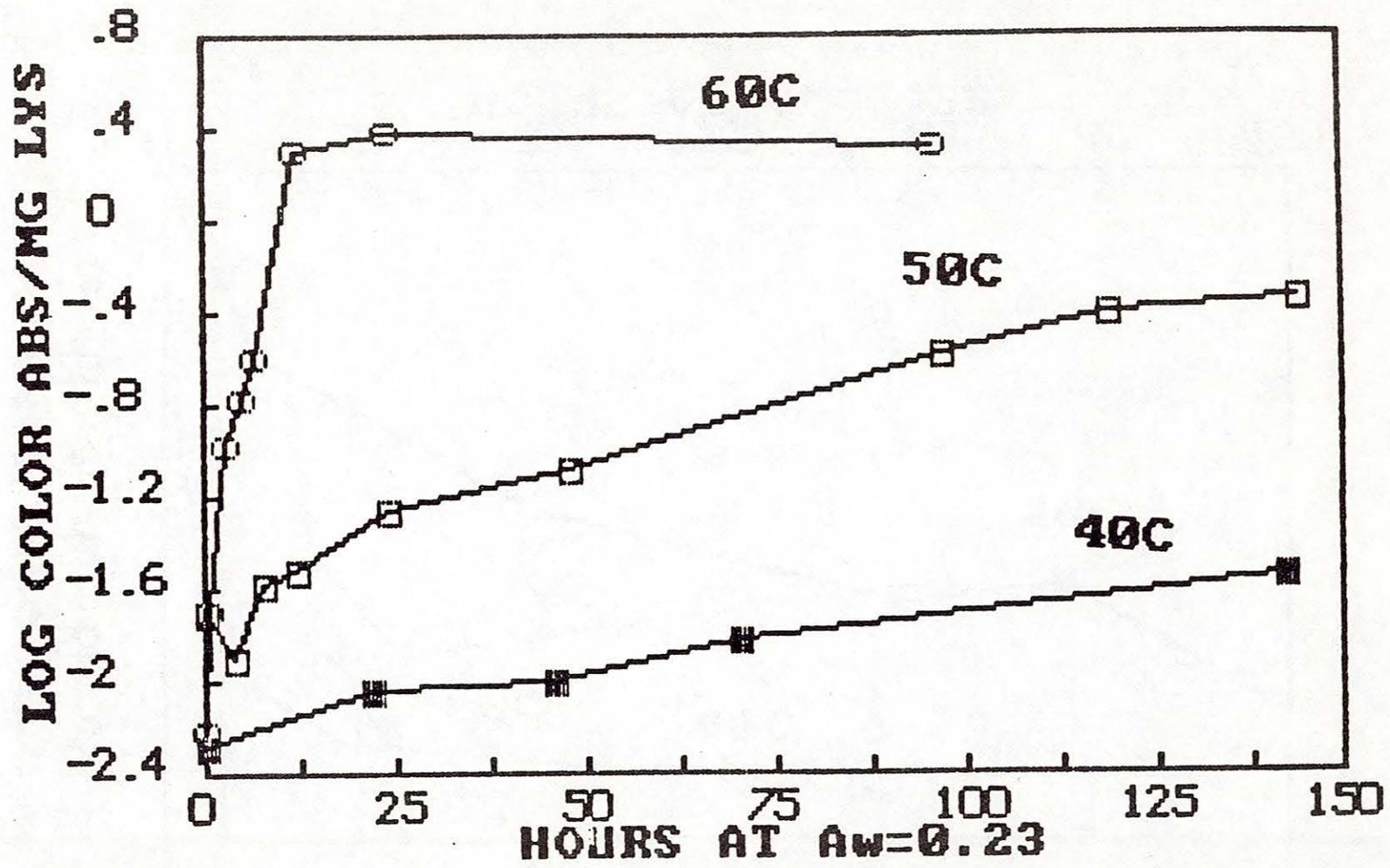
Figure 12. Semilog plots of color vs time of the data shown in Fig. 11.
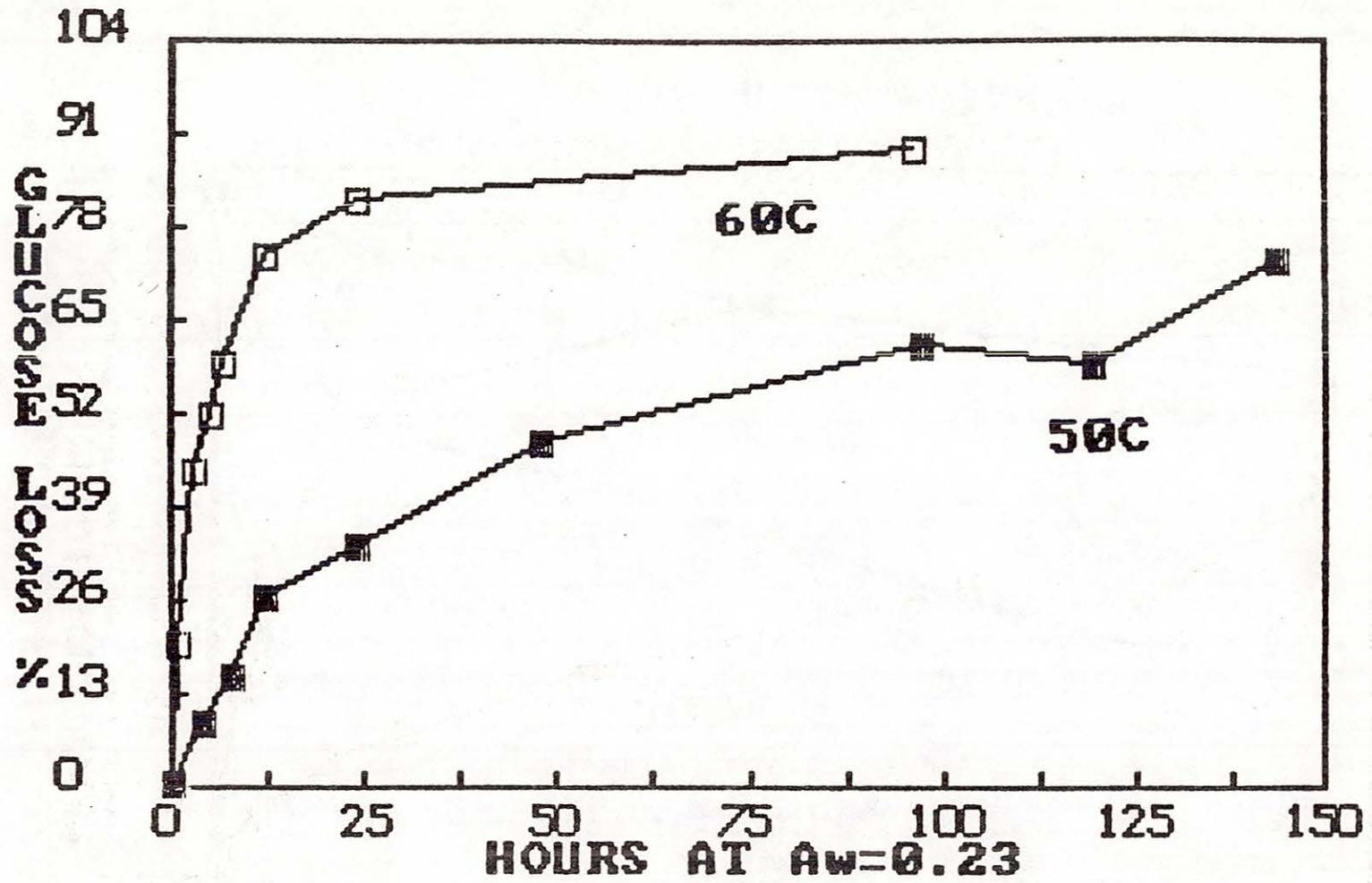
Figure 13. Rates of losses (%) of glucose in the lysine-glucose-cellulose model at 50 and 60 C and a_w 0.23.
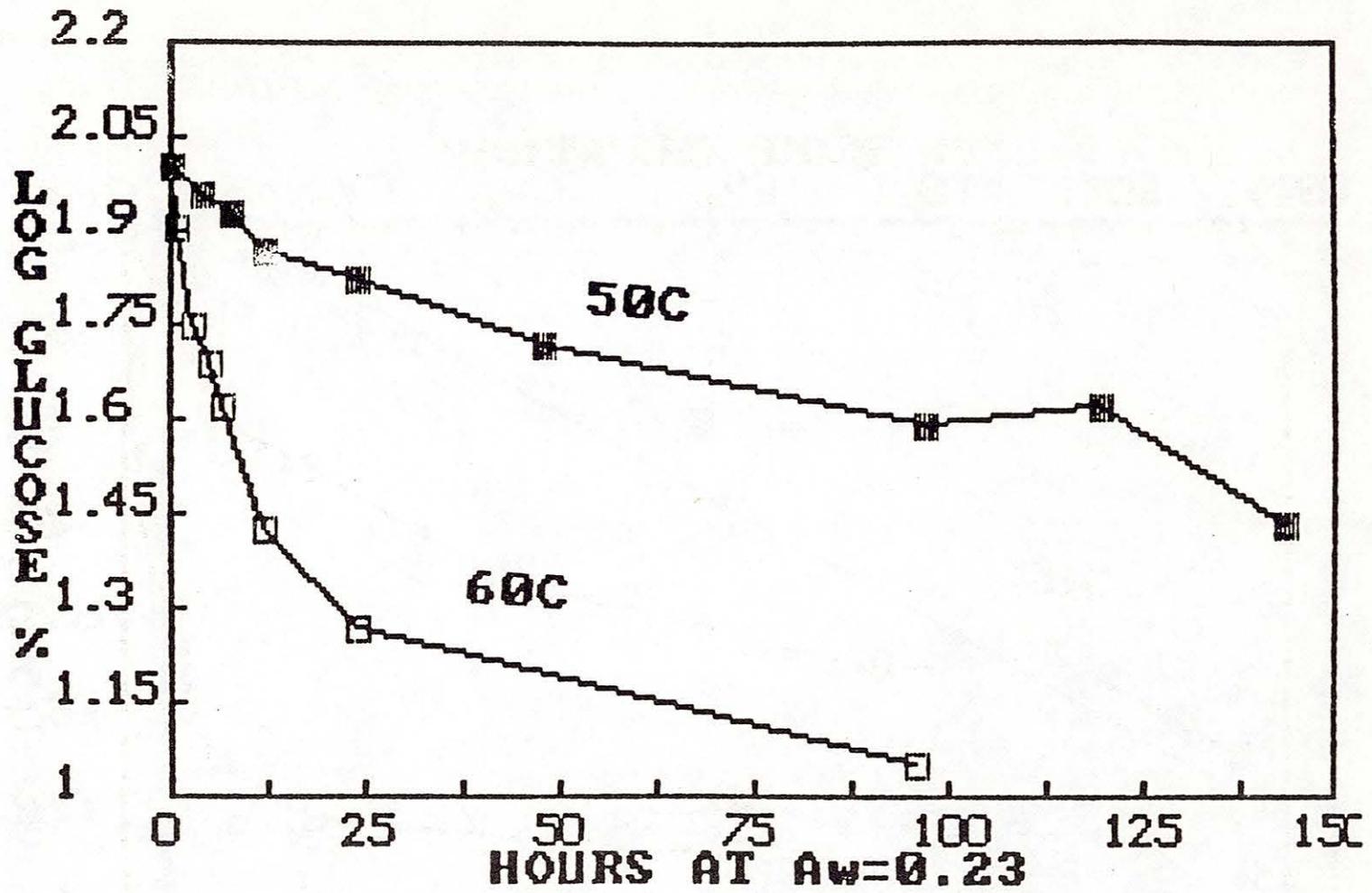
Figure 14.   Semilog plots of glucose vs time of data shown in Fig. 13.
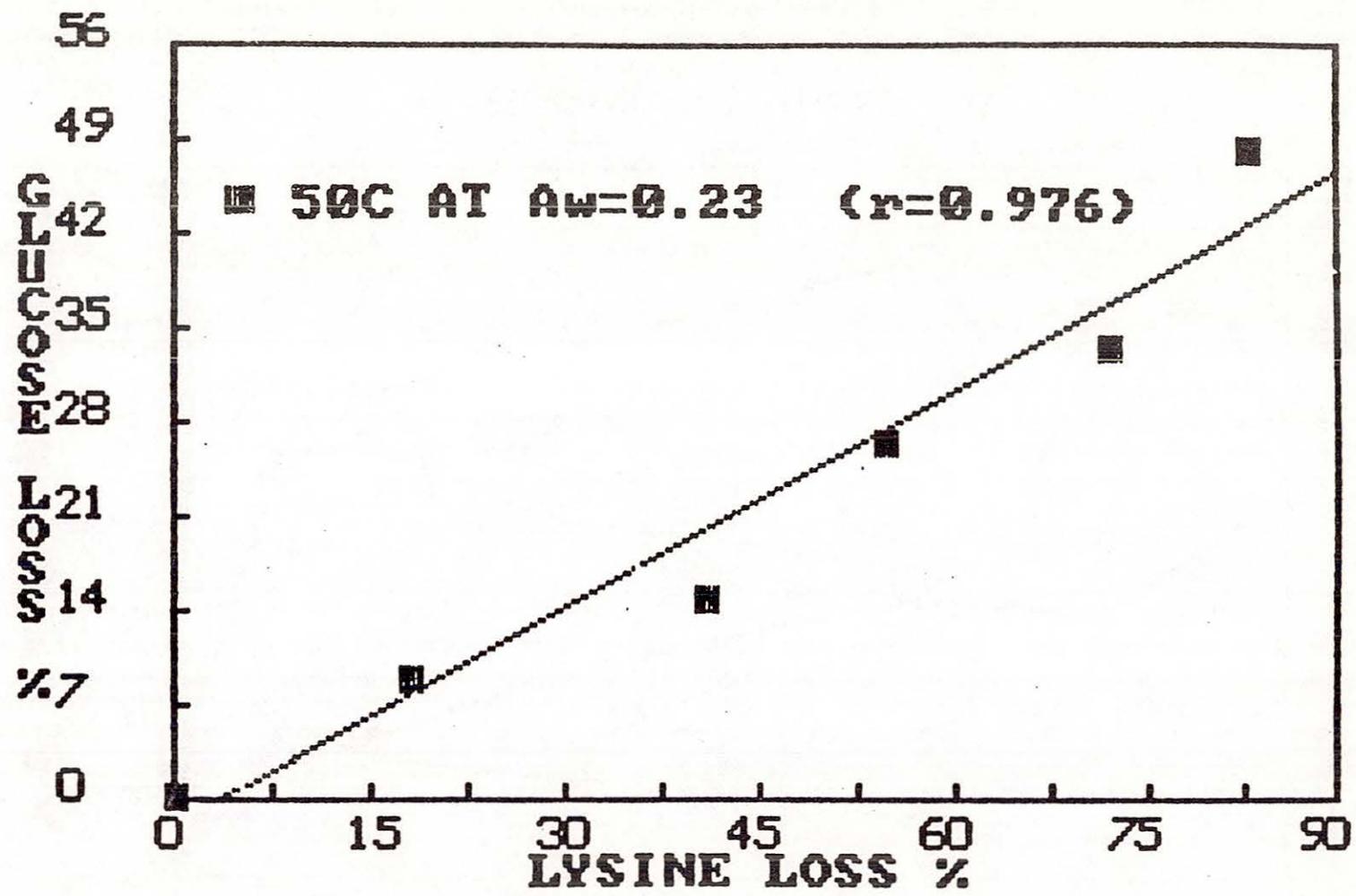
Figure 15. Correlation between the decrease in glucose and the decrease in lysine with time in the lysine-glucose-cellulose model at 50 C and a_w 0.23 (r=0.976).
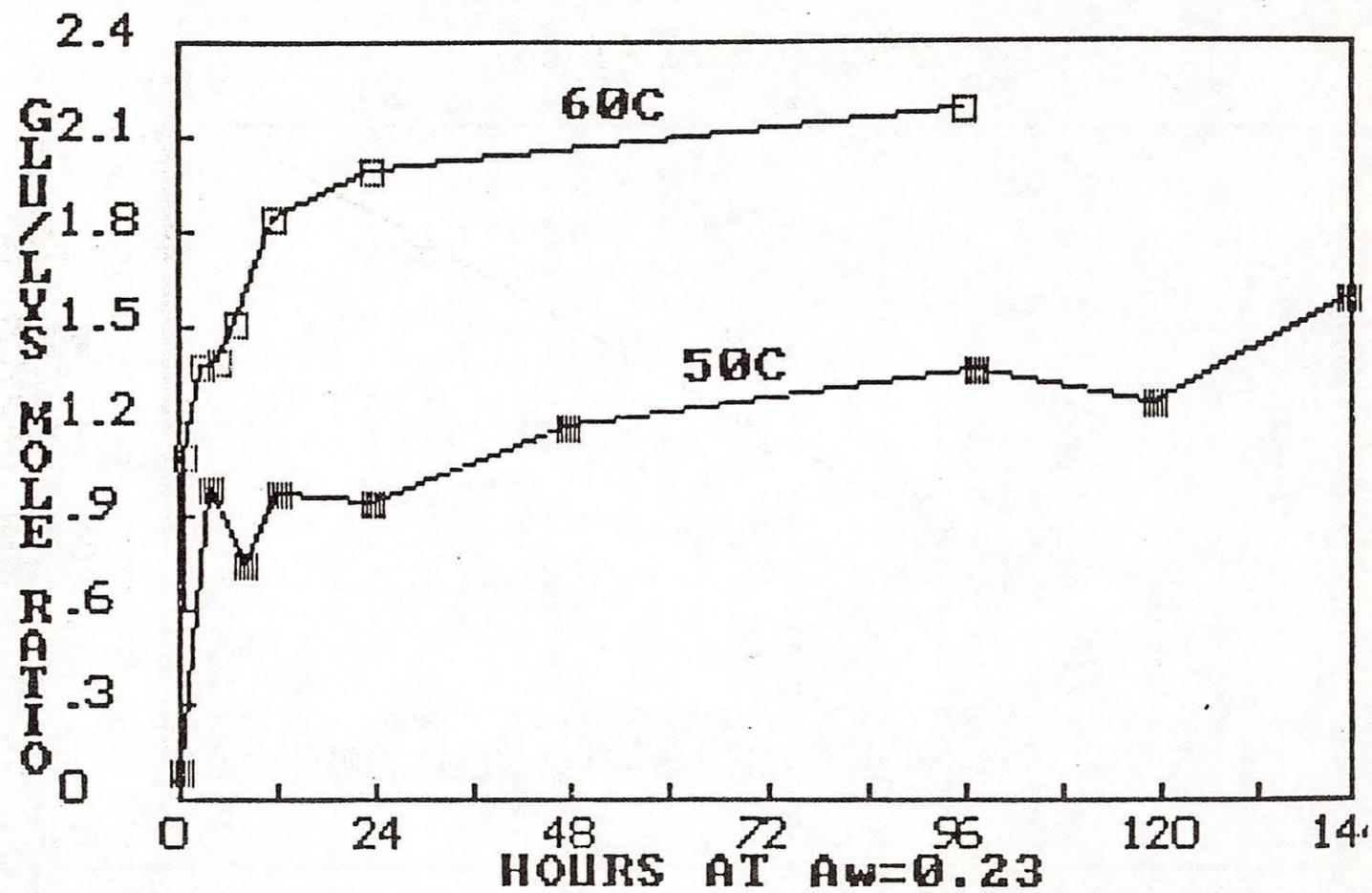
Figure 16.   Changes in the mole ratio of glucose to lysine as a function of time and temperature in the lysine-glucose-cellulose model at a_w 0.23.

Lysine and reducing capacity. The reducing capacity correlated well (r=0.984) with lysine (Fig. 17). The last two data points of the experiment at 120 and 144 hours were dropped in order to get a good fit of the data below 92% lysine loss. As seen in Fig. 5, these two points deviate significantly from the rest of the curve at 50 C. With all data points included, the correlation coefficient is 0.960, but there is much more scatter than that seen in Fig. 17. In any case, the reducing capacity appears to be a good indicator for the estimation of lysine degradation and possibly may be useful for assessing protein quality in model systems at comparable temperatures.

Lysine and furosine. A very good linear correlation (r=0.984) between lysine loss and furosine area units was seen in the models at 50 C even without dropping the last two points (Fig. 18). With the last two points omitted, an r value of 0.988 is obtained. Thus, furosine appears to be an excellent indicator for prediction of lysine availability in similar model systems at temperatures close to 50 C.

Lysine and fluorescence. By linear regression, fluorescence correlates poorly (r=0.838) with lysine loss (Fig. 19). The shape of the curve suggests that exponential regression would provide a reasonable fit, and, indeed, the correlation obtained with a semilog plot indicates an r of 0.982. However, the value of the information in Fig. 19 is in demonstrating that there is only weak fluorescence until about 70% of the lysine is lost. Therefore, fluorescence is not as good an indicator as reducing capacity or furosine in predicting lysine availability in compressed systems at low a_w.

Lysine and color. By linear regression, color formation also correlated poorly (r=0.746) with lysine loss in the models stressed at 50 C (Fig. 20). By exponential regression, the fit was considerably better (r=0.893). As in the case of fluorescence, the intensity of color is very low until most (85%) of the lysine is lost. Of special interest is the observation that there is delay in the appearance of color in relation to the appearance and fluorescence. These findings confirm and extend earlier data in the literature that there is considerable loss in lysine before the developments of brown pigments (Labuza and Saltmarch, 1981).

Correlations at other temperatures. Similar correlation (not shown here) has been obtained between lysine loss and reducing capacity or furosine in models at 60 C. At 40 C, these correlations were only moderately good (r approximately equal to 0.9), possibly because of few data points and the leveling off of the lysine rate within two time intervals.

Correlations obtained with data combined from models stressed at 40, 50 and 60 C. While it is necessary with model systems to work at precise
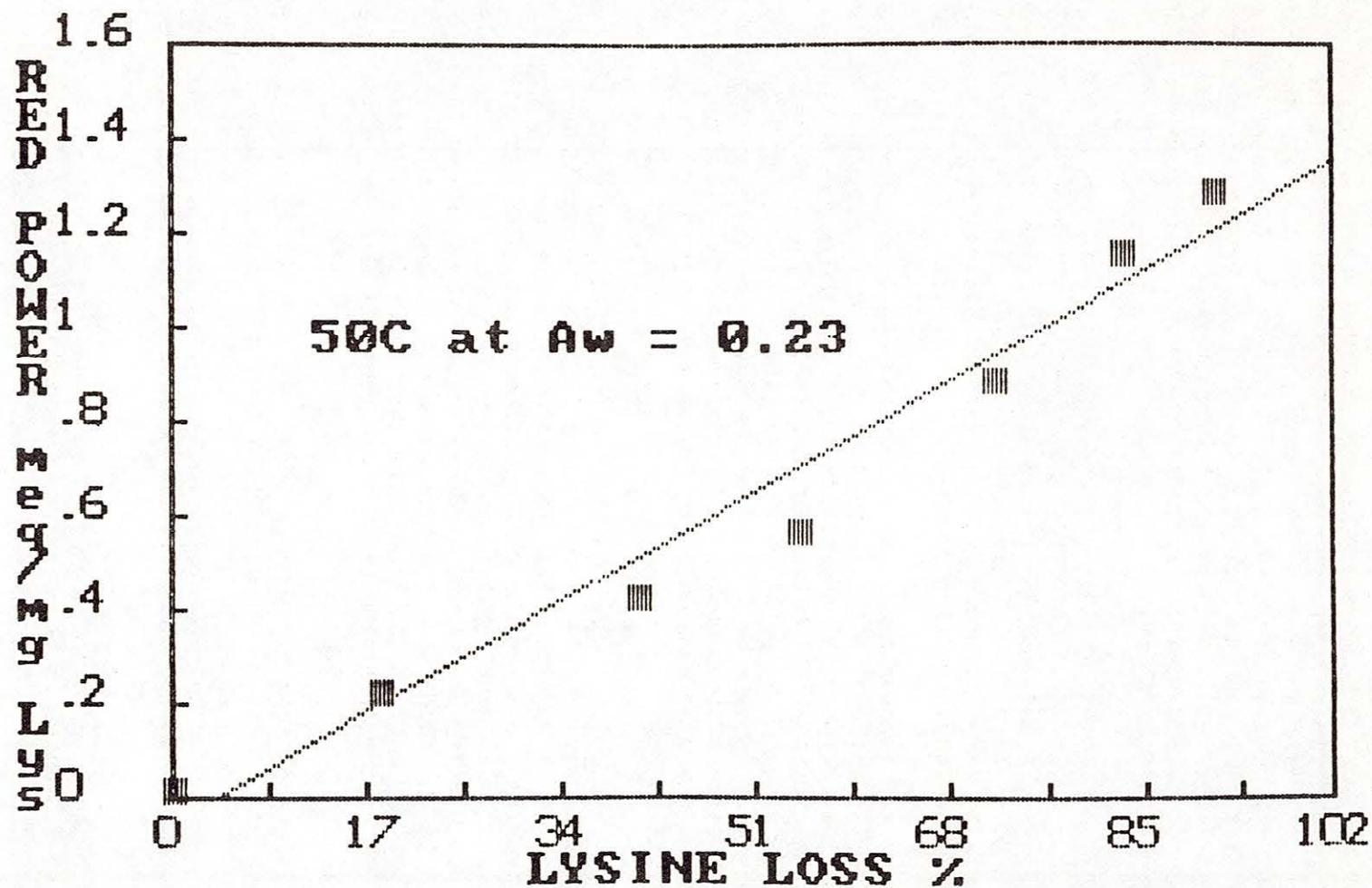
Figure 17. Correlation between the increase in reducing capacity and the decrease in lysine with time in the lysine-glucose-cellulose model at 50 C and a_w 0.23 (r=0.984).
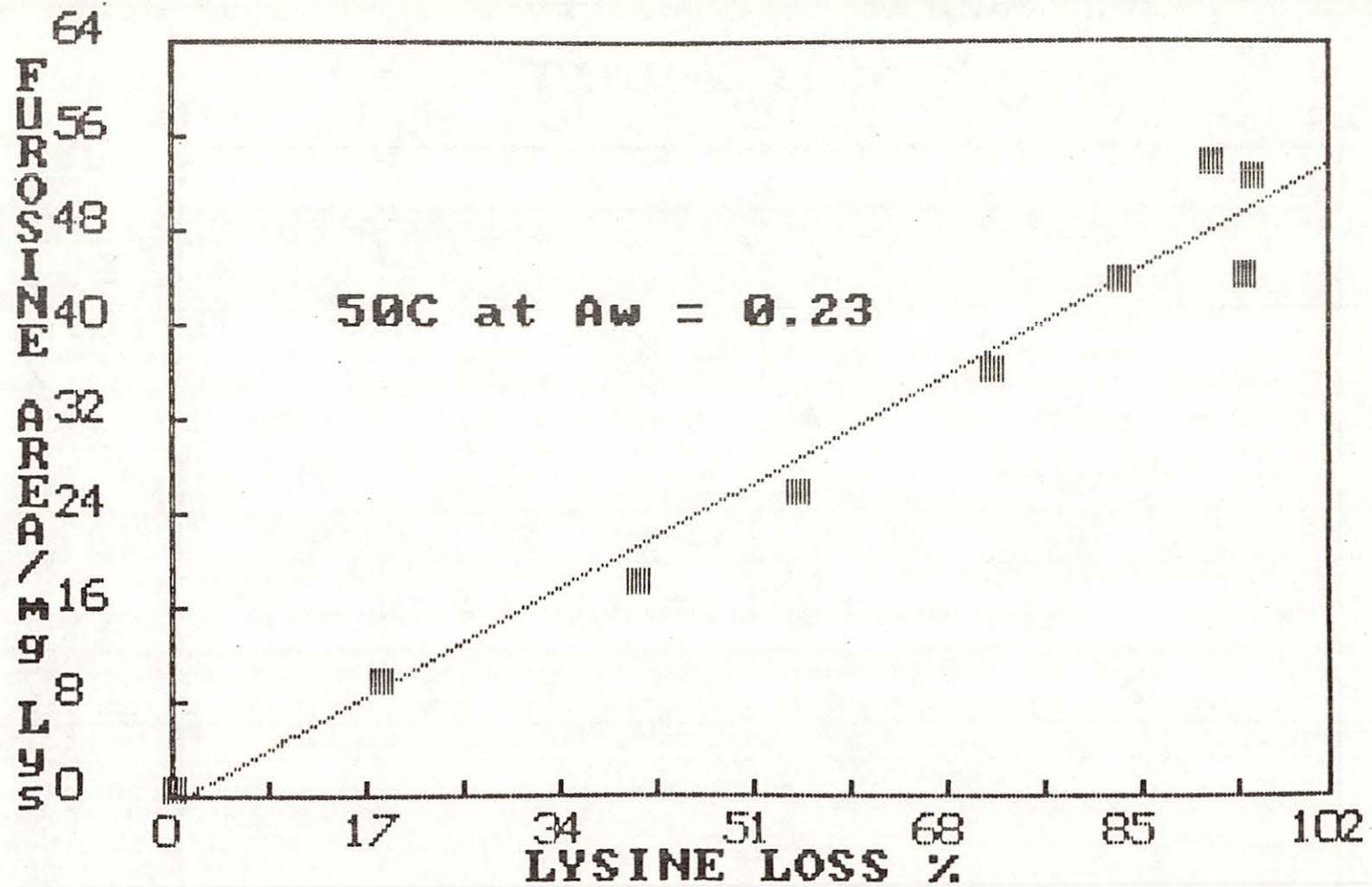
Figure 18. Correlation between the increase in furosine and the decrease in lysine with time in the lysine-glucose-cellulose model at 50 C and a_w 0.23 (r=0.984).
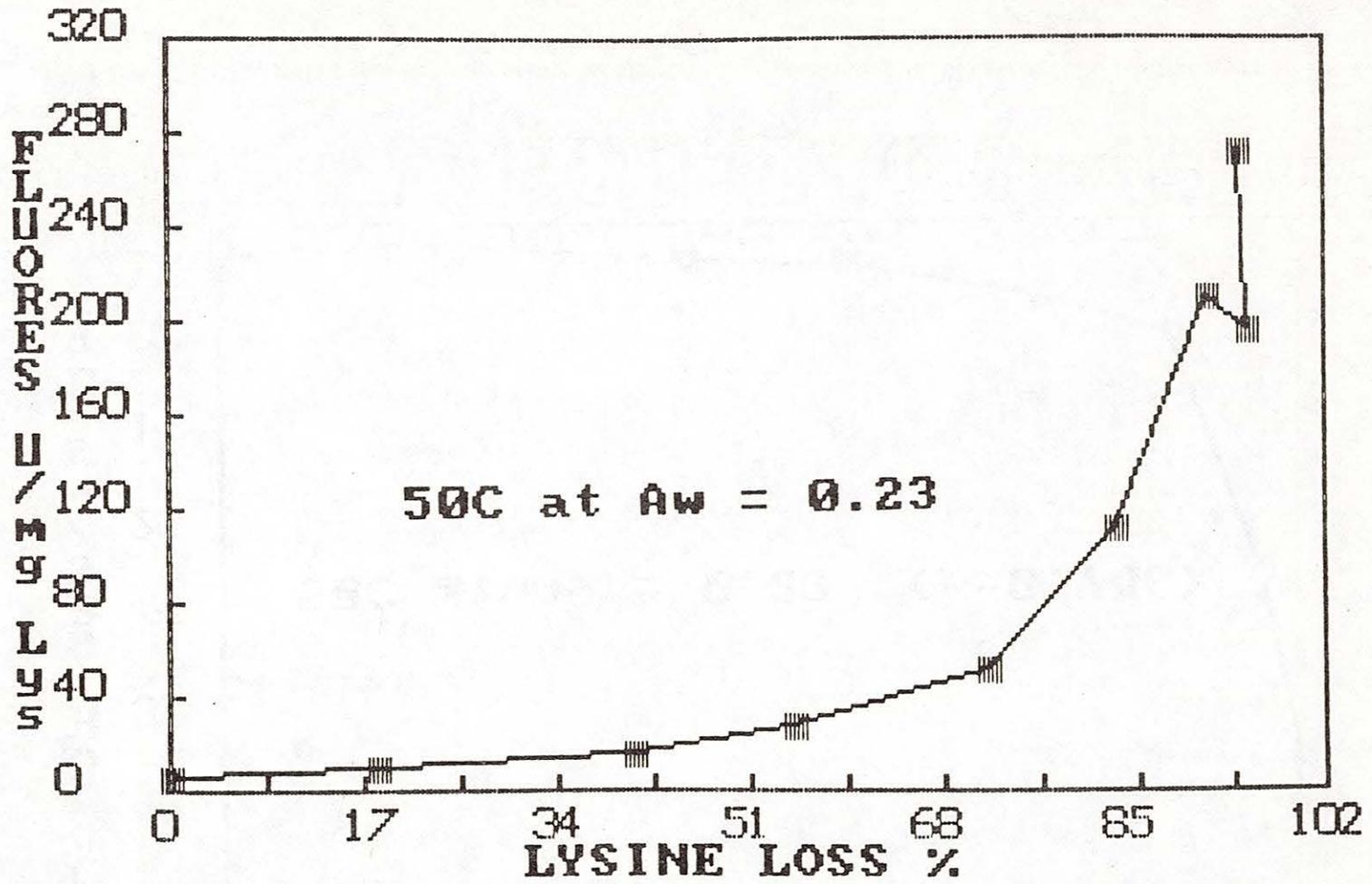
Figure 19. Correlation between the increase in fluorescence and the decrease in lysine with time in the lysine-glucose-cellulose model at 50 C and a_w 0.23 (r=0.838).
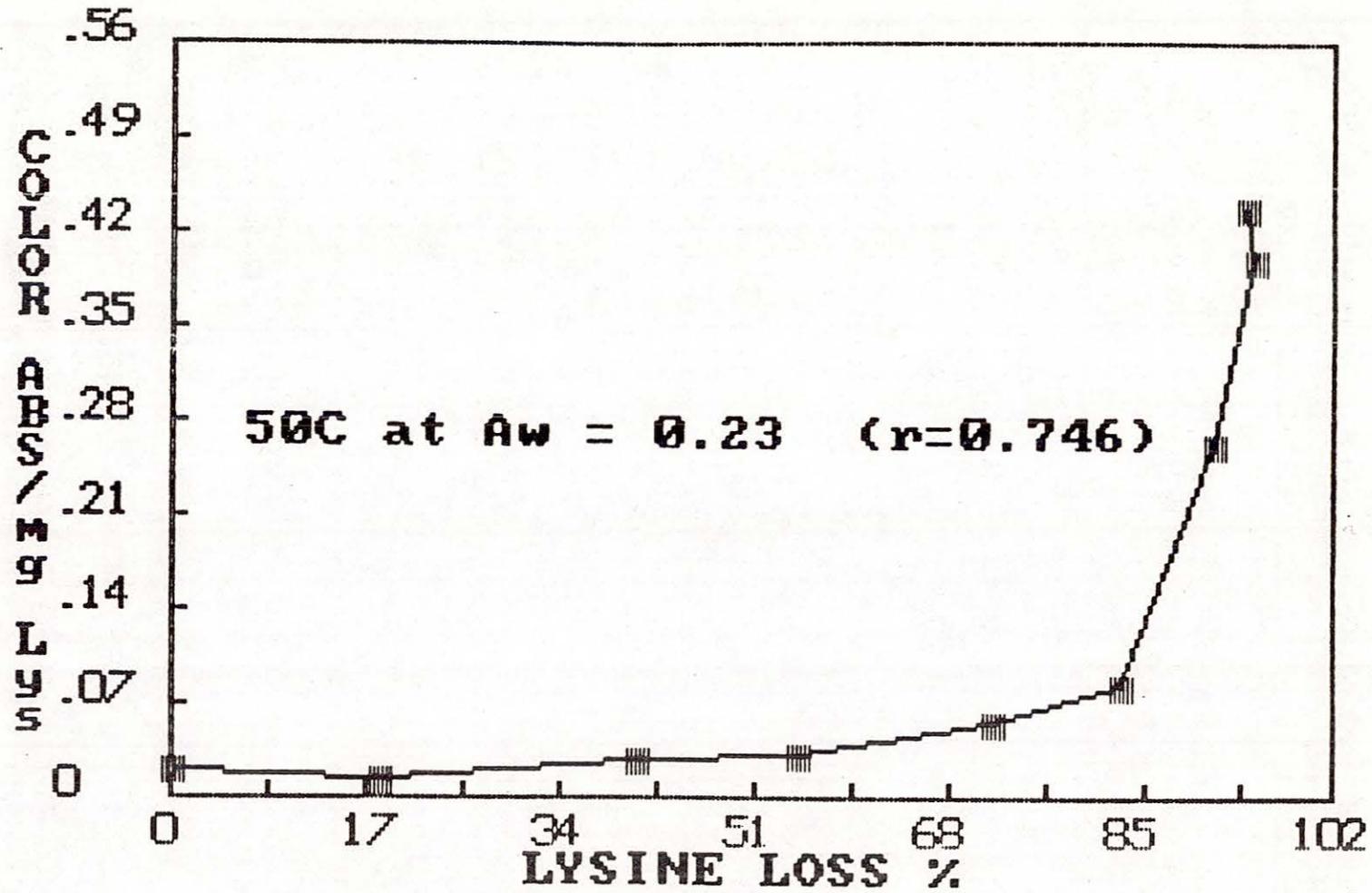
Figure 20. Correlation between the increase in color and the decrease in lysine with time in the lysine-glucose-cellulose model at 50 C and a_w 0.23 (r=0.746).

fixed temperatures, the real world situation is quite different with unpredictable fluctuations and periodic cycling of environmental temperature. It was therefore decided to pool data from all three temperature experiments and observe how the data would interact.

The overall correlation coefficient obtained with the pooled data between lysine and glucose losses was 0.936; between lysine loss and reducing power, 0.925; between lysine loss and furosine, 0.953 (Fig. 21); between lysine loss and fluorescence, 0.421; between lysine loss and color, 0.560 (Fig. 22). Therefore, it appears that even for mixed temperature exposures both furosine and reducing capacity are reasonably good indicators of lysine availability in a simple model system. Fluorescence, color and even reducing capacity may be affected by other constituents in a complex food. Among the markers tested, furosine seems to offer the best potential for a lysine availability indicator in food proteins.

Kinetics of lysine degradation. Fig. 3 suggests a first order deterioration of lysine in the model due to Maillard reaction. However, upon closer scrutiny (Fig. 4), it is seen that only the 40 C curve exhibits first order relationship. The 60 C curve is biphasic and the 50 C curve is only approximately linear. Since a straight line relationship was not obtained, a choice had to be made among the many different possibilities, i.e., the cut-off data points. Based upon existing literature, it is clear that most kinetic data evaluations (Wolf, Thompson and Reineccius, 1977; Warren and Labuza, 1977; Labuza and Saltmarch, 1981) are based upon the initial linear portion (50-75% nutrients loss) of the first order plot. The linear portions based upon a good least squares fit (46 hours at 40 C, 24 hours at 50 C and 7 hours at 60 C), yielded an E_a of 44.7 kcal/mole and a Q_{10} (50 C) of 8.2. Over 72 and 92% of lysine was exhausted at these reaction times at 50 and 60 C, respectively, and meet the criterion used by others in the the literature. Even though only 20% of lysine was lost at 40 C at 46 hours, the near perfect fit of the Arrhenius plot (r=0.999) indicates some confidence in the E_a value. The computed first half-time (Table 1) was close that observed in Fig. 3 for 50 C and 60 C but appeared to be low for 40 C. If this was rectified by using all data points for 40 C, then an E_a of 55.6 kcal/mole was estimated and was rejected because it is an unusually large value. The plot shown in Fig. 23 is a reasonable compromise. This was computed on the basis of all data points for 40 C and 50 C which show reasonable linearity. For 60 C, only the last data point which deviates too much from the first linear phase was omitted. On this basis an E_a of 45 kcal/mole and a Q_{10} (50 C) of 8.5 was computed (Fig. 23). The computed half-times (Table 1) were however, much higher than observed values for 50 and 60 C. If all data points at 40 C, 50 C and 60 C are used, a low E_a of 28 kcal/mole was estimated but would not be justified due to gross deviation of the last data point at 60 C. The probable reasons for nonlinear behavior of solid compressed systems at low a_w have already been described under METHODS. To emphasize, these include high diffusional resistance
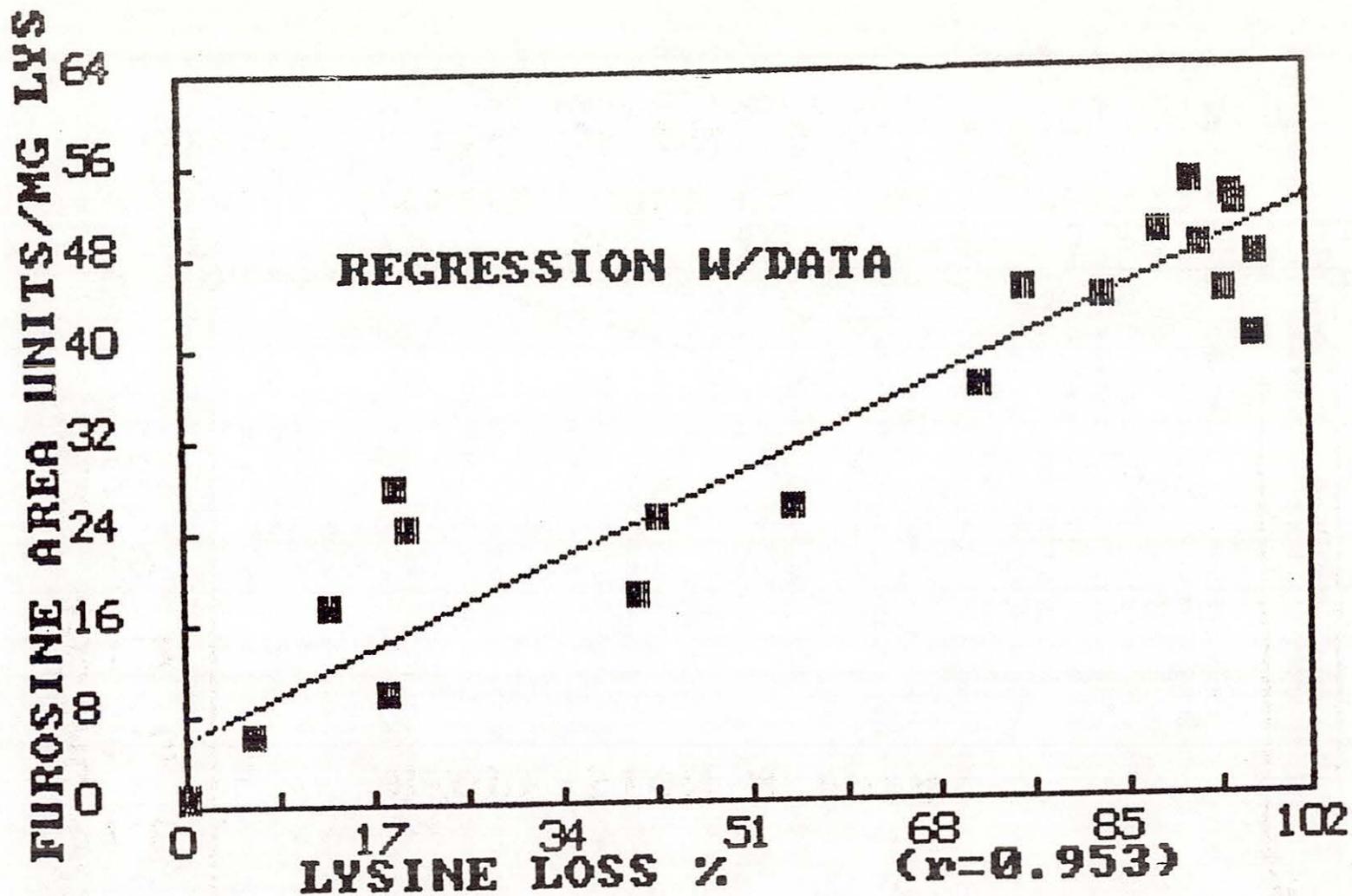
Figure 21.   Correlation between the increase in furosine and the decrease in lysine with time
with pooled data from all temperatures (40, 50 and 60 C) in the lysine-glucose-
cellulose model at a_w 0.23 (r=0.953).
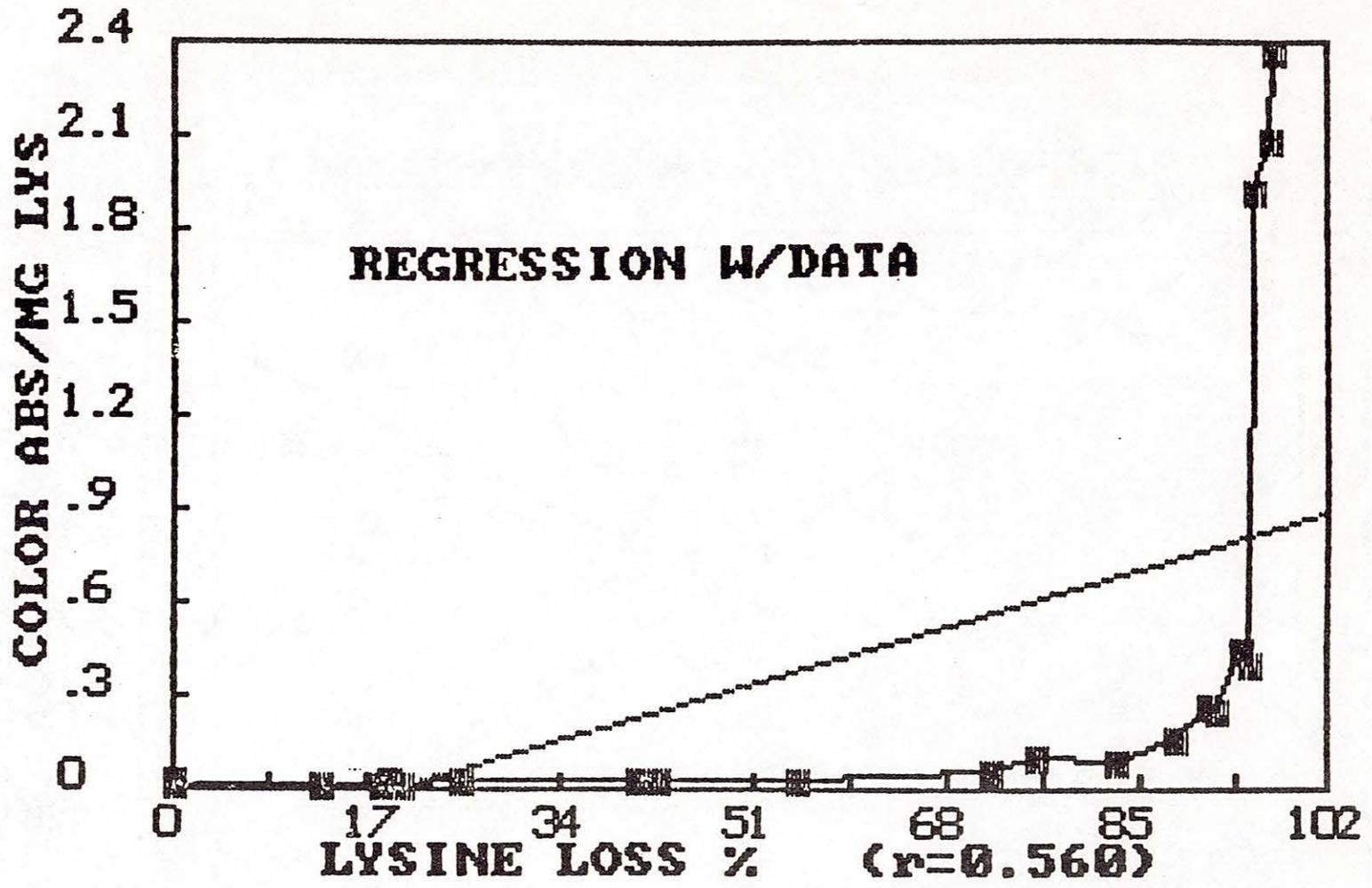
Figure 22. Correlation between the increase in color and the decrease in lysine with time with pooled data at all temperatures (40, 50 and 60 C) in the lysine-glucose-cellulose model at a_w 0.23 (r=0.560).
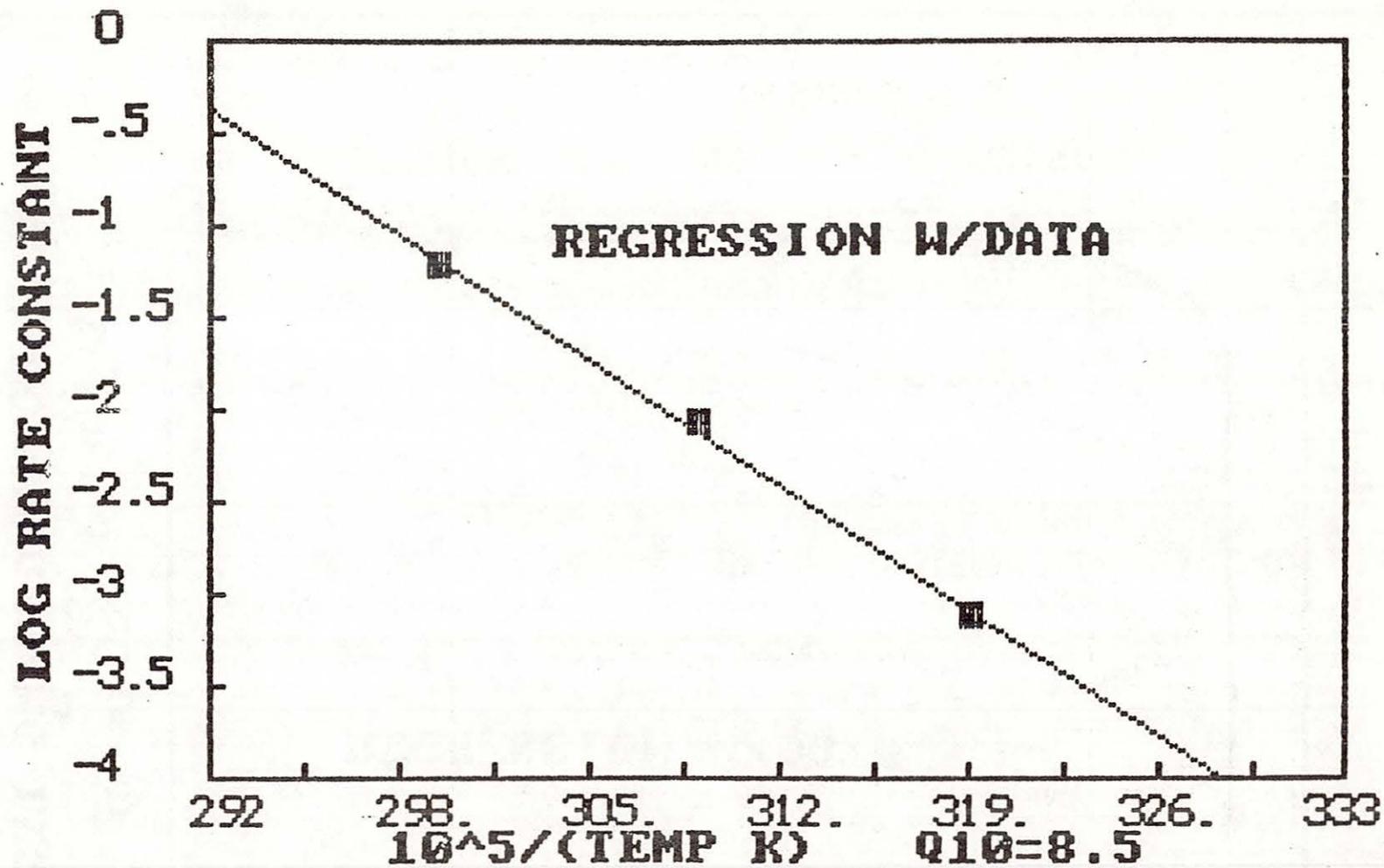
Figure 23. Effect of temperature (40, 50 and 60 C) on lysine degradation in the lysine-glucose-cellulose model at a_w 0.23 vs 10^5/temperature K shown yielded an E_a of 45 kcal/mole and Q_{10} of 8.5.

TABLE 1. First Order Rate Constants and Estimated First Half-times
at 40, 50, and 60 C

Temperature (°C)	Time Interval Hr	No. of Data Points	Regression Coefficient	Rate Constant (Hr -1)	t 1/2 Hr Computed	t 1/2 Hr Observed
40	0-46	3	-0.988	0.0049	140	
40	0-70.5	4	-0.890	0.0030	230	
40	0-142	5	-0.861	0.0017	400	>300
50	0-8	3	-0.991	0.066	10.5	
50	0.12.5	4	-0.996	0.065	10.6	10
50	0-24	5	-0.991	0.054	13	10
50	0-48	6	-0.967	0.037	19	10
50	0-97.5	7	-0.949	0.024	29	10
50	0-119	8	-0.971	0.023	30	10
50	0-143	9	-0.961	0.020	34	10
60	0-3	3	-0.998	0.47	1.5	1.2
60	0-5	4	-0.996	0.47	1.6	1.2
60	0-7	5	-0.988	0.37	1.9	1.2
60	0-12	6	-0.948	0.26	2.7	1.2
60	0-24	7	-0.872	0.14	5.0	1.2
60	0-96	8	-0.601	0.025	27	1.2

due to a tightly bound water layer restricting the mobility of reactants, zonal effects and selective inhibition spots. A highly compressed solid system at a low a_w is far different from a homogeneous reaction perform- ed with constant mixing provided by a shaking incubator or a stirrer under rather ideal conditions. It is therefore, clear that marked nonlinearity of the first order plots can cause substantial errors in the estimating of rate constants, and consequently, of E_a and Q_{10} values.

Since a poor fit was obtained by first order kinetics, an attempt was made to determine whether the second order plot would produce a better fit of the data. Further, approximate calculations of half-times values esti- mated from the 50 C and 60 C rate curves (Fig. 3) or from attempted fit of data (see METHODS) suggested that the reaction was possibly of the second order (equation 10). From Fig. 24, it is once again seen that a straight line fit is not obtained, especially at 60 C. Based upon the initial por- tion of the curves (24 hours at 50 C and 7 hours at 60 C) an E_a value of 39.4 kcal/mole and a Q_{10} (50 C) of 6.4 was estimated.

Labuza and Riboh (1982) have computed that, for up to 50% loss, the statistical difference between zero and first order for computed losses of nutrients is small (Labuza, 1979). Further, at 50% loss, the error in rate constant, due to analytical precision of measuring nutrients from $\pm$ 2 to $\pm$ 5%, ranges from 6 to 15%. The combined error for calculated E_a for food deterioration reactions due to analytical precision and the error in choosing the appropriate order of the reaction was shown by them to be about $\pm$ 25%.

Based upon the linear portions (46 hours at 40 C; 12.5 hours at 50 C and 3 hours at 60 C) of the lysine loss rate curves (Fig. 3), the zero order rates constants were also computed. This resulted in an E_a esti- mate of 41.6 kcal/mole and a Q_{10} (50 C) of 7.1.

It is not intended here to suggest that comparisons of E_a values derived from different orders of the reaction is appropriate for chemical reactions carried under near ideal conditions. However, in view of the nonlinear behavior of the present heterogeneous model, it was considered a permissable and useful exercise. There are instances in the literature, such as the hydrogen-bromine reaction where the rate expressions are of such complex type that the concept of reaction order does not apply (Frost and Pearson, 1953).

The activation energies for lysine loss in food and model food systems reported in the literature vary over a wide range of 10-38 kcal/mole (Labuza and Saltmarch, 1981). The present study is based upon a lysine model and is different from previous studies where only the epsilon amino group is free for reaction with reducing sugars. In lysine, from a theore- tical standpoint, as many as four glucose moles can react with each mole of lysine. Whether this will have any effect on activation energies is
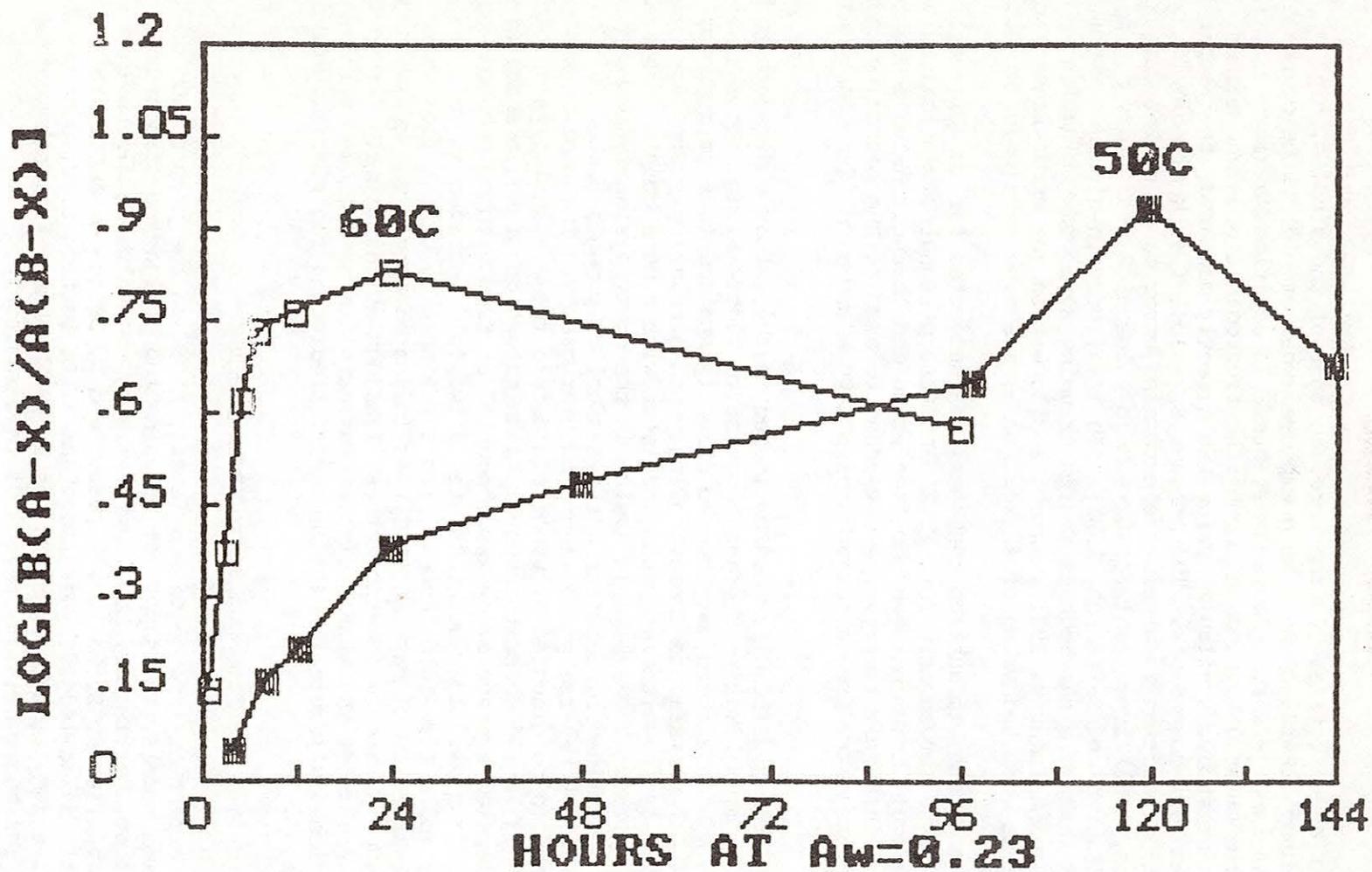
Figure 24. A plot of the second order function (see figure above and METHODS) vs time for the lysine-glucose-cellulose model at 50 and 60 C and a_w 0.23.

not clear at this time. Furthermore, in most of the studies, high temperatures (80-184 C) have been employed where rapid lysine degradation can cause large errors in rate constants. In addition, available lysine has been estimated by bioassay or by the fluorodinitrobenzene method. In the present study, available lysine was directly measured after separation of the Amadori components. The present E_a value of 45 kcal/mole for a first order reaction is within the estimated error range of 25% (Labuza and Riboh, 1982) from the literature high value of 38 for a dry cod muscle system (Labuza and Saltmarch, 1981). In a soy protein-glucose system, an E_a of 35 kcal/mole has been estimated assuming zero order kinetics (Labuza and Saltmarch, 1981), which is also within the error range from the present computed value of 42 kcal/mole, assuming zero order kinetics.

One possible explanation that has been suggested for the high activation energy observed here (Dr. F. W. Robbins, personal communication) is that the equilibrium between the free amino and the protonated amino form of lysine is highly temperature dependent because of the necessary change in stereochemistry from a tetrahedral SP_3 to a trigonal SP_2 configuration.

The large Q_{10} (50 C) values estimated in this study underscore the importance of minimizing storage temperature fluctuations in the handling of foods. Before these data can be directly applied to food systems, it is essential to validate these findings with a relatively simple N-α-acetyl-lysine-glucose system and later with a more complex protein-glucose system. The available lysine in the acetyllysine system can be readily determined by separating the Amadori components either by ion-exchange or by reverse phase liquid chromatography. The protein systems would have to be digested by proteases before the available lysine can be resolved by liquid chromatography. As an extention of the present work, an accelerated storage study was conducted at 52 C with compressed yogurt bars for 14 days. The data indicated a two-fold increase in reducing capacity and a five-fold increase (in furosine area units) from their initial values in 14 days at 52 C. As indicated above, the present model is not appropriate to interpret these findings at this time. Currently, studies are under way with a simple N-α-acetyllysine-lactose-cellulose model which may provide a rapid means of predicting the stability of dairy products.

ACKNOWLEDGEMENTS

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TITLE: A Comparison of Different Methods for Uncovering Sensory
Attributes of Ration Components

RICHARD D. POPPER, DR.* AND EINAR RISVIK, MR.

ABSTRACT: .

Two multivariate statistical techniques, multidimensional scaling and
partial least squares regression, were applied to the problem of identifying
the sensory attributes of foods. The techniques are illustrated by an
analysis of data on the sensory characteristics of food bars. In Experiment 1,
trained sensory panelists judged 12 food bars (8 commercial bars and 4 military
ration bars) on 31 sensory attributes. In Experiment 2, untrained subjects
first judged the dissimilarity among food bars without using predefined
sensory attributes, and then judged the bars on the same attributes the trained
panelists used. Multidimensional scaling was used to identify the sensory
characteristics that most distinguished the bars, and partial least
squares regression was used to relate these characteristics to the physical
and chemical properties of the bars. Other potential applications of these
statistical techniques are discussed.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Research Psychologist, Human Engineering Branch,
Behavioral Sciences Division, Science and Advanced Technology Directorate
PAST EXPERIENCE: Research Associate, Psychophysics Laboratory, Columbia
University
DEGREES HELD: B.A. Philosophy, Columbia University; M.A. Psychology,
Columbia University; Ph.D. Psychology, Columbia University.

A COMPARISON OF DIFFERENT METHODS FOR UNCOVERING SENSORY ATTRIBUTES
OF RATION COMPONENTS

RICHARD D. POPPER, DR. AND EINAR RISVIK, MR.

Introduction

Multivariate statistical techniques comprise a class of procedures whose main purpose is to abstract from a large amount of data the few important relationships among the variables studied. Such techniques have been applied in all domains of science, including the natural and behavioral sciences as well as history and archeology. The area of food research constitutes a natural application for many of these methods, because of the many variables that enter into the data base that a food researcher must consider. This data base spans several scientific domains, from microbiology, chemistry, and physics to physiology and sensory psychophysics. In each domain information is often collected on a large number of variables.

The present paper is concerned with methods for identifying sensory attributes of foods, applied in particular to the study of food bars. The objective of each of the methods discussed is to uncover the salient relation-ships among the sensory attributes and among the products studied in order to characterize the essential similarities and differences among the products. Such a characterization can play an important part in the development of new products and in their continued improvement. Portions of the results reported here have been reported by Briggs et al. (1) and by Risvik and Cardello (2). The emphasis of the present paper is on the illustration of the multivariate techniques rather than on the evaluation of any specific food item.

Why Study Food Bars?

The need for military rations that are light and compact has led to the development of a number of ration systems that include food bars as important components. The Nutritional Sustainment Module (1) consists of a number of different bars (for example, an Almond Dairy Bar and a Nacho Crunch Bar) engineered to be high in caloric density. The 30-Day Light Weight Ration (3) also contains a variety of food bars, in the form of dessert bars (for example, an Apple Cinnamon Bar) and bread-alternative bars (for example, Pizza Crisp) among others.

Food bars have also been available commercially to the consumer. They have been variously marketed as breakfast bars, quick-energy boosts, or as more nutritious alternatives to the typical candy bar. One question to be addressed here is how the sensory characteristics of the military ration bars compare to the commercial ones.

Approximately 50 commercial bars were considered for investigation, as were bars currently under development by the U.S. Army and intended for future ration systems. Among these 50 bars, 12 bars (8 commercial, 4 military) were selected for inclusion in the study and are listed in Table 1. The selection process consisted of identifying a manageable number of products that were judged informally to represent the widest range of products considered.

TABLE 1. Food Bars

1. APPLE SPICE ENERGY CRUNCH BAR
2. NUTTIN' BUT NATURAL BAR
3. APPLE CINNAMON GRANOLA CLUSTER
4. PLANTER'S JUMBO BLOCK
5. QUICK GAIN BAR
6. CARNATION BREAKFAST BAR
   (CHOCOLATE CHIP)
7. APPLE CINNAMON BAR (RATION)

8. PIZZA CRISP (RATION)
9. NACHO CHEESE CRUNCH
   (RATION PROTOTYPE)
10. FIGURINES DIET BAR (VANILLA)
11. APPLE BAKES
12. ALMOND DAIRY BAR
    (RATION PROTOTYPE)

An Example of Multidimensional Scaling

Various descriptive methods have been developed for the purpose of characterizing sensory attributes (for reviews, see Powers (4) and Pangborn (5)). Wine tasters and perfumists practice a form of descriptive analysis when they apply an elaborate nomenclature system to the description of their respective products. Highly structured and systematized descriptive methods have been developed and are used by the food industry and others in the sensory evaluation of their products. In these procedures, a sensory profile of a product is developed by having trained judges rate the product on a multitude of different sensory dimensions. The sensory profile, based on the average ratings of the judges, constitutes the description of the product.

The development and continued popularity of the profiling method attests to the need in sensory analysis for ways to capture the multidimensional or multi-attribute quality of foods. However, sensory profiling by itself is often not sufficient if the goal is to discover the relationships between sensory attributes or the differences and similarities between products. The reason for this is that a single profile may consist of as many as 30 to 40

attributes, and for a large number of products these profiles can differ in many ways. In such cases, the underlying organization in the data cannot be obtained from a visual inspection of the profiles; rather, some data-analytic method is necessary to extract such relationships statistically. Thus, sensory profiling is commonly followed by one of a variety of multivariate techniques of data reduction and analysis (4). One such method is that of multidimensional scaling (6,7).

The rationale underlying multidimensional scaling is best understood through an example. Fig. 1 shows a map of the United States on which are located a number of cities; also shown are the intercity airline distances. Given the map and a ruler, it is a simple matter to obtain the intercity mileages by measuring the distance between the points on the map. Multi-dimensional scaling reverses this process. Given as input the intercity distances, the multidimensional scaling algorithm will construct a map depicting the locations of the cities.
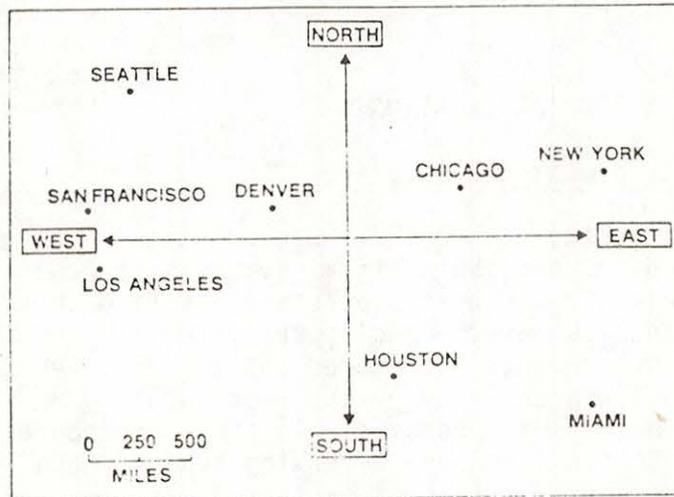
(A) LOCATION OF SELECTED U.S. CITIES

CITIES	CHIC.	DENV.	HOUS.	LA.	MIAMI	N.Y	S.F.	SEAT.
CHIC.		920	940	1745				
DENV.	920		879	831			ETC.	
HOUS.	940	879						
L.A.	1745	831						
MIAMI								
N.Y.		ETC.						
S.F.								
SEAT.								

(B) INTER-CITY AIRLINE DISTANCES

Figure 1.   Intercity distances and their geometric representation.

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In applying multidimensional scaling to the profile data, the objective is to obtain a spatial representation of the similarities and differences among products. This spatial representation takes the form of a map on which the products are positioned in such a way that the similar products are close together and the different products far apart. Thus, the products correspond to the cities on the map of the United States, and the size of the product differences correspond to inter-city distances. All that multidimensional scaling requires for constructing such a map is the equivalent of the inter-city mileage chart: a measure of the differences between the products. This information can be obtained from the sensory profiles using a method described below. The profiling and subsequent multidimensional scaling of food bars is illustrated in the first experiment.

Experiment 1: Profiling and Multidimensional Scaling of Food Bars

Subjects: Eight subjects were recruited to form a sensory panel. Their prior experience with sensory profiling ranged from considerable to none. However, all subjects participated in several training sessions. In these sessions, the meanings of the sensory attributes were explained, in some cases by having subjects taste substances (for example, quinine) that typified the sensory attribute in question (bitter). In addition, subjects rated samples of food bars (not the ones included in the study proper) and discussed their ratings afterwards. These discussions were intended to establish a consensus in the interpretation of the attributes when applied specifically to food bars and in the use of the numeric scale used for making the ratings.

Sensory Attributes: Prior to the training sessions, the sensory panel was asked to generate a list of sensory descriptors applicable to food bars, based on a range of samples. A subset of 31 sensory attributes was culled from this list and literature sources. The final list was organized into separate sections describing visual appearance, flavor, and texture attributes.

Procedure: Samples of the 12 food bars were evaluated along each attribute using a 10-point category scale of intensity, ranging from 0 to 9. The number "0" was labelled "none" and indicated the complete absence of the attribute in the sample rated; the numbers "1" and "9" were labelled "low" and "high", respectively. Samples were identified to the subject by code number only. Three samples of each food bar were presented in a random order over several sessions.

Results and Discussion: As an example, the average profile for one of the commercial products, the Apple-Cinnamon Granola Cluster, is shown in Fig. 2 The attribute ratings indicate that the bar has a rough outer surface (a visual characteristic), has a predominantly sweet taste, fruity, nutty, and cereal flavors, and a grainy texture while being chewed.

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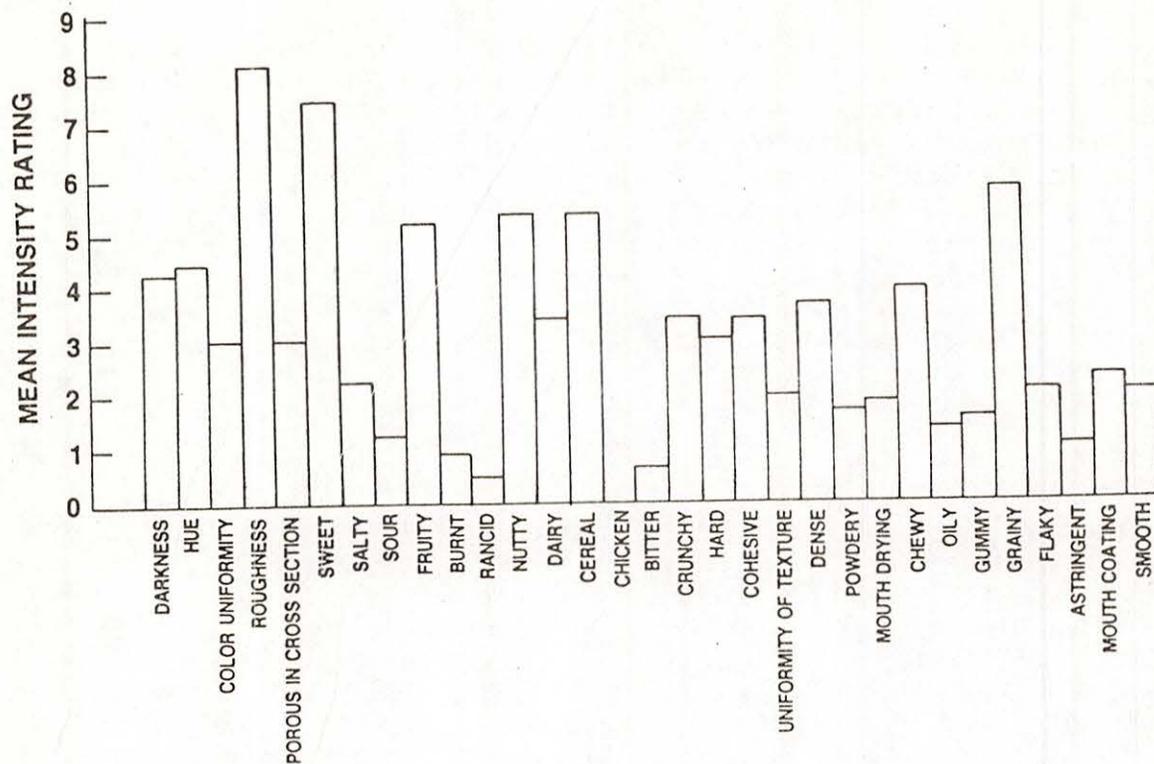
Figure 2.   Sensory profile of Apple Cinnamon Granola Cluster

In order to apply multdimensional scaling (MDS) to the data, a measure of the differences between two food bars was required. The profile data were used to calculate such a distance measure between food bars by considering each sensory attribute as a separate spatial dimension and applying the Euclidean distance formula (8). This formula computes the overall distance between two food bars by considering the difference between the bars on each individual attribute, squaring that difference and summing the squared differences over all attributes. Before computing the Euclidean distances in this way, each subject's ratings on an attribute were standardized. This step reduced the amount of noise in the data and led to a more interpretable solution.

The multidimensional scaling of the food bars was accomplished using the program KYST (9). The program allows one to choose the number of dimensions for the solution and provides an index of the degree of fit between the data and the spatial representation. A three-dimensional solution was chosen because it gave a good fit statistically, although the third dimension was not very interpretable.

Fig. 3 shows the location of the food bars in the first two dimensions of this solution. The Nacho Crunch and Pizza Crisp are located in the upper right quadrant; the others are arranged along the minor diagonal of the space, with Apple Bakes located in the upper left and the Almond Dairy Bar in the lower right. Note that the only two products falling into the lower right quadrant are the Vanilla Bar and the Almond Dairy Bar.
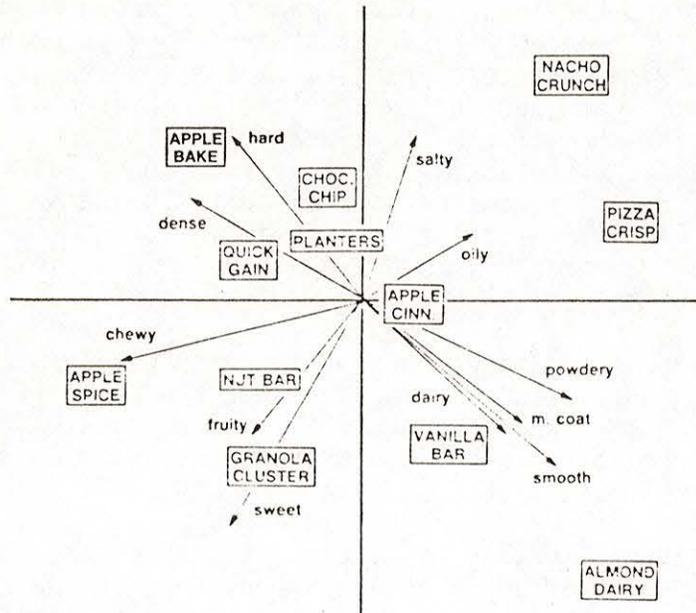
Figure 3. MDS plot based on sensory profiles.

An interpretation of the spatial arrangement shown in Fig. 3 requires one to impart meaning to the dimensions comprising the space. The meaning of the north-south or east-west dimensions is far from evident, but the directions along the diagonals can be interpreted based upon a familiarity with the bars. (The overall orientation of the space is arbitrary and the axes may therefore be rotated). The direction from lower left to upper right seems to correspond to a flavor dimension, ranging from the sweeter bars (Apple Spice and Granola Cluster) to the saltier and more savory ones (Nacho Crunch and Pizza Crisp). The other diagonal appears to represent a textural dimension, with the smooth and mouthcoating items in the lower right, and the harder, denser items in the upper left. This dimension may be correlated with a dairy/nondairy dimension.

A quantitative interpretation of the space is possible by projecting the profile attributes from which the space was derived into the space. This is accomplished by computing the multiple regression coefficients between the dimensions of the space and the profile attributes. Following the procedures outlined by Schiffman et al. (10) and Young and Hoffman (11), the profile attributes were represented as vectors in the two-dimensional space shown in Fig. 3. The direction of a vector indicates the direction in which the attribute increases, and the length of the vector is proportional to how well the attribute fits the space. Vectors that are close to each other represent positively correlated attributes, opposite vectors represent negatively correlated attributes, and perpendicular vectors represent uncorrelated attributes. The placement of the attribute vectors supports the previous, intuitively made, interpretation. Note that the Almond Dairy Bar, a bar of high caloric density, is considered similar to the less calorically-dense Vanilla Bar, most likely on account of its similarity in texture and dairy flavor. The Nacho Crunch and Pizza Crisp are viewed as similar on account of their salty flavor.

The above analysis was based on profile ratings by trained judges. Ratings by trained judges are often needed when the sensory judgments are particularly difficult or when a product is undergoing sensory development and modification. In the latter case, the need for consistency and continuity makes a trained panel essential.

However, in other situations, the emphasis may be on what similarities and differences untrained judges, representative perhaps of the consumer population, perceive among a set of products. In that context, sensory profiling may be inappropriate, since it defines the salient characteristics for the observer in advance, thereby possibly biasing his judgment.

One alternative method to sensory profiling is direct dissimilarity rating. In this procedure, naive subjects are asked to judge dissimilarity between bars directly, using whatever perceptual criteria for dissimilarity seem appropriate to them. These dissimilarity ratings are then submitted to a multidimensional scaling analysis. The application of this method to the scaling of food bars is illustrated in the second experiment.

Experiment 2: Direct Dissimilarity Ratings of Food Bars

Procedure. Twelve subjects in this study were presented with pairs of samples of food bars and asked to rate the overall difference between the samples, taking into account all the properties of the bars that they felt contributed to their difference. The same food bars were used as in Experiment 1. Subjects were presented once with each of the 66 pairs of samples constructible from the 12 bars and rated the difference between samples by making a hash mark on a line whose left and right endpoints were labelled "no difference" and "extremely different", respectively. None of the subjects had previous experience rating food bars.

After completing the difference ratings, subjects were presented with one sample of each food bar and asked to rate the sample using the profile attributes that the trained panelists had used.

Results and Discussion. The graphic ratings were transformed to numerical values by measuring the distance of each hash mark from the left endpoint of the line. These values were then averaged and submitted to KYST for multidimensional scaling. Fig. 4 shows the first two dimensions of a three-dimensional solution. The overall pattern is similar to that found on the basis of the profile ratings, showing the Nacho Crunch and Pizza Crisp off to one side and the other bars group predominantly along one dimension. The Vanilla Bar and Almond Dairy Bar are at the bottom of this group, and Planters and Apple Spice at the top.
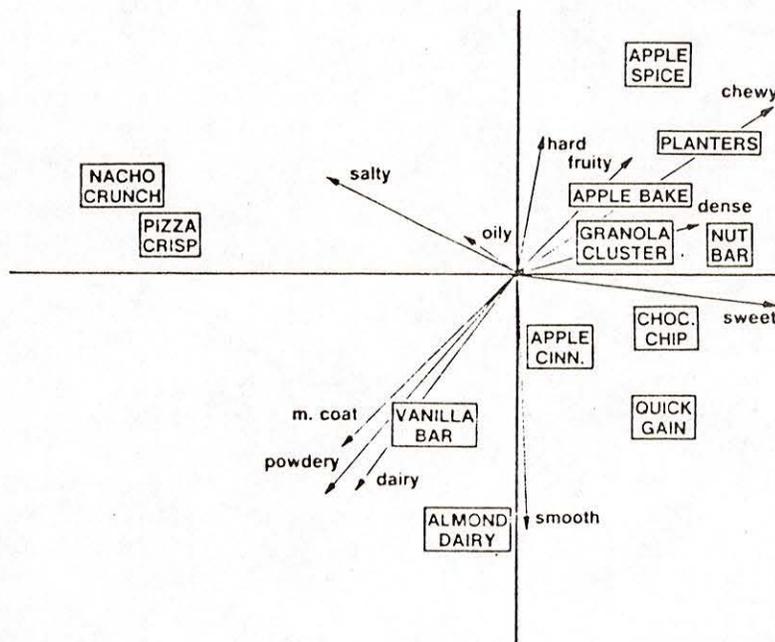
Figure 4. MDS plot based on dissimilarity ratings.

Multiple regression analysis was again used to project the product attributes into the multidimensional space, using the attribute ratings provided by the naive subjects at the end of the experiment. The major directions in this space correspond to those obtained with the trained panelists: one direction corresponds to flavor (sweet vs. salty), the other to texture (chewy vs. powdery/mouthcoating).

While the placement of the bars along these directions shows some similarities, there are also many differences whose nature is difficult to characterize. However, the existence of such differences is not surprising in light of the different procedures used for generating the multidimensional solutions. Several methods exist (10,11) for determining statistically the agreement among dimensional solutions such as those shown in Fig. 3 and 4, and these methods could be applied to further investigate the differences between the judgments of trained and untrained observers.

It should also be obvious by now that the process of interpreting a multidimensional space, although aided by statistical techniques, is not precise and leaves much to the discretion (and imagination) of the investigator. Sometimes the only clearly interpretable differences are the obvious ones. The interpretation can be especially problematic in situations where many of the sensory attributes involved are highly correlated. The Almond Dairy Bar, for example, was perceived as smooth and mouthcoating in texture and having a dairy flavor. Other bars consisted of other, equally unique combinations of sensory attributes. The presence of such complex intercorrelations makes it difficult to extract one or two orthogonal dimensions in a multi-attribute space.

Relating Sensory Attributes to Chemical Characteristics

So far, the sensory attributes of the food bars have been considered without reference to any physical or chemical attributes of the bars. Often it is desirable to relate these two kinds of attributes to each other. This can lead to an understanding of what chemical properties are important to the sensory experience and can also suggest what effect changes in the chemical properties might have on sensory characteristics. The chemical properties also provide information about the objective similarities and differences among food bars. This can be demonstrated by a multidimensional scaling analysis of the chemical properties.

In the present study, each bar was submitted to chemical and other instrumental analyses which yielded measurements on 14 variables (for example, carbohydrate content, sodium content, etc.); these measurements constitute an instrumental profile for each bar. After standardizing the variables in order to equate the units of measurement, these profiles were subjected to multidimensional scaling. Fig. 5 shows the result: a pattern quite similar to the previous two scaling solutions, which were based on the sensory characteristics of the bars. Clearly, the similarities and differences in the physicochemical nature of these bars largely mirror their perceptual similarities and differences. How then can one combine the information from the sensory and chemical domains in order to assess the relationships between the specific instrumental and sensory variables?
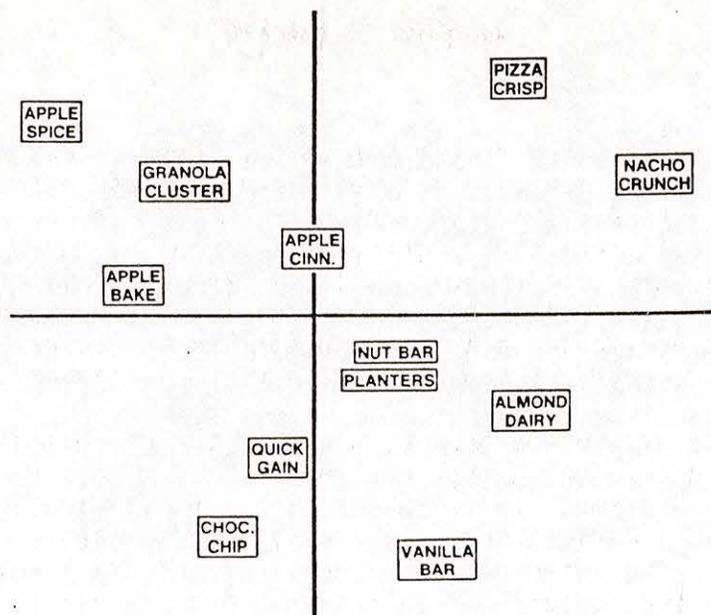
Figure 5. MDS plot based on chemical/instrumental measures.

One approach (8, 10) is to use multiple regression to project the chemical properties into the multidimensional space derived from the sensory analysis. Another, quite different approach, is to use both the sensory and chemical properties to derive a "psycho-chemical" space. This can be accomplished using Partial Least Squares Regression (12,13), a relatively new technique, which is applied here using the chemical properties together with the sensory profiles provided by the trained judges.

Partial Least Squares (PLS) Regression yields two kinds of plots. The first type of plot is identical in nature to the plots obtained with multidimensional scaling. Fig. 6 shows the location of the food bars in the case of a two-dimensional solution.
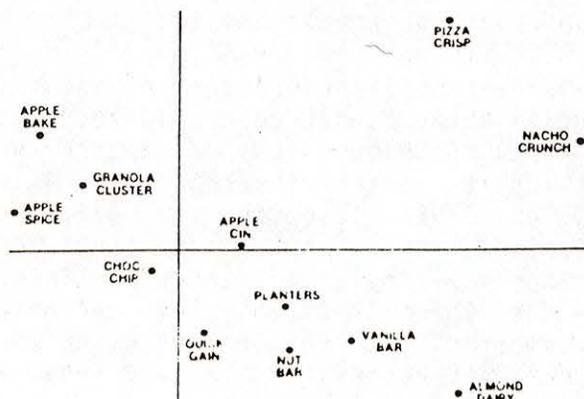
Figure 6. PLS plot based on sensory and chemical profiles.

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In addition, PLS provides a plot that depicts the location of the attributes in relation to the dimensions. Fig. 7 shows the results for a selected number of the chemical and sensory attributes. In this figure, it can be seen that sodium content and the perception of saltiness are positively related and together define the region in the upper right hand corner where both the Pizza Crisp and the Nacho Crunch were located in the previous figure. The attributes dairy, smooth, mouthcoating, and oily are grouped near the instrumental measures of fat content and caloric density; these attributes together define the region on the far right. Carbohydrate content is negatively correlated with fat content and is located in the upper left corner. No chemical/instrumental measures were included that captured the textural attributes of hard and dense.
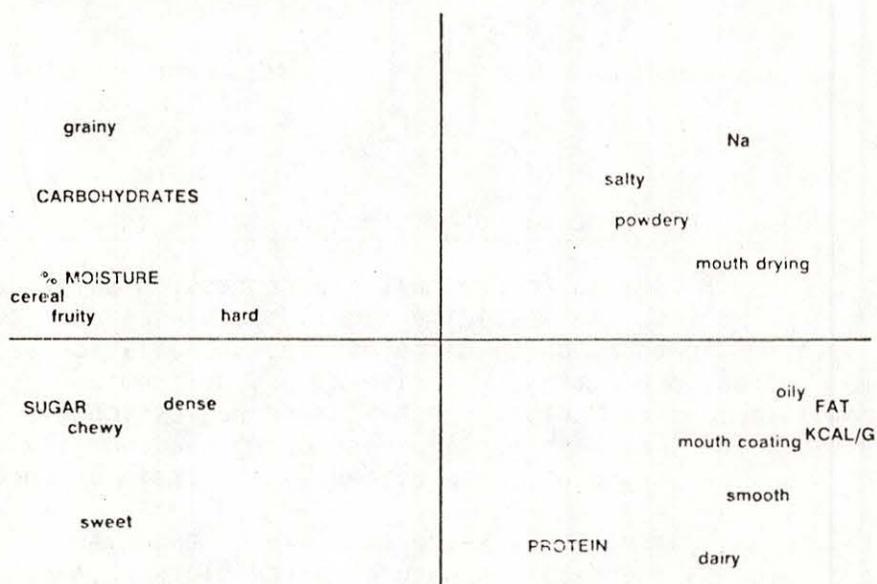
Figure 7. PLS plot of sensory and chemical/instrumental attributes.

Practical Applications of Multivariate Techniques

Several methods have been outlined for identifying sensory attributes; however, attribute identification is not an end in itself. The results from such analyses have been applied to the study of sensory systems, to process and product development, and to market research (14). Analyses such as those presented here can also be used for selecting from a large number of sensory attributes those important ones that should be included in future descriptive analyses of the product domain. While the food bars differed on almost all the profile attributes used, the multidimensional scaling and PLS analyses point to a subset of attributes that are more important than others in describing overall product differences.

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One important question in the application of these scaling techniques is how the sensory and chemical attributes relate to peoples' preferences for different products. This is a critical question for the developer of military rations who wants to know how to change a property of a ration component so as to alter its sensory characteristics and thereby enhance its acceptance by the soldier.

The acceptance of the food bars was determined by asking the untrained subjects in Experiment 2 to judge the acceptance of each bar on a 9-point hedonic scale ranging from "dislike extremely" to "like extremely". No simple relationship was found between the acceptance of the bars and the sensory attributes or the dimensions of the multivariate space. However, it was noted that the Nacho Crunch, a component of the proposed Nutritional Sustainment Module, was considered less acceptable by these subjects than other military ration components that were tested. In particular, the acceptability of the Nacho Crunch was in contrast to the high acceptability of Almond Dairy Bar, another of the components of the Nutritional Sustainment Module. Both components are high in caloric density. It may be that, for whatever reason, a high concentration of fat is more acceptable in a dairy-flavored, yogurt-type product than in a salty one. It is also the case that the Nacho Crunch was unique in that it was rated the most oily of all the bars. Thus, one could try to improve the acceptability of the bar by masking or reducing its oilness.

Another application of these techniques, not yet attempted, is the design of entire ration menus. One concern in the design of a ration system is that there be sufficient variety from meal to meal, so as to forestall the onset of monotony that may occur with prolonged consumption of the ration. Of particular importance is the variety in the entree, which is perceived as the central component of a meal. Ratings of the overall similarity and differences among a large number of entrees could be collected, and these ratings analyzed via multidimensional scaling or partial least squares regression. In the multidimensional space, entrees highly similar to each other would be clustered together. One could then try to compose a ration by selecting entrees from different and distinct clusters so as to maximize the dissimilarity, and thereby variety, among the entrees in the ration.

The scaling methods that have been discussed also have application outside the areas of food and flavor research. For example, consider the problem of sustaining an individual in an artificial, climatically controlled environment, for example a shelter. What are the important determinants of perceived air quality? There are several dimensions to consider: ambient temperature, humidity, air flow, chemical composition, and odor characteristics. How do these dimensions interact to create the most acceptable air quality? These problems are, in principle, amenable to analysis by the methods reviewed here.

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TITLE: Use of Polyamide Fluorescence Comparative Stability Tests and Sensory and Acceptance Evaluations in Storage Life Tests for Oils in the Food Emulsions: Mayonnaise and Salad Dressing

WILLIAM L. PORTER,* E.D. BLACK, C. SHAW, J. JARBOE, AND C.P. DUNNE

ABSTRACT:

Measurement and extension of stability of salad dressing is of financial and logistical importance to the military. Polyamide coated plates develop characteristic fluorescence when exposed over cobalt- and heat-accelerated oxidizing sald oil extracted from mayonnaise and salad dressing, at the onset of rapid phase oxidation and rancidity. Solid sample techniques permit measurement of the course of oxidation and comparative accelerated stability (ASL) of salad dressings. The following conditions were compared using oils stored three and six months: hydrogenated versus nonhydrogenated salad oils, mayonnaise versus salad dressing, 21°C versus 38°C, glass versus plastic jars.
In all cases, hydrogenated oils extracted from stored mayonnaise or salad dressing showed greater ASL than nonhydrogenated oils. Similarly, in almost all cases, oils from stored mayonnaise showed greater ASL than those from salad dressing. Generally, oils from mayonnaise or salad dressing stored at 21°C showed greater ASL than those stored at 38°C. Finally, storage in glass jars resulted in greater ASL in a majority of cases. The fluorescence ASL test separated hydrogenated from nonhydrogenated oils more strongly than sensory and classic chemical tests, whereas sensory and chemical tests more sharply discriminated glass from plastic containers. Comparative tests on four samples are complete in three hours. Fluorescence tests on unextracted emulsions are also possible.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Research Chemist, Biological Sciences Division, Science & Adv. Tech. Dir., Natick Research, Development & Engineering Ctr.
PAST EXPERIENCE: Airline Meteorologist, Braniff Airlines, Dallas,TX, 1946-1947. Research Meteorologist, Cameron Station, VA, 1952-1953. Research Meteorologist, U. S. Army Natick, RD&E Center, Natick, MA, 1953-1964. Research Chemist, U. S. Army Natick RD&E Center, Food Chemistry Division, Natick, MA, 1964-1974.
DEGREES HELD: Bachelor of Arts, Oberlin College, 1938. Master of Science, University of Chicago, 1951. Doctor of Philosophy, Harvard University, 1962.

USE OF POLYAMIDE FLUORESCENCE COMPARATIVE STABILITY TESTS AND SENSORY AND
ACCEPTANCE EVALUATIONS IN STORAGE LIFE TESTS FOR OILS IN THE FOOD
EMULSIONS: MAYONNAISE AND SALAD DRESSING

PORTER, W. L., BLACK, E. D., SHAW, C. P., JARBOE, J. & DUNNE, C. P.

INTRODUCTION

The Problem. Measurement and extension of stability of soybean oil
based salad dressing is of financial and logistical importance in military
food supply. This study was undertaken to determine the effect of hydro-
genation of salad oil, which is a relatively expensive procedure, on stabi-
lity of mayonnaise and spoonable salad dressing made from the oil. Polya-
mide fluorescence resulting from reaction with oxidized volatile compounds
was used as an accelerated comparative stability test in conjunction with
actual storage of the salad dressings at expected warehouse temperatures.
Peroxide values and a flavor-quality trained sensory panel as well as a
consumer acceptance panel were also employed in evaluation.

Backgound. The military currently purchases about 800,000 gallons of
spoonable salad dressing per year at a cost of about $2,500,000 (6). The
majority of this is in large metal cans. The dressing is quite acidic (pH
3.5 to 4.0) and is very close to coated metal surfaces of the lid or can.
These facts and particularly the emulsion form and the high polyunsatura-
tion of the soybean salad oil, result in the dressing's relatively low
stability to oxidative rancidity and reversion flavor. However, it is
designated semiperishable and kept in nonrefrigerated warehouses. Such
instability necessitates a five month rotation, frequent inspections and
sensory and chemical evaluations, all of which are expensive compared to
other semiperishable items. A current remedy is (Federal Specification
EE-M-131G) partial hydrogenation of soybean (the major salad oil for the
military), reducing linolenic acid content from about 7% to 3.0%, an
expensive procedure. The dressing's short rotation time is also expen-
sive. The extended military logistics chain may result in products
arriving at overseas locations with most of the nominal shelflife expired.
There has even been considered a designation as a perishable item, necessi-
tating expensive refrigerated storage.

The Cooperative Storage Test. Under the auspices of Ms. Barbara
Preston of the Association for Dressings and Sauces, a cooperative test
was arranged, by which the Lexington, NC plant of Hudson Industries, Inc.

prepared mayonnaise and spoonable salad dressings made either from partially hydrogenated soybean oil to meet the requirements of Fed. Spec. EE-M-131G, or nonhydrogenated oil. Both clear glass jars and plastic jars were used, with storage and sensory evaluation originally planned for 40°, 70° and 90°F (5°, 21° and 32°C) at cooperating facilities, of which U. S. Army Natick Research, Development and Engineering Center, Food Engineering Directorate was one.

TEST DESIGN AND MEASUREMENT METHODS

Preparation of Salad Dressings and Storage Test Design. Mayonnaise and salad dressing were prepared from standard ingredients by standard methods (Fed. Spec. EE-M-131G), including metered mixing and nitrogen sparging before the colloid milling stage, although screw tops were attached in an atmosphere of air. No EDTA or antioxidants were added. As noted above, both partially hydrogenated (ca. 3-3.5% linolenic acid) and nonhydrogenated soybean oils (ca. 7-7.5% linolenic acid) were used. They were standard production oils from Cargill. Standard 1/2 gallon glass and plastic jars were used, the glass jars being sealed by hand with waxed-cardboard caps coated with some plastic at the rim. The plastic jars were sealed by heating a plastic coated aluminum liner. The mayonnaise and spoonable salad dressing were prepared at the plant of Hudson Industries, Inc., Lexington, NC. Although the exact proportions and mixing details were proprietary, the following is an estimate of approximate proportions conforming to Federal Specification EE-M-131G, July 24, 1979. Mayonnaise, Type I: soybean oil (80%), sucrose (8%), egg yolk (7%), water and vinegar (4%), and salt (1%). Spoonable salad dressing, Type II: soybean oil (35%), vinegar (21%), water (20%), sucrose (15%), starch (4%), egg yolk (4%), and salt (1%).

The statistical design (Fig. 1) at Natick was planned to test the effect of salad dressing type (mayonnaise or spoonable dressing), of hydrogenation, package type (glass or plastic) and storage temperature (21°C and 38°C--70°F and 100°F) on salad dressing quality, as measured by both a trained flavor quality panel and a consumer acceptance test, by peroxide value and by the oxidative polyamide fluorescence accelerated comparative stability test. The latter is properly a comparative stability or prognostic, rather than a current abuse level test. Analysis of variance, including mean and standard deviation, was applied to the consumer acceptance data, but not to that of the flavor quality panel.

Polyamide Fluorescence Accelerated Shelf Life Test. Details of this reaction and associated accelerated stability testing have been reported (7). Glass or plastic plates coated with a thin layer of polyamide powder, commonly used for thin layer chromatography (TLC) are exposed to the vapor phase over oxidizing oils to develop characteristic fluorescence at the onset of rapid phase lipid oxidation when rancid odor also becomes

noticeable. Solid sample fluorescence techniques permit measurement of the course of oxidation and determination of comparative accelerated stability (ASL).

Several lines of chemical evidence are consistent with the hypothesis that the initial fluorescence is associated with amino-imino-propene compounds of the type formed from the reaction of malonaldehyde resulting from oxidation of unsaturated fatty acids with free primary amine groups (Fig. 2). The polyamide polymer (Fig. 3) contains about one terminal free amino group per 100 monomer units; thus the surface is reactive with several types of amine-sensitive compounds like quinones, reducing sugars and aromative aldehydes. Fluorescence emission, which for our system is initially maximal at about 430 nm for an excitation wavelength of 360 nm, can be produced by authentic malonaldehyde generated from acidified tetraethoxypropane. In addition, oxidizing sonicated soybean lecithin emulsions will not produce the fluorescence in the vapor phase if the pH of the emulsion is buffered at 9, although a plate in the oxidizing aqueous phase shows strong fluorescence. If the emulsion is titrated to pH 2.6, fluorescence rapidly appears on the plate in the vapor phase. The pH of malonaldehyde is 4.65 and it is therefore not volatile in alkaline conditions. However, the fluorescence emission maximum undergoes a red shift from 430 nm to about 455 nm during oxidation, which is hardly consistent with the generation of a single, stable fluorephore.

The fluorescence of the indicator plate can be measured by standard solid sample fluorescence spectrophotometry techniques like those developed by Sawicki and Guilbault (11, 12). Fluorescence can be measured within or over an oxidizing oil or within or over an emulsion of lipid in water provided in the latter case the pH is below 5.5. We used two instruments: 1) a Hitachi Solid Sample Holder Attachment (Fig. 4) for a Model MPF-2A HitachiPerkin Elmer Fluorescence Spectrophotometer or 2) a custom-build Solid Sample Holder for a Baird-Atomic Model SF-1 Fluorescence Spectrophotometer. Typical settings on the Perkin Elmer instrument were: excitation wavelength 360 nm producing emission at wavelength 430 nm; excitation slit width 2 nm; emission slit width 4 nm; filter 39; sensitivity setting from 2 to 4. Calibration using plates spotted with 30 µL quinine sulfate solution (1 µg/mL in 0.1N H_2SO_4) compared to the relative fluorescence intensity of known model compounds (13) suggested a sensitivity of 10 ng of the presumed malonaldehyde-amine moiety.

Oil Extraction. Oils were extracted from the stored mayonnaise samples by freeze-breaking the emulsion as described by Min and Tickner (4). Oils were extracted from the spoonable salad dressing samples by mixing with approximately a double volume of methylene chloride. The extract was filtered and the solvent removed by rotary evaporator. This procedure was necessary because freeze-breaking was unsatisfactory with the lower oil content dressings.

Peroxide values on the oils were performed in conformance with AOCS Official Method Cd. 8-53 (14).

Accelerated Comparative Stability of Oil. For the measurement of accelerated comparative stability of oils extracted from stored salad dressing, we have used a 5 μL sample of oil deposited by micropipette at the center of a typical glass-backed polyamide-coated (TLC) plate, 2 x 3 cm (LS254, with UV indicator, procured from Schleicher and Schuell, Inc.). A Teflon ring of 2 cm diameter and 2.5 mm thickness surrounds the test spot and a similar polyamide top plate covers the ring with polyamide facing the oxidizing oil (Fig. 5). The "sandwich" so constructed is secured by strips of metallized pressure sensitive adhesive tape 1.3 cm in width (Scotch Brand No. 850, Polyester Film, Silver, 3M Company). The sandwich may be exposed for periods of over a week at oven temperatures of $65^{\circ}C$ without failure. It is thin enough to be inserted in the average solid sample holder without distortion of the fluorescence focal point. We have found that readings may be dependably made through the glass backing of the receiver plate, a procedure that permits rapid removal, reading and reinsertion into the oven within one minute. Solid sample fluorometry, however, is much more sensitive to sample position than liquid cuvettes, and it is necessary to have a means of precise movement of the solid sample plate into and away from the fluorescence focal point.

For accelerated comparative stability testing, the plate which is to hold oil is pre-impregnated with cobaltous chloride hexahydrate (by dipping 1 minute in 2.5 mg/mL solution, draining and oven drying). This produces about a 30 fold reduction of induction period, from over one day at $65^{\circ}C$ for typical cottonseed oil, without cobalt, to less than one hour. Sandwiches containing oil-spotted plates, together with suitable blank sandwiches, are placed in the $65^{\circ}C$ oven, oil side down and read at zero time and intervals of 10 minutes thereafter until fully oxidized.

Consumer Panel. The consumer acceptance panel consisted of 36 randomly selected employees of Natick RD&E Center. Mayonnaise was prepared for evaluations by spreading 1 tablespoon (14 g) over a slice of bread and dividing the bread into quarters. Each panel member was given 1/4 slice of mayonnaise-coated bread. Salad dressing was prepared for evaluation by putting 1 tablespoon (15 g) over 1 oz. (28 g) of shredded lettuce for each panel member. Ratings were made on a 9 point hedonic scale in which 1 = dislike extremely, 9 = like extremely, and 5 = neither like nor dislike. Results were analyzed by product (mayonnaise or salad dressings) by an analysis of variance after each withdrawal and at the end of the study.

Sensory Panel. The trained sensory panel consisted of six food technologists who evaluated the products as is (i.e. without a carrier such as bread or lettuce). Salient characteristics and quality ratings for the products as received were established and deviations from the

established characteristics and quality ratings were recorded after each storage withdrawal. Panel members made independent ratings and then discussed them with other members of the panel. Ratings given represent a consensus of the panel members, and as such, do not lend themselves to statistical analysis.

RESULTS AND DISCUSSION

It cannot be too strongly emphasized that the results of the fluorescence test as used in this project reflect an accelerated comparative stability test, suitable for determining the relative susceptibility to future oxidative stress of two oils or whole emulsions. It is not a measure of present status, as are the peroxide values, the quality ratings of the trained sensory panel, or the acceptability ratings of the consumer panel. The fluorescence test, as used here, is used to compare stability of two oils differing in one parameter. It is not intended, in the work reported here, to be used for kinetic analysis and absolute predictive shelf-life extrapolation through activation energies to nonaccelerated conditions and lower temperatures of storage.

Typical spectra produced by the Hitachi Perkin Elmer instrument are shown in Fig. 6, for linolenic acid, and in Fig. 7 over oxidizing, rancid potato chips and freeze-dried carrots. Similar spectra result when recorded on the Baird Instrument, but the double monochromator grating of the latter suppresses the pattern of diffraction bands seen for all powder samples with the Perkin Elmer.

For an internal standard on the Perkin Elmer instrument, we have been able to use the filter-suppressed scatter residual of the 360 nm excitation peak. From this we have derived a fluorescence index (F. I.), the ratio of emission intensity at 430 nm to that of the suppressed 360 nm scatter peak. The latter is observed to decrease as fluorescence increases, thus enhancing the F. I. increase, perhaps because the powder particles become coated with absorbing fluorescent compounds, with resulting loss of scatter and Raman peak intensity. The 390 nm cutoff filter was not available to us on the Baird instrument, and we resorted to a fluorescence index derived from emission peak height divided by the intensity at the valley between the scatter peak at 360 nm and the true fluorescence peak.

Both of these types of fluorescence index are highly reproducible for a given level of fluorescence, providing the plate is reproducibly positioned at the excitation beam focal point. Since for quantification we sought an event marker, the time to the end of the induction period for oxidation of lipids and appearance of carbonyl compounds and rancidity, a close correspondence of the F. I. with bound fluorescent compound concentration was not necessary and would be very difficult to quantify. Rela-

tive mean deviation of replicate fluorescence index measurements (repositioning the plate) is $\pm$ 5%. Emission wavelength, which varies nearly linearly with fluorescence index (Fig. 11), may be used as a dependable monitor of the progress of oxidation, although with slightly less favorable signal-to-noise ratio than fluorescence index.

When a series of fluorescence indices or maximal emission wavelengths measured over an oxidizing lipid is plotted against time, there is always a typical oxidative induction period before rapid increase of F. I., whether the system does not contain antioxidant (linolenic acid, Fig. 8) or has endogenous or added antioxidant (cottonseed oil, Fig. 8 and lecithin plus BHA, Fig. 9). Figure 10a shows a typical emission spectra obtained over oxidizing salad oils extracted from stored mayonnaise and salad dressing. Also shown (Fig. 10b) is the spectrum obtained when the detector plate is exposed over the intact salad dressing rather than the extracted oil, a procedure we have recently found feasible and reproducible. Although the results reported in this study were obtained on extracted oils, it is probably much preferable to monitor oxidation over the intact salad dressing, since in the latter case, the egg phospholipids may be the most prone to oxidation, the first to produce fluorogenic compounds, and therefore, the more probable correlates with the onset of rancid odor or changes in flavor.

As a measure of induction period for accelerated comparative stability tests, we have used the time in minutes for a cobalt-accelerated system incubated at 65°C to increase 0.1 F. I. units over its lowest consistent F. I. reading. For spectra in which the maximal emission wavelength is used as a monitor, the comparable induction period is based on increase of 5 nm over lowest consistent baseline maximal emission wavelength.

Figure 11 shows development of polyamide fluorescence over oxidizing soybean oils extracted from mayonnaise stored in glass containers at 70 and 100°F for three months. The data are plotted as emission wavelength versus time as a demonstration of the wavelength method. The induction period is clearly shown for all four oils as is the onset of rapid fluorescence development. This onset, in our experience, coincides with the first detectable rancid odor from oil contained in the opened polyamide sandwich and the time to its appearance is a good measure of accelerated comparative stability.

It is evident that hydrogenated oil has the much longer induction period compared to nonhydrogenated oil. Also clear is the differentiation, for both unsaturation levels, of the oil stored at 21°C (70°F) from that at 38°C (100°F). What is not shown here is that, other parameters being the same (temperature, packaging and hydrogenation), mayonnaise has the longer induction period compared to salad dressing. Figure 12 shows fluorescence development for oils from mayonnaise stored

in plastic containers for six months. Here, the data are plotted as fluorescence index versus time. Many of the features appear similar, but what is striking is that hydrogenated oil stored six months at 38°C (100°F) has a sharply reduced induction period and is now less stable than nonhydrogenated oil stored at 21°C (70°F). All of the oils, however, have dropped in stability compared to oils stored in glass at three months.

Figure 13 shows fluorescence development for oils from salad dressing stored in plastic containers for six months. Here, the same overtake of the nonhydrogenated sample stored at 21°C (70°F) by the hydrogenated sample stored at 38°C (100°F) has occurred, and three of the four oils have dropped in stability compared to mayonnaise oils. If induction period derived from fluorescence accelerated comparative stability tests is plotted against storage time for three and six months (Figs. 14, 15, 16, 17), it is evident that at three months, this stability test can easily discriminate in all cases between hydrogenated and nonhydrogenated oils, between oils from salad dressings stored at 21°C (70°F) and 38°C (100°F) (with one exception in 8 cases), between all mayonnaise and salad dressing cases (the latter of each pair having less stability) and did not discriminate dependably at this storage time, between oils from salad dressings stored in glass and those stored in plastic containers (the latter showing less stability with hydrogenated but not with nonhydrogenated oils).

However, it is clear from inspection of Figs. 14-17, that an apparent increase in stability with time of storage occurs for certain samples. It should be reiterated that at present, the test is more dependable for comparison of stability of two samples at the same time of storage, than of the same sample at different times (Figure 14, control values versus three month samples). The accelerated test is also not intended at present for absolute shelf life predictions at typical storage temperatures.

At six months, plots of induction period versus time show clearly the changes mentioned above in connection with the fluorescence development graphs (Figs. 12, 13). In 14 out of the 16 possible combinations (hydrogenation, temperature, salad dressing type, and container type) stability dropped with doubled storage time. The drops in stability were most pronounced in the hydrogenated samples, to the extent, as mentioned above, that at six months hydrogenated oil stored at 38°C (100°F) became lower in accelerated stability test rating than nonhydrogenated oil stored at 21°C (70°F), for all cases except mayonnaise stored in glass containers. However, all other parameters being the same, each nonhydrogenated oil had lower stability at 6 months than its corresponding hydrogenated oil. Finally, other parameters being the same, in six out of eight pairs, oils from plastic containers had lower stability than those from glass containers and this was particularly pronounced at 38°C (100°F).

One could thus tentatively predict the lowest stability for nonhydrogenated oils extracted from salad dressing stored in plastic containers at 38°C (100°F) and this was indeed the case (Fig. 17). The range of accelerated induction periods covered in this study is thus from 148 minutes for hydrogenated oil from mayonnaise stored in glass at 21°C (70°F) for three months to 30 minutes for nonhydrogenated oil from salad dressing stored in plastic at 38°C (100°F) for six months.

It would appear from these data that two factors contribute most to the cobalt- and temperature- accelerated comparative stability value (lipid oxidation induction period). One is the level of existing peroxidation and the other the innate autoxidation tendency of the particular polyunsaturated triglyceride substrate as determined by degree of unsaturation and added or endogenous antioxidants and synergist. Existing peroxidation level is affected most by packaging, salad dressing type, time, and temperature, while the innate autoxidation susceptibility is of course dependent on degree of hydrogenation, oil type (triene, diene, or monoene) and additives. In other studies not reported here, we have found that the rate-limiting step in formation of oxidative polyamide fluorescence at high temperatures is not the reaction of volatile carbonyls with the polyamide surface, since we have shown this reaction to be very rapid with synthesized malonaldehyde or aromatic aldehydes. Thus, the rate limiting step is formation of volatile carbonyls from oxidizing lipids. Oxidative polyamide fluorescence appearance coincides with the appearance of volatile carbonyls and rancidity. The measurement of comparative stability is only as dependable as the accelerated test used to reach this point.

It should be noted in comparing oil stability values for mayonnaise and spoonable salad dressing, that oils from the former were extracted by freeze-breaking the emulsion, whereas methylene chloride extraction was used for the latter. Also, it should be noted that the sensory panel flavor quality ratings and consumer acceptance ratings were performed on the whole emulsion, in contrast to the fluorescence tests and peroxide values.

The sensory panel flavor quality ratings are shown for samples stored three and six months in Figs. 18, 19, 20, 21. The only conspicuous differences other than that between 70 and 100°F storage are those between glass and plastic containers, flavor quality for oils from the latter of each pair being lower at each time point. There is not a consistent flavor quality difference between dressings with hydrogenated versus nonhydrogenated oils.

The mean consumer acceptance ratings for the same storage times are shown in Figs. 22, 23, 24, 25. Again, the only conspicuous differences are between ratings for dressings in glass and plastic containers, neither temperature nor hydrogenation level being a dependable differentiator. Also shown on these figures are the peroxide values at the same time

points. Again, no dependable trend is evident, other than that the values for oils in plastic packaged salad dressings are higher than those of oils in glass jars.

We have found that a useful summary of trends for the fluorescence accelerated stability test is by pair comparison of oils similar in all except one test parameter. Table I shows the frequency with which the stated stability rank order is observed in these "other parameters equal" pairs.

The extension of such pair comparisons to the sensory panel flavor quality and consumer acceptance ratings does not seem justified, because, as noted above, the ratings are measures of current status and are not comparable with a stability-to-stress test.

Analysis of variance was performed on the consumer acceptance data. For the 36 subjects, for a given stored item score, standard deviation was high (1.3 to 1.9) compared to range of the data (5.2 to 6.9). For mayonnaise, length of storage had a noticeable effect and the indisputable container effect was obscured by the fact that samples stored in plastic containers at $38^{\circ}C$ ($100^{\circ}F$) for six months were not taste tested because of separation of oil and brown color. For salad dressing, length of storage was significant and salad dressings stored in plastic containers were significantly lower in score than those stored under glass.

Thus, for both graphical and statistical analysis of the organoleptic tests, the conspicuous effect was that of container. Since dressings in the plastic containers were discolored both at the container surface and on the upper surface of the dressing, not in contact with the container, it is probable that the effect is related to oxygen permeability of the plastic. Control of the gas atmosphere thus emerges as a vital preventive measure (1), whether by impermeable containers or by addition of oxygen consuming substances like glucose oxidase. The latter was recently tested by an independent laboratory for the Association for Dressings and Sauces (10). Peroxide values were kept lower in the treated samples, but flavor scoring did not detect the difference after storage for six months at $21^{\circ}C$ ($70^{\circ}F$).

From these tests, it would appear that special processing by hydrogenation did not produce significant flavor differences for storage at $21^{\circ}C$ ($70^{\circ}F$) and $38^{\circ}C$ ($100^{\circ}F$) for three and six months (cf. 1, 3, 5, 10). Recent statistical analysis of variance of the $21^{\circ}C$ ($70^{\circ}F$), 15 month consumer acceptance data again showed that only the container made a significant difference and only in salad dressing, while no significant difference was found between acceptance scores of hydrogenated versus nonhydrogenated oils in either mayonnaise or salad dressing.

The polyamide indicator oxidative fluorescence test of accelerated comparative stability was demonstrated here to discriminate quite consis-

TABLE I.

Fluorescence Accelerated Comparative Stability Test

Frequency of Stability Rank Order

	FREQUENCY* OF RANK ORDER	
STABILITY RANK ORDER	THREE MONTHS	SIX MONTHS
MAYONNAISE > SALAD DRESSING	8	7
GLASS > PLASTIC	4	6
70^OF > 100^OF	7	8
HYDROGENATED > NON-HYDR.	8	8

*OUT OF POSSIBLE 8

tently in "other parameters equal" pairs of extracted salad dressing oils between hydrogenated and non-hydrogenated samples, mayonnaise and salad dressing, glass and plastic container, and 21°C versus 38°C (70 versus 100°F). It is facile and simple, and can be applied to intact salad dressings as well as to the extracted oils, an advantage where polar lipids of the added egg may contribute to early rancidity. In the latter mode (intact food), it requires little preparative chemistry, as contrasted to gas chromatography of volatiles (2,4), which has been recently used in an accelerated flavor stability test (9). The polyamide test, in addition, has significant potential applications in "in-package" monitoring of stability.

As noted above, however, the polyamide fluorescence accelerated comparative stability test uniformly predicted greater stability for hydrogenated versus nonhydrogenated oils in salad dressings. This radical difference from organoleptic results may arise because a much longer time base is needed for the predicted greater comparative stability to manifest itself. On the other hand, it must be recalled that the organoleptic tests were performed on the whole emulsion, while the fluorescence tests were made on extracted oils. As a third possibility, cobalt- and heat-acceleration may not be valid accelerated comparative stability test modes for salad dressing oils. Polyamide indicator fluorescence, itself, however, will always be a dependable monitor of the commencement of rapid phase lipid oxidation, even though less drastic stability test conditions prove necessary.

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TYPE OF DRESSING	TYPE OF CONTAINER	HYDROGENATION	STORAGE TEMPERATURE (°F)
MAYONNAISE	GLASS	HYDROGENATED	100
			70
		NON-HYDRO.	100
			70
	PLASTIC	HYDROGENATED	100
			70
		NON-HYDRO.	100
			70
SALAD DRESSING	GLASS	HYDROGENATED	100
			70
		NON-HYDRO.	100
			70
	PLASTIC	HYDROGENATED	100
			70
		NON-HYDRO.	100
			70
STORAGE TIME TO EVALUATION (MONTHS) 70, 100°F - INITIAL, 3, 6 70°F - 9, 12, 15			

Figure 1. <u>Statistical design – mayonnaise and salad dressing storage stability test.</u>

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$$O = CHCH = CHOH + RNH_2 \xrightarrow{-H_2O} O = CHCH = CHNHR$$

MALONALDEHYDE   N · HEXYL-   ENAMINE
(ENOL FORM)   AMINE OR
α · N · ACETYL-
LYSINE

$$O = CHCH = CHNHR + RNH_2 \xrightarrow{-H_2O} RN = CHCH = CHNHR$$

ENAMINE   N,N' · DISUBSTITUTED
1 · AMINO · 3 · IMINOPROPENE
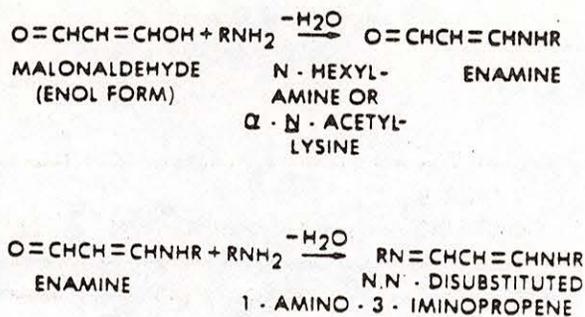
WHERE
$R = (CH_2)_5CH_3$

Figure 2.   <u>Malonaldehyde-amine reactions</u>.   (Reproduced from Ref. 7
Copyright 1969, American Chemical Society.)
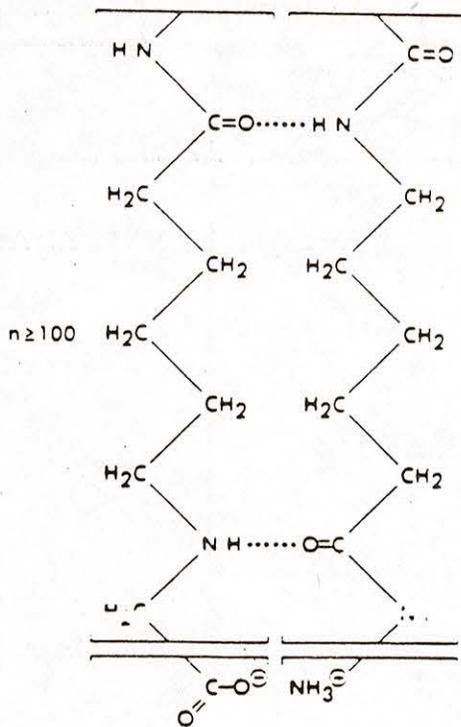
Figure 3.   <u>Polyamide-6 (nylon-6, perlon or polycaprolactam)</u>.

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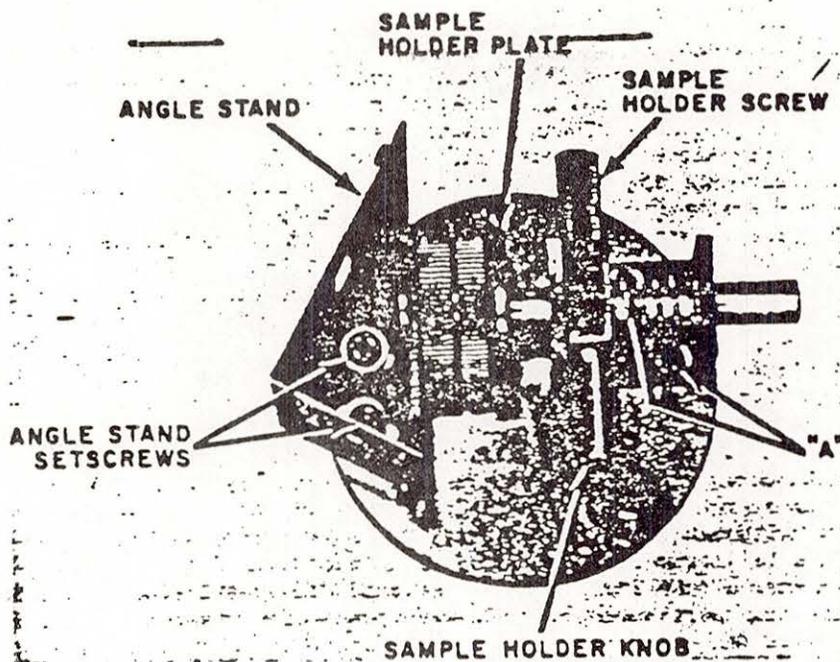
Figure 4.   Solid-sample holder attachment.
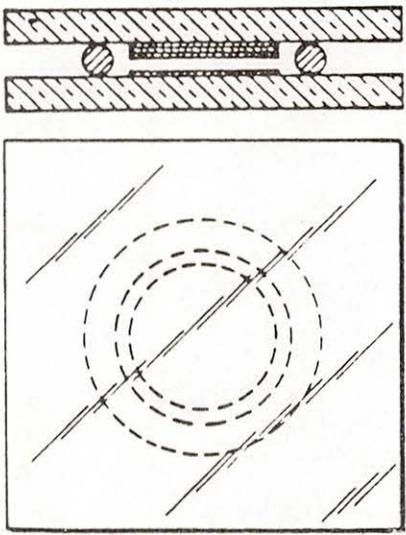
Figure 5.   Plate assembly for oxidative fluorescence assay.
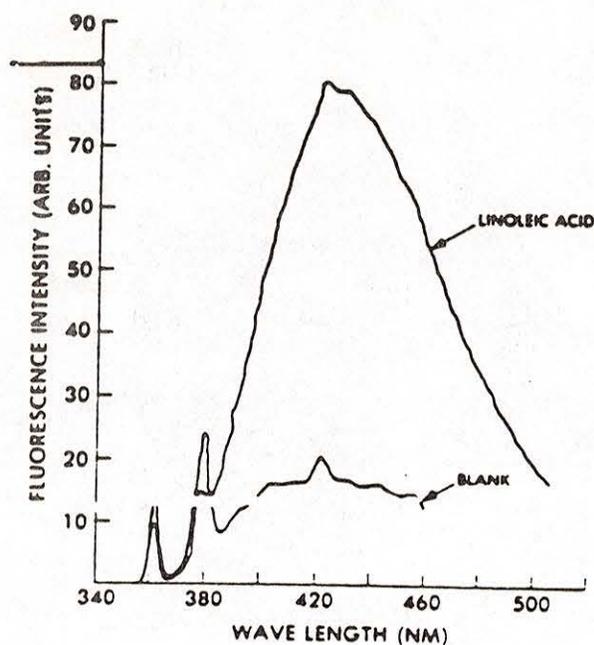
Figure 6. Fluorescence emission spectrum for polyamide on plastic facing oxidizing linoleic acid-conditions: 69°C for 20 h.
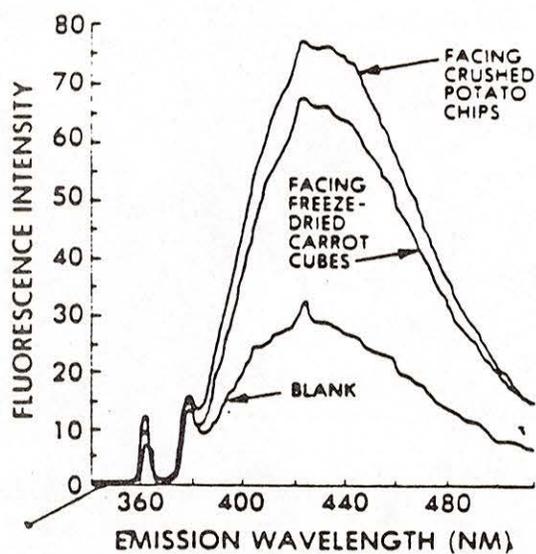
Figure 7. Oxidative polyamide fluorescence emission spectra in packaged foods.

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Key: O, linoleic acid; Δ cottonseed oil.
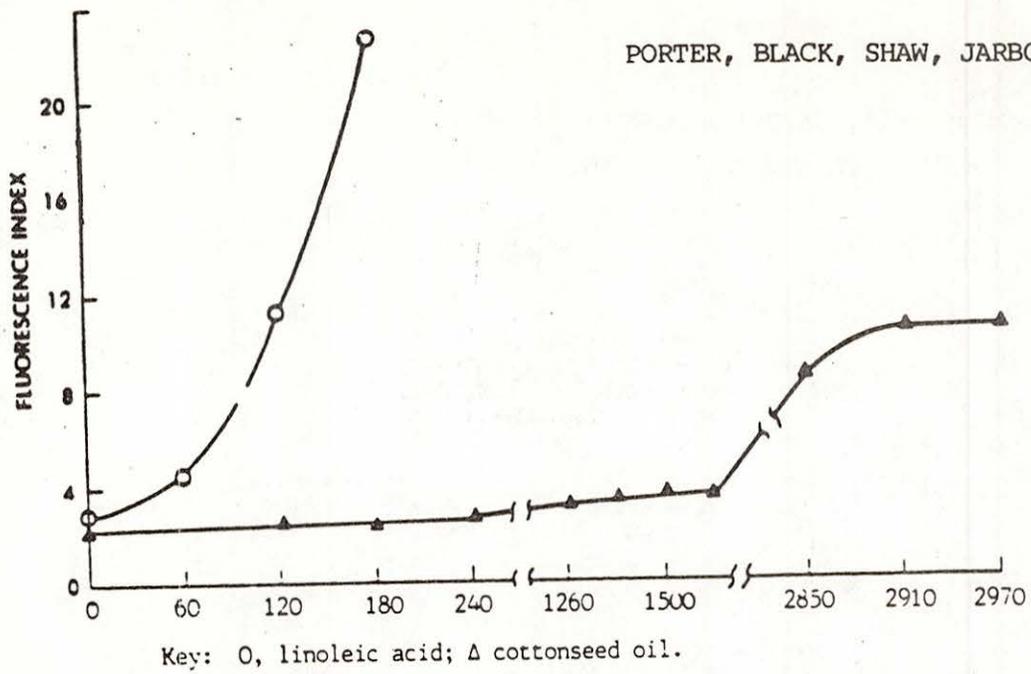
Figure 8. Oxidation polyamide fluorescence production over oils.

Key: O, blank; □, lecithin plus hematin; Δ, lecithin—hematin plus 0.1% BHA.
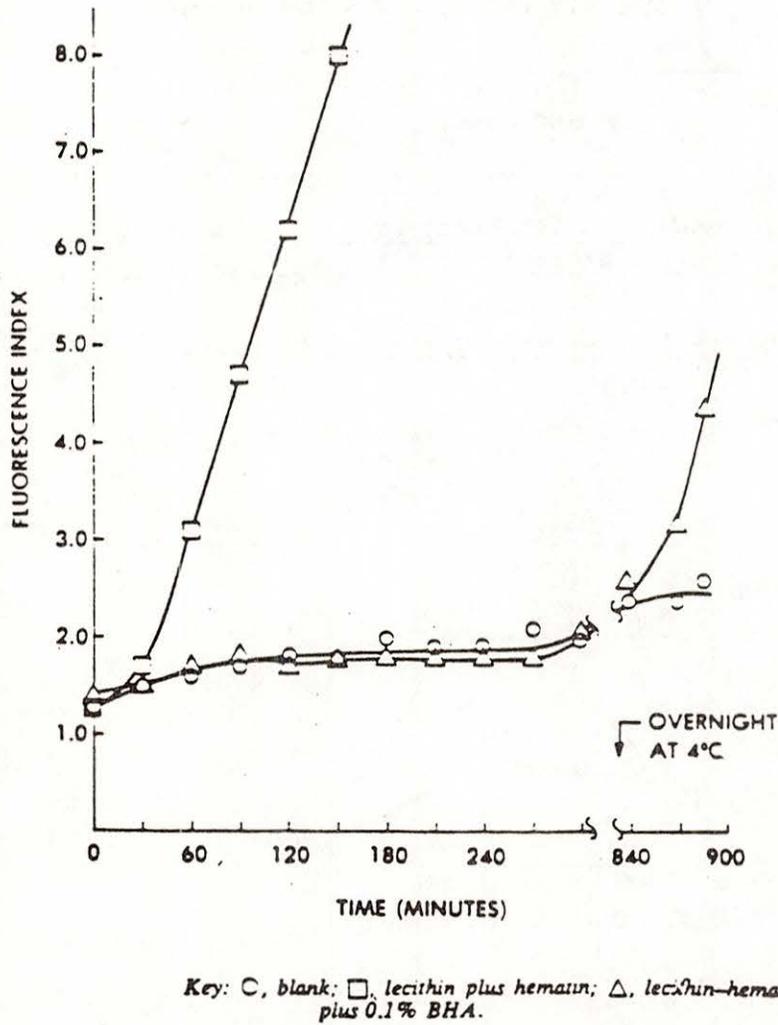
Figure 9. Antioxidant evaluation by oxidative polyamide fluorescence from soy lecithin liposomes.
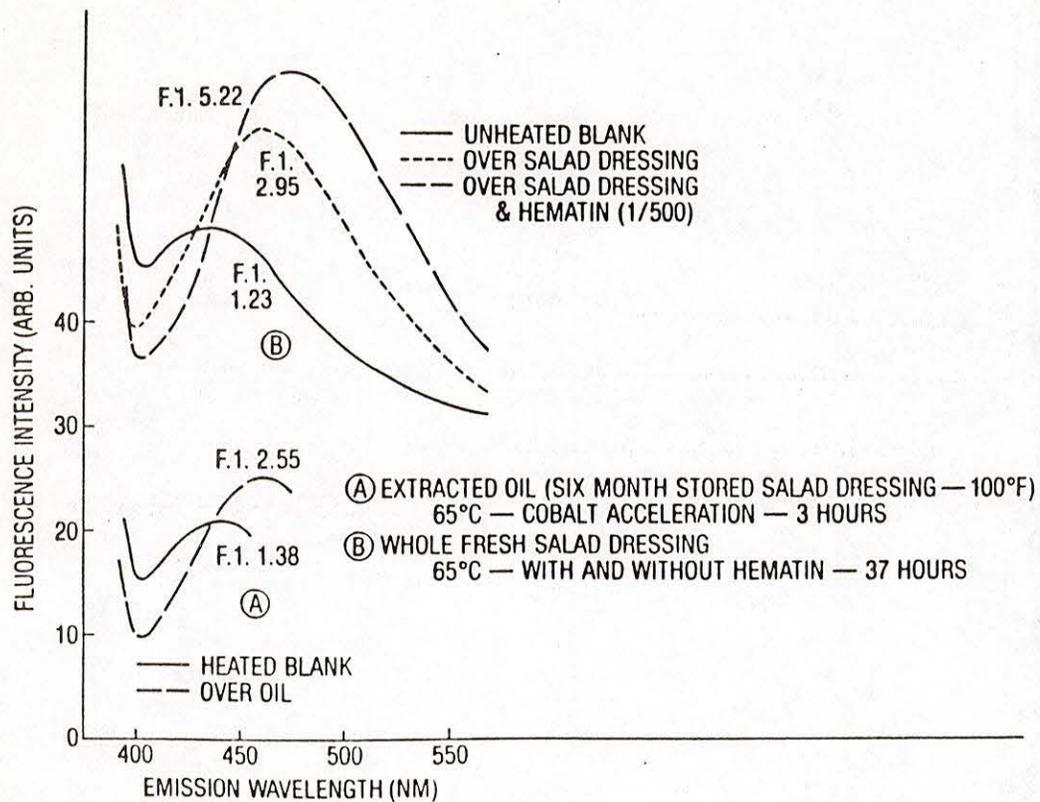
Figure 10. Polyamide fluorescence spectra over oxidizing substrates.
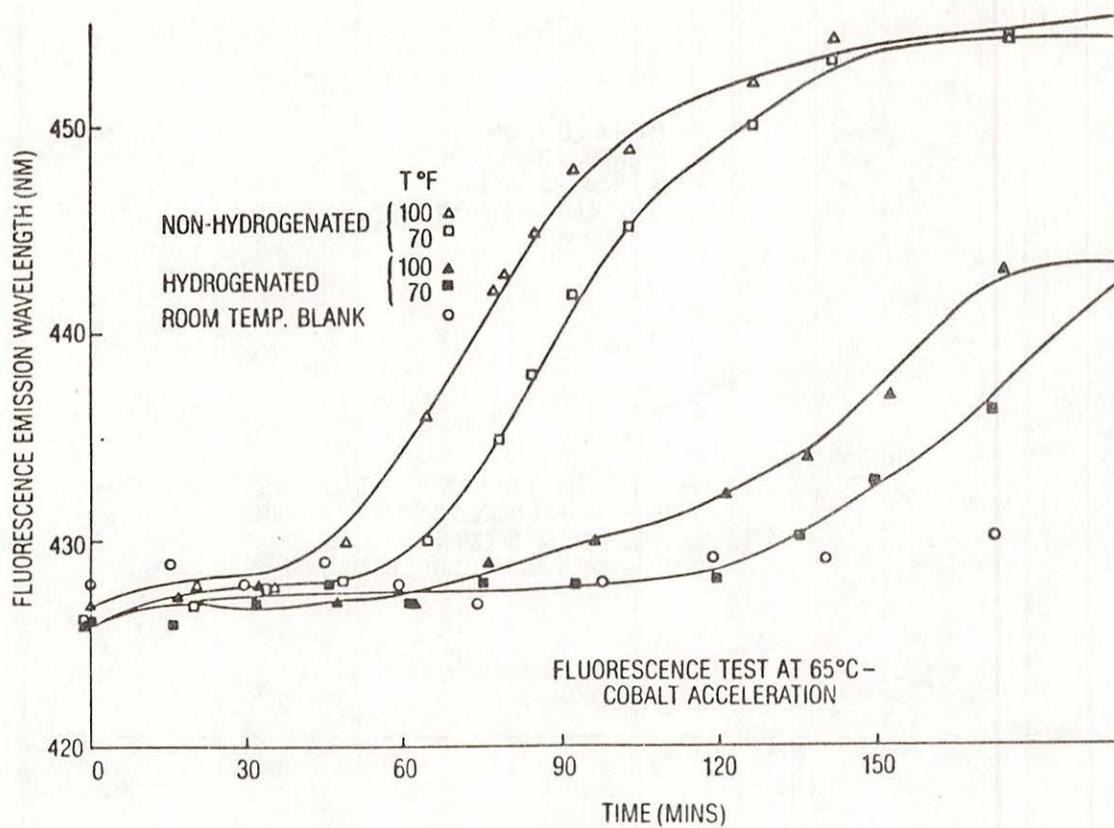
Figure 11.   Development of polyamide fluorescence over oxidizing salad oil from mayonnaise stored in glass containers three months.
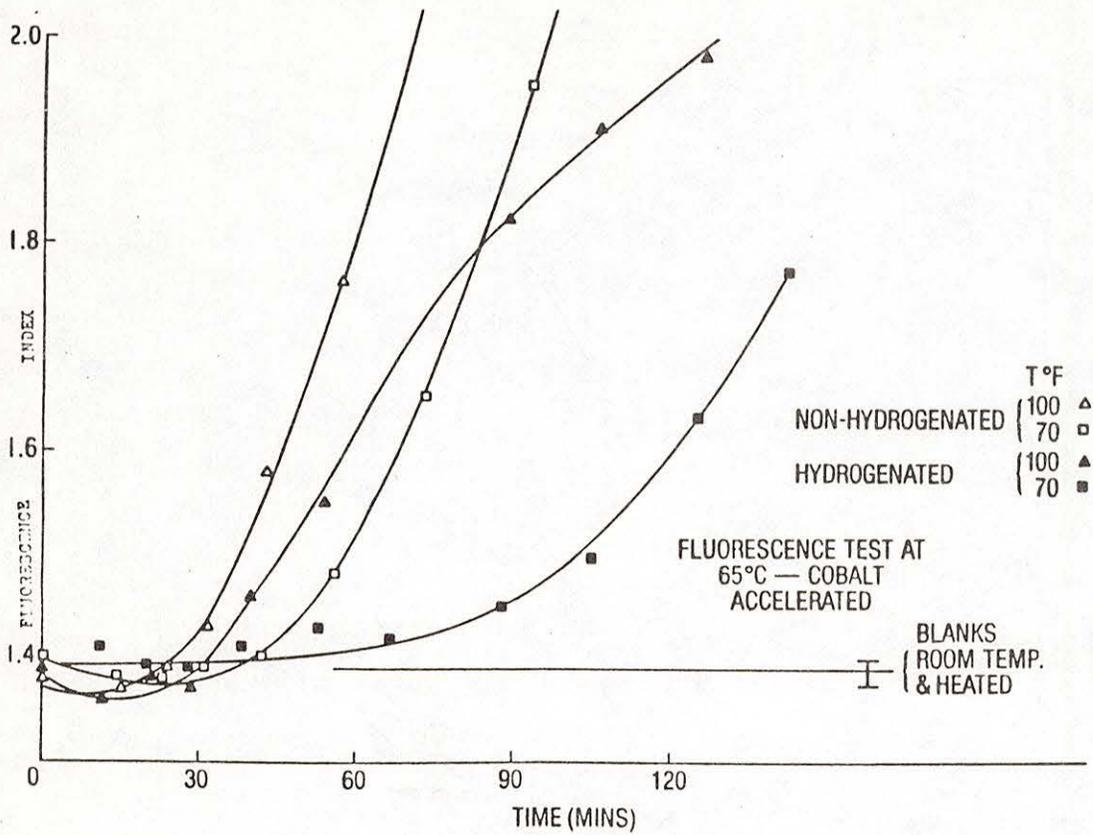
Figure 12. Development of polyamide fluorescence over oxidizing salad oil from mayonnaise stored in plastic containers six months.
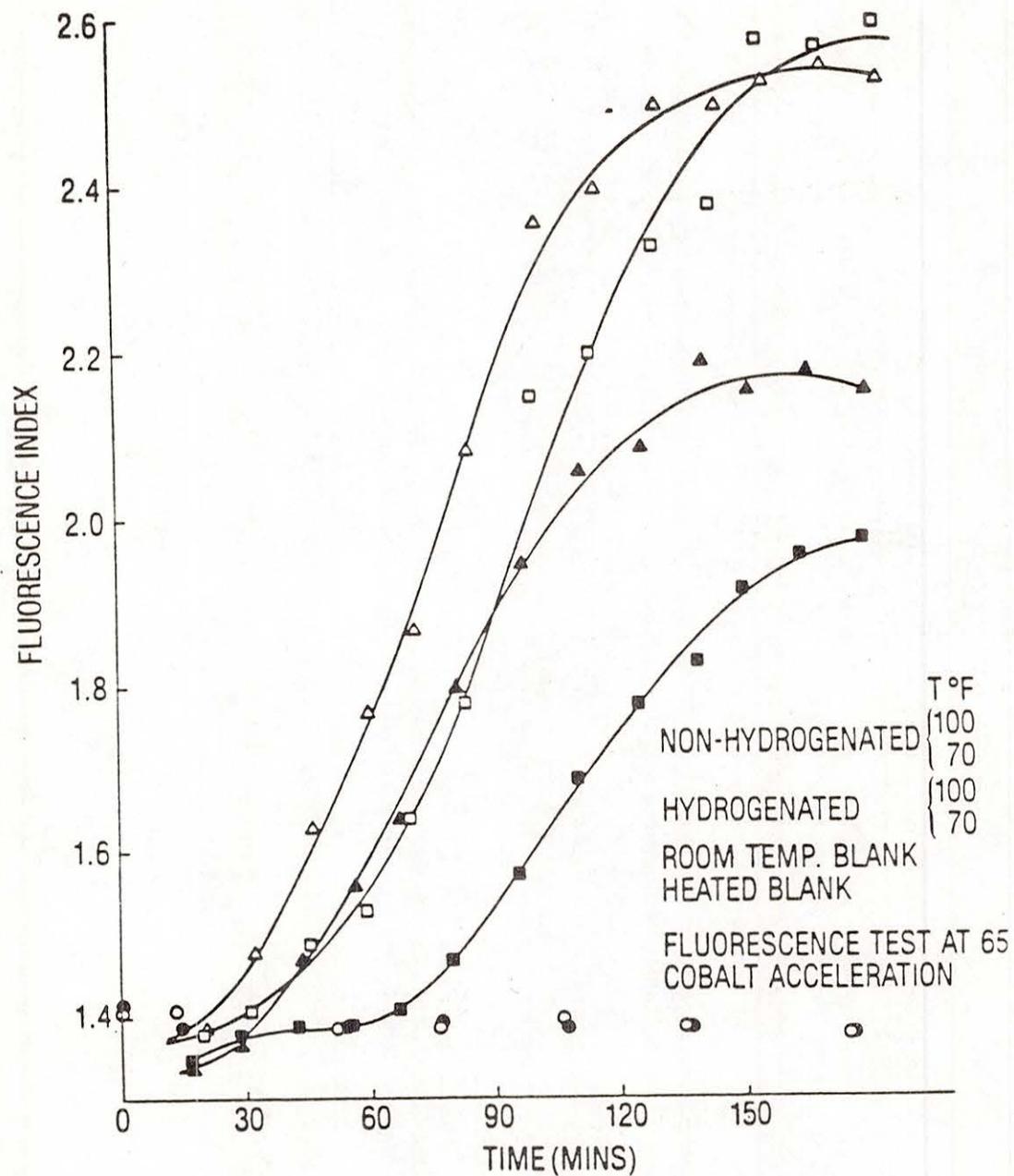
Figure 13.   Development of polyamide fluorescence over oxidizing salad oil from salad dressing stored in plastic containers six months.
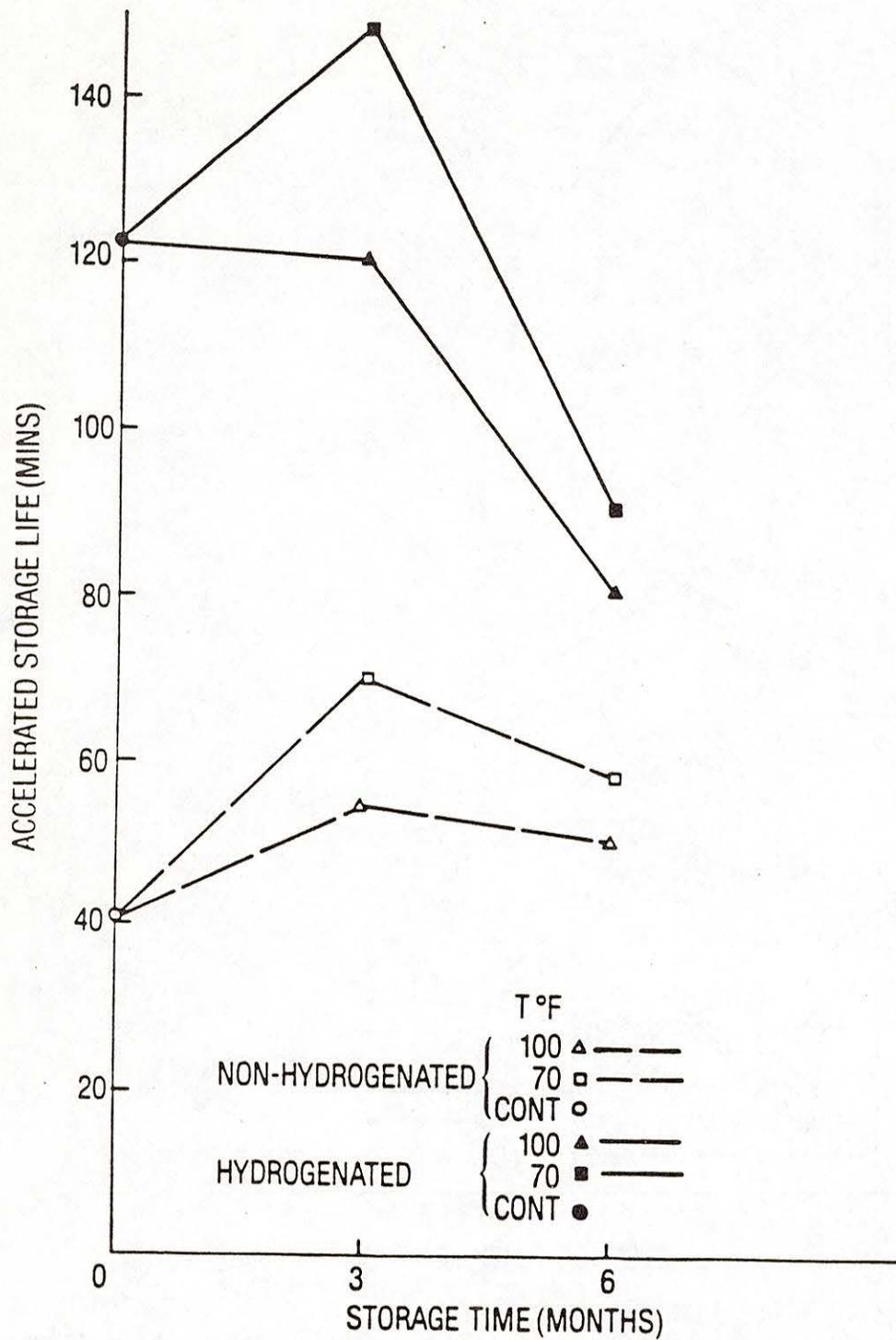
Figure 14. Comparative accelerated stability – polyamide fluorescence – mayonnaise – glass container.
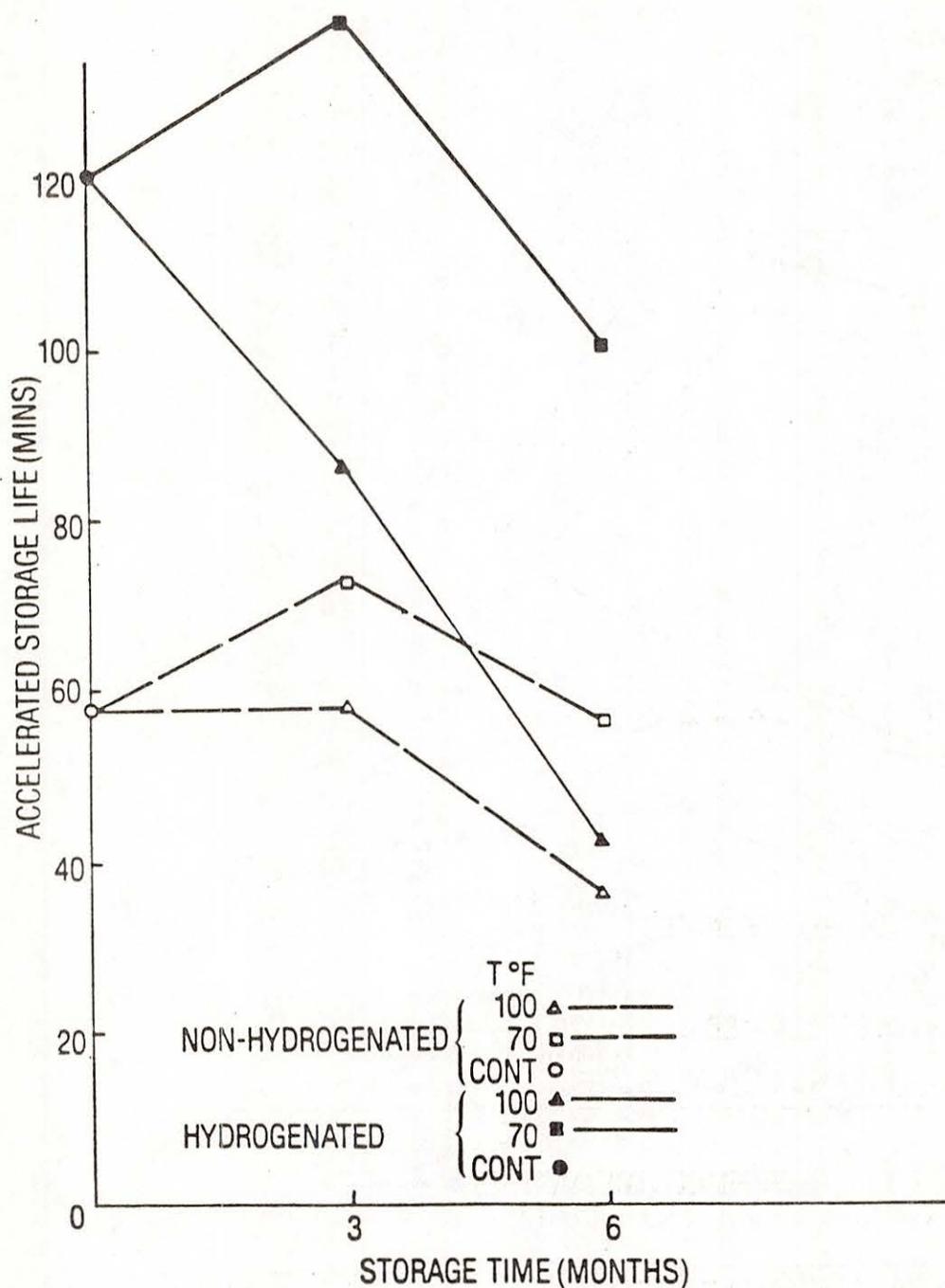
Figure 15.   Comparative accelerated stability – polyamide fluorescence – mayonnaise – plastic container.
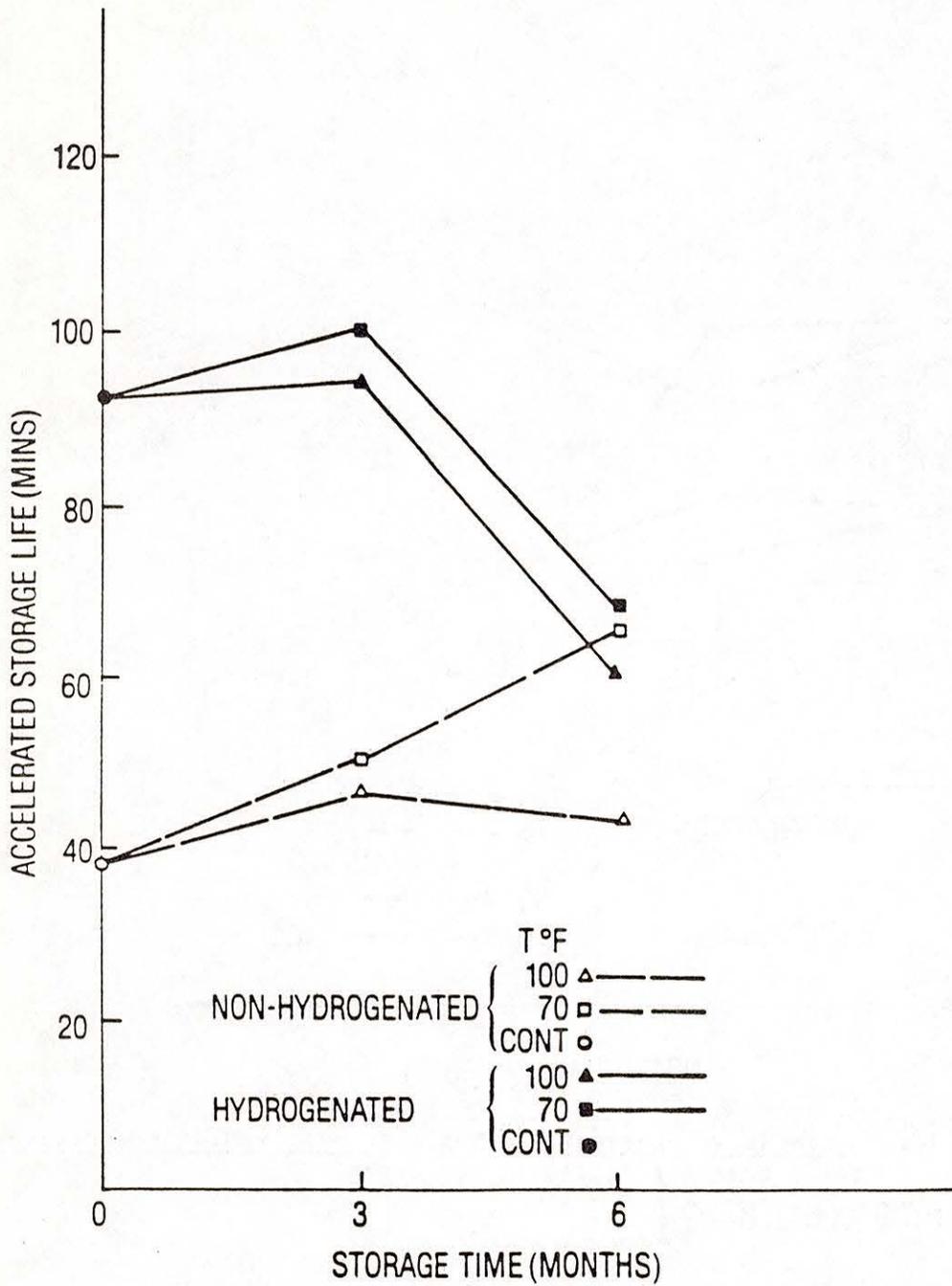
Figure 16. <u>Comparative accelerated stability - polyamide fluorescence - salad dressing - glass container.</u>
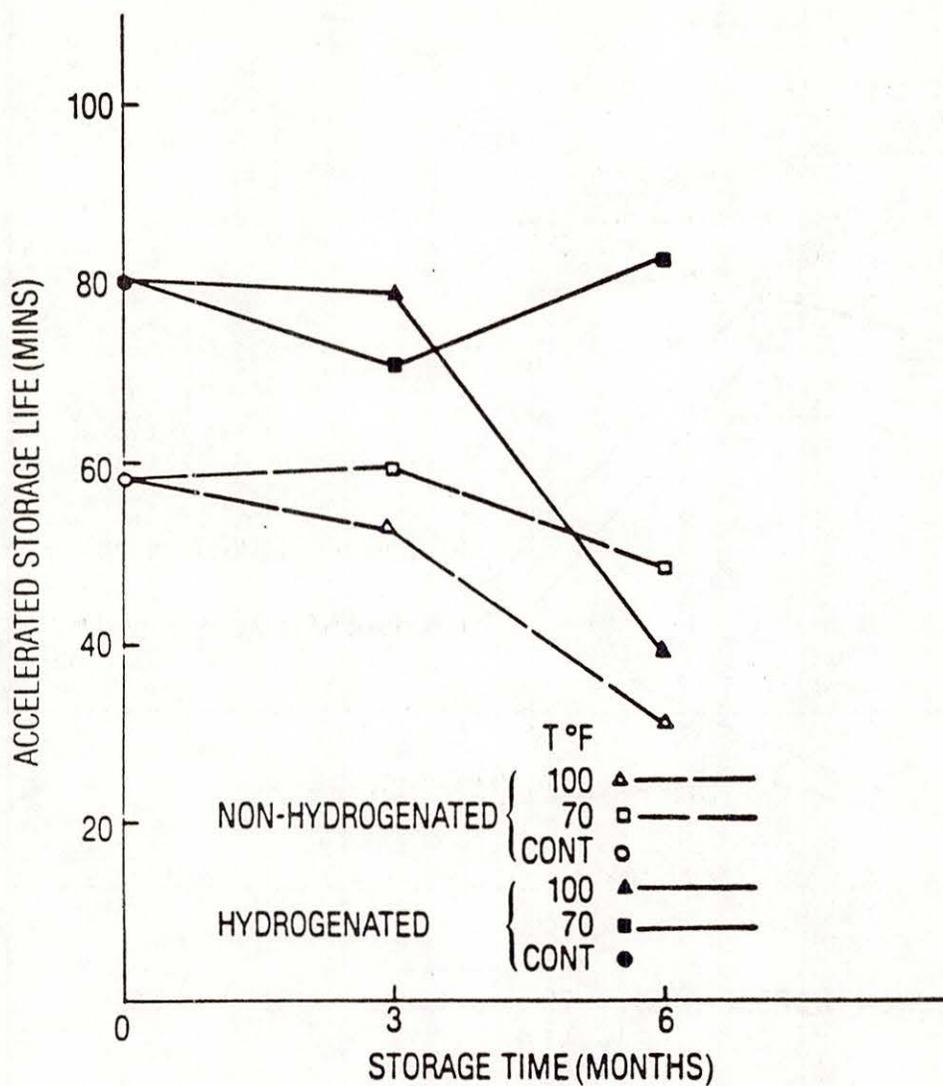
Figure 17. Comparative accelerated stability - polyamide fluorescence - salad dressing - plastic container.
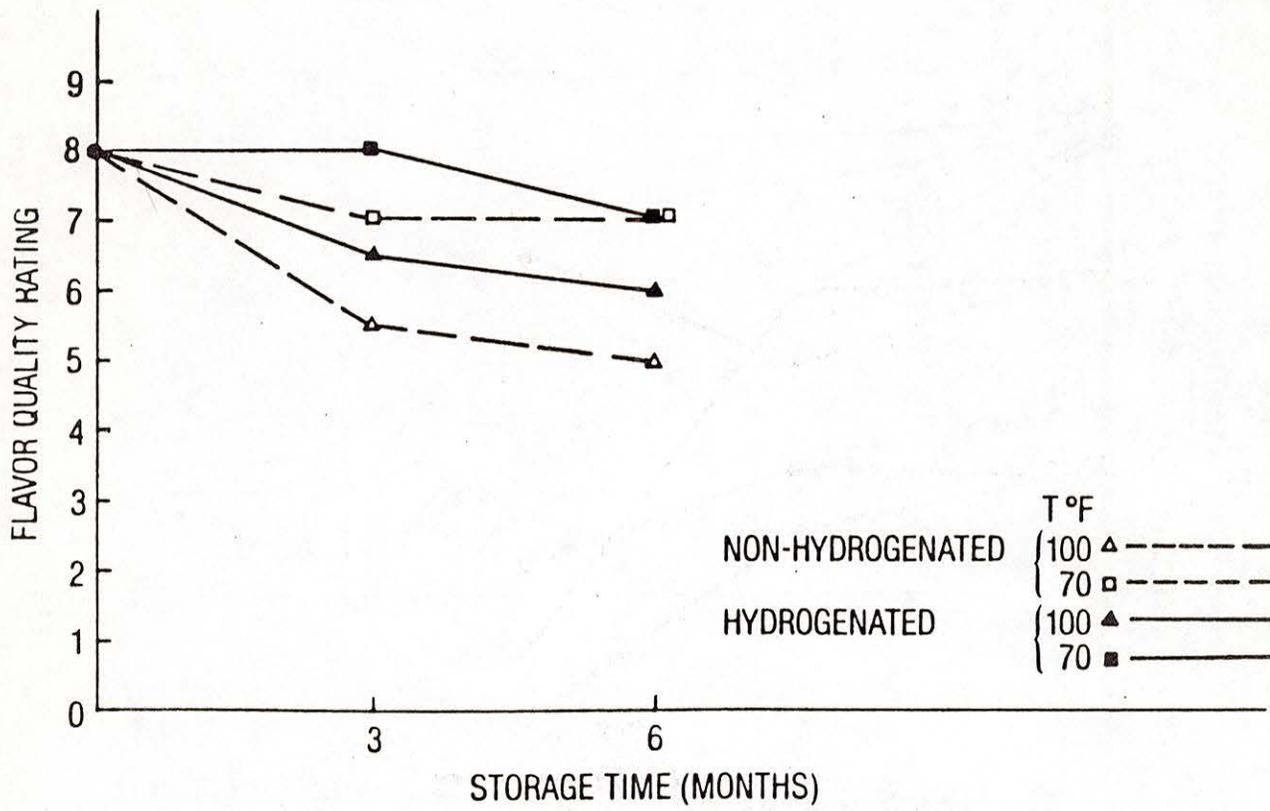
Figure 18.   Sensory panel flavor quality rating – mayonnaise, glass
             container.
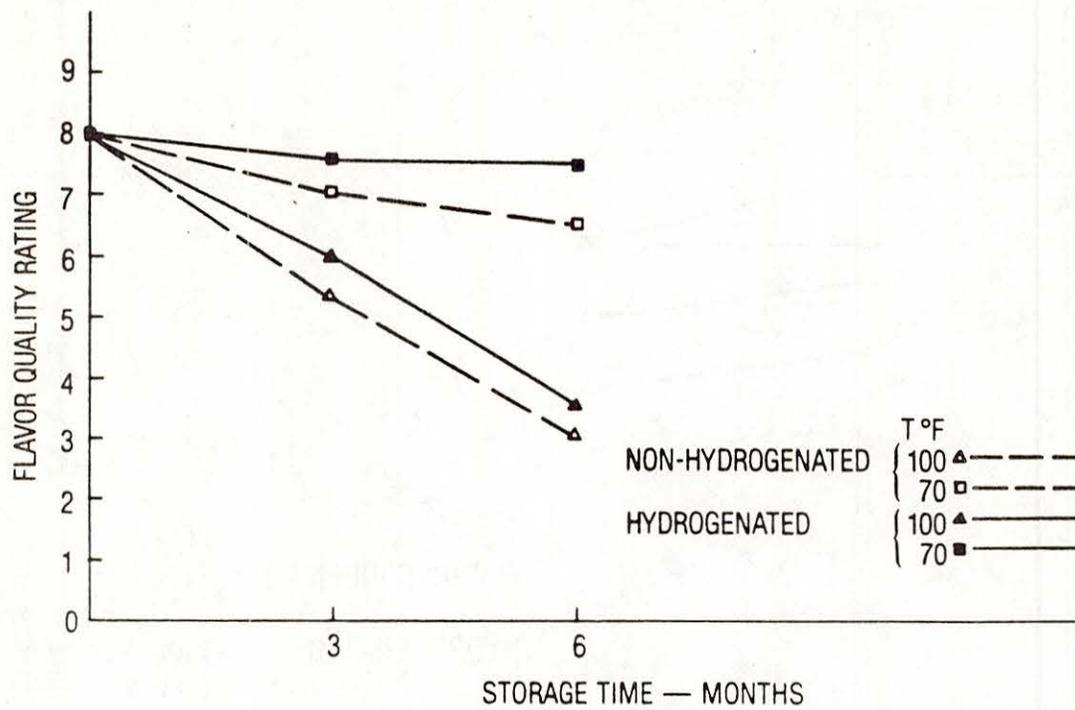
Figure 19.   Sensory panel flavor quality rating – mayonnaise plastic container.
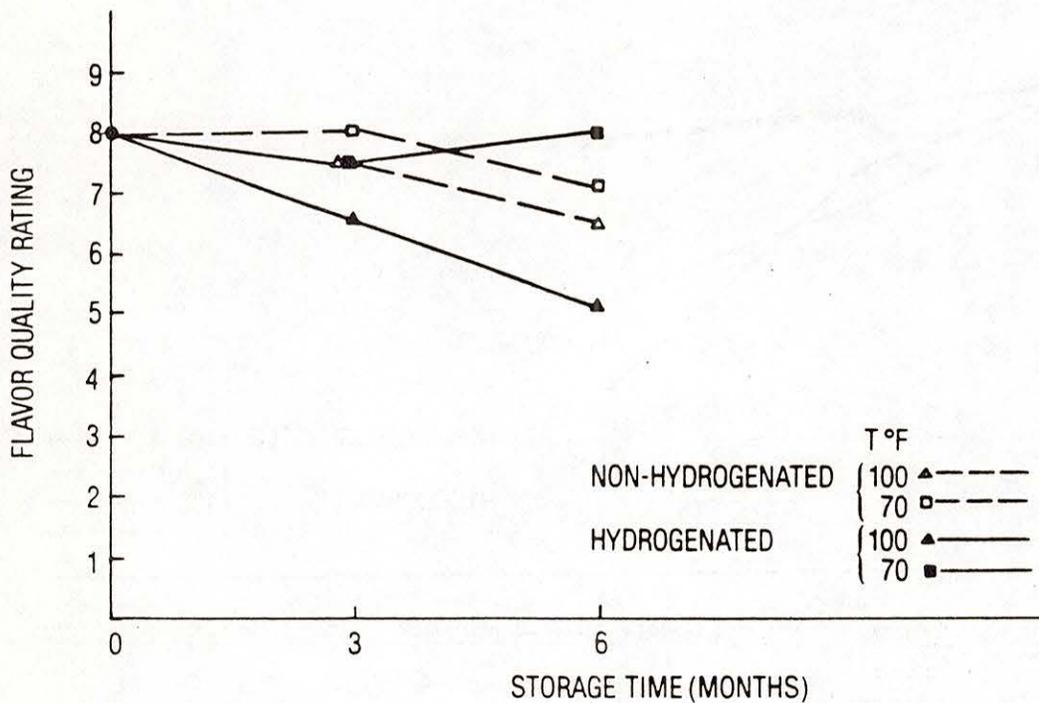
Figure 20. Sensory panel flavor quality rating-salad dressing glass container.
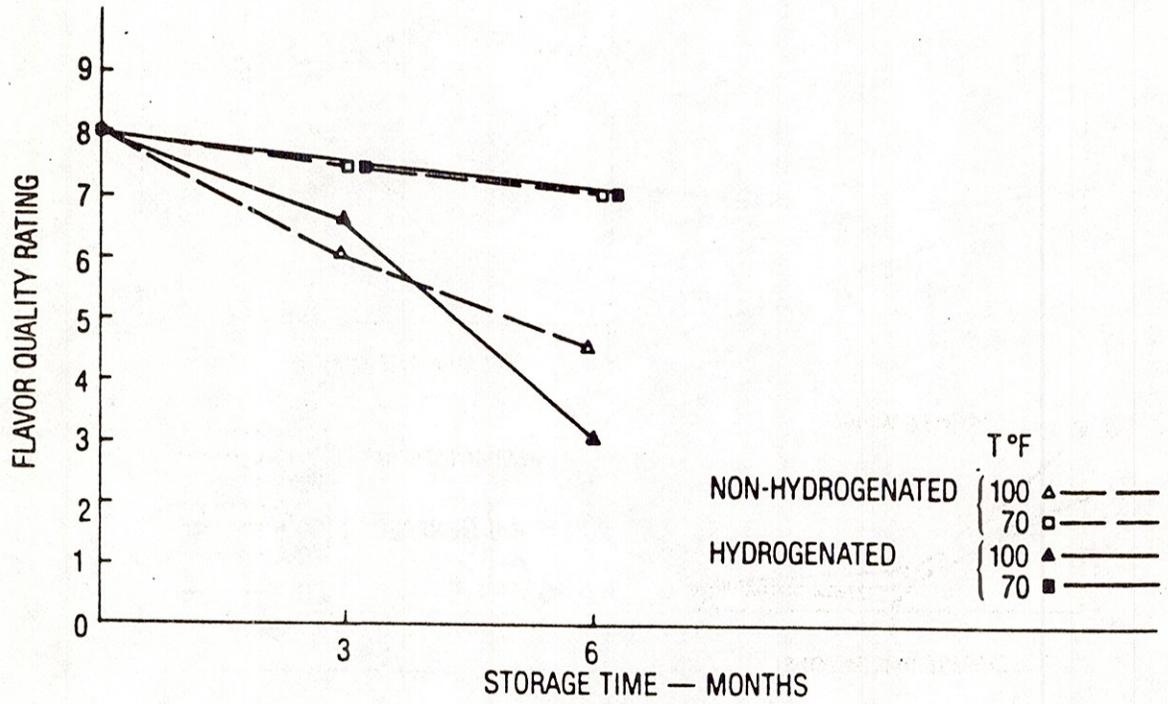
Figure 21.   Sensory panel flavor quality rating-salad dressing plastic
container.

MAYONNAISE
GLASS CONTAINER

FIGURE 22

PEROXIDE VALUE

PV (meg./kg.)

STORAGE TIME (MONTHS)

ACCEPTANCE SCORE

CONSUMER
ACCEPTANCE

STORAGE TIME (MONTHS)

	T °F	
NON-HYDROGENATED	100 ▲	
	70 ▫	
	CONT ○	
HYDROGENATED	100 ▲	
	70 ▪	
	CONT ●	
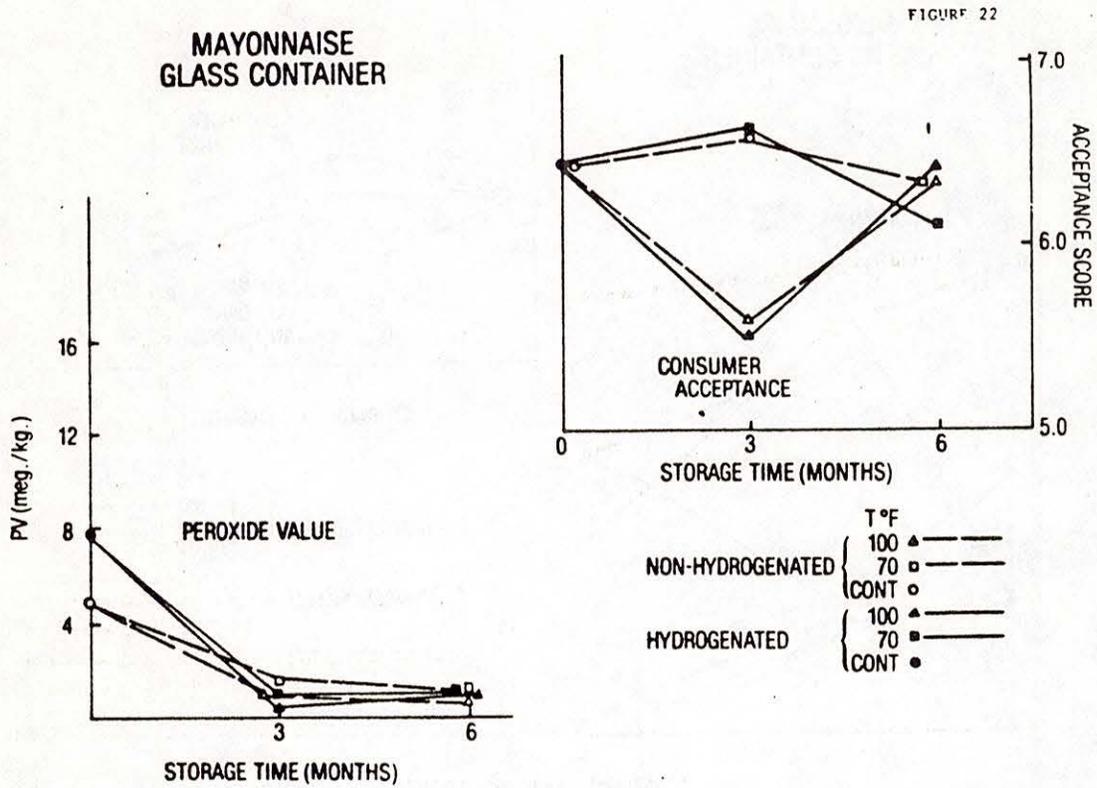
Figure 22. Consumer acceptance ratings and peroxide values, mayonnaise in glass container.

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MAYONNAISE
PLASTIC CONTAINER
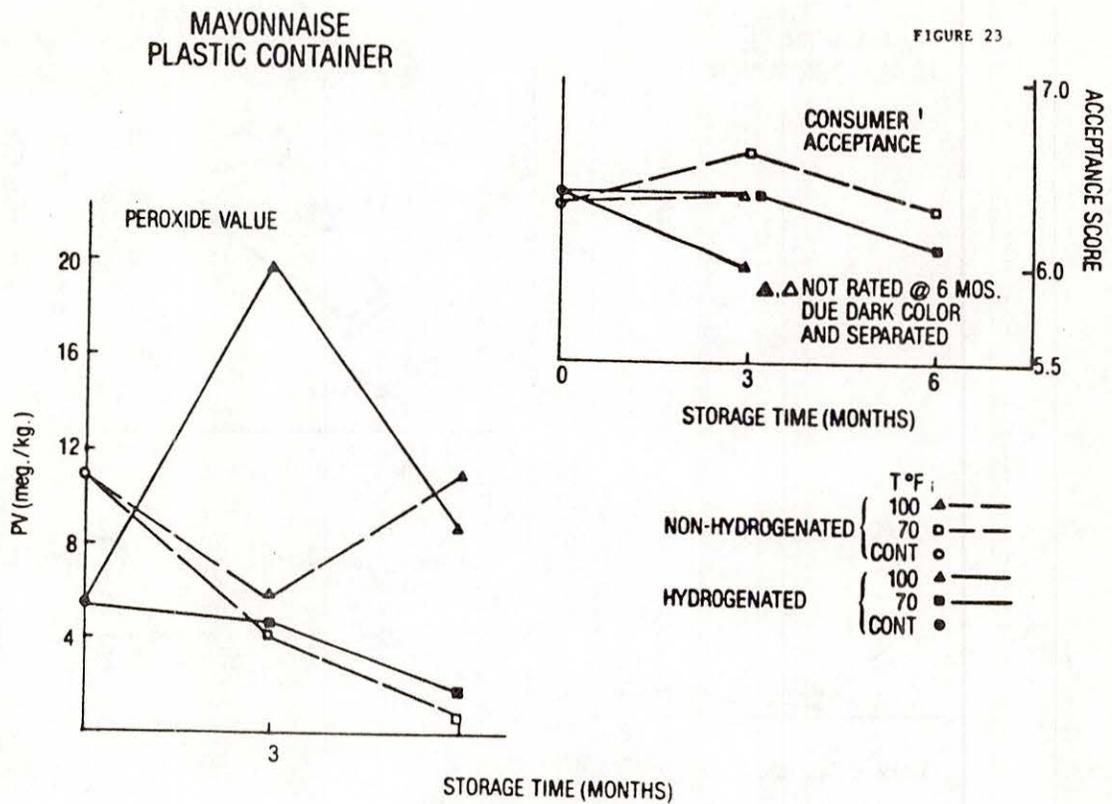
FIGURE 23

Figure 23. Consumer acceptance ratings and peroxide values, mayonnaise in plastic container.

SALAD DRESSING
GLASS CONTAINER

FIGURE 24

CONSUMER ACCEPTANCE

ACCEPTANCE SCORE

STORAGE TIME (MONTHS)

PV (meg./kg.)

PEROXIDE VALUE

STORAGE TIME (MONTHS)

T °F

NON-HYDROGENATED
100
70
CONT

HYDROGENATED
100
70
CONT
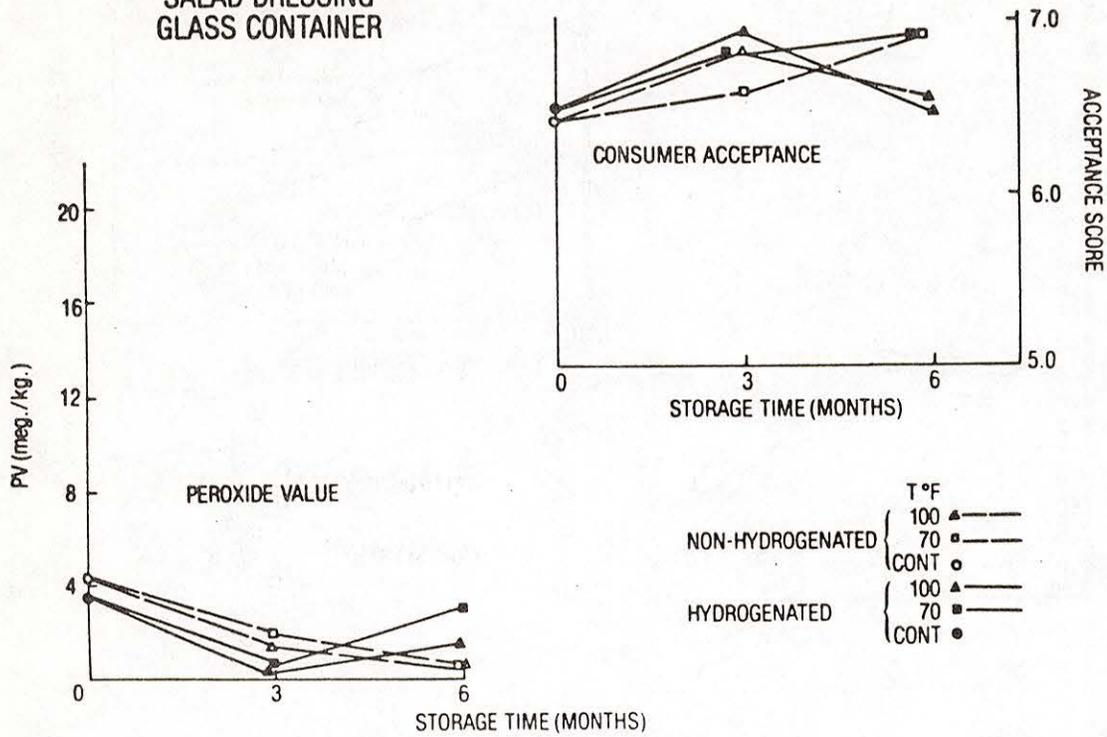
Figure 24.   Consumer acceptance ratings and peroxide values, salad dressing in glass container.

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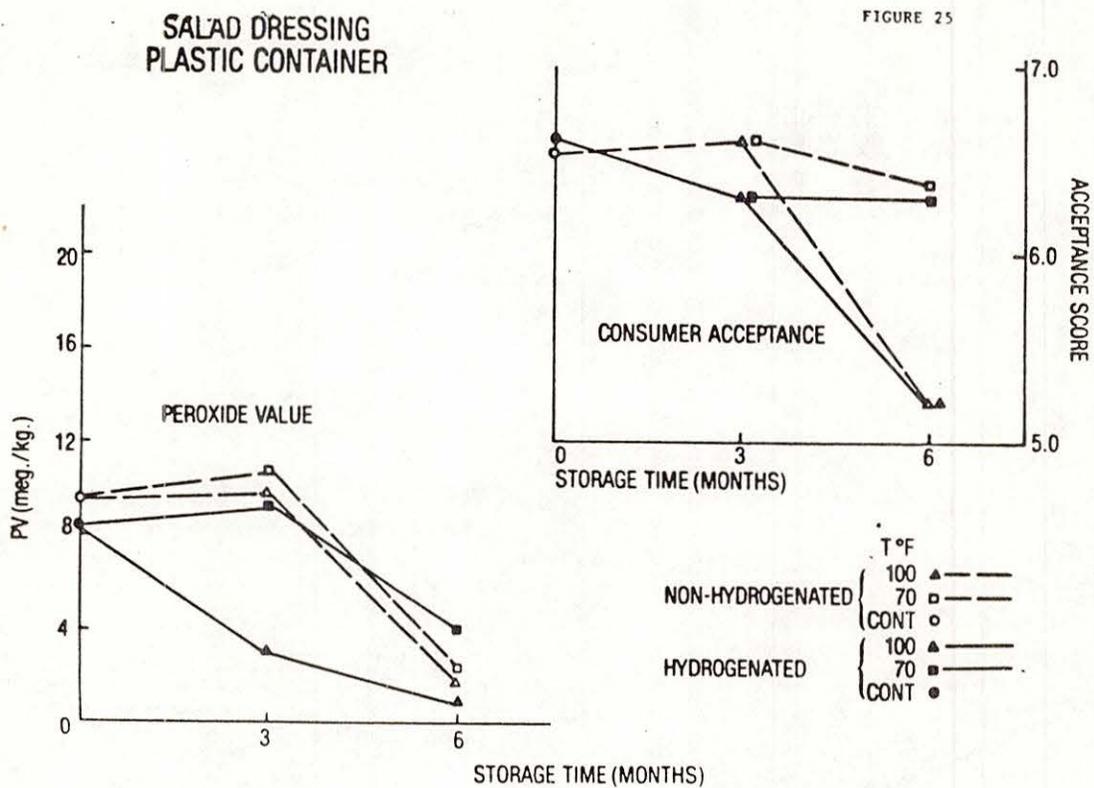
Figure 25.   Consumer acceptance ratings and peroxide values, salad dressing in plastic container.

TITLE: Thermal Inactivation and Injury of Spores of <u>Bacillus</u>
<u>stearothermophilus</u>

DURWOOD B. ROWLEY, DR.*, FLORENCE E. FEEHERRY, MRS. and
DONALD T. MUNSEY, MR.

ABSTRACT:

A thermal process which would be adequate to insure the inactivation
of thermophilic spores would have an adverse effect on quality. Although
thermophiles are not a health problem they may be a spoilage problem that
could impact on logistical efficiency and morale. The purpose of this
study was to determine the thermal resistance of <u>Bacillus stearothermophilus</u>
spores (ATCC 12980), the extent of the injured spore population at various
processing temperatures, and the significance of the injured spore popula-
tion as regards the thermophilic spoilage of temperature-abused ($>35^{\circ}$C),
low acid Tray Pack components.

Aqueous spore suspensions were heated at different temperatures for
various time intervals in a resistometer, spread plated on Antibiotic
Assay Medium supplemented with 0.1% soluble starch without (AAMS) or with
0.9% NaCl (AAMS-S), and incubated at 55°C unless otherwise indicated.
Uninjured spores formed colonies on AAMS and on AAMS-S; injured spores
formed colonies only on AAMS. D- values (time in min to inactivate 90% of
the spores) obtained when survivors were recovered on AAMS were 62.04,
18.00, 8.00, 3.33, and 1.05 min at 112.8°C, 115.6°C, 118.3°C, 121.1°C, and
123.9°C, respectively. Recovery on AAMS-S resulted in reduced D- and z-
values (change in temperature which will alter the D- value by a factor of
10). The computed z- value for spores recovered on AAMS and AAMS-S was
8.3°C and 7.6°C, respectively. The rates of inactivation and injury were
similar. Injury was a linear function of the heating temperature.

Heat-injured but viable spores would not be able to cause spoilage at
storage temperatures $\leq 45^{\circ}$C or at optimum temperatures in low-acid ration
components having about 0.9% NaCl, a pH ≤ 6.6 and/or hermetically sealed.
However, various pre- and post-processing control factors must be followed
to assure freedom from thermophilic spoilage.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Chief, Biological Sciences Division, Science
and Advanced Technlogy Directorate, U. S. Army Natick RD&E Center
PAST EXPERIENCE: Assistant Professor, Hartwick College, Oneonta,
New York, 1956-1959. Assistant Professor, University of Massachusetts,
Amherst, Massachusetts, 1962-1963. Research Microbiologist, Natick RD&E
Center, Natick, Massachusetts, 1963-1969. Chief, Food Microbiology Branch,
Natick RD&E Center, Natick, Massachusetts, 1969-1981.
DEGREES HELD: Bachelor of Science, Hartwick College, Oneonta,
New York, 1951. Master of Science, Syracuse University, Syracuse,
New York, 1953. Ph.D., Syracuse University, Syracuse, New York, 1962.

THERMAL INACTIVATION AND INJURY OF SPORES OF <u>BACILLUS</u> <u>STEAROTHERMOPHILUS</u>

Durwood B. Rowley, Dr.
Florence E. Feeherry
Donald T. Munsey

INTRODUCTION

Denny (12) reported that as early as 1913, Barlow demonstrated that thermophilic bacteria were the prime cause of spoilage of canned corn. Although thermal processes have been developed which generally assure the safety of low-acid (pH 4.6 and above) canned foods from <u>Clostridium</u> <u>botulinum</u> (20) and freedom from spoilage due to <u>C</u>. <u>sporogenes</u> (27), spores of the thermophilic organism <u>Bacillus</u> stearothermophilus can, and do survive thermal processing in a "commercially sterile" product (7, 12, 27). Since many products cannot withstand the heat treatment required to inactivate thermophilic spores, other measures are required to prevent thermophilic spoilage. Such measures include (i) control of thermophilic contamination of ingredients, (ii) rapid cooling to 43°C subsequent to thermal processing, and (iii) controlled storage.

During the course of the thermal process, spores may be inactivated, sublethally injured, or remain uninjured. The exponential death rate resulting from thermalization of spores forms the basis of calculations used in thermal processing in the food industry (27); however, the injured spore population is not always considered in these calculations. Sublethal injury caused by various food processing techniques affects either the germination or the outgrowth capability of the spore as manifested by (i) a requirement for nonnutritive germination stimulants, (ii) modified optimum temperature for enumeration, (iii) increased sensitivity to inhibitors, and (iv) altered nutritional requirements (2). Spore injury may have beneficial effects in food processing by taking advantage of increased sensitivity to food ingredients such as sodium chloride. Such injury may play a role in reducing thermophilic spoilage of temperature-abused foods.

The purpose of this study was to determine the thermal resistance of <u>B</u>. <u>stearothermophilus</u> spores and the extent of the injured spore population at various processing temperatures, and the significance of the injured spore population as regards the thermophilic spoilage of temperature-abused, low-acid canned foods.

MATERIALS AND METHODS

Spore preparation. The medium of Cook and Brown (9) was used to prepare the spores of B. stearothermophilus ATCC 12980. This medium had the following composition (grams per liter): Bacto-tryptone (Difco), 3.0; Bacto-peptone (Difco), 6.0; Bacto-yeast extract (Difco), 3.0; 'Lab Lemco' beef extract (Oxoid), 1.5; Mn++, 1.0 μg/ml; agar (Difco) 15.0 for slants or 25.0 for Fernbach flasks.

Stock cultures were maintained on agar slants on the medium of Cook and Brown at 5°C. Growth was washed off stock slants with water (10 mL), heated at 75°C for 10 min, diluted (100 mL total), and 3 mL of the diluted suspension inoculated onto a solid agar (250 mL) surface in a 2800 Fernbach flask. Incubation was at 55°C for 4 days.

The cultures from approximately 25 Fernbach flasks, containing a mixture of cell forms, were harvested by scraping the agar surface with a bent glass rod and rinsing off the growth with water. The combined suspensions were centrifuged at 1000 x g for 30 min in the swinging bucket rotor in an International Equipment Co. (IEC) refrigerated centrifuge at 5°C. The supernatant was decanted and the pellet was washed by resuspension in chilled water and recentrifugation. This washing procedure was repeated two times. Subsequently, the washed pellets were resuspended in 200 mL of 0.05 M potassium phosphate, pH 7.0, containing lysozyme (100 μg/mL) and incubated with stirring at 37°C for 1 h. Enzyme treated spores were water washed four times to remove vegetative debris.

Twenty spore suspensions prepared as above were lyophilzed, pooled, (ca. 8 g of spores) and stored in an evacuated desiccator over silica gel at 5°C. The lyophilzed spores had no detectable vegetative cells, no spores in sporangia, and fewer than 5% germinated spores.

Spore activation. Aqueous suspensions of spores (1.0 mg lyophilized spores/mL sterile distilled water or ca. 2.0×10^8 spores/mL) were mixed thoroughly with a Vortex mixer and were filtered through a coarse sintered glass funnel (Pyrex) to remove spore clumps. Spores were activated by heating at 100°C for 15 min in a free flowing steam cabinet (G.H. Wahmann Manufacturing Co., Baltimore, MD), and subsequently were chilled in an ice bath until used.

Heat treatment. A volume (0.5 mL) of activated spore suspension was placed in a stainless steel cup (I.D. 17.4 mm, Ht. 13 mm) and heated in a Biological Indicator Evaluator Resistometer (BIER; Joslyn Valve, Co., Macedon, NY) at different temperatures for various time intervals. After

heating, these cups were aseptically dropped into tubes (11 x 203 mm), containing 9.5 mL of chilled, sterile distilled water as the first dilution.

Recovery conditions. Diluted samples (0.1 mL) were spread plated (duplicate plates) on Antibiotic Assay Medium supplemented with 0.1% soluble starch (AAMS; 9) which had the following composition (grams per liter) Bacto-peptone (Difco), 6.0; Bacto-tryptone (Difco), 4.0; Bacto-yeast extract (Difco), 3.0; 'Lab Lemco' beef extract (Oxoid), 1.5; dextrose 1.0; soluble starch (Difco), 1.0; and agar (Difco), 15.0, pH 6.8-6.9. This was the optimal or nonselective medium for growth under aerobic conditions. CFU on this medium represented growth from the total viable population (uninjured and injured spores). Addition of NaCl to concentrations as high as 0.9% in AAMS (AAMS-S) had little effect on the number of colonies formed by unstressed cells (Fig. 1). Increasing the concentration of NaCl above 0.9% progressively decreased the CFU/mL. CFU on this selective medium represented only the uninjured spore population -- those cells not sensitive to 0.9% NaCl.
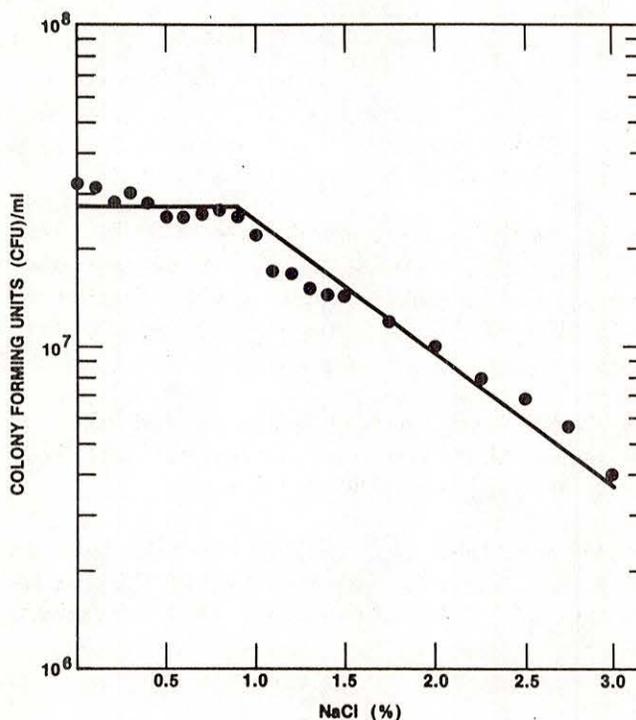

Figure 1. Effect of NaC1 concentration in a recovery medium (AAMS) on the percentage survivors of uninjured spores of Bacillus stearothermophilus ATCC 12980. Heat-activated (100°C - 15 min) spores were plated on AAMS supplemented with various concentrations of NaC1 and incubated at 55° C for 24 h. The CFU/ml plotted were the average of three experiments.

Incubation temperatures ranged from $40^{\circ}C$ to $65^{\circ}C$ with $55^{\circ}C$ being the optimum temperature of incubation. Incubation time was approximately 24 h except in the case of the lower temperatures such as $40^{\circ}C$ and $45^{\circ}C$ where the time increased to 6-7 days and 2-3 days, respectively.

In some experiments, the pH of AAMS or AAMS-S was adjusted to lower values with HCl prior to autoclaving. Since autoclaving may have an effect on the pH, all given values represent those after autoclaving.

Incubation was under aerobic conditions unless otherwise noted. Anaerobic conditions (spread plates) were maintained with GasPak (Baltimore Biological Laboratory).

Calculations. Percentage of spores injured was calculated according to the following: Injured Cells (%) = I =

$$\left(1 - \frac{CFU/mL_{selective}}{CFU/mL_{nonselective}}\right) \times 100$$

where the term selective means either selective medium (AAMS-S) or selective temperature of incubation ($^{\circ}C$), selective pH (<6.9), or anaerobic conditions, and the term nonselective means either nonselective medium (AAMS) or nonselective temperature of incubation ($55^{\circ}C$), nonselective pH (pH 6.9), or aerobic conditions.

D- and D'- values. The time in minutes required at a given temperature to destroy 90% of the cells when the survivors were recovered on AAMS (D) or under selective conditions such as AAMS-S (D').

All experiments were repeated 2-3 times, and the results represent the average of all experiments. In all figures except for Fig. 1, the best straight line was determined by the method of least-squares.

RESULTS

Thermal inactivation. The kinetics of thermal inactivation of spores of B. stearothermophilus in aqueous suspension are shown in Fig. 2. The survival curves had an initial shoulder portion preceding a logarithmic decline when spores were heated at $112.8^{\circ}C$, $115.6^{\circ}C$, and $118.3^{\circ}C$. D-values ranged from 62.04 min at $112.8^{\circ}C$ to 1.05 min at $123.9^{\circ}C$.
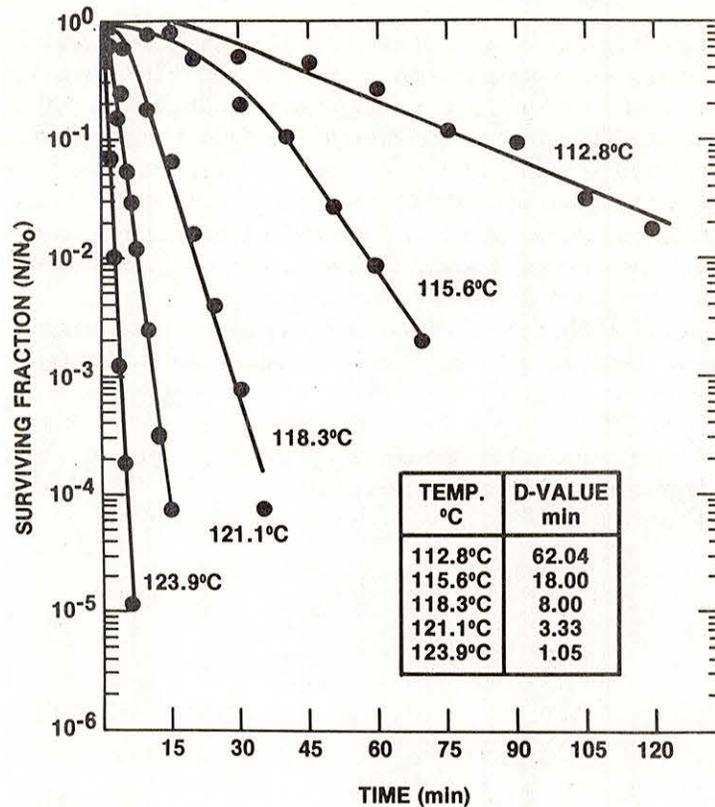
Figure 2. Thermal inactivation of spores of Bacillus stearothermophilus ATCC 12980. Heat-activated (100° C - 15 min) spores were treated at various temperatures for various time intervals, plated on AAMS and incubated at 55° C for about 24 h. D-values were computed by the method of least-squares for the rectilinear portion of the curve.

Thermal injury determined by salt-sensitivity or temperature of incubation-sensitivity. The kinetics of thermal injury (as judged by inability to form colonies on AAMS-S) as compared to inactivation at two temperatures, 115.6°C, and 121.1°C are shown in Fig. 3. At 115.6°C, it was evident that injury preceded inactivation. There was an initial shoulder in the survival curve during which some spores were injured, but not inactivated. For example, there were ca. 83% survivors on AAMS when spores were heated for 10 min at 115.6°C. However, 68% of these surviving spores were injured, as judged by their inability to form colonies on AAMS-S. Rapid inactivation and injury resulted upon exposure to 121.1°C, thus no shoulder was evident. D'-values at 112.8°C, 118.3°C, and 123.9°C were 44.04, 5.36, and 0.82 min, respectively (data not shown). The smaller D'-values are "pseudo" D-values as compared to the true D-values and are an indication of injury.

As shown in Fig. 3, there was at least 95% inactivation of the spore population when heated at 121.1°C for 6 min. Furthermore, 95% of the surviving 5% was injured as judged by inability of cells to grow on AAMS-S. When sensitivity to incubation temperature was used as a criterion of injury, the same extent of injury was not shown (Table 1). Incubation temperatures did not affect the total number of CFU/ml of either unactivated or activated spores except that incubation time for colony visualization was increased at lower temperatures. However, incubation temperature did have an effect on the ability of heat-treated spores to produce colonies on AAMS. For example, spores heated at 121.1°C for 6 min formed fewer colonies at 40°C than at 55°C, and ca. 62% of the surviving fraction was injured as judged by inability of cells to grow at 40°C. Even a prolonged incubation of 14 days at 40°C did not increase the recoverable cells (data not shown). The results in Table 1 indicate that the inhibitory effect of temperature on recovery of heat injured cells was most pronounced at 40°C and that incubation temperatures of 65°C had little, if any, effect.
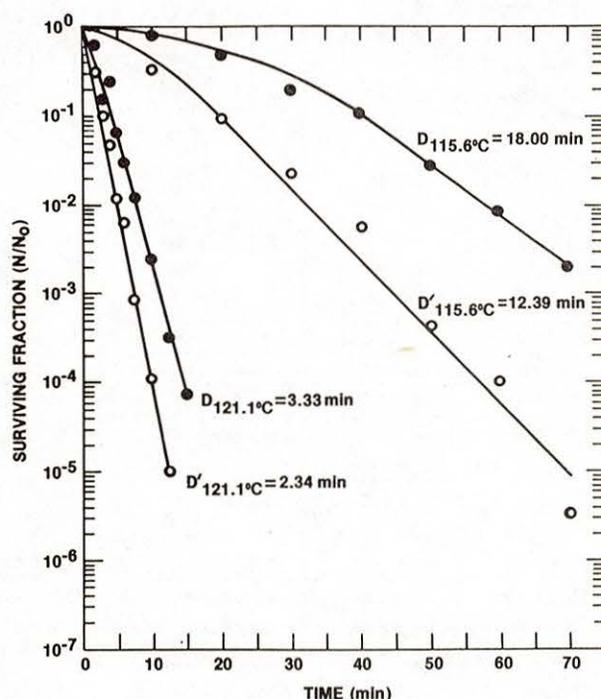

Figure 3. Thermal inactivation and injury of spores of Bacillus stearothermophilus ATCC 12980. Heat-activated spores were treated at 115.6°C or 121.1°C for various time intervals, plated on AAMS without (●) or with 0.9% NaCl (○), and incubated at 55°C for about 24 h. The D- and D'-values were computed as described in Fig. 2.

TABLE 1. Effect of Incubation Temperature on Recovery of Uninjured
and Thermally Injured Spores of B. stearothermophilus

Incubation Conditions				CFU/mL[a]		
Temperature $^\circ$C	Time Days	Unactivated	Activated[b]	Heat-Treated[c]	Injured Cells (%)[d]
40	6-7	1.35×10^8	2.61×10^8	3.28×10^6	62.3
45	2-3	1.38×10^8	2.76×10^8	4.86×10^6	44.1
55	1	1.52×10^8	2.50×10^8	8.70×10^6	0
65	1	1.31×10^8	2.49×10^8	6.57×10^6	24.5

a. Colony forming units per mL in AAMS.
b. An aqueous suspension of spores was heated at 100°C for 15 min.
c. Activated spores were heated at 121.1°C for 6 min resulting in a spore population of inactivated, injured and uninjured cells.
d. Injured cells (%) =

$$\left(1 - \frac{CFU/mL_{x\ ^\circ C}}{CFU/mL_{55\ ^\circ C}} \right) \times 100$$

Effect of pH or anaerobiosis on recovery of heated spores. As shown in Table 2, recovery medium with a pH value of 6.6 had no effect on the percent recovery of activated spores of B. stearothermophilus as compared to unadjusted AAMS, pH 6.9. However, as the pH of the recovery medium was reduced below 6.6, there was a progressive decrease in percent recovery until at pH 5.8 only ca. 1% of the spores formed colonies.

Heat-injured spores not only showed an increased sensitivity to 0.9% NaCl and an incubation temperature of 40°C, but also to two other conditions (pH 6.6 and anaerobiosis) having no effect on the recovery of activated spores (Table 3). This sensitivity of heat-injured spores was also demonstrated in Table 4 by reduced D'-values of 2.34 min (NaCl), 1.54 min (anaerobiosis) and 2.36 min (pH 6.6). When the pH of the recovery medium was below 6.6, the D'-values result from not only inactivation and injury, but also pH inhibition. The presence of 0.9% NaCl in the recovery medium or anaerobiosis further reduces D'-values.

TABLE 2. Effect of pH on the Recovery of Activated[a] Spores
of B. stearothermophilus[b]

Recovery Medium pH	Percent Recovery
6.9 (unadjusted)	100
6.6	98
6.4	62
6.2	38
6.0	20
5.8	1

a. 100°C for 15 min.
b. AAMS plates were incubated aerobically at 55°C for 1 to 2 days.

TABLE 3. Effect of Various Selective Conditions of Recovery
on the Percent of Activated[a] B. stearothermophilus
Spores Injured by Heating at 121.1°C

PERCENT INJURY[b]

Selective Conditions

Minutes at 121.1°C	NaCL (0.9%)	pH (6.6)	Anaerobic (GasPack)	Incubation Temperature (40°C)
0.0	0.0	0.0	0.0	0.0
2.0	70.8	37.9	62.0	–
4.0	85.7	55.4	93.0	–
6.0	91.3	76.5	98.2	62.3
7.5	95.7	89.9	99.7	–

a. 100°C for 15 min.
b. % Injury =

$$\left(1 - \frac{CFU/mL_{\text{Selective Conditions}}}{CFU/mL_{\text{AAMS, pH 6.9, }55^\circ\text{C, Aerobic}}}\right) \times 100$$

TABLE 4. Effect of the Recovery Medium pH Alone or in Combination with
NaCl or Anaerobiosis on the Decimal Reduction Time of
Activated and Heated[a] B. stearothermophilus Spores

Recovery Medium pH	Decimal Reduction Time (min)		
	AAMS Aerobic	AAMS-S	AAMS Anaerobic
6.9	3.33[b]	2.34	1.54
6.6	2.36	1.46	1.15
6.4	1.57	1.07	0.95
6.2	1.11	0.79	0.73

a. Activated (100°C for 15 min) aqueous spore suspensions were heated
for various time intervals at 121.1°C, diluted, plated, and incubated
aerobically at 55°C for 1 to 2 days and anaerobically at 55°C for 3 to 4
days.

b. This is the only "true D-value", that is obtained by recovery of heated
spores under optimal conditions; all other values are D'-values.

Estimation of heating time to attain 90-95% injury. In an effort to
compare the extent of injury at various heating temperatures, when at least
90% of the total population was thermally inactivated, the time required to
achieve 90-95% injury (detected by salt-sensitivity) was plotted vs. heating
temperature. The logarithm of the time required to attain 90-95% injury was
a linear function of the temperature of heating and ranged from 120 min at
112.8°C to 2 min at 123.9°C (Fig. 4).
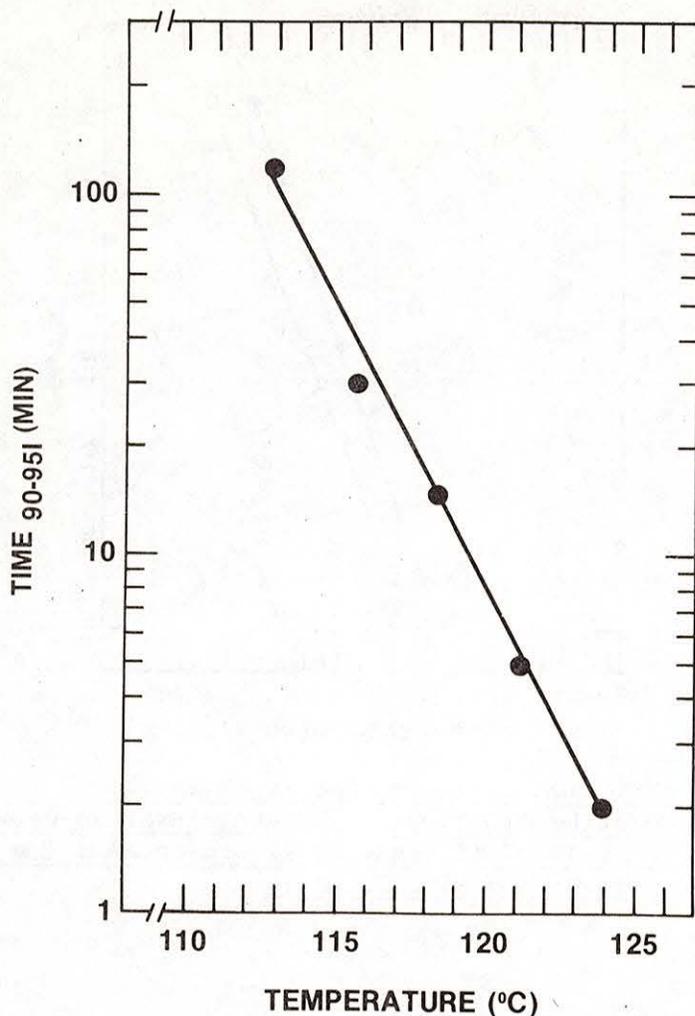
Figure 4. Effect of heating temperature on the time required to attain 90-95% Injury (90-95I) of spores of Bacillus stearothermophilus ATCC 12980.

Thermal destruction curves. D- and D'-values were plotted vs. temperature in Fig. 5 in order to generate z-values (the change in temperature which will alter the D- or D'-value by a factor of 10). In the temperature range of 115.6 to 121.1°C a z-value of 8.3°C was obtained for spores recovered on AAMS compared with a z-value of 7.6°C for spores recovered in AAMS-S. The rates of inactivation (z-values) and injury (the area between the two curves) were similar.

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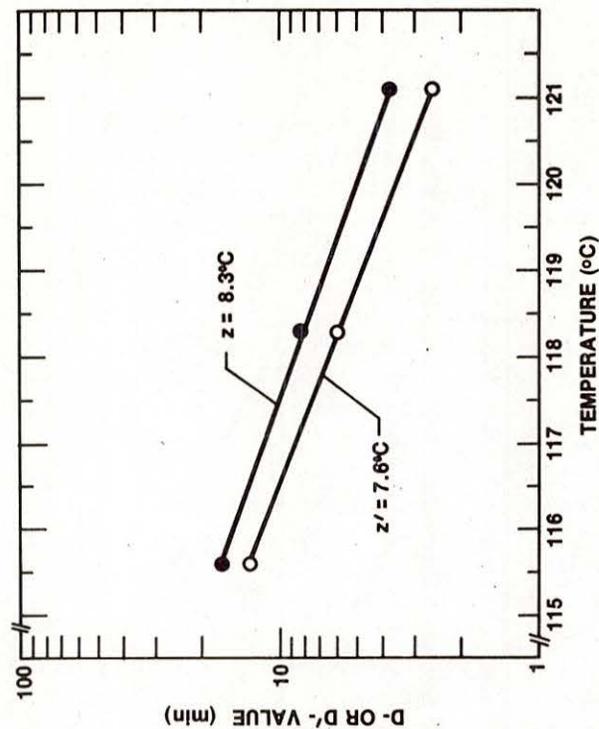
Figure 5.   Thermal destruction curve for spores of Bacillus
stearothermophilus ATCC 12980.   D- and D'-values were based on
the recovery at 55° C of total survivors on AAMS (•), and
uninjured survivors on AAMS-S (o).

DISCUSSION

The thermal resistance of water suspensions of B. stearothermophilus as
characterized by D- and z-values confirmed other work (5, 10, 15, 21, 22,
28) indicating that these spores are extremely heat resistant and that a 12D
process for C. botulinum would not provide a 5D process as used for B.
stearothermophilus (D. J. Goeke.   Paper presented at the Second Annual
Eastern Research Highlights Conference,   National Canners Association,
Washington, D.C. 1977).   Note, however, that differences in computed
D-values can exist due to variations in strains of B. stearothermophilus
(21), conditions (sporulation medium or temperature) under which spores were
produced; suspending menstrua (water, buffer, or organic material) during
heating, or; recovery conditions (medium, atmospheric conditions, pH or
incubation temperature) employed.   The z-value reported in our study was
8.3°C as compared to the range of 6.9 to 7.8°C reported for various
strains of B. stearothermophilus (21).   Briggs (5) and Pflug et al. (24)
published z-values of 7.0 and 8.4°C for water suspensions of spores of
strains NCIB 8919 and ATCC 7953, respectively.

Many researchers (5, 13, 18, 22) have demonstrated that survival curves of spores, heated at temperatures below 121.1°C, frequently consist of an initial shoulder portion succeeded by a logarithmic decline. Theories regarding the explanation for such shoulders include (i) the effect of spore clumping, (ii) the result of an activation process counteracting the inactivation process, or (iii) the existence of an intermediate state of thermal susceptibility between the normal viable state and the dead state (e.g., injured cells capable of repair). In our studies, all spore suspensions were filtered (sintered glass filter) to remove any possible spore clumps and activated under experimentally determined optimal conditions (100°C for 15 min) prior to any heating experiments determining survival. Therefore, we believe the intermediate state of thermal susceptibility or the injured spore population capable of repair accounts for the shoulder portion of our survival curves.

The addition of a stressing substance (e.g., NaCl, antibiotics) to a good medium (17) or certain stressful conditions have been used for assaying spore injury. In our studies, the presence of thermally injured spores was routinely judged by the inability of these spores to form colonies in the presence of 0.9% NaCl. Heat-stressed B. stearothermophilus spores not only showed an increased sensitivity to NaCl, but to other post-processing environmental factors such as pH 6.6, anaerobic conditions and incubation temperatures below 55°C; all factors that had little if any effect on the recovery of unstressed cells. Cook and Gilbert, (11), Briggs and Yazdany (6), and Labbe (19) have previously demonstrated that heated spores of B. stearothermophilus are sensitive to NaCl in the recovery medium. This increased sensitivity of heat injured cells to post-processing environmental factors had an effect on the "apparent" heat resistance of the spores as evidenced by reduced D-values, referred to as "pseudo" or D'-values (Fig. 3, Table 4).

The germination system (1, 3) as well as the outgrowth system (4) of heat injured spores may be damaged. Labbe (19) pointed out that lysozyme added to a nutrient agar recovery medium did not enhance the recovery of heat injured B. stearothermophilus spores. Duncan et al., (14) demonstrated that lysozyme circumvents both the triggering and cortex lytic systems involved in the germination of C. perfringens spores. Thus, Labbe's results indicate that the thermal injury of B. stearothermophilus spores was not due to the thermal inactivation of these two systems associated with germination. He postulated that a substance produced in nutrient broth by B. stearothermophilus enhanced the recovery of heat injured spores due to its effect on the outgrowth system. In the present studies, no attempt was made to determine the spore system(s) affected by thermal injury.

What is the significance of the injured spore population? Clearly injured spores are sensitive to any one of an array of typical post-processing factors such as NaCl, temperature, pH, and anaerobiosis -- all of which result in fewer survivors as evidenced by reduced D- and z-values. Cook and Gilbert (11) suggested that the presence of 1 to 3% NaCl may play an important role in the control of thermophilic spoilage of low-acid (pH 4.6 and above) canned foods. Spore injury and subsequent sensitivity to the surrounding environment is one of numerous factors (e.g., nitrite and brine concentration, pH, storage temperature) associated with the inhibition of C. botulinum and reduced thermal requirements in cured meats (8).

Although the recovery of unstressed B. stearothermophilus spores was not affected by anaerobic conditions, 93% of those spores surviving 121.1°C for 4 min were unable to proliferate under these conditions (Table 3). Thus, injury should play a role in the delay and/or reduction of thermophilic spoilage of hermetically sealed foods.

If heat-treated B. stearothermophilus spores were recovered at 40°C, there was always a reduction in count as compared to recovery at 55°C (Table 1). This inability of injured spores to outgrow at lower temperatures may be of benefit to the common practice of rapidly cooling thermally processed cans to a temperature of 43°C in order to aid in the elimination of thermophilic spoilage (12).

The phenomenon of autosterilization (23) or sterilization by means of spore deactivation (25) has been reported for flat-sour thermophiles, i.e., B. stearothermophilus. Pearce and Wheaton (23) have defined the term autosterilization as the drying out, or loss of viability, of spoilage spores which have never grown in the product. This was accomplished at a sub-optimum incubation temperature of 21.1°C. It is conceivable that spore injury may play an important role in autosterilization.

It does appear that thermal injury would reduce the potential of B. stearothermophilus spoilage of foods having a pH $\leq$ 6.6, $>$ 0.9% NaCl, hermetically sealed and/or stored at $\leq$ 40°C. Effects of the interactions of these post-processing conditions on the recovery of injured spores was not investigated in these studies. We did demonstrate the effect of the medium pH alone or in combination with NaCl or anaerobiosis on the decimal reduction time of heated B. stearothermophilus spores (Table 4). Where the pH of the recovery medium was $\leq$ 6.6 and contained 0.9% NaCl, or was incubated under anaerobic conditions, the reduced D'-values resulted not only from injury, but also from inhibition by pH alone and in combination with NaCl or anaerobic conditions.

Gombas (16) appropriately stated, "preventing proliferation of injured spores is a double-edged sword". He further emphasized that one must assure (i) that all of the surviving population is injured, (ii) all injured spores are inhibited by the post-process treatments, and (iii) repair of the injured spores must be prevented. After repair, an injured pathogen or spoilage microorganism has the potential to cause a health hazard or spoilage.

It is evident that one must maintain a low indigenous thermophilic spore population in the formulation since if the spore level is too high one cannot be sure that all of the thermophilic spores are either inactivated or injured during a thermal process (e.g., 6 min at 121.1°C). Thermal treatment (121.1°C for 6 min) of a water suspension of B. stearothermophilus spores inactivated $\geq$ 90% of the spore population and $\geq$ 90% of the survivors were injured, as judged by their inability to proliferate in the presence of 0.9% NaCl (Fig. 3, Table 3). If one assumes 100 spores per container of food (e.g. peas with ca. 0.9% NaCl), it is conceivable that after 6 min at 121°C the container could contain one viable and uninjured spore capable of germination, outgrowth, and of causing subsequent spoilage. This is assuming no protective effect by ingredients during heating. A protective effect could result in more than one viable and uninjured spore. Haldeman (G. R. Haldeman, M. S. Thesis, Pennsylvania State University, University Park, 1978) demonstrated that low numbers (<2/g) of thermophilic spores were capable of causing spoilage in canned mushrooms. In some of our studies (data not reported), cans containing ca. one C. thermosaccharolyticum spore/100 g of beef strips with green peppers and gravy spoiled within four days at 65°C.

Other control factors include temperature control after processing and during storage, use of ingredients with minimal levels of thermophilic spores and appropriate cleaning of vegetables (26). Foods produced for the military services are controlled by purchase documents which, when appropriate, assure strict enforcement of (i) temperature control after processing, (ii) Military Standard MIL-STD-900 (Bacterial standards for starches, flours, cereals, alimentary pastes, dry milks, and sugars used in the preparation of thermostabilized foods for the Armed Forces, 9 April 1985, Class 89GP GL) to assure that ingredients such as starches, flours, cereals, alimentary pastes, dry milks, and sugars are free from or have low numbers of thermophilic spores, and (iii) washing of vegetables to minimize the introduction of thermophiles. Control of storage temperatures is not always possible in the military environment.

The actual significance of injury and treatment interactions reducing thermophilic spoilage must eventually be verified by inoculated pack studies dealing with the product(s) under concern.

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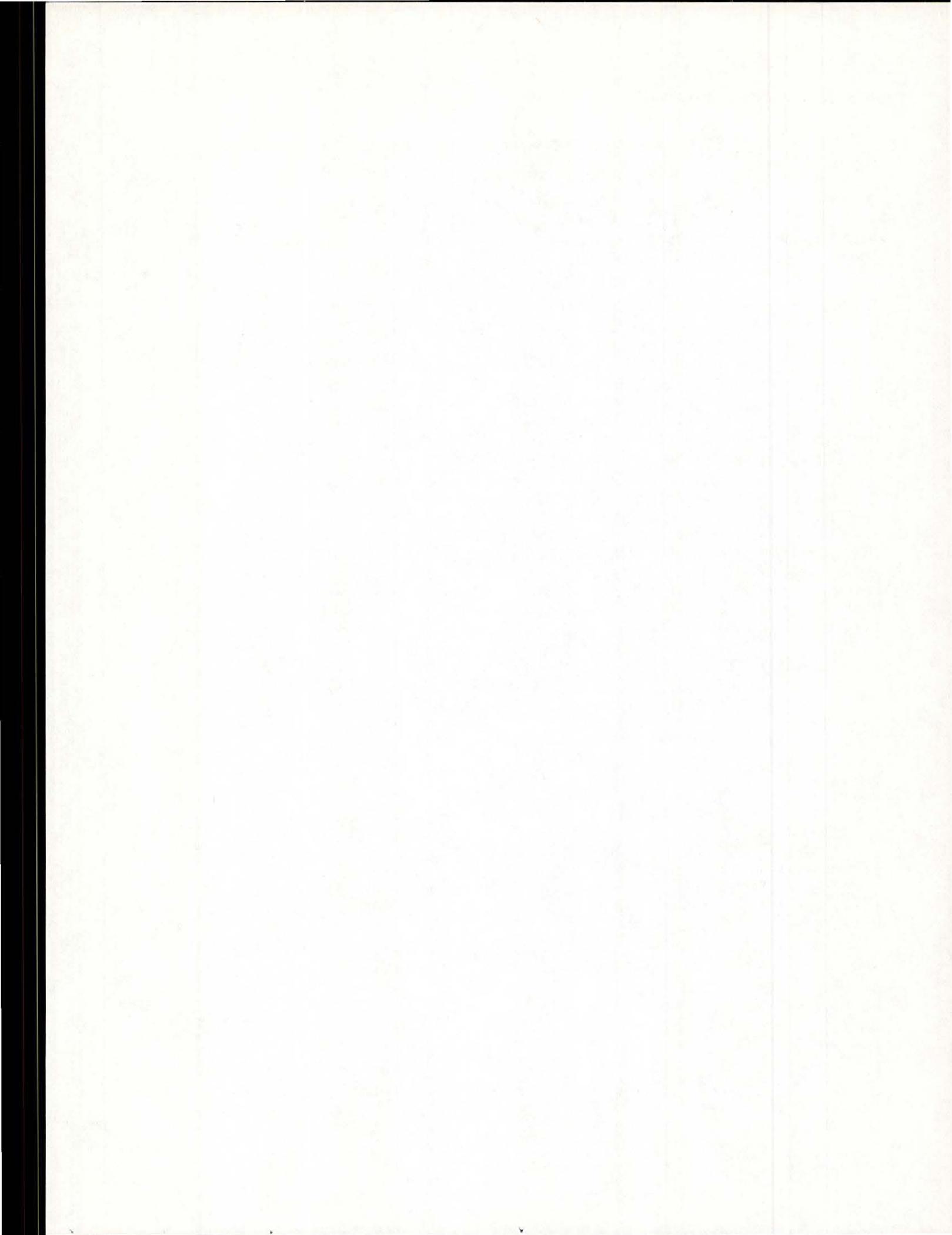
TITLE: Nondestructive Measurement of the Variation in Carbon Distribution and Vapor Adsorption Capacity of Chemical Protective Fabrics

RONALD SEGARS,* ERNEST JOHNSON, & DAVID NORDQUIST

ABSTRACT:

Uniform distribution of the activated carbon in fabrics designed for chemical protection (CP) is essential for optimum safety and performance. A novel nondestructive test method has been developed and applied to the determination of the distribution patterns of several carbon impregnated foams used as inner layers of CP battlefield uniforms.

The amount of light transmitted through the material from a fixed source was detected by a photocell and displayed on a signal analyzer. The signal trace was related to the amount of carbon in the path between the light source and the detector; high voltage for low carbon content and low voltage for high carbon content.

Light transmittance data correlated highly with both the areal density of the foams and with their CCl_4 adsorption capacity. Surface area data from nitrogen gas adsorption studies also correlated with areal density of the foams and with light transmittance. Calculations based on these experimental correlations showed that it is possible, using light transmission measurements, to determine the amount of any vapor a fabric will adsorb if only the cross-sectional area of an adsorbed molecule of that vapor is known.

*BIOGRAPHY:
PRESENT ASSIGNMENT: Research Physicist, Biological Science Div., Science & Adv. Tech. Dir., Natick Research, Development & Eng. Center.
PAST EXPERIENCE: Research Physicist (Fluid Mechanics, Thermal Properties) PRL, NRDEC, 1960-1970. Research Physicist (Food Rheologist) Food Science Lab, NRDEC, 1970-1983.
DEGREES HELD: Bachelor of Arts, Bowdoin College, Brunswick, ME, 1958. Master of Science, Northeastern University, Boston, MA, 1970.

NONDESTRUCTIVE MEASUREMENT OF THE VARIATION IN CARBON DISTRIBUTION
AND VAPOR ADSORPTION CAPACTTY OF CHEMICAL PROTECTIVE FABRICS

RONALD SEGARS, ERNEST JOHNSON, AND DAVID NORDQUIST

INTRODUCTION

Much work has been done on the development of fabrics to protect the
combat soldier in toxic environments. Many of these fabrics are laminates
in which one layer has been impregnated with an adsorber of toxic agents.
The adsorbent found generally to be the most satisfactory is activated
carbon (1). Fabrics intended for use in combat uniforms must be designed
to meet the requirements and objectives of the final product. In general
this means a maximum reduction in weight, reduced heat stress, assured
protection from toxic agent challenges of specific concentration, flexi-
bility, water repellency, ability to accept camouflage dyes, etc. Several
of these factors are affected by the amount of carbon in the fabric. If
there is too little carbon, or if it is poorly distributed, protection
cannot be assured. If there is too much carbon, the objective of minimum
weight will not be achieved. It is possible that too much carbon will
increase heat stress and reduce the flexibility. These requirements and
objectives place upper limits on the amount of carbon that can be used in
a combat uniform. To insure complete coverage with a limited amount of
carbon, the application process must be monitored and controlled to main-
tain and verify a uniform carbon distribution.

The distribution of activated carbon in chemical protective fabrics
and foams is a critical factor in their functional performance. If re-
gions with less carbon than was intended exist in the material, the expect-
ed level of protection is compromised. Toxic agents may penetrate through
these voids and cause injury, incapacitation, and sometimes death. Voids
may exist even though the material, on a larger scale, contains the appro-
priate amount of activated carbon and would by most quality control tests
satisfy all procurement specifications.

Often the manufacturer, to insure that adequate protection is provided
and that the product passes specification requirements, will "overload"
the material with carbon in order that samples taken from "weak" zones
will not fall below the 1.6 mg/cm^2 adsorbence minimum stated in the speci-
fication. This is undesirable from the economic point of view. It also
works against the ultimate goal of minimizing weight.

There is much to be gained by controlling the deposition and distri-
bution of carbon in fabrics to be used for chemical protection. In this
paper, we describe a simple and inexpensive method for evaluating the
distribution of activated carbon in the carbon-impregnated foams used as
inner layers of battlefield uniforms. The method is readily adaptable to
on-line monitoring of the final product. The method provides a continuous
feedback which in theory could be used to control the manufacturing pro-
cess. The method also provides a simple nondestructive test for inclusion
in specifications for quality assurance.

EXPERIMENTAL APPROACH

This research describes a light transmission measurement method, the most promising of several ideas which were evaluated in this study. In addition to light transmission, various sound attenuation studies, investigations of wave propagation characteristics, and elecrical resistance and capacitance measurements were considered. Of these methods, both sound attenuation and wave propagation showed some promise but were abandoned in favor of concentration on the light transmission approach.

Several interrelated experiments were conducted to establish the applicability of light transmission to the evaluation of carbon distribution in chemical protective foams. These experiments were designed to demonstrate as a first step the relationship, if any, between adsorption of CCl_4 (by methods described later) and the areal density of the fabric. The areal density was assumed to be directly proportional to the amount of carbon, binder and other additives present since earlier studies had shown the density of the unfilled foam to be nearly constant. Other experiments were aimed at demonstrating a relationship between light transmission and the areal density of the fabric. Included in this was the need to determine the sensitivity of the instrument and to show that variations in areal density could in fact be detected. As will be shown, these experiments also suffice to relate CCl_4 adsorption to light transmittance. A final set of experiments dealt with the relationship between the above measures, particularly the light transmittance and the presently used standard evaluation of CCl_4 adsorption.

The standard evaluation method for CCl_4 adsorption uses a "breakthrough" test (MIL-C-4385B(GL), Ref.2) in which a foam fabric containing activated carbon is used as a diaphragm through which a known flow of a carefully controlled gas mixture of nitrogen and CCl_4 is passed. The effluent is monitored and the amount of CCl_4 adsorbed by the diaphragm at the time CCl_4 is detected in the effluent is taken as the adsorbancy of the material. These tests were performed by the Individual Protection Directorate at NRDEC on samples carefully selected to (1) be uniform in light transmission and (2) cover the full range of expected light transmittance values.

Both type II and type III foams are unpigmented polyester based polyurethane foams impregnated with a slurry containing activated carbon and the necessary dispersing agents and binders. For type II foams, Phos Check[R] P-30 is added to the slurry to produce a flame resistant product. Type III foams, in addition to being flame resistant, have a 2[d] additive, Polyox WSRN-80[R], which gives a repellent finish to the impregnated foam.

In addition to the standard breakthrough test to determine the amount of CCl_4 which a sample of material containing activated carbon would

adsorb, an in-house system was devised which continuously monitored the weight of CCl_4 vapor adsorbed by the sample. A 1 by 8 cm strip of material containing the activated carbon was suspended from the weighing mechanism of an Ainsworth analytical balance. The samples weighed approximately 0.2 g and the balance read to 0.1 mg. The sample hung inside a glass container which was carefully positioned in the weighing chamber of the balance in such a way that the support wire holding the sample did not touch the small hole in the top of the glass container when the sample moved up and down. An inlet tube near the bottom of the glass allowed a few drops of liquid CCl_4 to be introduced into the chamber. The vapor from the CCl_4 was adsorbed by the foam and the increase in weight of the foam was recorded manually as a function of time.

Plots of the sample weight versus time (Fig. 1) clearly showed two distinct regions of adsorption. In both regions the weight gain was nearly linear with time but near the start of the adsorption process, the weight gain was almost five times faster than in the later stages. Presumably the initial adsorption corresponds to the filling of the monolayer. The intersection of the two linear segments was taken as the monolayer adsorption value and used as a measure of the adsorptive capacity of the sample.

The two direct measures of CCl_4 adsorption were supplemented by a measure of the total surface area of the samples. A Micromeritics gas adsorption apparatus (Accusorb model 2100E) was used to determine the total surface area of the 1 by 8 cm sample strips described above. Replicate runs taken on several samples were in excellent agreement and suggest that surface area data are highly reproducible.

The total surface areas obtained with the Micromeritics instrument were used to estimate the amount of CCl_4 that would be adsorbed in the monolayer. McClellan and Harnsberger (3) give the cross-sectional area of an adsorbed CCl_4 molecule as 39.2 A^2. Multiplying this area by the number of molecules per mole and dividing by the molecular weight of CCl_4 gives 1535 square meters as the surface area required to adsorb 1 gram of CCl_4. The reciprocal of this value multiplied by the total surface area obtained from the Micromeritics instrument was taken as the weight of adsorbed CCl_4 for the 1 by 8 cm sample strips and is denoted as ADSORP-CAL in the figures.

The apparatus and measurements described above are part of the tests used to validate the application of a nondestructive light transmission method to determine the amount and distribution of activated carbon in carbon containing foams. In this method, a photocell was positoned directly above the sample to be measured. An ordinary incandescant light bulb was positioned approximately 3 cm below the sample. The photocell was mounted on a tri-axial positioner to facilitate locating the detector directly over the center of the light bulb and to allow the photocell to

be lowered close to the sample to reduce the amount of stray light reaching the detector. The electrical leads from the photocell were attached to a Wavetek 804A signal analyzer which was used to display, record and save on disk the voltage output from the photocell, (Fig. 2).

The drive mechanism from a recorder was used to pull a strip of foam approximately 20 cm wide by 50 cm long at a constant velocity past the photocell detector. Moving the sample at a constant speed made the time axis of the signal analyzer proportional to distance traveled or position on the sample since the starting point was carefully marked on both the sample and the analyzer trace.

RESULTS AND DISCUSSION

The traces produced clearly showed the variations in light transmission and indicated the amount of carbon present at each location. The voltage peaks indicate high light transmission and low carbon content while the low voltage points indicate low light transmission levels and high carbon content. Uniform regions of high, intermediate, and low light transmission levels were identified, evaluated and selected for subsequent gas adsorption studies using this procedure.

A plot of the experimental adsorption of CCl_4 (determined from the wight gain) vs the areal density (weight per unit area), Fig. 3, shows a highly correlated linear dependance for both the type II and type III fabrics. Adsorption for the two types is quite different with the type II material adsorbing less CCl_4 for a given areal density. There is also evidence that the two samples of type II fabric give slightly different adsorption-density values. The type II material represented by +'s adsorbs slightly less CCl_4 at a given areal density than that represented by the o's.

The above description applies equally well to a plot of surface area (which is determined using nitrogen gas adsorption) vs areal density as shown in Fig. 4.

A similar plot for the samples subjected to the standard breakthrough test is shown in Fig. 5. With the exception of two data points, one for each type of foam, the plots for these materials are linear. Correlation coefficients, with the two points omitted, are 0.97 for type II foam (only one type II foam was evaluated by this procedure) and 0.99 for the type III. The omitted points are shown on the plot but are not included in the regression line. Again, the type II material shows less adsorption of CCl_4 at a given areal density.

A comment needs to be made regarding the omitted data points. It is obvious from the above plot that the two points deviate sharply from the

two others in their respective groups. Dixon (4) and Dean and Dixon (5) suggest that for small groups of data such as these, the median is a better indicator of the expected value or population average than is the mean value. The regression line shown on the plots lies very close to the median values.

Three plots (Figs. 3,4,5) show a strong linear correlation between CCl_4 adsorption and areal density of the fabric for three very different measures of gas adsorption. Part of the reason for this high degree of correlation, particularly for the larger samples used in the breakthrough test, is that fact that the samples were carefully selected to have a uniform distribution of carbon, at least within the capability of light transmittance to measure the distribution. This selection procedure may explain the high correlations of this work and why similar correlations are not always found by others (McKinney (6), Hepfinger (7)).

For example, one can imagine a sample disk to be cut from a uniform region of a given areal density. For this sample, breakthrough would occur uniformly over the exposed area of the sample and would give a true breakthrough time. A true adsorption value for that areal density would also be obtained. Now suppose a sample disk was taken from a region of a steep carbon gradient. One side of the sample disk has very little carbon while the other has too much. The total weight could easily be the same as the wieght of the uniform sample and hence its calculated areal density will be the same. Its breakthrough time however will be much lower since nearly half of the exposed sample is below the average value and will allow premature breakthrough of the CCl_4. Hence there are two very different breakthrough times for the same areal density. A few nonuniform samples like this would greatly reduce any correlations.

Figure 6 is a plot of areal density vs light transmittance. The relationship for both types of fabric is linear and highly correlated. A significant difference is shown between the two types, and in this plot, a marked difference is also observed between the two samples of type II fabric. The reasons for this latter difference need separate investigation.

Figure 7 is a plot of areal density vs light transmittance for the samples prepared for the standard CCl_4 breakthrough test. The curve for the type III fabric is very linear while that for the type II material is concave upward. In spite of this obvious curvature, the linear correlation is still high at r = 0.95. Again the type II material exhibits a greater areal density at a given light transmittance than does the type III.

The adsorption of CCl_4 as determined from the weight gain of sample strips suspended in vapor is plotted vs light transmittance in Fig. 8. This plot is very similar to the plot of areal density vs light transmit-

tance, (Fig. 6). Similarity would be expected due to the high correlations between all measures of adsorption and areal density and between areal density and light transmittance, but here all three sets of data (two type II samples and one type III) are quite linear, well-correlated, and are located in the same relative positons in both plots. It should be noted that in the high adsorption region)low light transmittance) type III material adsorbs less CCl_4 than type II. This appears inverse to the expected trend since throughout the range studied, type III material adsorbed more per unit of areal density than type II (Fig. 3). However, the much higher areal density of the type II foam when plotted vs light transmittance (Fig. 6) more than offsets this difference and in Fig. 8, type III materials, at least in the high adsorption region, adsorb less CCl_4 vapor than type II per unit of light transmittance.

Figure 9 is a plot of the CCl_4 adsorption at breakthrough vs light tansmittance. With the two previously mentioned points plotted but omitted from the regression analyses, the type III material exhibits a linear dependence with high correlation ($r = 0.99$). The type II material is clearly concave upward (as observed in Fig. 7) but in spite of this curvature, the linear correlation coefficient is high ($r = 0.88$). For these breakthrough test samples, the areal density of type II foam as a function of light transmittance (Fig. 7) was not sufficiently higher than the areal density of type III to offset type III's higher adsorption (Fig. 5). For these data, the type III foam adsorbs more per unit of light transmittance than the type II.

Plots of the calculated and experimental adsorption vs light transmittance for both type II and type III fabric show that the regression lines are parallel (Figs. 10 and 11) and therefore the two methods (calculated from surface area data, actual adsorption of CCl_4 vapor) differ by a constant. This is further illustrated by the linear relationship shown in Fig. 12 where the calculated adsorption (as described in the previous section) is plotted vs the experimental adsorption (as determined with the in-house adsorption system) for both types of foam.

Figures 8, 9, 10, 11 and 12 carry strong implications. It is quite clear that the light transmittance can be used to accurately predict the adsorption of CCl_4 whether this adsorption is determined by the standard breakthrough test or by some other method such as the in-house system used in this work. It is also clear from Fig. 12 that the amount of CCl_4 adsorbed, and undoubtedly other gases as well, can be accurately calculated if the total surface area available and the cross-section area of an adsorbed molecule are known. It is then possible to determine the theoretical amount of adsorption of any gas of known molecular area from a measurement of the light transmittance value. The foundation for this possibility lies in the fact that the light transmittance probably measures the amount of carbon present in the sample. The activated carbon in the foams has all been subjected to very similar treatments and thus has nearly the same surface area per unit weight. Knowing the weight or amount of carbon

present from the light transmittance measurements thus gives an accurate measure of the surface area available for adsorption and allows the calculation of the adsorption capacity for any gas.

The above discussion has shown that the light transmittance is directly related to the adsorption capacity of the activated carbon impregnated foams. Figures 13 and 14 show the variation in light transmittance, and hence in adsorption capacity, of typical type II and type III foams. It is clear in these figures that a cyclic pattern of high transmittance (low adsorption) followed by low transmittance (high adsorption) occurs along the length of the roll. These high transmittance regions extend across the width of the roll and thus constitute a sizeable area of low adsorption in every yard of material. These low adsorption regions might allow the toxic agents to penetrate the material and thus constitute a serious defect, which must be corrected. Continuous on-line monitoring of the production process could warn of such defects and permit removal of material for additional testing before dangerously defective materials get into the supply line.

CONCLUSIONS

A simple, inexpensive, nondestructive method to determine the adsorptive capacity of activated carbon impregnated foams has been developed and tested. Its method of application is readily adaptable to on-line monitoring of production and in fact its use in this work was very similar to its use in production monitoring.

The light transmittance values provided by the new test method have been shown to correlate highly with the amount of carbon present in the material (areal density), and with its adsorptive capacity for CCl_4.

The adsorptive capacity of the foams has been shown to correlate highly with the total surface area available for adsorption. The amount of CCl_4 adsorbed can be accurately predicted from known values of the cross-section area of an adsorbed molecule and a measure of the total surface area as provided by the light transmitance.

Based on these findings, it should be possible to predict the adsorption by a carbon impregnated foam, of any gas of known molecular cross-section area, from a measurement of the light transmittance of the foam.

ACKNOWLEDGMENTS

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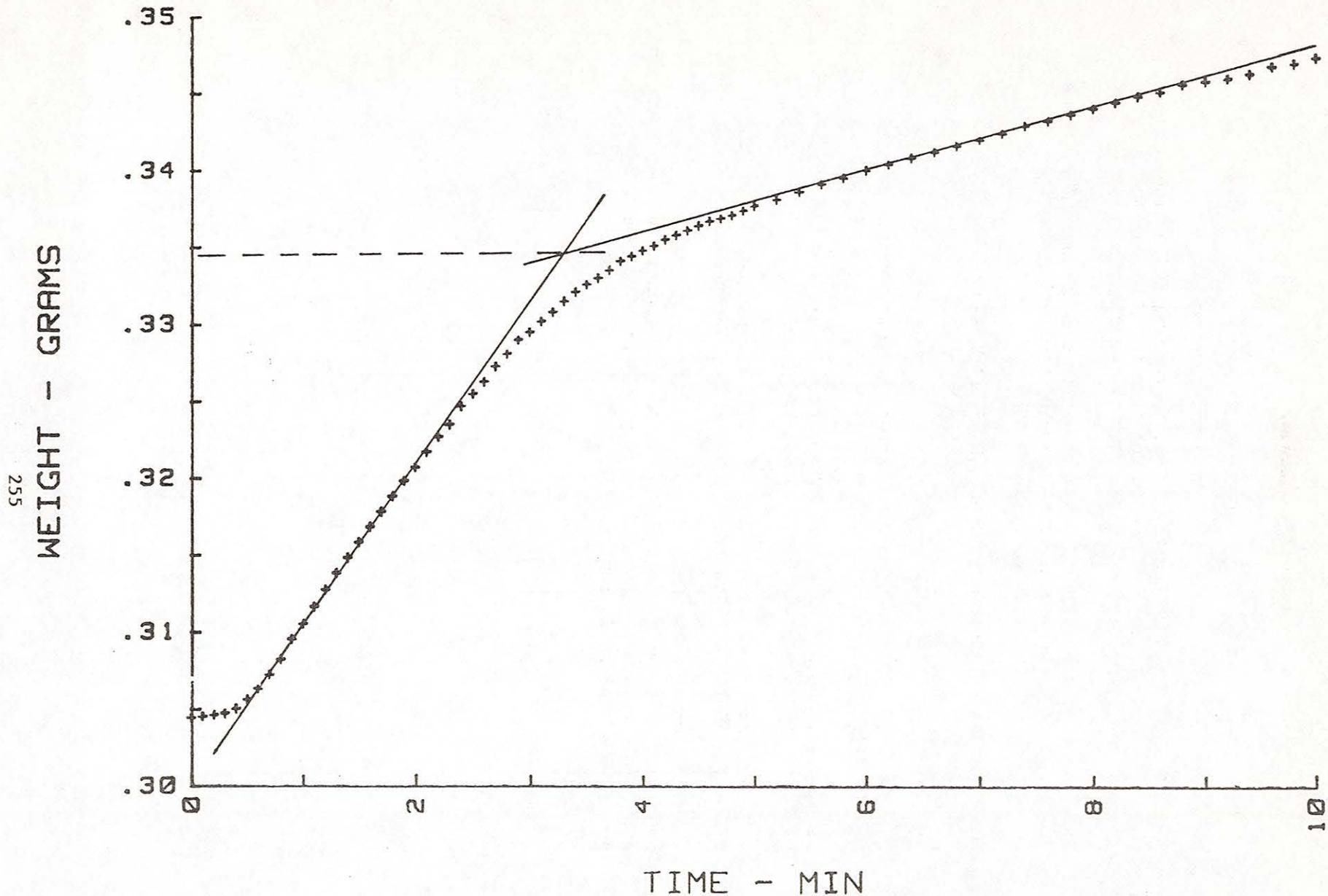
Figure 1. Plot of raw data from the in-house developed CCl_4 adsorption apparatus showing the weight gain of a 1 x 8 cm sample strip suspended in CCl_4 vapor plotted as function of exposure time. Intersection of the linear regions and the determination of monolayer adsorption weight are shown.
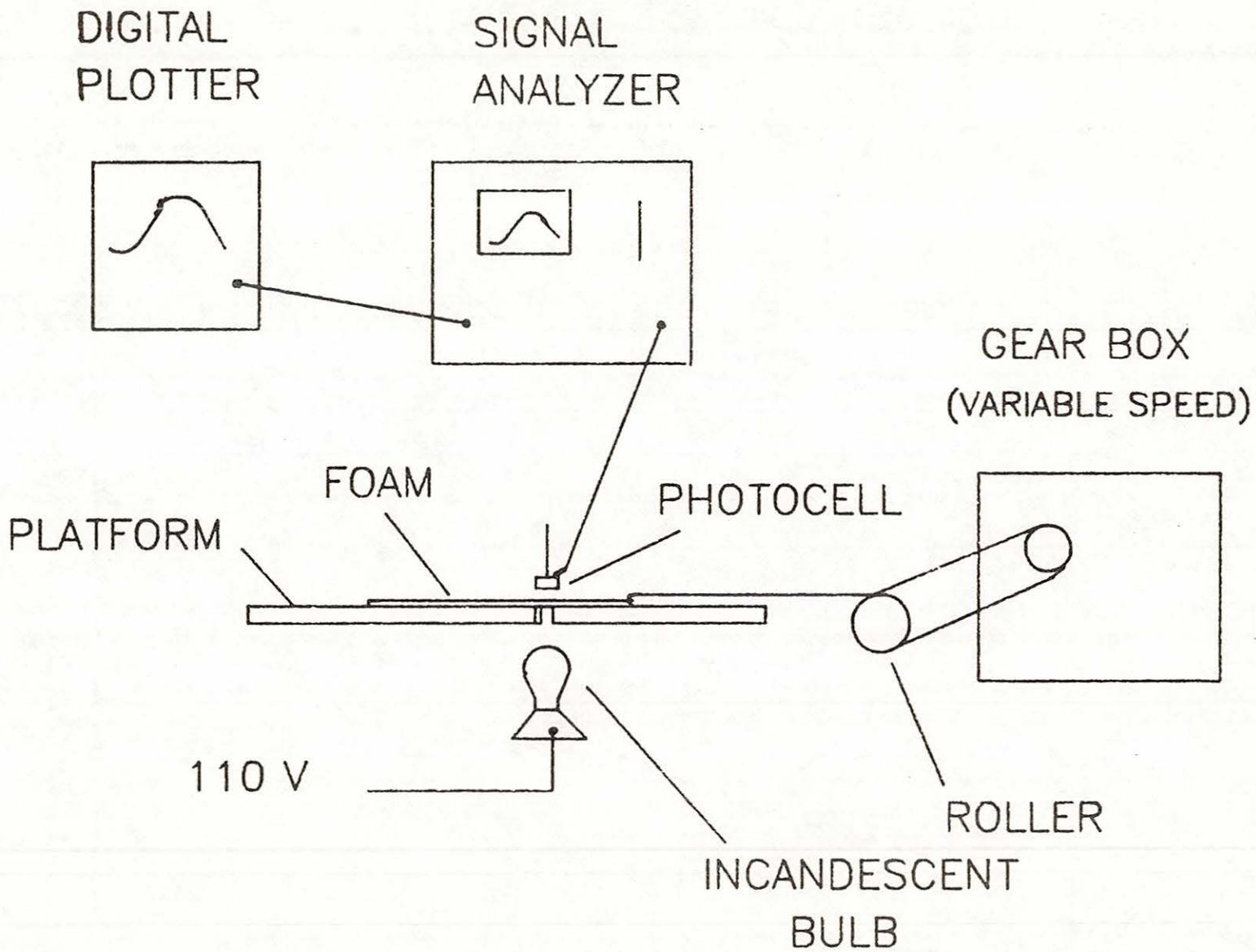
Figure 2. Schematic diagram of the Light Transmission Apparatus.
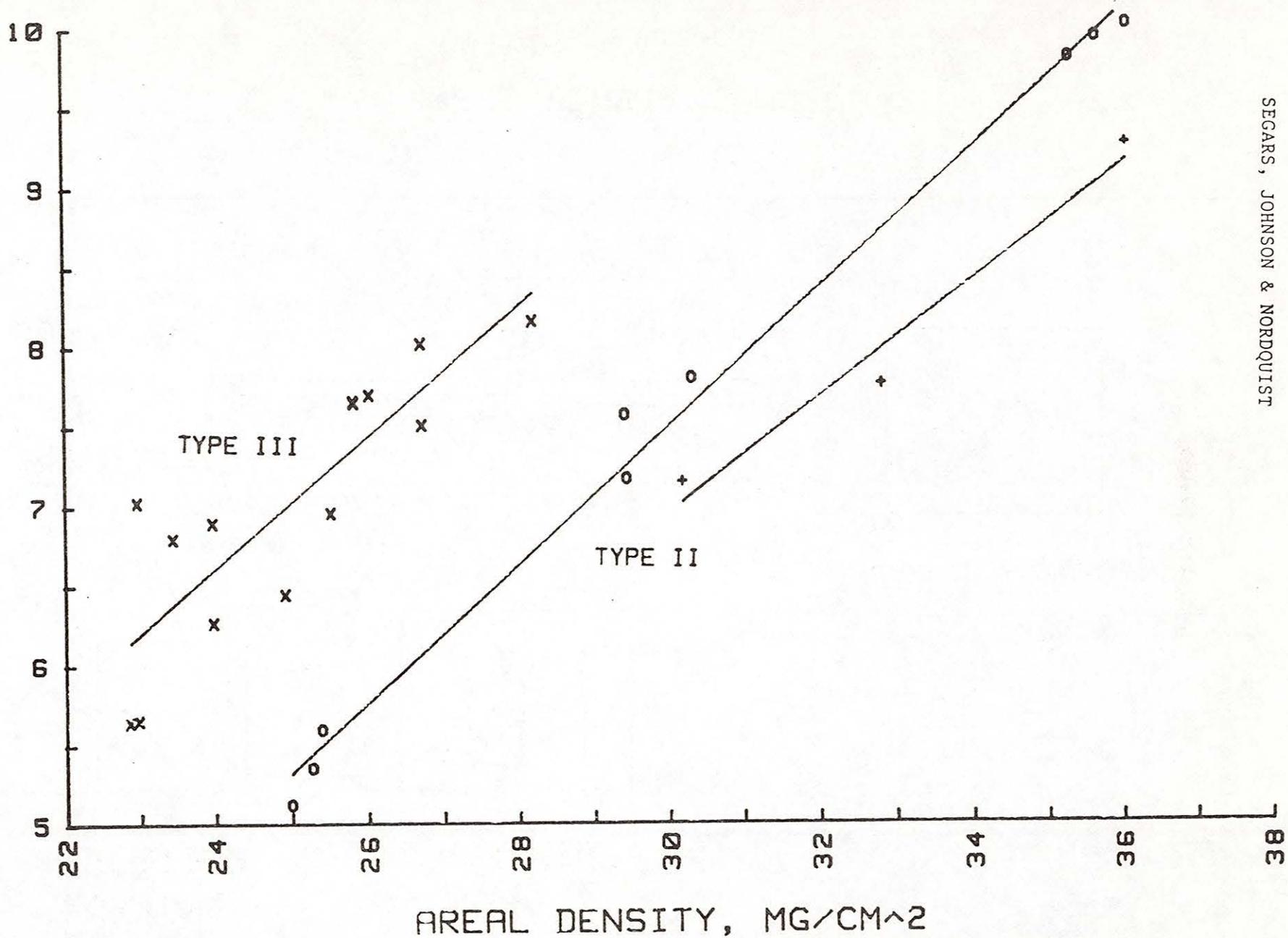
Figure 3. Experimental CCl adsorption values (from plots like Fig. 1) vs the areal density of the fabric for type II foam (o, +) and type III foam (x).
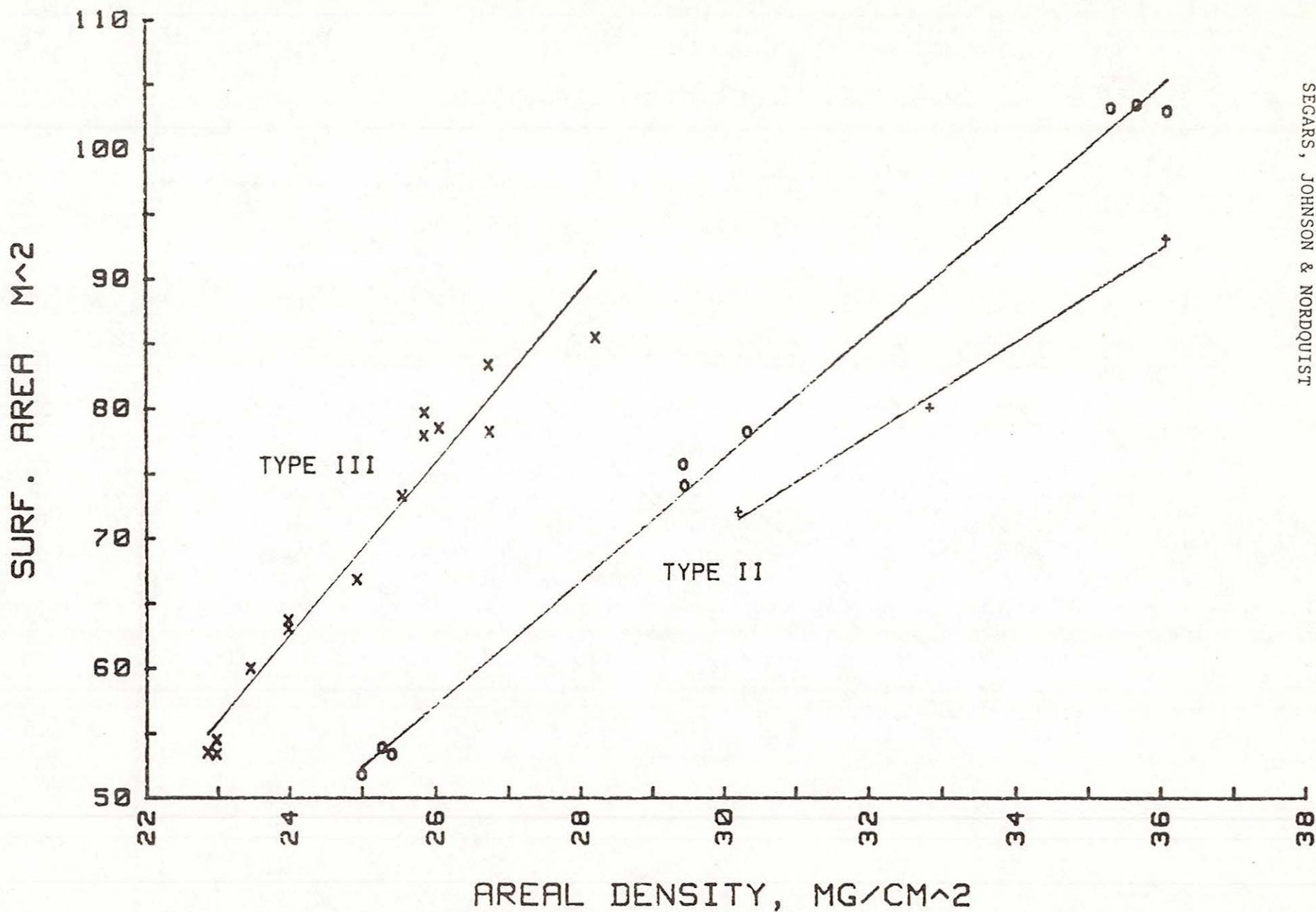
Figure 4.   Surface area of a 1 x 8 cm sample strip as determined by nitrogen gas adsorption (Micromeritics 2100 E System) vs the areal density of the fabric.   o, + = type II foam, x = type III foam.
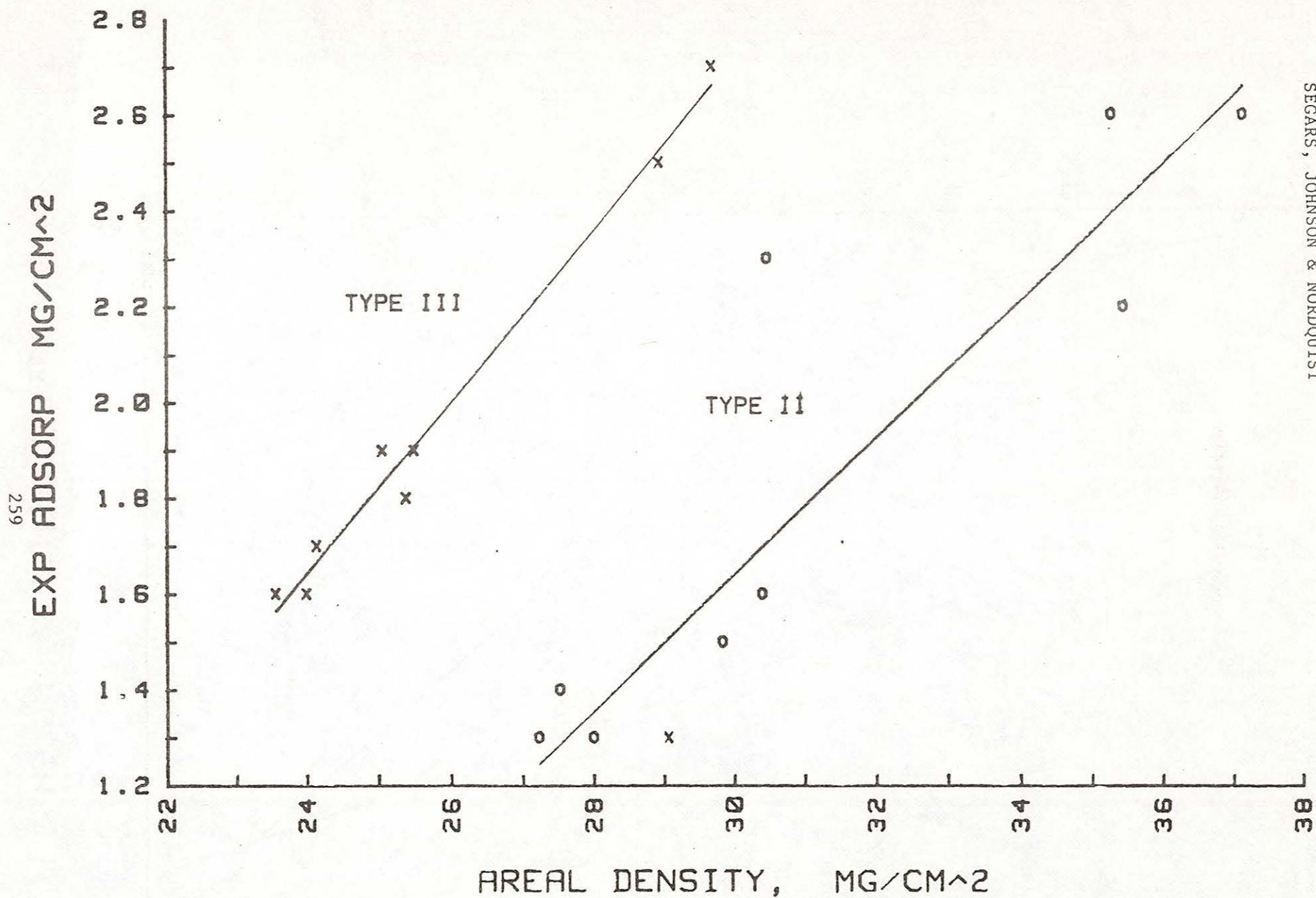
Figure 5. CCl_4 adsorption values from standard breakthrough tests vs areal density for type II (o) and type III (x) foams. The two outlying points (one for each type foam) are not included in the linear regression lines shown.
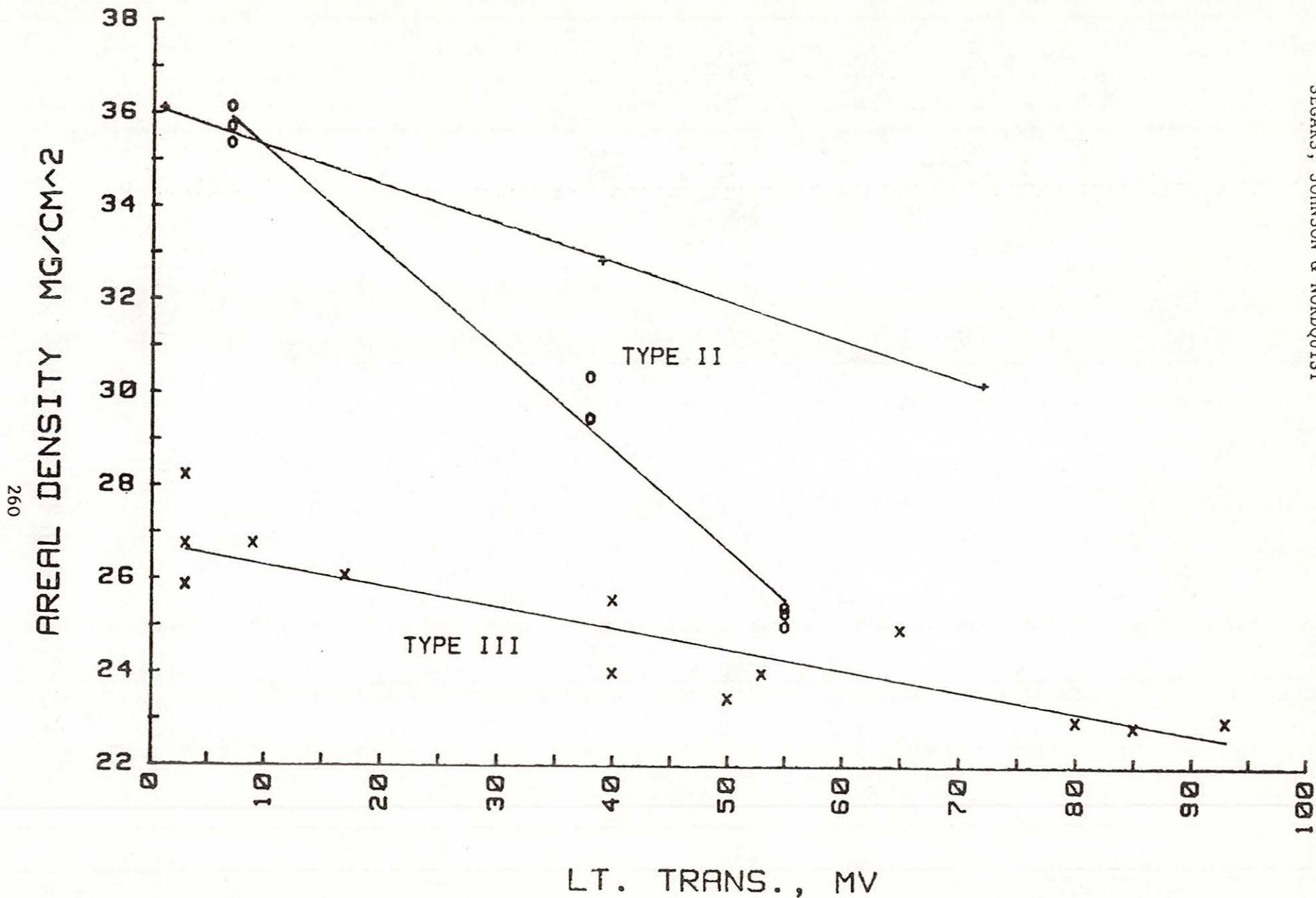
Figure 6. Areal density of the foams as a function of their light transmittance (output of photocell in millivolts). o, + type II foam, x type III foam.
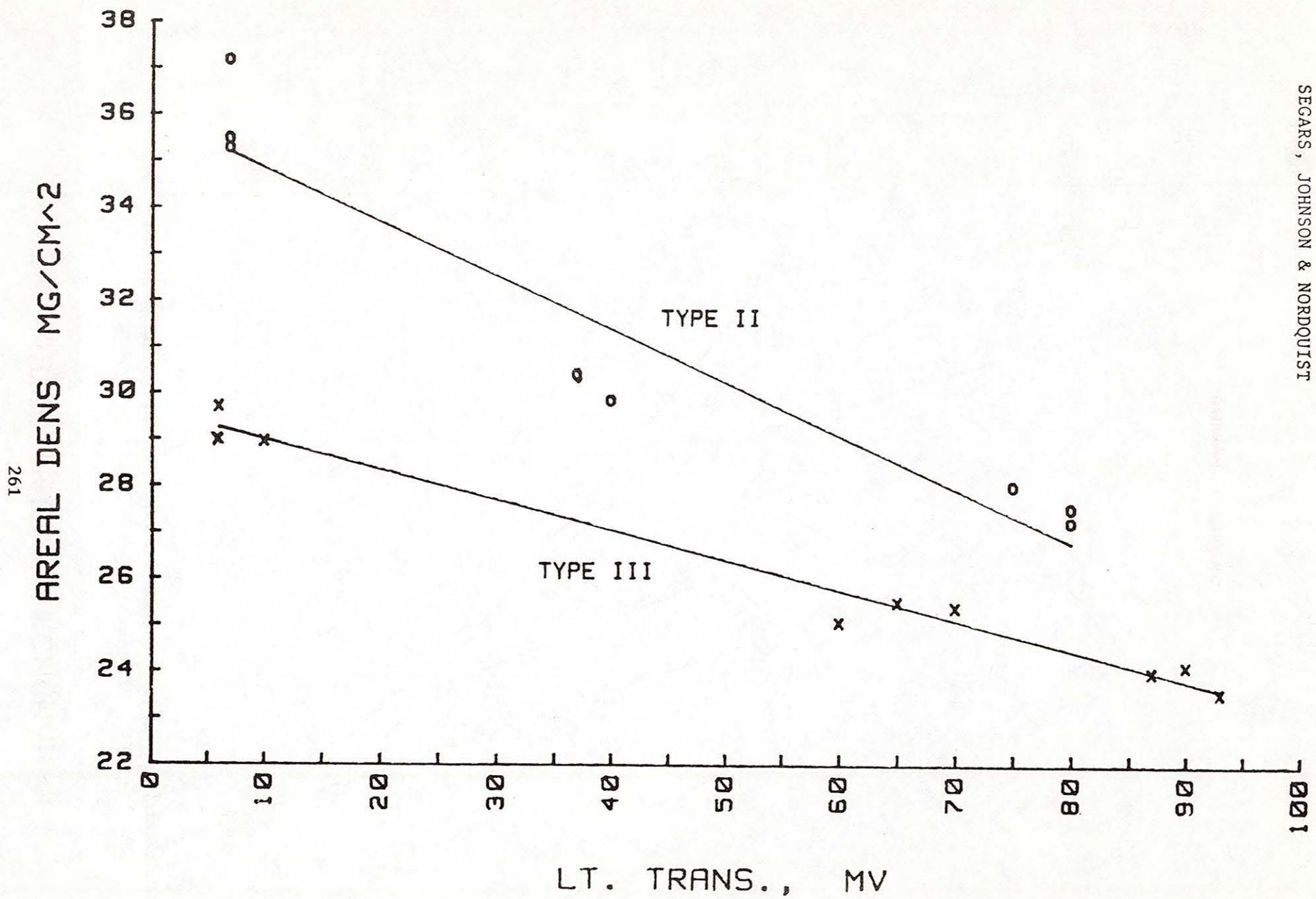
Figure 7. Areal density of samples submitted for standard (breakthrough) adsorption tests as a function of their light transmittance. o = type II foam, x = type III foam.
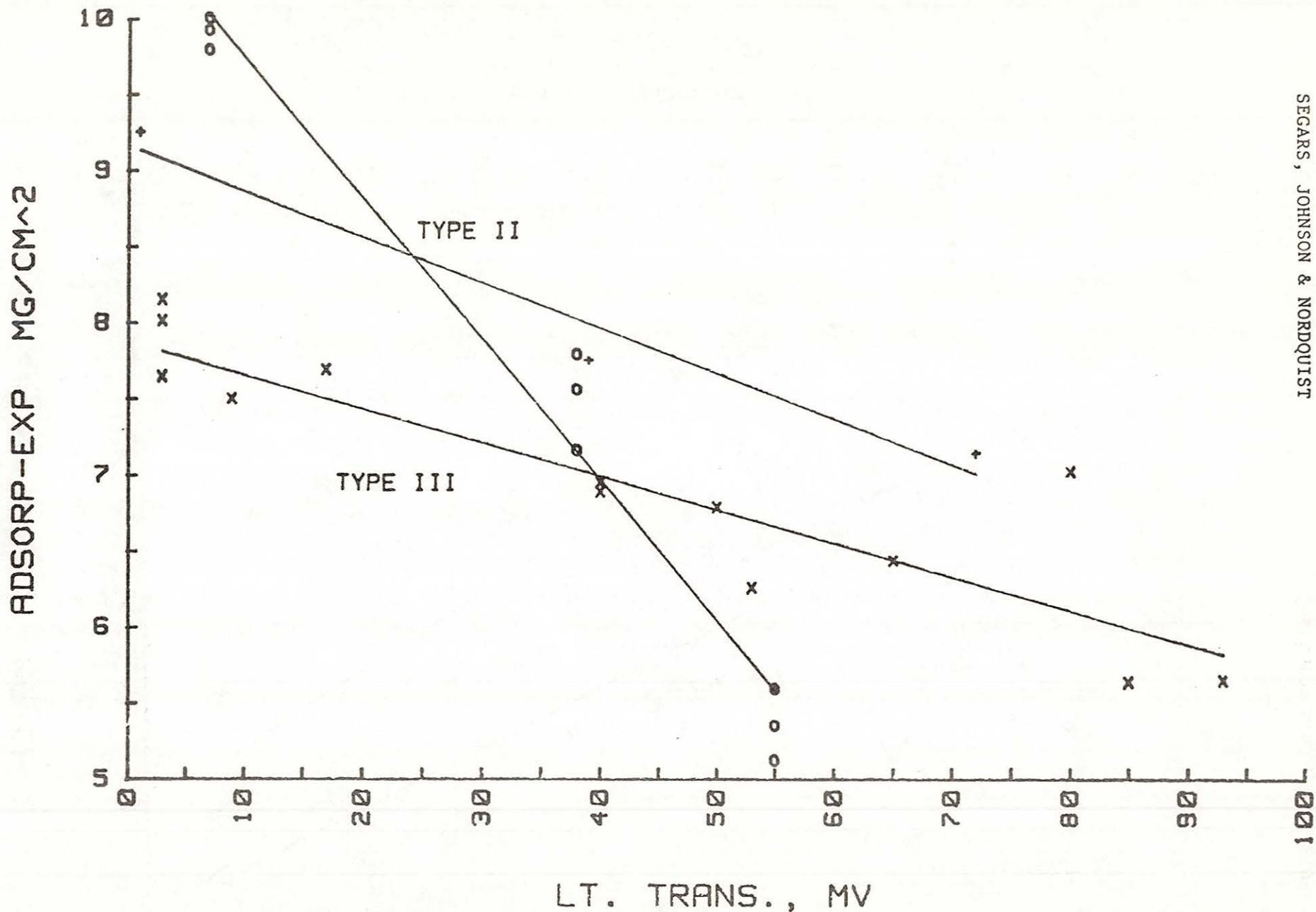
Figure 8. Experimental adsorption of CCl_4 vapor by 1 x 8 cm sample strips as a function of their light transmittance for type II (o, +) and type III (x) foams. (Adsorption data from plots as shown in Fig. 1).
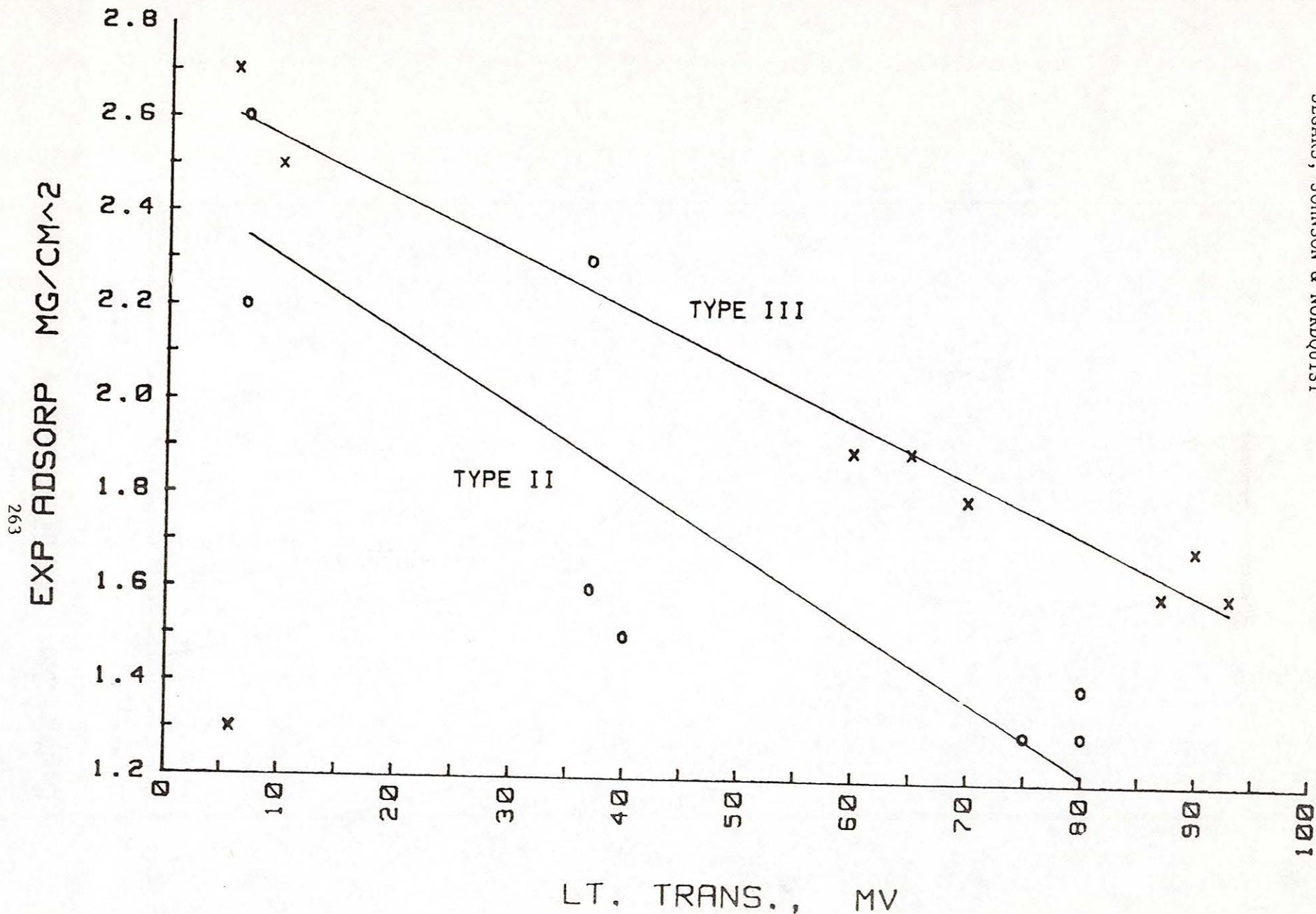
Figure 9. CCl_4 adsorption values obtained by the standard breakthrough test plotted vs the average light transmittance of the samples. o – type II, x – type III. The two outlying points, one for each type, are not included in the linear regressions.

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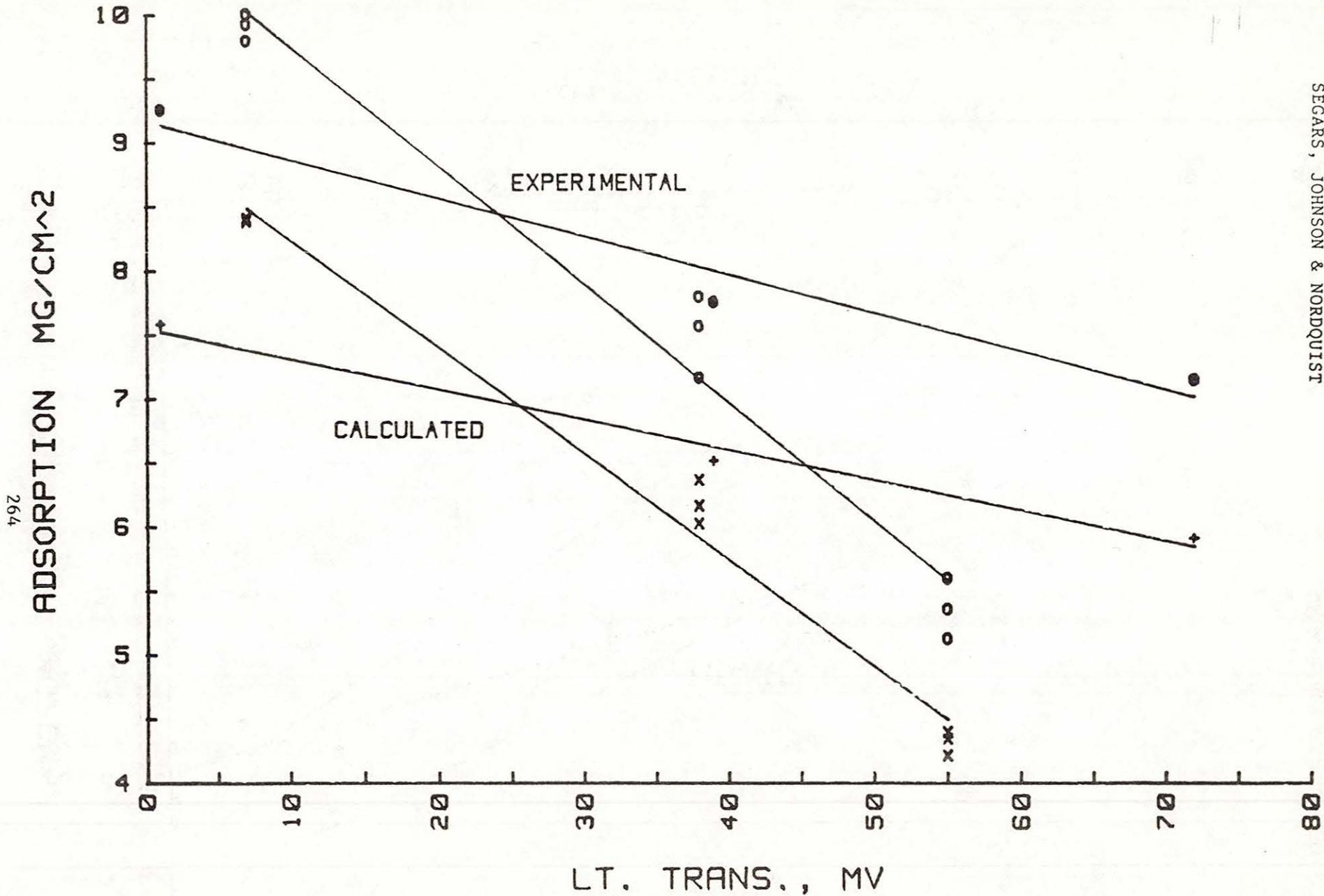
Figure 10. Adsorption of CCl_4 vapor from direct experiments (o, •) and calculated (x, +) from surface area data vs light transmittance for type II foam.
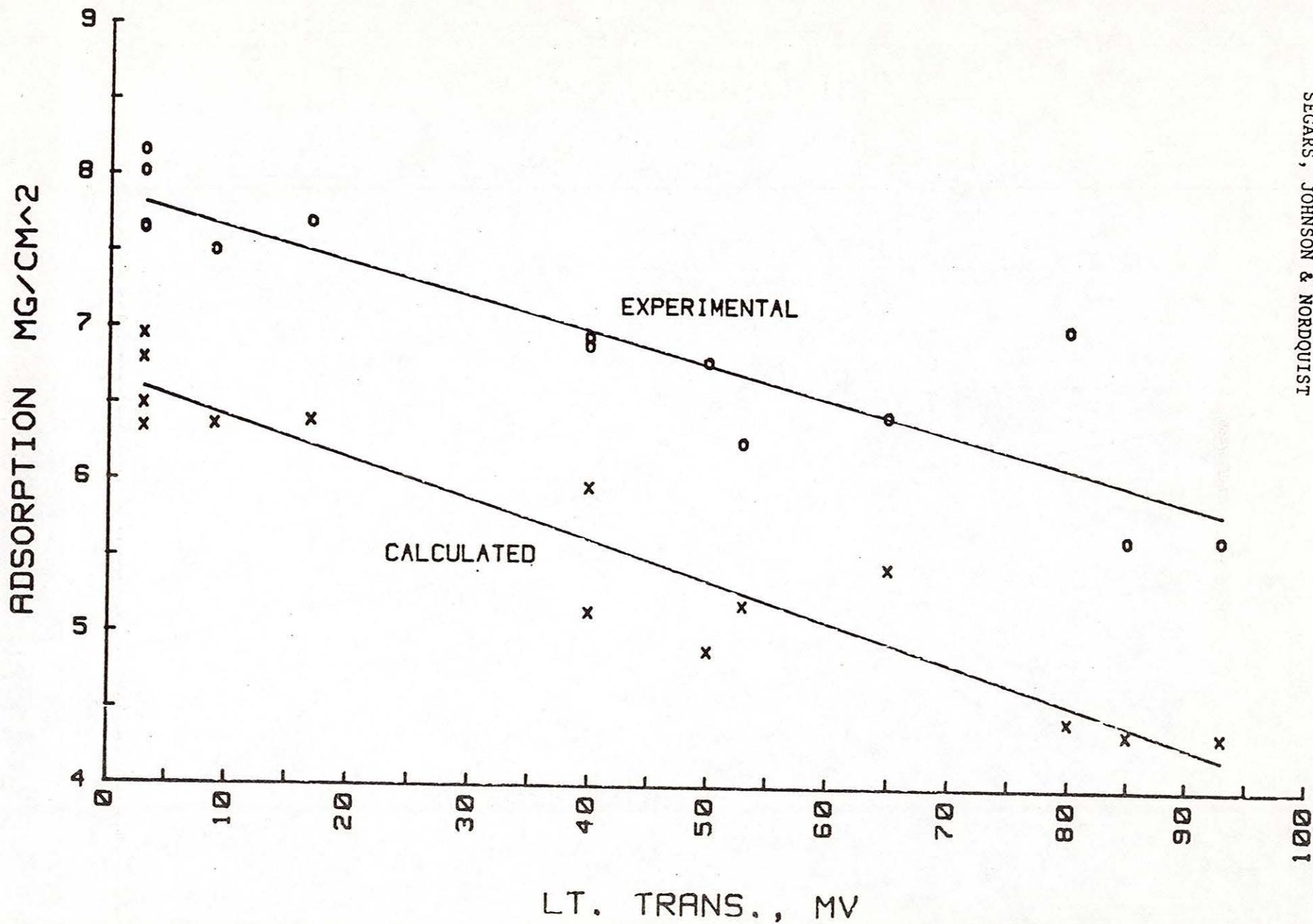
Figure 11. Adsorption of CCl_4 vapor from direct experiment (o) and calculated (x) from surface area data vs light transmittance for type III foam.
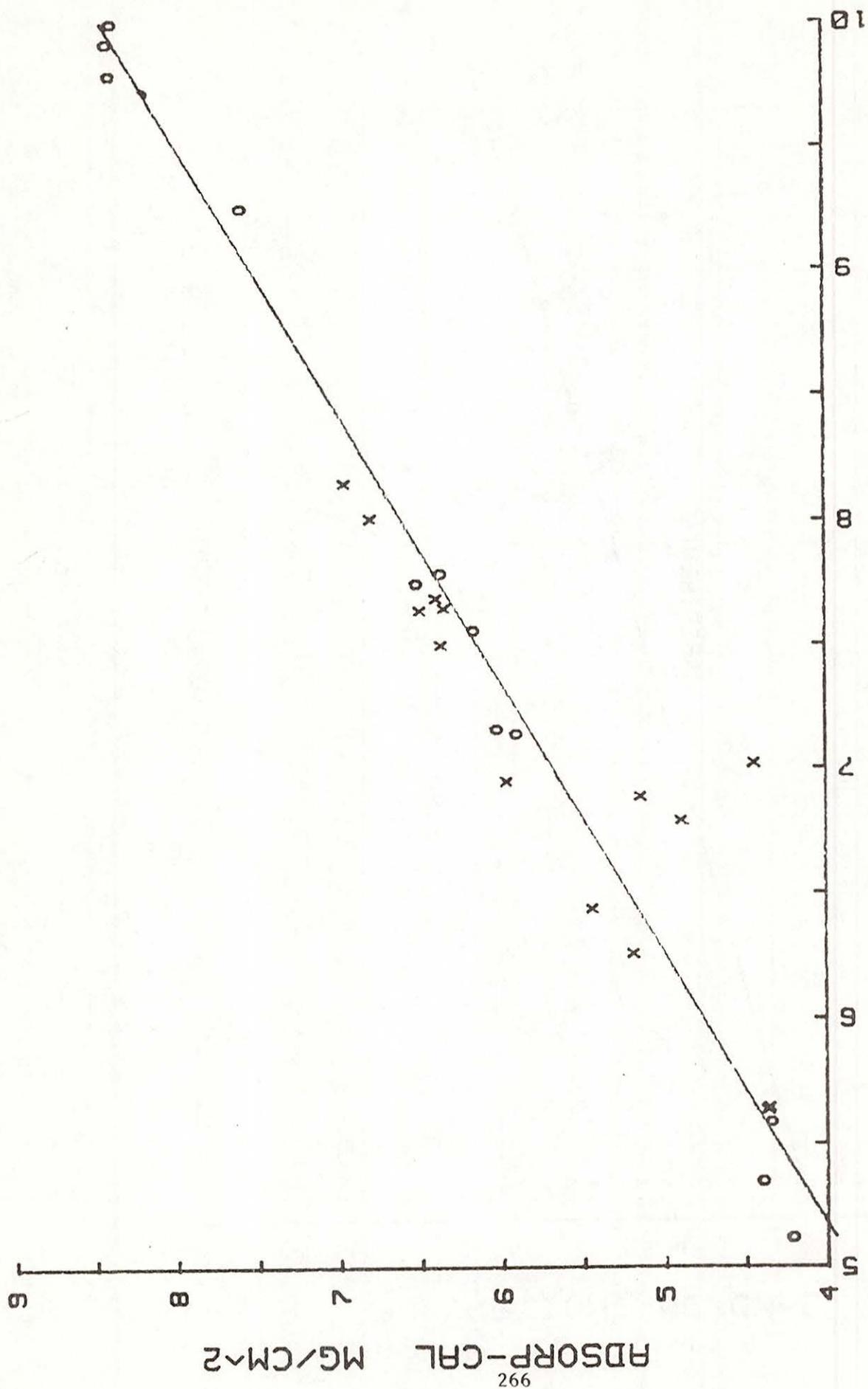
ADSORP-EXP, MG/CM^2

ADSORP-CAL MG/CM^2

Figure 12. Plot of calculated CCl_4 adsorption vs experimental adsorption. o = type II foam, x = type III foam.

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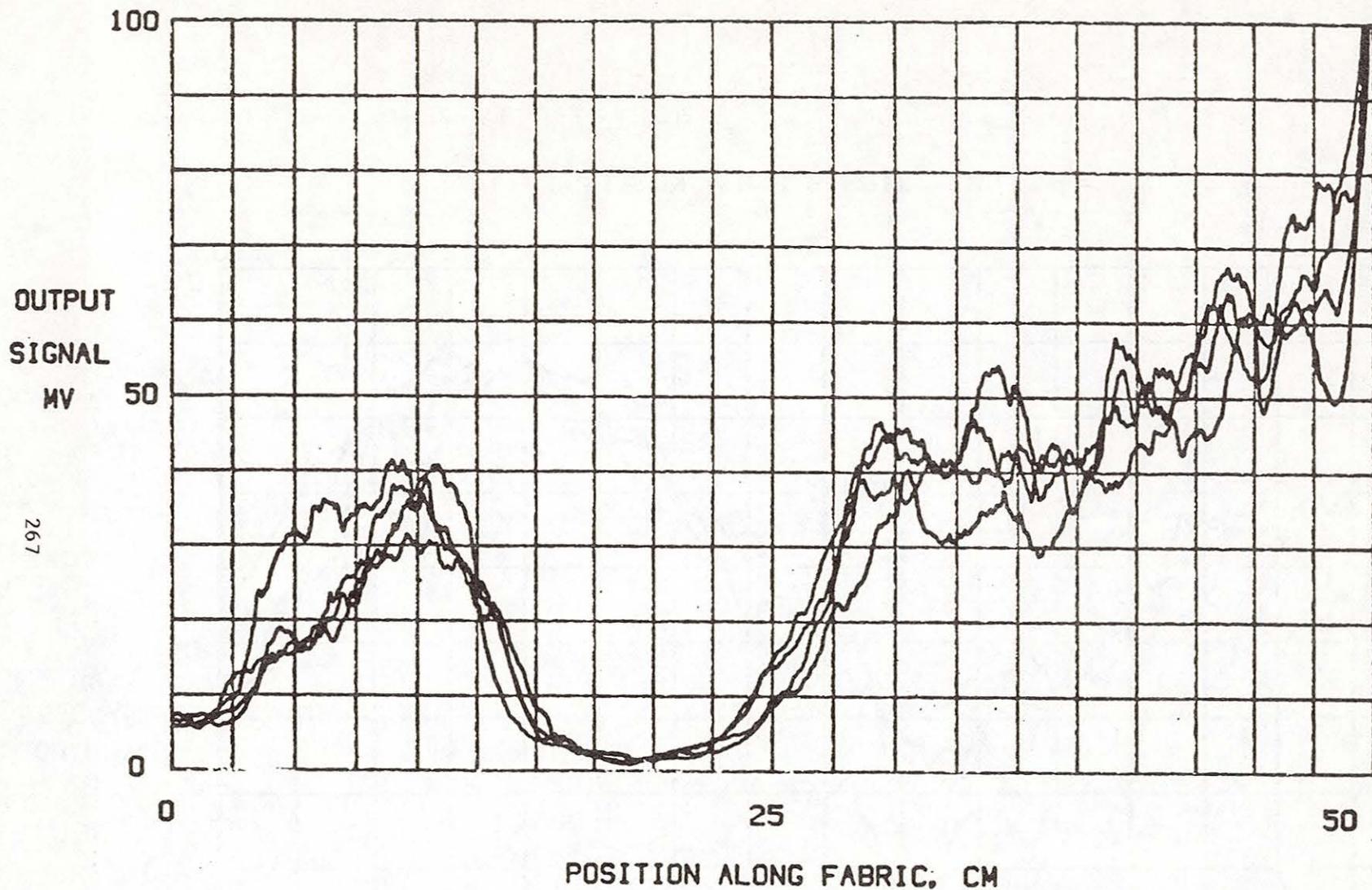
Figure 13. Typical plot of light transmittance (photocell output in millivolts) vs position along the length of the foam. Four tracings spanning approximately a 20 cm width of cloth are shown. Foam is of type II.
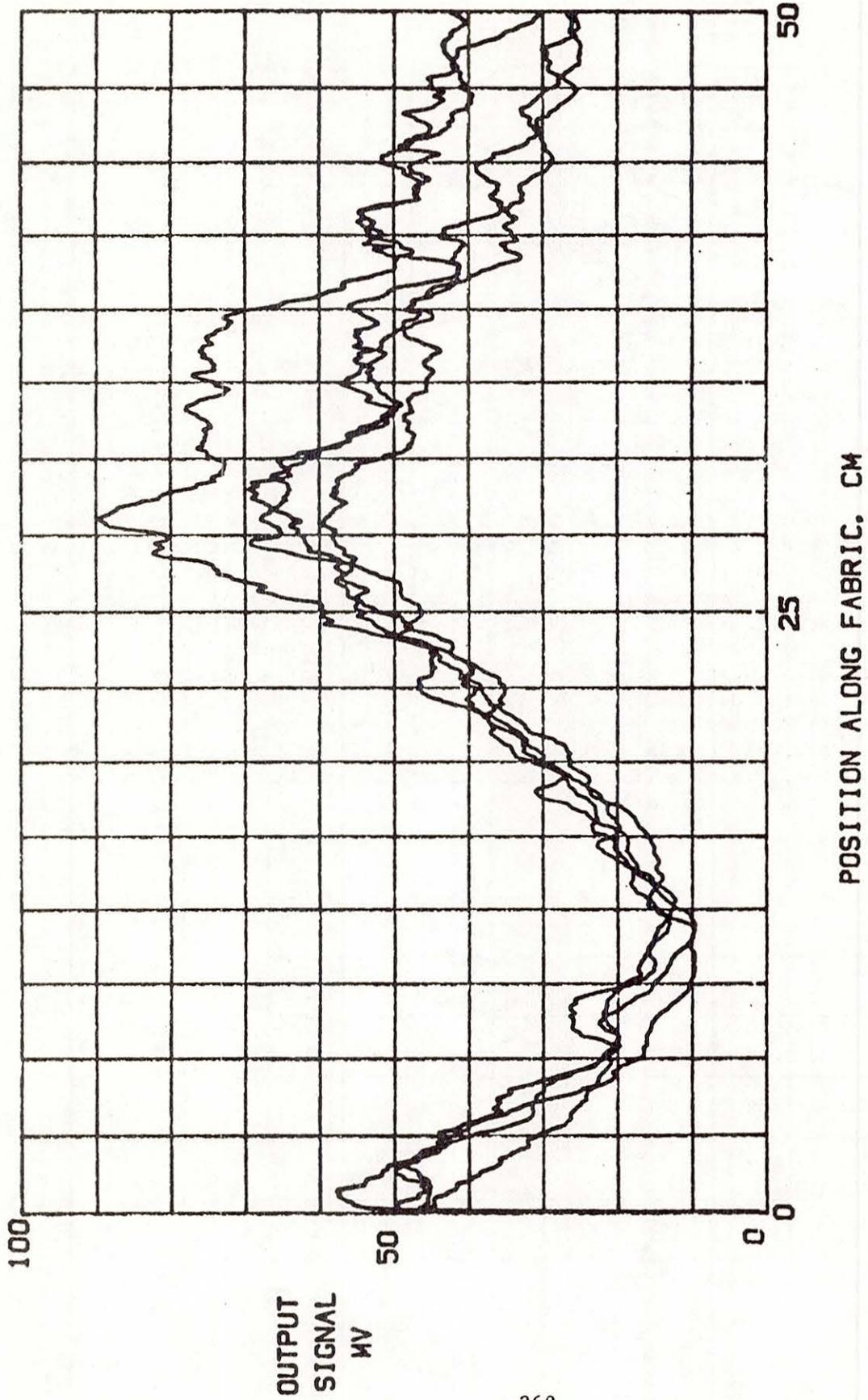
Figure 14. Similar to Fig. 13 but for a type III foam.

TITLE: Combat Encapsulation: Human Factors in Advanced Integrated
        Life Support Systems

LAWRENCE E. SYMINGTON, Ph.D*

ABSTRACT:

The U. S. Army Natick Research, Development & Engineering Center, (NRDEC), U. S. Army Human Engineering Laboratory, (HEL), and Field Artillery Board combined in a team effort to demonstrate advanced life support systems concepts providing combat vehicle crews the capability to survive and fight in toxic environments. In the October 1985 REDLEG Demo at Ft Sill, Oklahoma, NRDEC's life support systems concepts permitted continuous operation of a fire direction center in HEL's Command Post Vehicle for 72 hours in collective protection (closed vehicle with overpressure) and for 54.5 hours in full MOPP4 encapsulation. The collective protection life support system included custom packaged and calorie-dense foods, a water foraging system, an on-board toilet, and an attached crew rest shelter which allowed for MOPP4 crew entry and exit. The previous duration record for encapsulation in MOPP4 had been 24 hours with administrative breaks for eating and waste elimination. NRDEC's microclimate cooled, one-and two-piece suit ensembles, which incorporated through-mask eating and drinking and in-suit waste collection systems for both liquid and solid body waste, allowed this previous encapsulation duration to be more than doubled. REDLEG Demo was an excellent example of a cooperative effort to demonstrate and evaluate new life support technologies and concepts, which could lead to an entirely new doctrinal concept of how and how long the individual soldier can fight in a toxic environment.

*BIOGRAPHY:
   PRESENT ASSIGNMENT: Life Support Systems Technology Coordinator,
Behavioral Sciences Div., SATD, USANRDEC.
   PAST EXPERIENCE: Engineering Psychologist, Human Engineering
Branch, Behavioral Sciences Division, Science and Advanced Technology
Laboratory, USANRDC, 1972-1984. Research Psychologist, U.S. Army Human
Engineering Laboratory, 1969-1972.
   DEGREES HELD: Ph.D 1969, M.A. 1967 (Experimental Psychology)
University of California, Santa Barbara, A.B. 1964 (Psychology) Colby College.

COMBAT ENCAPSULATION: HUMAN FACTORS
IN ADVANCED INTEGRATED LIFE SUPPORT SYSTEMS

LAWRENCE E. SYMINGTON, Ph.D

Early in 1984, the U.S. Army Natick Research, Development and Engineer-
ing Center (NRDEC) first became involved with the U.S. Army Human Engineering
Laboratory (HEL) in a demonstration of life support systems concepts for
combat vehicles under a program then called New Thrust Demo. The objective
of that joint effort was the demonstration and evaluation of innovative NBC-
oriented life support systems in 24-hour field scenarios to allow for more
rapid integration of promising concepts into the Army system.

Lessons learned from this initial endeavor combined with inputs from the
Field Artillery School led to a field demonstration at Ft. Sill, Oklahoma in
October, 1985 called REDLEG Demo. Five NRDEC Directorates (Advanced Systems
Concepts, Aero-Mechanical Engineering, Food Engineering, Individual Protection,
and Science and Advanced Technology) combined with HEL, other Army Materiel
Command Centers, and the Field Artillery Board in running this demonstration,
which encompassed a much broader scenario than the original 24-hour tests
run at HEL.

NRDEC's objective in REDLEG Demo was to demonstrate advanced life support
systems concepts that would provide combat vehicle crews the capability to
survive and fight in toxic environments. It seems self-evident that unless
we protect the crewmembers and allow them to function, even the most sophisti-
cated weapon system will be a failure. We must ensure that systems designed
to protect, sustain, and shelter individual soldiers be human factored to
permit effective mission performance while not, in themselves, severely stress-
ing the soldier.

In the October 1985 REDLEG demonstration, NRDEC's advanced life support
systems concepts were integrated into HEL's human factored Command Post Vehicle
(CPV). The Demo plan called for the CPV to operate continuously as a field
artillery fire direction center in two separate 72-hour iterations. The first
iteration, Macro or Collective Protection, involved MOPP2 Level conditions
(closed vehicle with overpressure) and ran for the planned 72 hours. The

second iteration was conducted in full MOPP4 encapsulation and ran for 54.5 hours, being halted for reasons unrelated to the efficacy of NRDEC's life support equipment. The previous duration record for encapsulation in MOPP4 had been 24 hours with administrative breaks for eating and waste elimination. NRDEC's microclimate cooled individual protection systems, incorporating through-mask eating and drinking and in-suit waste collection systems for both liquid and solid body waste, allowed the previous encapsulation duration to be more than doubled.

COLLECTIVE PROTECTION

In the collective protection scenario, the six-man CPV crew performed the required fire direction combat tasks for the full 72 hours with no administrative breaks for eating, sleeping, or waste elimination. One crewmember was removed from the CPV because of a dental problem; the remainder of the crew appeared to be in excellent physical and mental condition at the end of the demonstration. The crewmembers stated that they could have continued to operate for periods far in excess of the 72 hours.

Custom packaged and calorie-dense foods were provided for the collective scenario. Thermostabilized meal trays consisted of three menus, each providing 770 to 1130 kcal, that were heated by the crew in a fabric ration heater. The heater was collapsible and easily stored -- a human factors feature appreciated by the crew. Custom assembled Meal, Ready-to-Eat rations provided larger entrees (eight ounces) than the normal MRE and were packaged to allow easy access to components and more efficient stowage in the CPV. The calorie-dense packet used ICE (infusion, compression, and extrusion) technologies for producing calorically and nutritionally dense shelf-stable bars. The resulting product provided 1400 kcal in 24 cubic inches of space. These three ration types were supplemented by shelf-stable bread and water flavorants. In general the crew responded quite favorably concerning the acceptability of these products. While the crew liked the concept of the calorie dense packet, two components, cream corn crunch and the tamale bread bar, were not well received; the other four components were judged to be acceptable. Fig. 1 shows the collective protection food concepts.

A prototype water foraging and collection system employing both reverse osmosis and individual NBC purification filters was demonstrated (Fig. 2). Such a system would allow a vehicle to forage for, decontaminate, bulk store, and distribute potable water to crewmembers in a contaminated environment.

A vehicular powered toilet system was mounted in the CPV to provide an innovative collection system for human waste and other refuse. The system was compact, waterless, drainless, odorless, and reliable. In addition, a sink

Figure 1.   Collective Protection Food Concepts

C.P.V. WATER FORAGING SYSTEM CONCEPT

50 GAL. BLADDER ②
(WATER STORAGE)

AUXILIARY OUTLET
(SHOWER/SINK)

③ WATER FILTRATION UNIT
• PRE-FILTERS
• R/O MEMBRANE
• N.B.C. FILTER

① PUMP
(WATER INLET)

④ 5 GAL. POTABLE WATER

⑤ HAND PUMP

⑥ N.B.C. CANTEEN

INDIVIDUAL HYDRATION SYSTEM

⑧ MASK W/DRINK TUBE

⑦ F.I.S.T. SYSTEM

⑥ N.B.C. CANTEEN
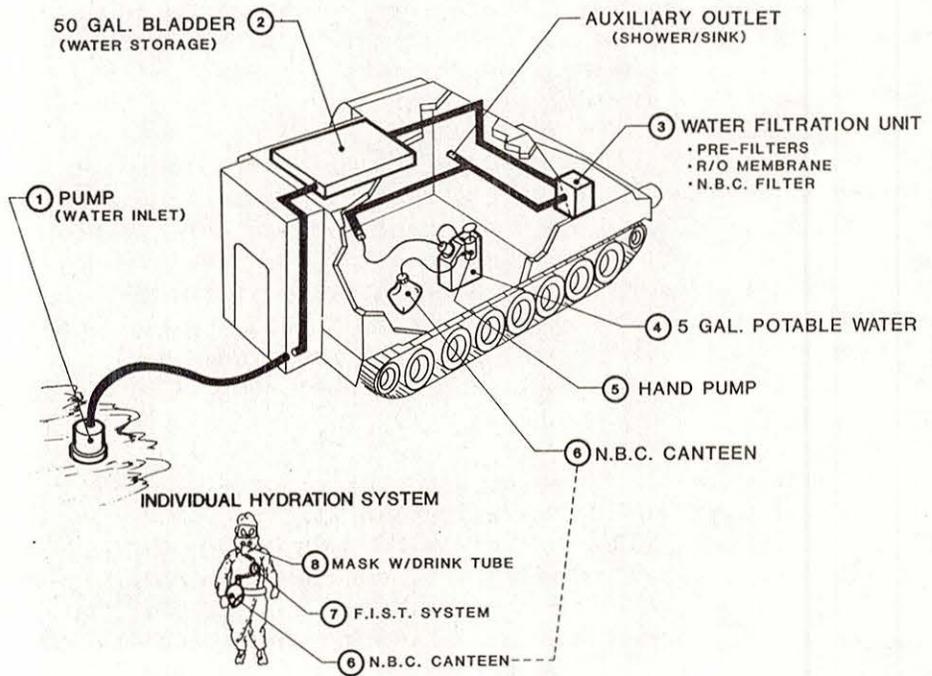
Figure 2.   Prototype Water Foraging, Collection, and Purification System

arrangement was designed and fabricated to mount directly above and empty into the toilet, thus eliminating the need for plumbing.

Three chemical protective crew rest shelters were designed and fabricated for demonstration during the collective protection scenario. Each shelter was deployable in a chemically contaminated or clean environment for attachment to the rear of the CPV in order to share its overpressure system.

A concept for entry/exit through the crew rest shelters using a four-way zipper was also demonstrated. Essentially, a crewmember outside the vehicle in full MOPP4 protection (one-piece ensemble only) zipped his suit into a zipper on the shelter. He then engaged the other part of the zipper, opening his suit and allowing him access to the interior of the shelter with environmental contamination effectively excluded from the shelter interior. His suit was left attached to the outside of the shelter, ready for him to exit if the mission so required (Fig. 3). In practice, the concept did work, but needs more extensive human factoring to increase the speed and ease of the entry/exit operation (e.g., initial engagement of the zipper was difficult and at an awkward height).
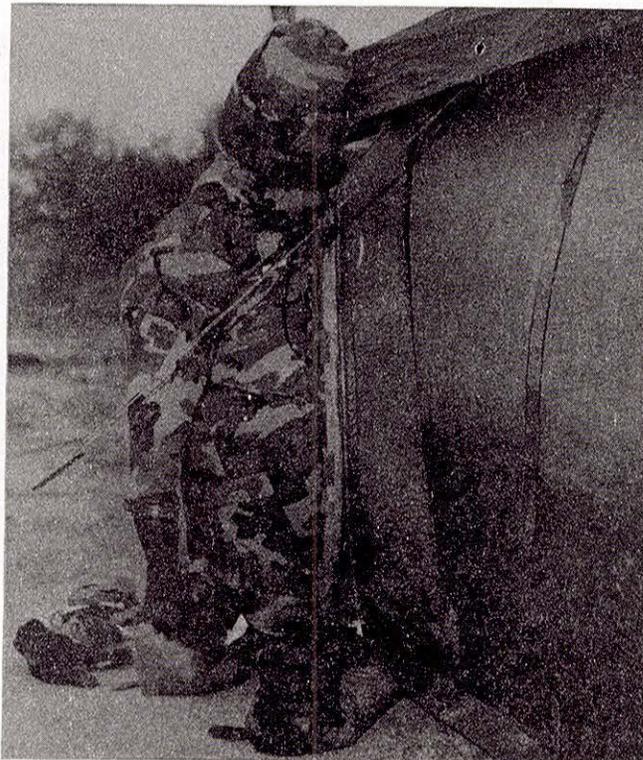

Figure 3.   Empty One-piece Protective Ensemble; Crewman has Entered the Shelter

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INDIVIDUAL PROTECTION

In the individual protection scenario the crew performed the required fire direction combat tasks for 54.5 hours with no administrative breaks for eating, sleeping, or waste elimination. The demonstration protocol called for stopping if the crew was reduced by 50% for any reason. One crewmember was terminated for motion sickness occurring during a sustained movement of the CPV, a second for irritation caused by the medically required wear of a rectal temperature probe, and a third for an eye irritation problem that may have been related to the air being blown into his mask. None of the subjects were terminated because of physical, mental, or emotional fatigue due to their encapsulation or due to the NRDEC life support equipment under demonstration. The remaining crew could have continued and actually expressed a desire to do so.

NRDEC designed two fully integrated protective ensembles for REDLEG, each comprised of both developmental and standard items. Fig. 4 shows crewmembers in MOPP4 in the CPV. Both systems utilized the standard microclimate cool air vest (from the M1A1 tank) which used filtered air from the vehicle for heat stress reduction while mounted. A developmental battery-powered backpack provided filtered ambient air for cooling during dismounted operations. The one-piece ensemble included a sorptive, flame resistant, chemical protective undergarment; an integrated combat vehicle crewman's (CVC) helmet incorporating a subsistence portal for through-mask feeding; 14-mil butyl chemical gloves; improved string-knit cotton glove liners; black one-button overboots; and the Fluid Intake Suction Tube (FIST) hydration

Figure 4.   Crewmembers in MOPP4 in the CPV

system for improved through-mask drinking. A one-piece, self-expanding camouflage shell included a retractable arm capability which, along with internal storage pockets and an air lock pocket, provided a means for waste elimination. Interfaces for feeding, drinking, microclimate cooling, and communications were integrated in the suit.

The two-piece ensemble included a two-piece, two-layer, chemical protective, self-expanding garment with similar waste elimination capabilities, a permeable chemical protective hood compatible with the XM40 masks, black vinyl speedlace boots, and a hybrid chemical protective glove designed to reduce heat stress in the hand area.

Both one and two-piece ensembles were equipped with a viable system for within-suit waste management while in full MOPP4. Using a retractable arm concept and an integrated waste management system consisting of both urine and fecal collection devices and associated items of personal hygiene, crewmembers were able to safely and effectively eliminate wastes while remaining within their chemical protective suits. Bellows, both under the arms and in the crotch, provided ample room within the suit for these activities. The pockets inside the suit, intended to carry the waste elimination devices, toilet paper, and personal hygiene wipes, were actually too small for the 72-hour mission and need to be enlarged. The two-way air lock pocket designed to pass waste bags out of the suit was more functional on the one-piece suit (with a vertical pocket) than on the two-piece suit (with a horizontal pocket).

An innovative prototype food system concept consisting of six major elements allowed the soldiers to consume a variety of food products while in MOPP4. The individual protection food concepts are shown in Fig. 5. Subsistence portals were furnished to provide a mechanism to allow foods and beverages to pass through the mask (Fig. 6). The portal contained a standard NATO thread adaptor, which permitted the device to be easily spun into either existing side port of the protective mask. Food transfer units, which allowed foods/beverages to safely pass from the contaminated environment through the portal to the consumer, were also provided. Semi-solid, shelf-stable foods contained in aluminum tubes equipped with food transfer units were also made available. These included such items as Chicken a la King, Corn, Potatoes, and Apple Pie. In conjunction with these foods, a heating device was installed in the test vehicle to heat these products prior to consumption. Three flavors of electrolyte beverage, designed to replace body fluids lost due to excessive perspiration while in MOPP4, were furnished to crewmembers. Tubes (6.5-ounce) equipped with food transfer units allowed the soldier to consume this beverage through the mask. Also included was a solid-food dispensing device. This device offered the crewmembers either red licorice or beef jerky and was designed to be compatible with the subsistence portal.
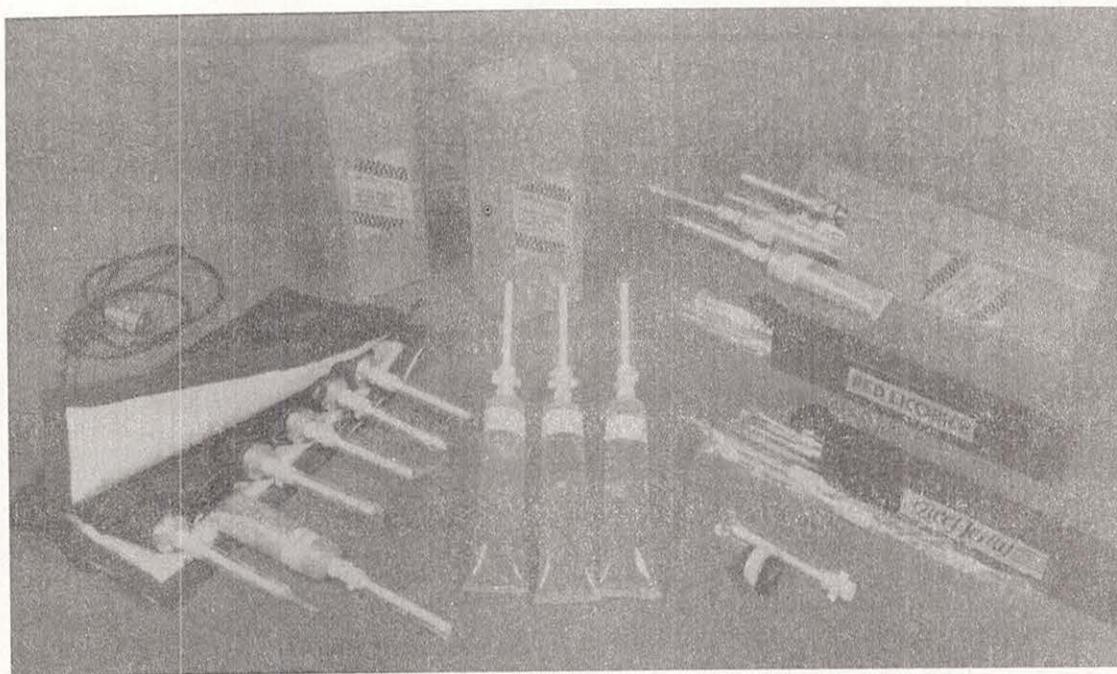
Figure 5.   Individual Protection Food Concepts
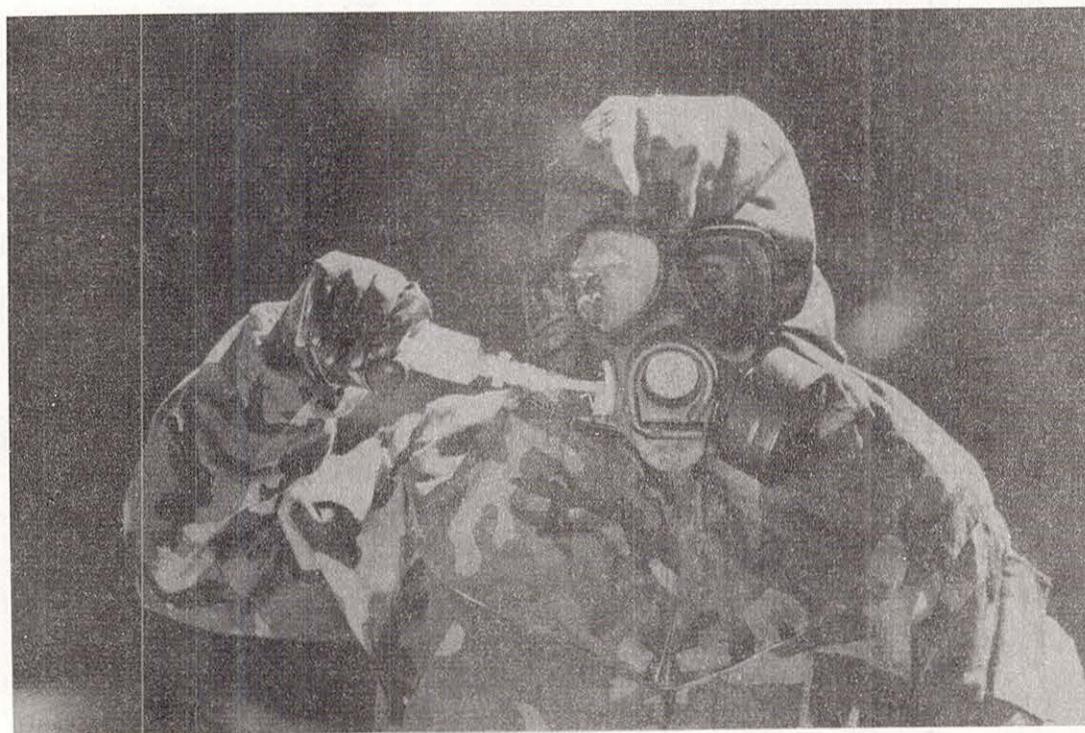
Figure 6.   Crewmember Consuming a Tube Food in MOPP4

CONCLUSIONS

1. REDLEG Demo was an excellent example of what can be achieved in a cooperative effort among Army organizations.

2. The life support concepts demonstrated are capable of leading to an entirely new doctrinal concept of how and how long the individual soldier can fight in a toxic environment.
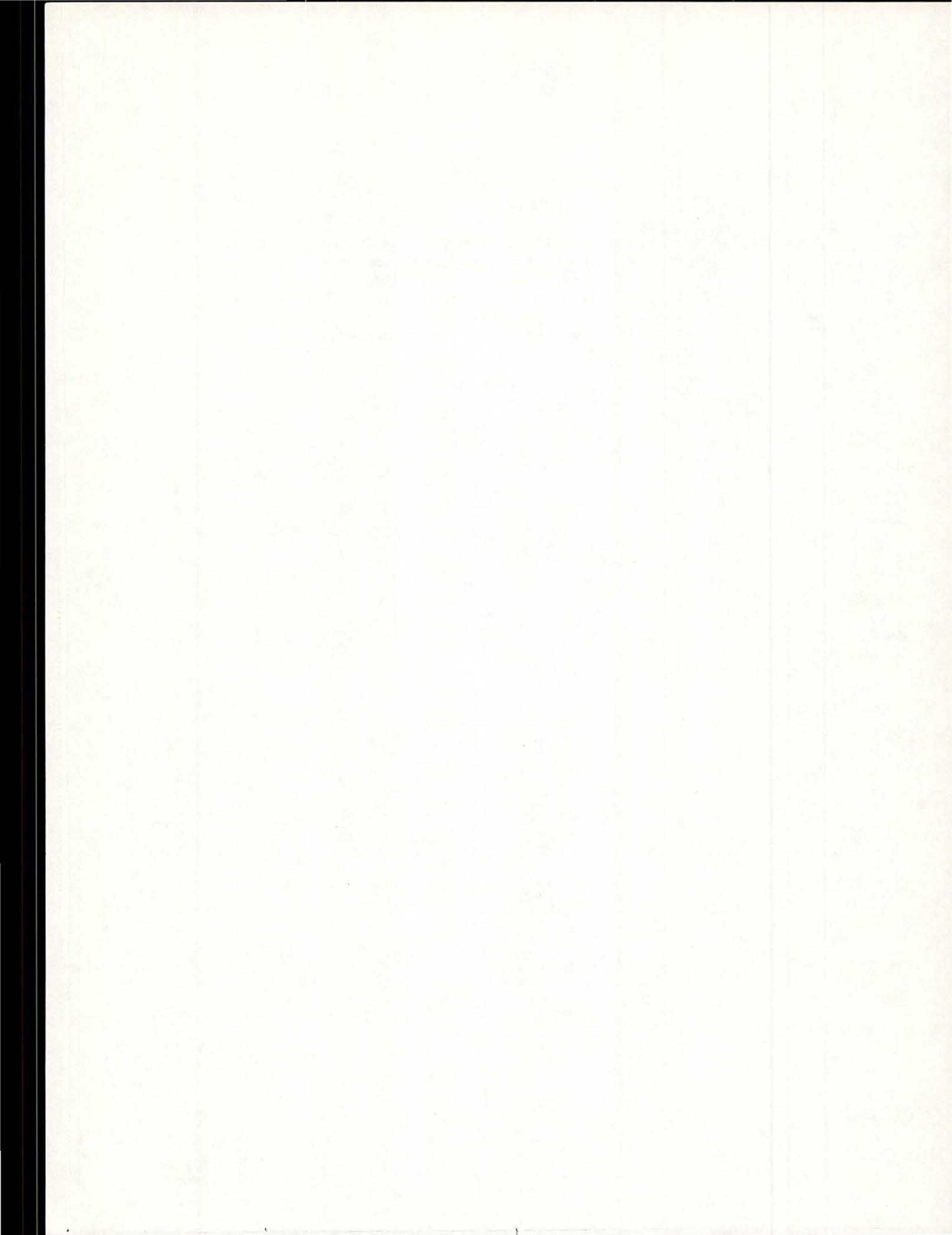
TITLE: Hi-Tech Fibers for Improved Ballistic Protection

JANET E. WARD, MRS.,* AND WALTER KOZA, MR.

ABSTRACT:

A high priority need exists for lighter weight body armor to provide increased protection against multiple ballistic threats. Optimization of the current state of the art material will offer limited improvement. To achieve a quantum leap in ballistic protection, a new fiber material will be required.

Fiber developers are pursuing the development of fibers with high strength and high tensile and compressive moduli for use in high strength industrial yarns, aerospace and low weight, high strength composite applications. These hi-tech fibers appear to be likely candidates for the improved ballistic materials required.

Natick RD&E Center has developed a single yarn impact test to evaluate small amounts of fiber at ballistic speeds. The single yarn impact test and scanning electron microscopy were used to evaluate several new hi-tech fibers early in their development.

Based on preliminary evaluations, the potential for substantial ballistic improvement has been identified in four new hi-tech fibers. Continued developmental work has been recommended.

* BIOGRAPHY:
    PRESENT ASSIGNMENT: Textile Technologist, U.S. Army Natick Research, Development and Engineering Center
    PAST EXPERIENCE: Textile Technologist, Singer Co., Elizabeth, NJ, 1980-1981; Textile Technologist, Levi Strauss & Co., San Francisco, CA, 1975-1977.
    DEGREES HELD: Bachelor of Science, 1970; Master of Science, 1971; Indiana State University, Terre Haute, Indiana.

HI-TECH FIBERS FOR IMPROVED BALLISTIC PROTECTION

JANET E. WARD, MRS., AND WALTER KOZA, MR.

INTRODUCTION

Thousands of lives saved have proved that personnel body armor is effective in reducing combat casualties. Therefore, the Army continues to support research and development efforts to improve this type of ballistic protection for the individual soldier. Substantial gains in fragmentation protection were achieved when Kevlar[E], a high-strength aramid fiber, was identified as a superior ballistic-resistant material and replaced nylon as the state of the art in body armor.

However, to improve a soldier's mobility, lighter weight body armor systems are needed. Advances in weapons technology also require increased protection against multiple ballistic threats. Efforts to optimize the ballistic performance of Kevlar through systems engineering have potential for satisfying those needs in part. The achievement of another quantum leap in ballistic protection, like that seen in Kevlar over nylon, will most likely be accomplished through the development of hi-tech fibers.

Research groups, world wide, are pursuing the development of fibers with high strength, high tensile modulus, and high compressive modulus for the aerospace industry as well as for other low weight, high strength composite applications. Those fiber properties, essential for industrial needs, have also been shown through previous studies to be important in ballistic protective materials. Smith (1) stressed high strength, elongation, and work-to-break properties; while Laible, Figucia, and Ferguson (2) added high modulus and heat resistance to the desired properties for a better impact-resistance fiber.

Kevlar[E] is a registered trademark of E.I. duPont deNemours & Co., Inc.

By nature of the development criteria for the new hi-tech fibers, most would meet, at least in part, the physical properties for a "better" ballistic fiber. This does not automatically ensure, however, that the new materials will surpass the ballistic resistance capabilities of Kevlar. It is not known how to weight the relative importance of strength, modulus, elongation, heat resistance, and even denier per filament to ballistic resistance. This is especially true when the mechanical properties are known only for strain rates decades below those of interest. For this reason the body armor developer has a responsibility to conduct studies capable of identifying the more promising new fiber candidates.

Natick RD&E Center has developed a single yarn impact test to evaluate small amounts of fiber at ballistic speeds. This single yarn impact test and scanning electron microscopy (SEM) of the ballistically impacted yarns have been used to evaluate several new hi-tech fibers early in their development. The fiber samples were obtained through cooperative efforts with several fiber developers.

EXPERIMENTAL TEST METHOD

Single Yarn Impact Test

The Natick RD&E Center Single Yarn Impact Test has proven to be a useful method of evaluating the ballistic impact properties of textile yarn materials at an early stage in their development.

In this method, a single yarn is impacted in a crosswise direction by a speeding .22 caliber fragment simulating projectile (Figure 1) that elongates the yarn to rupture in microseconds time as illustrated in Figure 2 on the next page.

Figure 1. Fragment Simulating Projectile
.22 caliber (4.5X)

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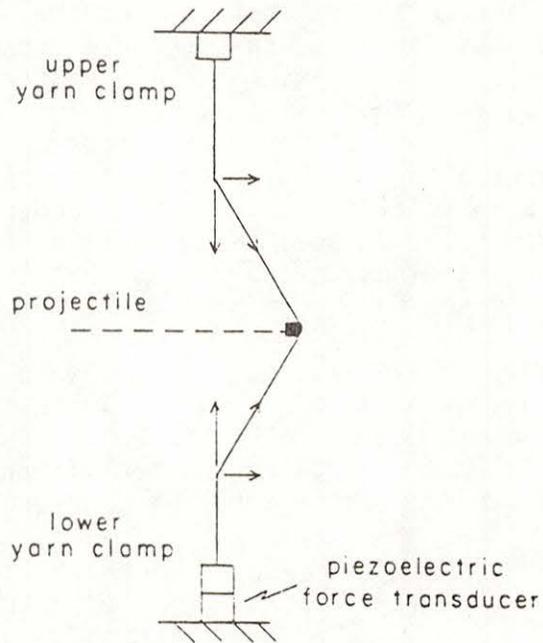
Figure 2. Schematic of Single Yarn Impact Test

During the impact process, the tensile force in the yarn is continuously measured and recorded with a piezoelectric force transducer and oscilloscope as shown in Figure 3.
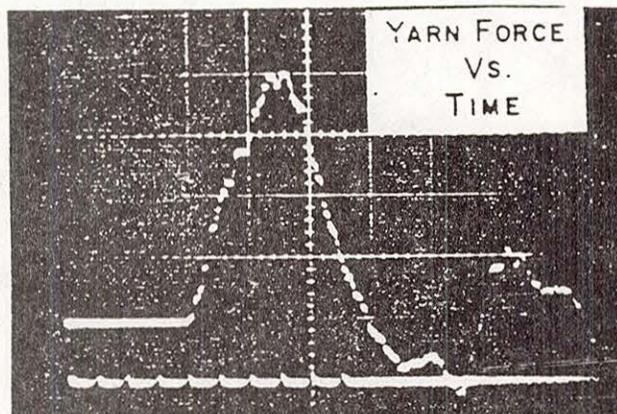

Figure 3. Oscilloscope trace showing
Yarn Force vs. Time

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At the same time, yarn elongation to rupture is periodically
photographed by high frequency microflashes as seen in Figure 4 below.
From these data, the ballistic properties of the yarn material are defined
in terms of breaking tenacity, breaking elongation, time to break, initial
tensile modulus, and strain wave velocity.
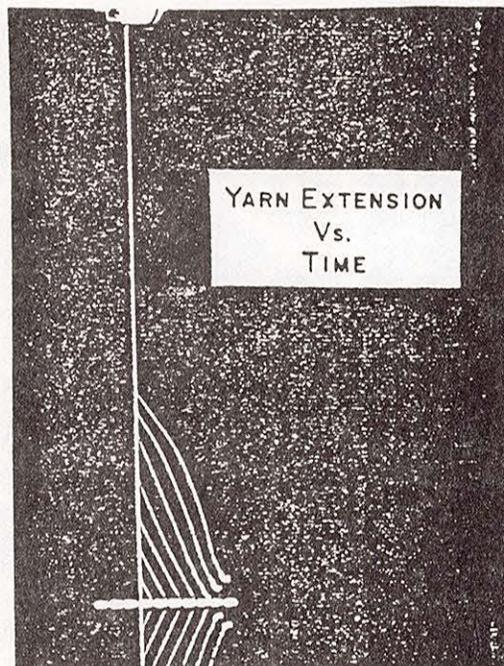
Figure 4. High Speed Photograph of Impacted Yarn
Used in Measurement of Yarn Extension vs. Time

Scanning Electron Micrographs

Scanning Electron Micrographs were used to analyze the mode of
failure, melting or fibrillation, occurring in each fiber after rupture.
To obtain the micrographs, the fractured ends of the impacted yarns were
mounted on specimen studs using silver paint and single-faced adhesive
aluminum tape. The samples were coated in a vacuum evaporator with a thin
layer of gold palladium. The samples were coated for a total of 15 minutes
with each being rotated approximately 120 degrees at 5-minute intervals
to obtain a uniform and complete coating. The fracture patterns of the
coated samples were observed in an AMR Model 1000A Scanning Electron
Microscope using the secondary electron mode.

MATERIALS EVALUATED

Four new hi-tech fiber variants have been examined by the single yarn impact test and SEM procedures. The fibers were as follows:

PBT (polybenzthiazole), an experimental aromatic heterocyclic fiber developed in two forms by the U.S. Air Force -- As Spun (PBT/AS) and Heat Set (PBT/HS).

Spectra®, an ultrahigh molecular weight polyethylene (gel spun) fiber developed by and commercially available in two forms from Allied Corporation -- Spectra 900 (S/900) and Spectra 1000 (S/1000).

Although exact methods for achieving the high modulus in the above fibers are not known, it is speculated that two separate methods were employed in achieving that property. It is our understanding that the approach taken by Allied in the production of Spectra is that of chain extension applied to a conventional polymer, in this case, polyethylene. On the other hand, the Air Force uses a different approach, that of processing liquid crystalline polymers using molecules that form thermotropic or lyotropic mesophases (3). Either method would result in extended chains and, in turn, high modulus and strength along the fiber axis.

Nylon 66 (T/728) and Kevlar 29 (K/29) yarns were also included in the evaluation as controls. Nylon was added to this evaluation for the failure mode analysis because of its low heat resistance. The acronyms in parenthesis will be used to designate fiber types in the following tables.

RESULTS AND DISCUSSION

The physical properties listed in Table 1 were obtained from static (low strain rate) tests completed by the fiber producers and are used here to illustrate the substantial improvements in physical properties of the hi-tech fibers over Kevlar and nylon. When compared directly, the properties of the four new materials are also different, especially in melting points. As shown in Table 1, the melting points of the polyethylenes are substantially lower than that of nylon.

Spectra® is a registered trademark of Allied Corporation.

Table 1. Physical Properties of Hi-Tech Fibers

Fiber Type	Fiber Density (g/cc)	Brkg. Ten'y (g/d)	Brkg. Elong. (%)	Initial Modulus (g/d)	Melting Point (°C)
PBT/HS	1.59	29.3	1.5	2000	370°
PBT/AS	1.58	25.4	1.8	1430	370°
S/1000	0.97	36.0	2.8	1900	147°
S/900	0.97	29.0	3.6	1400	147°
K/29	1.44	22.0	3.6	525	427°
T/728	1.14	9.8	18.2	45	254°

When the properties generated at ballistic speeds listed in Table 2 are compared to static properties of the same fibers in Table 1, significantly different values are seen. Differences between static properties and ballistic properties exist due to the added elements (cutting, flexing, and crushing) to which a specimen is exposed during ballistic testing. In this case as in most, the properties are generally lower for ballistic impact testing. More important, however, are the rates of change. In no case did the breaking tenacity or the initial modulus of the four hi-tech fibers fall below that of Kevlar. The levels of tenacities and moduli retained by the new fibers suggest the potential for substantial improvement over Kevlar in ballistic resistance capabilities.

Table 2. Ballistic Properties * of Hi-Tech Fibers

Fiber Type	Yarn Size (d)	Brkg. Ten'y (g/d)	Brkg. Elong. (%)	Initial Modulus (g/d)	Strain Wave Velocity (m/s)
PBT/HS	1808	19.6	1.4	1100	10,160
PBT/AS	1822	22.2	2.5	750	8,710
S/1000	645	24.6	2.2	840	8.710
S/900	1215	17.0	2.5	520	8,130
K/29	1502	11.2	2.6	475	6,770
T/728	1080	6.7	13.0	43	2,540

*Results of Single Yarn Impact Tests at 305 m/s.

Strain wave velocity is considered by many to be the most influential parameter in the ballistic performance of a material (4,5). It is the rapid propagation of stress away from the point of impact that incorporates more material into the impact resistance process. Strain wave velocities generated by the Single Yarn Impact Test on the four new hi-tech fibers are listed in Table 2 in descending order of expected ballistic performance. The strain wave velocities support the potential for improved ballistic performance in fabrics for all four of the new hi-tech fibers: PBT Heat Set, PBT As Spun, Spectra 1000, and Spectra 900.

Of notable interest is the earlier speculation that two different approaches were used in processing the new fibers. It appears from this preliminary analysis that either the chain extension method or the liquid crystalline method can achieve the property profile required for improved ballistic performance.

In addition to comparing the ballistic tensile properties of the evaluated fibers, the mode of failure that occurs in the new materials as a result of ballistic impact was determined. The response of PBT fibers, Heat Set and As Spun, appears to be very similar to that of Kevlar. Figures 5 and 6 illustrate the similarities of PBT As Spun and Kevlar with both demonstrating fibrillation as the form of failure.
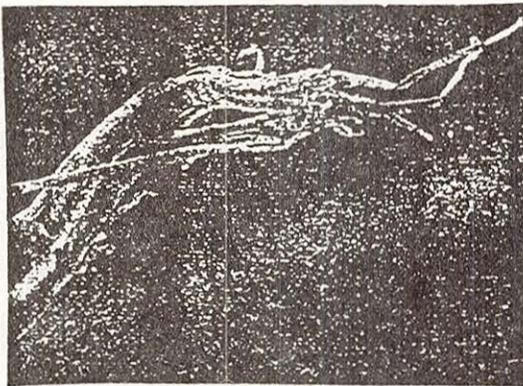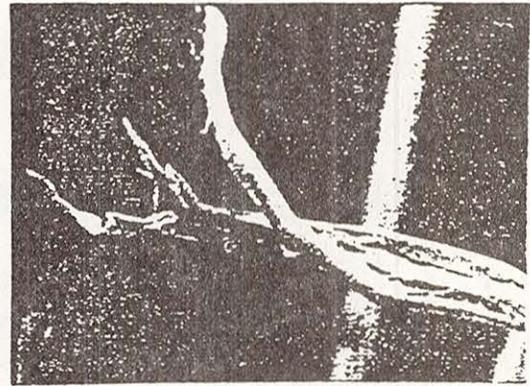
Figure 5. PBT As Spun   Figure 6. Kevlar 29

As shown in Figure 7, fusion from melting is extremely evident at the point of rupture on nylon fibers. That failure mechanism is commonly attributed to the low melting point of nylon. However, the other fiber of this group with an even lower melting point does not demonstrate the same failure trends as nylon. The polyethylene fiber, as seen in Figure 8, shows only slight evidence of fusion. Its high modulus to density ratio appears to increase its ability to respond quickly to high speed impact, thereby mitigating the extreme localized deformation (6). The high-modulus polyethylenes appear to have the capacity for plastic deformation which should be advantageous for improved ballistic behavior. Interpretation of results in Table 2 and the above SEM analysis shows that the low melting point of the polyethylene fiber has little effect on the ballistic resistance capabilities of that material.
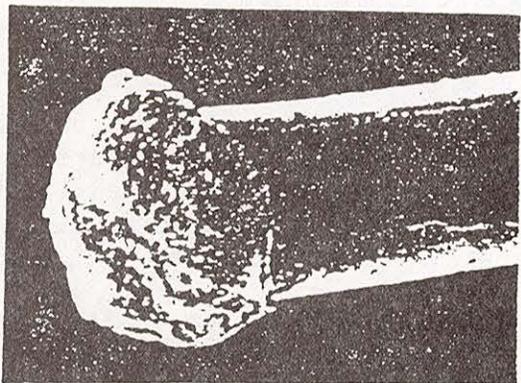

Figure 7.   Nylon 66

Figure 8.   Spectra 900

As indicated earlier in this paper, the ballistic evaluations being reported are preliminary, but provide a reliable indication as to the ballistic performance potential of a new fiber. Conclusions drawn from the single yarn impact test and SEM analysis will determine when additional testing will be accomplished on the fiber in woven fabric and/or laminate form. For any new candidate ballistic fiber, the next phase of the evaluation would include the establishment of a V50 ballistic limit, the velocity at which 50% of a simulated threat completely penetrates a target material. Given satisfactory V50 results, a casualty reduction analysis would be conducted to validate the improved ballistic performance. The casualty reduction analysis is the final phase in the ballistic evaluation of a new material. The analysis provides an indication as to the relative percentages by which current and new materials reduce casualties in a given battlefield scenario.

It is well documented (7,8) that obtaining the maximized ballistic potential of a material in a fabric or non-woven form requires considerable research and development work in yarn geometry, fabric geometry, systems engineering, and surface modifications, as well as in other areas. The objective is to maximize filaments in the target impact cross-section. Improved theoretical models are being developed to help in the transitioning process.

CONCLUSIONS

There is a high priority requirement for lighter weight armor systems with improved protection against multiple ballistic threats.

A quantum leap in ballistic protection over that of Kevlar may be accomplished through new hi-tech fibers. The best source for such hi-tech fibers are the research and development efforts of producers of fiber products for use in aerospace and in low weight, high strength composite material applications.

Natick RD&E Center has developed a single yarn impact test to predict the ballistic potential of hi-tech fibers. Four new hi-tech fibers have been evaluated. Based on the single yarn impact test results, all four fibers, PBT As Spun, PBT Heat Set, Spectra 900 and Spectra 1000, have potential for substantial improvement in ballistic protection.

The next stage for these candidate materials includes V50 and casualty reduction analyses as well as studies in yarn geometry, fabric geometry, surface finishing, and systems engineering.

Natick RD&E Center will continue to maintain an awareness of new or emerging hi-tech fibers, evaluate their ballistic potential via our screening tests, and plan further ballistic evaluations as warranted.

ACKNOWLEDGEMENTS

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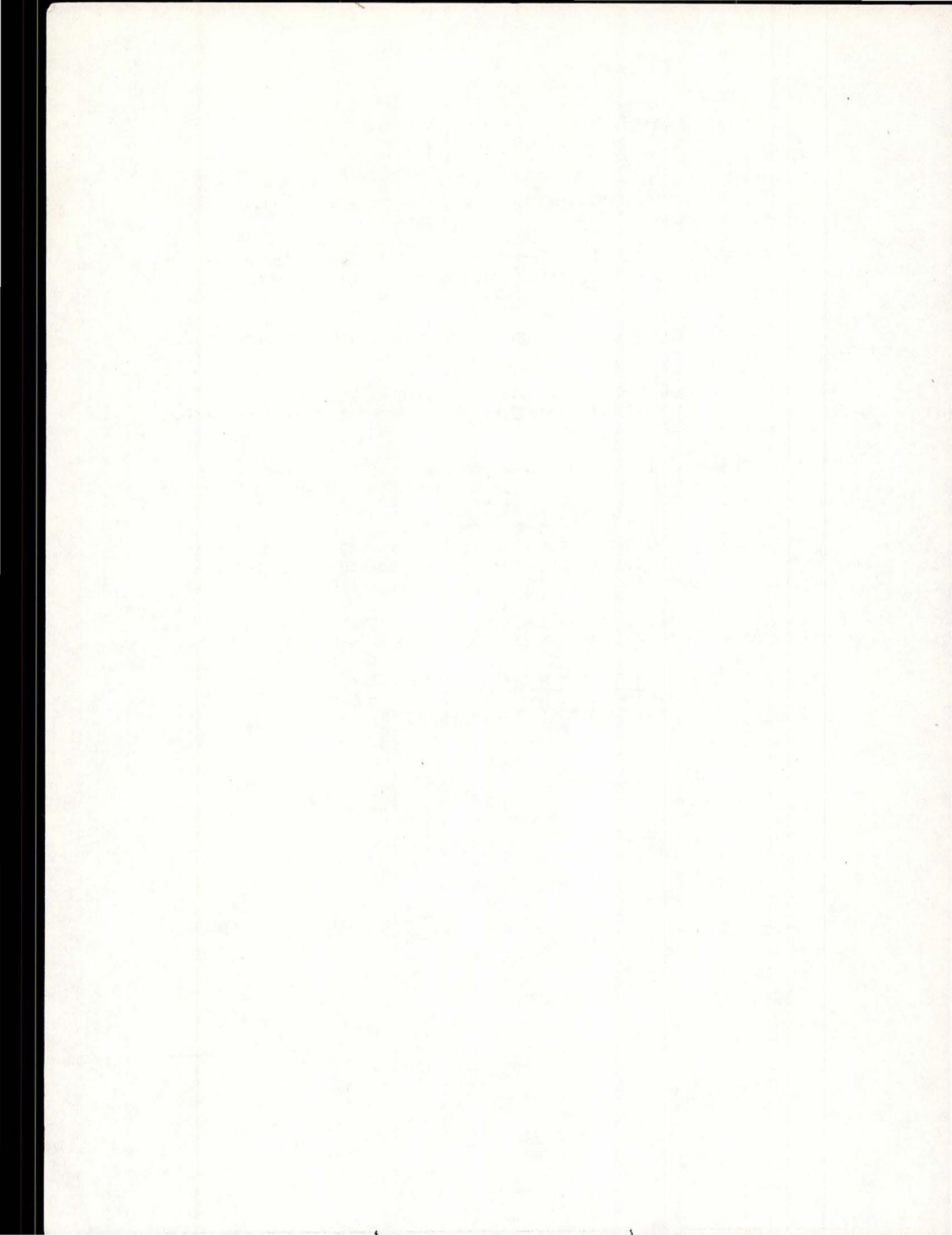
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