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Edited by T. P. Labuza, University of Minnesota

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# JOURNAL OF FOOD PROCESSING AND PRESERVATION

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# CONCEPTS OF PREFERENCE MAXIMIZATION IN COMPUTER-ASSISTED MENU PLANNING

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## ABSTRACT

*Computer assistance for menu planning has evolved to the stage where analytical representations of food preferences can be used in a mathematical optimization procedure. The model presented in this paper can be used to determine serving frequencies of menu items while ensuring budgetary and nutritional control.*

## INTRODUCTION

The tools of mathematical optimization were first applied to human diet planning with the seminal contribution of Stigler (1945). The development of the simplex algorithm by Dantzig (1963) and the increasing speed and availability of digital computers set the stage for Balintfy (1964) to define the "menu problem," which was based on the recognition that human beings consume menu items, and the "feed mix" approach used successfully for planning intakes for cattle and chickens fails to capture the complexity and cultural evolution of human diet patterns.

Recent advances in mathematical programming models and software, the increasing complexity of a food service manager's job, the unstable price patterns of foods, the growth of consumer awareness of diets in preventive health care, breakthroughs in modeling food preferences, and the declining costs of electronic computation are conjointly spawning a new generation of models and software for computer-assisted menu planning.

Earlier forays into computer-assisted menu planning methodology used a mathematical programming formulation of the problem where cost was minimized subject to nutritional requirements and other constraints. Meal acceptability was ensured by enforcing a minimum time



interval between successive appearances of the same menu item. It has been demonstrated (Gelpi *et al.* 1972) that even cost-minimized menu plans show an acceptability level not significantly different from conventionally planned ones, and in addition, savings of 10% of raw food cost were realized during a period in which the wholesale food price index rose 3.9%.

In spite of this impressive performance, cost-minimizing models have had limited acceptance. Such a model tends to bring in inexpensive items at their upper bounds, whereas more expensive items are unduly depressed in their serving frequencies. Moreover, separation ratings are only an incomplete substitute for the true nature of food preferences, and food preferences are critical to the estimation of production estimates, attendance, etc.

### MODELING FOOD PREFERENCES

Most investigations of food preferences (Meiselman *et al.* 1972; Moskowitz 1974) assess the preference on a hedonic scale. Some studies also elicit the preferred serving frequencies of menu items. Such approaches fail to capture the effect of serving frequency on food preferences. It has been recognized that serving frequency does indeed affect acceptability (Benson 1960; Siegel and Pilgrim 1958). This led to the development of analytical functions that capture this relationship (Benson 1960; Balintfy *et al.* 1974; Sinha 1974).

Several forms of this relationship can be illustrated graphically (Fig. 1). One can relate total preference to serving frequency. This function increases at first, reaches a maximum value, and then decreases. The value of frequency at which the function reaches its maximum value is the preferred frequency. Dividing total preference by the serving frequency yields the average preference per serving. In addition, we can look at incremental preference, or the change in preference due to one additional serving of an item.

The 3 forms of the preference-quantity relation are all related and any 2 can be obtained from the third. The basic assumption behind these functions is that inter-service items are approximately equal. However, if preferences are to be evaluated with arbitrary inter-service times, the preference-time function can be used. This is illustrated in Fig. 2, where the changing preference for an item is shown with the item being served on days 1, 7, 10 and 20 of a feeding schedule.

The methods of estimation of the parameters of preference-time and quantity functions, together with possible analytical forms, can be found in Balintfy *et al.* (1974) and Sinha (1974).

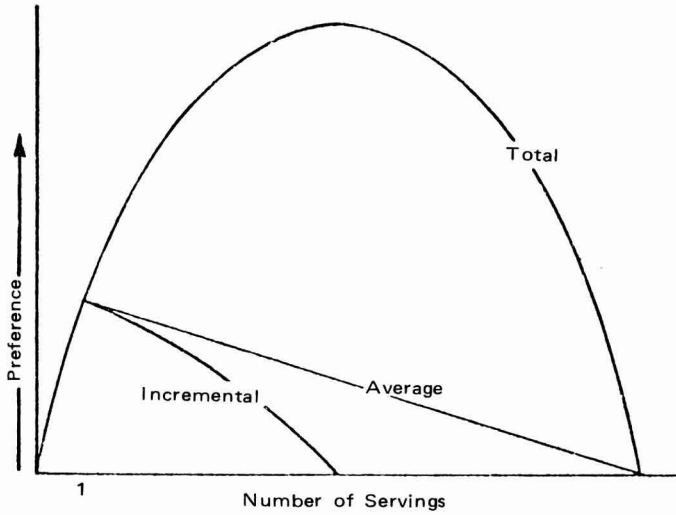


FIG. 1. RELATIONSHIP BETWEEN SERVING FREQUENCY, TOTAL PREFERENCE, AVERAGE PREFERENCE, AND INCREMENTAL PREFERENCE

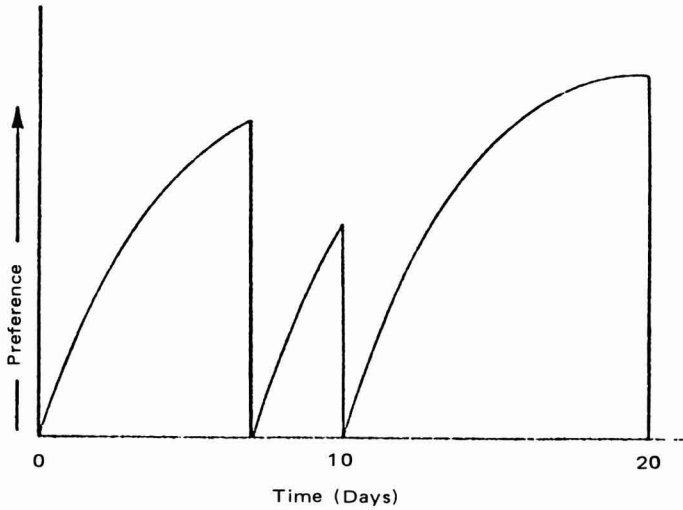


FIG. 2. PREFERENCE FOR MEAT LOAF SERVED ON DAYS 1, 7, 10, AND 20 OF A FEEDING SCHEDULE

**QUANTITY-CONSTRAINED OPTIMIZATION**

When an individual furnishes estimates of preferred serving frequencies, these are the unconstrained optimum serving frequencies for the item. With the large number of menu items commonly available at food-

service systems, the first thing that moves a person's actual eating habit away from this unconstrained optimum is the person's capacity to consume food. By using the capacity to consume as a constraint, quantity-constrained optimum frequencies can be obtained.

### Single-stage Model

Suppose that an individual is to eat one entree at a meal for each of  $s$  days. If  $x_1, x_2, \dots, x_n$  are the serving frequencies for the  $n$  entrees, and  $G_j(x_j)$  represents the total preference exhibited by the individual if the  $j$ -th item is served  $x_j$  times in the  $s$  days,  $G_j(x_j)$  is the total preference-quantity function with each item having its own set of parameters. The individual's total preference for all the entrees, with the  $j$ -th one served  $x_j$  times, is  $\sum_{j=1}^n G_j(x_j)$ . The quantity-constrained optimization problem can then be stated as

$$\text{maximize } \sum_{j=1}^n G_j(x_j), \text{ subject to } \sum_j x_j = s, x_j \in I, \quad (1)$$

where  $I$  is the set of nonnegative integers.

The contribution of the  $j$ -th item to the objective function is  $G_j(x_j) = x_j [H_j(x_j)]$ , where  $H_j(x_j)$  is the average preference as a function of the serving frequency  $x_j$ . If  $y_{ij}$  is the marginal contribution to preference of the  $i$ -th serving of the  $j$ -th item,

$$y_{ij} = i[H_j(i)] - (i-1)[H_j(i-1)] \quad (2)$$

As indicated by Fig. 1, these marginal contributions decrease as the number of servings in  $s$  days increases. In fact, if the frequency of serving becomes sufficiently large, the marginal contribution of an additional serving becomes negative. This property of diminishing marginal preference contribution makes it easy to solve the knapsack problem (1), as the "greedy solution" will be optimal. The problem can be solved by (1) constructing a table of marginal preference contribution of each additional serving of each item, as illustrated in Table 1, and (2) selecting successively the largest element in the matrix at each step to fill up the  $s$  days.

The preference-time function parameters for 48 dinner entrees from a study by Moskowitz (1974) were used to formulate examples for such a problem for 84 days.

Table 2 shows the optimum serving frequencies for the items. A noticeable feature of the entries in the columns of Table 2 is that zero frequencies occur frequently. If the integrality conditions were dropped

Table 1. Marginal preference of additional serving of menu items. This table is used to determine the quantity-constrained optimal serving frequencies

Item	1	2	3	4	5	6	7	8	9	10		
Number	Item Name	Serving	1	2	3	4	5	6	7	8	9	10
	Marginal Preference of Serving											
	Number (in 84 days)											
1	Meat loaf	8.0	6.3	5.5	5.0	4.6	4.3	4.1	3.8	3.7	3.5	3.5
2	Chop suey	5.9	4.8	4.2	3.9	3.6	3.4	3.3	3.1	3.0	2.9	2.9
3	Liver	5.1	4.3	3.9	3.6	3.4	3.3	3.2	3.1	3.0	2.9	2.9
4	Swiss steak	8.3	7.1	6.4	6.0	5.8	5.5	5.4	5.2	5.1	5.0	5.0
5	Pizza	7.7	6.6	6.1	5.8	5.5	5.3	5.2	5.0	4.9	4.8	4.8
6	Roast pork	7.4	6.1	5.5	5.1	4.8	4.6	4.4	4.2	4.1	4.0	4.0
7	Chow mein	5.3	4.5	4.0	3.8	3.6	3.4	3.3	3.2	3.1	3.0	3.0
8	Corned beef	5.4	4.4	3.9	3.6	3.4	3.3	3.1	3.0	2.9	2.6	2.6
9	Beef pot pie	7.3	6.1	5.5	5.2	4.9	4.7	4.5	4.4	4.2	4.1	4.1
10	Lasagna	6.8	5.8	5.3	4.9	4.7	4.5	4.4	4.3	4.1	4.0	4.0
11	Veal scallopini	4.0	3.4	3.1	2.9	2.8	2.7	2.6	2.5	2.4	2.4	2.4
12	Corned beef hash	5.4	4.6	4.1	3.8	3.6	3.5	3.4	3.3	3.2	3.1	3.1
13	Polish sausage	6.9	5.8	5.2	4.9	4.6	4.4	4.3	4.1	4.0	3.9	3.9
14	Veal roast	7.5	6.3	5.7	5.4	5.1	4.9	4.7	4.6	4.4	4.3	4.3
15	Fish sticks	7.6	6.5	5.9	5.5	5.3	5.1	4.9	4.7	4.6	4.5	4.5
16	Barbecued beef cubes	7.3	6.2	5.7	5.3	5.1	4.9	4.7	4.6	4.5	4.4	4.4
17	Roast beef	7.9	6.6	5.9	5.5	5.2	5.0	4.8	4.6	4.5	4.4	4.4
18	Salmon	6.1	5.1	4.6	4.3	4.1	3.9	3.7	3.6	3.5	3.4	3.4
19	Pot roast	7.9	6.5	5.9	5.5	5.2	4.9	4.7	4.6	4.4	4.3	4.3
20	Seafood platter	7.8	6.5	5.9	5.5	5.2	4.9	4.7	4.6	4.4	4.3	4.3
21	Pepper steak	6.9	5.9	5.3	5.0	4.8	4.6	4.4	4.3	4.2	4.1	4.1
22	Shrimp creole	5.3	4.5	4.1	3.9	3.7	3.5	3.4	3.3	3.2	3.2	3.2
23	Salisbury steak	8.0	7.0	6.4	6.1	5.9	5.7	5.5	5.4	5.3	5.2	5.2
24	Macaroni and cheese	7.5	6.3	5.7	5.3	5.1	4.8	4.7	4.5	4.4	4.3	4.3

(Continued)



Table 1. Marginal preference of additional serving of menu items. This table is used to determine the quantity-constrained optimal serving frequencies (Continued)

Item Number	Item Name	Serving 1 (in 84 days)	2	3	4	5	6	7	8	9	10
25	Ham	8.2	7.0	6.4	6.0	5.8	5.6	5.4	5.2	5.1	5.0
26	Fried chicken	8.5	7.4	6.8	6.5	6.2	6.0	5.8	5.7	5.6	5.5
27	Grilled steak	8.7	7.7	7.2	6.9	6.6	6.5	6.3	6.2	6.1	6.0
28	Veal parmesan	5.2	4.4	4.0	3.8	3.6	3.4	3.3	3.2	3.1	3.1
29	Ravioli	7.3	6.2	5.7	5.4	5.1	4.9	4.8	4.6	4.5	4.4
30	Barbecued Spare Ribs	8.1	7.0	6.4	6.0	5.8	5.6	5.4	5.3	5.2	5.1
31	Hungarian goulash	4.3	3.6	3.3	3.1	2.9	2.8	2.7	2.6	2.5	2.5
32	Baked tuna and Noodles	6.1	5.0	4.5	4.1	3.9	3.7	3.5	3.4	3.3	3.2
33	Chicken a la king	6.8	5.8	5.2	4.8	4.6	4.4	4.2	4.1	4.0	3.9
34	Sweet and sour pork	4.5	3.8	3.4	3.2	3.0	2.9	2.8	2.7	2.6	2.6
35	Chili con carne	6.6	5.6	5.1	4.8	4.6	4.4	4.3	4.2	4.1	4.0
36	Fried oysters	4.3	3.8	3.5	3.4	3.3	3.2	3.1	3.0	3.0	2.9
37	Breaded shrimp	7.6	6.8	6.3	6.0	5.8	5.7	5.6	5.5	5.4	5.3
38	Stuffed cabbage	4.4	3.8	3.5	3.3	3.1	3.0	2.9	2.8	2.8	2.7
39	Breaded veal steaks	7.5	6.4	5.7	5.4	5.1	4.9	4.8	4.6	4.5	4.4
40	Vealburger	6.1	5.2	4.7	4.4	4.2	4.1	3.9	3.8	3.7	3.6
41	Turkey pot pie	7.8	6.5	5.9	5.5	5.2	5.0	4.8	4.6	4.5	4.3
42	Chicken cacciatore	4.8	4.1	3.7	3.4	3.2	3.1	3.0	2.9	2.8	2.7
43	Swedish meatballs	6.3	5.3	4.7	4.4	4.1	4.0	3.8	3.7	3.6	3.5
44	Italian sausage	5.7	4.9	4.4	4.2	4.0	3.8	3.7	3.6	3.5	3.4
45	Stuffed green peppers	5.5	4.7	4.2	4.0	3.8	3.6	3.5	3.4	3.3	3.2
46	Turkey slices w/gravy	7.8	6.5	5.8	5.4	5.1	4.8	4.6	4.5	4.3	4.2
47	Spareribs w/sauerkraut	6.0	5.1	4.6	4.3	4.1	4.0	3.8	3.7	3.6	3.5
48	Chili macaroni	5.3	4.4	3.9	3.6	3.4	3.3	3.1	3.0	2.9	2.8

(Concluded)

Table 2. Optimal serving frequencies using preference-time function data from Table 1

Item Number	Item Name	Optimal Number of Servings in 84 Days by Single-Stage Approach
1	Meat loaf	2
2	Chop suey	1
3	Liver	0
4	Swiss steak	4
5	Pizza	3
6	Roast pork	2
7	Chow mein	0
8	Corned beef	0
9	Beef pot pie	2
10	Lasagna	1
11	Veal scallopini	0
12	Corned beef hash	0
13	Polish sausage	1
14	Veal roast	2
15	Fish sticks	3
16	Barbecued beef cubes	2
17	Roast beef	3
18	Salmon	1
19	Post roast	3
20	Seafood platter	2
21	Pepper steak	2
22	Shrimp creole	0
23	Salisbury steak	4
24	Macaroni and cheese	2
25	Ham	4
26	Fried chicken	6
27	Grilled steak	11
28	Veal parmesan	0
29	Ravioli	2
30	Barbecued spare ribs	4
31	Hungarian goulash	0
32	Baked tuna and noodles	1
33	Chicken a la king	1
34	Sweet and sour pork	0
35	Chile con carne	1

(Continued)

Table 2. Optimal serving frequencies using preference-time function data from Table 1 (*Continued*)

Item Number	Item Name	Optimal Number of Servings in 84 Days by Single-Stage Approach
36	Fried oysters	0
37	Breaded shrimp	4
38	Stuffed cabbage	0
39	Breaded veal steaks	2
40	Vealburger	1
41	Turkey pot pie	3
42	Chicken cacciatore	0
43	Swedish meatballs	1
44	Italian sausage	0
45	Stuffed green peppers	0
46	Turkey slices w/gravy	2
47	Spareribs with sauerkraut	1
48	Chili macaroni	0

(*Concluded*)

in (1), the optimal solution would have the marginal preferences at the optimum frequencies equal for all the items.

### A SINGLE-STAGE MENU PLANNING MODEL

#### The Variables and Cost Constraint

Let  $X$  represent the vector of  $n$  decision variables, where the  $j$ -th element of  $X$  is  $x_j$ , the number of times the  $j$ -th menu item is to be served in the  $s$  days of the menu plan. If  $C^T$  represents the  $n$ -vector of unit portion costs of menu items, the cost of the solution vector  $X$  is the scalar  $C^T X$ .

#### The Nutritional Constraints

Let  $A$  be the  $m \times n$  matrix of nutrient contents of the menu items, where an element  $a_{ij}$  of  $A$  is the amount of the  $i$ -th nutrient in a unit portion of the  $j$ -th item. Let  $B$  represent the  $m$ -vector of nutritional requirements for a reference individual over the  $s$  days. The set of  $m$  nutritional constraints is then  $AX \geq B$ .

**The Structural Constraints**

Let  $M$  be a  $K \times n$  incidence matrix indicating the availability of items for different courses. If  $m_{kj}$  is the general element of  $M$ ,  $m_{kj} = 1$  if the  $j$ -th item is available for the  $k$ -th course, and  $m_{kj} = 0$  otherwise. If menu items could be divided into mutually exclusive sets by course, and each meal consisted of exactly one item from each of the  $K$  courses, the matrix  $M$  would consist of just staggered rows. But sometimes the occurrence of one item from a particular course on a meal excludes the need for any item from another course. For example, if the entree is lasagna, no item from the starch category is needed in the meal. In such a case, lasagna would have unit coefficients in the rows of  $M$  corresponding to entrees and starches. If  $S$  is the  $K$ -vector of components indicating the number of items needed for a course in  $s$ -day cycle, the structural constraints are defined by  $MX = S$ .

**Auxiliary Constraints**

Let  $R$  be an  $L \times n$  matrix of coefficients for assorted attribute constraints, proportionality constraints, production constraints etc., that define other feasibility conditions together with a right-hand-side  $L$ -vector  $D$ . If, for example, manpower availability forces the food-service system to serve precooked entrees at least three times a week, such a constraint could be incorporated in the set  $RX \leq D$ . There may be limits on bake-shop items, casseroles, or ground-meat items, or the serving of certain entrees may require some highly compatible items to be forced into the solution.

**The Objective Function**

The preference of individuals for specific menu items in steady-state situation is a concave function of serving frequency. This implies that the marginal contribution of an additional serving of an item in a period of given length gets smaller as the number of servings of the item increases. This phenomenon is attributable to the effect of monotony, and its analytical representation is called the preference-frequency. One form of this function is

$$G_j(x_j) = x_j [a_j - b_j e^{-c_j T / x_j}] / (1 - e^{-r_j T / x_j}) \tag{3}$$

where  $G_j(x_j)$  is the preference derived by consuming the  $j$ -th item  $x_j$  times in a period of length  $T$ , and  $a_j, b_j, c_j$ , and  $r_j$  are parameters specific to the population-item combination.



With the  $n$  items partitioned into  $K$  subsets according to the course structure such as entrees, starches, vegetables etc., let  $w_k$ ,  $k = 1, 2, \dots, K$  be the relative weight of course  $k$  in the total preference of the meals. The total preference of the individual (or group of individuals) for the items is

$$G(X) = \sum_{k=1}^K w_k \sum_{j=n_{k-1}}^{n_k} G_j(x_j) \quad (4)$$

where  $n_0 = 0$ , and  $(n_k - n_{k-1})$  is the number of menu items in course  $k$ . This leads to a nonlinear-programming formulation for a single-stage model of menu planning

$$\text{maximize } G(X)$$

$$\text{subject to } C^T X \leq C_0, AX \geq B, MX = S, RX \leq D, X \geq 0 \quad (5)$$

where  $C_0$  is the cost limit per person for the cycle time of the menu plan.

The problem of elements of  $X$  assuming fractional values is not a serious one. The nonlinear program (5) is well suited for solution by piecewise linearization (Wolfe 1967) where the grid-points of the linearized variables can be conveniently selected to coincide with unit portions. In this way all the upper bounds of the auxiliary variables correspond to integer values, and experience with such upper-bounded linear-programming models for menu planning has shown that in such cases most of the bounds tend to bind, and thus most of the components of the vector  $X$  are integer-valued.

An alternate nonlinear programming formulation of menu planning can be derived from (5) and considered as useful for institutional feeding programs where the management objective is to maintain a given food preference-level at minimum cost. This version of the problem is

$$\text{minimize } C^T X$$

$$\text{subject to } G(X) \geq u_0, AX \geq B, MX = S, RX \leq D, X \geq 0 \quad (6)$$

where  $u_0$  is some minimal level of preference to be maintained, and the rest of the notation is the same as in (5).

## SAMPLE PROBLEMS

Problem (5), although nonlinear, and large in size, (well over 100 constraints and 400 variables for food service establishments), is amenable to efficient solution techniques in existence. The objective function is additively separable, and this makes the application of grid linearization (Wolfe 1967) suitable. Such an algorithm was coded in FORTRAN to operate on a batch-processing system on the CDC 6600, and was used to solve the sample problems. The grid-points were selected to correspond to unit portions of each item, and most of the variables are integer-valued in the optimal solutions.

The preference data for the sample problems was obtained from a study conducted on a U.S. Naval vessel off Greece (Moskowitz 1974). Since this study was incomplete in that no condition was available to estimate the parameter  $r_j$  in relation (3), an arbitrary value of 0.4 was assigned to  $r_j$  for all  $j$  in the sample problem. Nutrient and cost data were derived from Balintfy *et al.* (1972) and the costs were not meant to reflect today's market. All seven problems presented deal with planning a 35-day 6-course meal. Weights for the courses are obtained from Moskowitz (1974).

In the following summary of the sample problems solved, "nutrient constraints" refers to a minimum daily intake specification of 40% of the Recommended Daily Allowances (Nat. Acad. of Sci. 1974) for 19–22 year old males for protein, calcium, iron, vitamin A, thiamin, riboflavin, niacin, and vitamin C.

Problem Number	Calory Limit (900 KCal/day)	Structural Constraints	Nutrient Constraints	Cost Limit (\$/35 days)
1	no	yes	no	none
2	yes	yes	no	none
3	yes	yes	no	15.00
4	yes	yes	no	12.00
5	yes	yes	yes	none
6	yes	yes	yes	15.00
7	yes	yes	yes	12.00

Table 3 displays the optimum serving frequencies obtained for the 26 entrees of the sample problem under the seven constraint conditions. Although the problem uses a relatively small set of 126 items, it does

Table 3. Optimal serving frequencies for 26 entrees per 35-day period as obtained from the single-stage model under 7 constraint conditions.

General Problem Description		Structural Constraints Only		No Nutritional Constraints		With Nutritional Constraints		
Cost Limit		None	None	\$15	\$12	None	\$15	\$12
Item Number	Item Name	Number of Servings Every 35 Days						
1	Meat loaf	2	2	2	2	2	2	1.35
2	Grilled liver	0	0	1	3	1	2	4
3	Swiss Steak/Gravy	3	2	2	1	2	1	1
4	Rost pork	2	2	1	0.33	3	3	2.65
5	Corned beef	0	0	0	1	0	0	0
6	Beef pot pie	0	0	.23	1	0	0	0
7	Baked lasagna	0	0	1	2	1	1	3
8	Corned beef hash	1	0	0	0	0	0	0
9	Fish sticks	2	2	3	4	2	3	4
10	Roast beef	2	2	2	1	2	2	1
11	Post roast	2	2	2	1	2	1	0
12	Pepper steak	2	2	1	0	1	0.84	0
13	Shrimp creole	0	1	0	0	1	0	0
14	Salisbury steak	3	3	3	2	3	3	2
15	Baked macaroni	0	1	1	2	1	1	2
16	Roast ham	3	2	2	2	3	3	3
17	Fried chicken	3	3	3	3.67	3	3	3
18	Grilled steak	4	3	2.77	1	2	2	0
19	Sweet/sour pork	0	0	0	0	0	0	1
20	Chile con carne	2	2	2	2	1	2	2
21	Breaded veal steak	2	2	2	1	1	1	0
22	Chicken cacciatore	0	0	0	0	0	0	0
23	Swedish meatballs	0	0	0	0	0	0	0
24	Roast turkey	2	2	2	2	2	2	2
25	Ravioli/meat sauce	0	1	2	3	2	2.16	3
26	Spaghetti/meat sauce	0	0	0	0	0	0	0
Preference as a percentage of that for optimal solution of problem 1		100	96	94	72	90	86	63
Cost (\$/35 dinners)		18.26	16.82	15.00	12.00	16.55	15.00	12.00

provide insight into the use of such a model. As can be expected, nutritional and cost constraints have an adverse effect on preference. Figure 3 shows the change of preference as a function of cost with and without nutritional constraints. In the table and the figure, the preference level with only the structural constraints is taken as the reference point to express all other levels of preference as a percentage of this  $ad$

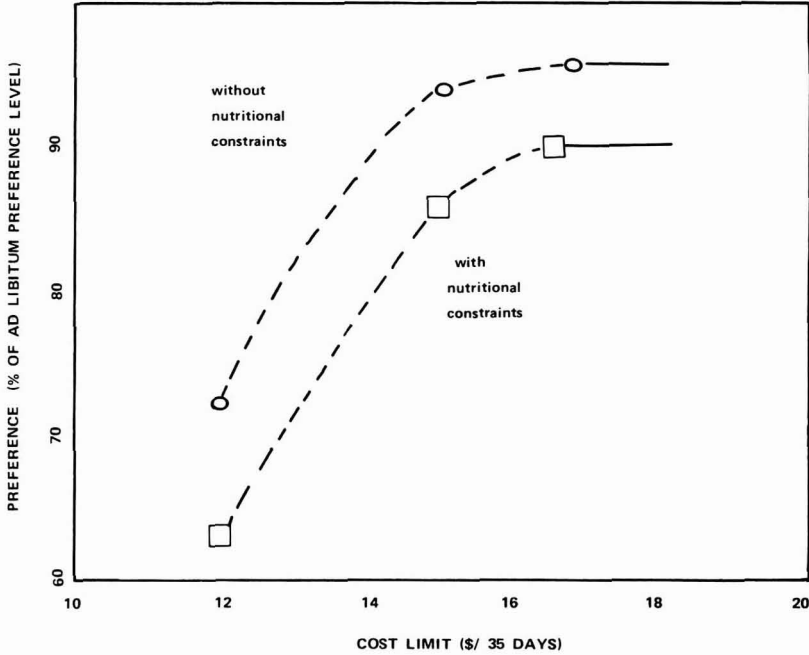


FIG. 3. THE CHANGE OF PREFERENCE FOR OPTIMUM MENU PLANS DUE TO BUDGETARY CHANGE WITH AND WITHOUT NUTRITIONAL CONSTRAINTS

The preferences are expressed as a percentage of the *ad libitum* preference level, i.e. the preference for the optimum menu plan without any cost or nutritional control.

*libitum* level. For example, at the \$15.00 level, the preference loss due to a budgetary drop from \$15.00 to \$12.00 is 22 percentage points without nutritional constraints, and 23 percentage points with them. Thus Fig. 2 highlights the tradeoffs among preference, cost, and nutrition. These tradeoffs are readily visible at the item-frequency level. For example, without nutritional constraints, the frequency of liver is 0 with no cost constraint, and 3 with a \$12.00 limit. On the other hand, grilled steak's frequency drops from 3 to 1.

### CONCLUSIONS

An optimum solution vector  $X$  obtained by solving either (5) or (6) has to be scheduled. The serving-frequency vector  $X$  meets the most significant conditions pertaining to population preferences, total cost,

nutrition, and other general aspects of feasibility. The remaining objective is to assure compatibility among the items on the meals and days of the planning horizon. Compatibility is a property of interactions among items, and therefore in scheduling we deal with the acceptability aspects of combinations of items. The single-stage model thus separates menu planning into two sequential optimization processes. In the first phase, food preferences are maximized using separable programming, and in the second phase, compatibility is to be maximized. Manual scheduling is feasible, but more automated approaches are conceivable by algorithms based on measures of compatibility.

The use of single-stage models goes beyond menu planning as it is defined here. The dual variables provide information on the changes management should consider in their list of menu items. One way of implementing this change is adding to or deleting from the existing list. Let  $V$  be the vector of dual variables, and  $q_{.r}$  be the column vector of attributes, as these would be defined in the nonlinear program (5). If  $y_{k_r}$  is the marginal preference for the item's  $k$ -th serving in  $s$  days, the reduced cost factor  $\bar{c}_r(k)$ , on which the evaluation of a menu item's  $k$ -th serving in  $s$  days can be considered, is

$$\bar{c}_r(k) = G_r(k) - G_r(k-1) - Vq_{.r} \quad (7)$$

If  $\bar{c}_r(k) < 0$ , for  $k = 1$ , even the first serving of the item has a negative contribution, and the item can be considered for elimination from the list. If for a new item  $\bar{c}_r(1) > 0$ , the item will appear in the solution to the nonlinear program with a positive contribution to preference. Another type of change is to modify existing menu items to increase their frequencies in the optimal solution. This can be achieved by increasing the people's preference for the item, etc., and by changing the elements of the column vector  $q_{.r}$  by recipe changes or nutritional fortification. In fact, recipes can be optimized by solving the problem

$$\begin{aligned} & \text{minimize } V_N (AZ)^T \\ & \text{subject to } Z_l \leq Z \leq Z_u \end{aligned} \quad (8)$$

where  $V_N$  is the  $k$ -vector of dual variables corresponding to attributes that depend on the recipe, such as nutrients and cost,  $A$  is the  $k \times n$  matrix of nutrients and costs per unit weight of the  $n$  foods in the recipe,  $Z$  is the  $n$ -vector of decision variables with  $z_i$  being the amount of the  $i$ -th food used in a unit portion of the menu item as specified in the standardized recipe, and  $Z_l$  and  $Z_u$  specify the lower and upper

bounds on the elements of the vector  $Z$ . These bounds have to be such that any variation of the recipe in the specified range would not detract from the item's acceptability. If fortification of the item by vitamin and mineral supplements is permissible, these too can be incorporated in the matrix  $A$ , and the decision variable  $Z$ . If a recipe is changed, the single-stage model's solution vector and dual variables will change too. So this calls for a decomposition scheme whereby recipes and serving frequencies are modified back and forth.

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## PREDICTION OF NUTRIENT LOSSES

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### ABSTRACT

*Once a food is processed it is subjected to a variable temperature-humidity-time distribution pattern which can cause further losses. If a truthful nutrition label is to be put on the food package knowledge of this distribution function is important in assessing the further loss that occurs. More important however, is some knowledge of the kinetics of the degradation of the particular nutrient being considered. The method presented in this paper is based on selecting certain criteria and then based on minimal data, decision rules are used to estimate the possible extent of loss. The steps are as follows: (1) Some estimate is made of the minimum, average and maximum temperatures and times for distribution of the food; (2) A decision is made as to whether moisture gain or loss is involved and can change the rate of degradation; (3) A literature search is made as to the kinetics of the degradation of the nutrient (even single point data, i.e., endpoint analysis are useful); (4) A decision is made as to the maximum amount of degradation tolerated for the average and maximum shelf life; (5) The amount of degradation in #4 is calculated based on both zero and first order rate constants estimated from #3; (6) If the amount lost is less than 50% in #5 then that data is used for the label. If it is greater, then the true order of the reaction must be determined in the lab for calculation in #5. Based on these rules a better estimate of losses can be made.*

Nutritional labeling of foods as is done voluntarily by most food companies in the United States has the implication that the consumer is getting what the label states. In the United States the label requires that certain nutrients be labeled as a percentage of the U.S. RDA. This RDA is based on the 1968 National Academy of Science/National Research Council (NAS/NRC) RDA with the value taken for that group with the highest requirement. Thus, for label purposes the U.S. RDA for iron is



that for females (18 mg) and for vitamin A it is based on the value for males (5000 IU). Table 1 lists the present NAS/NRS RDA's in comparison with the label U.S. RDA requirements (Packard 1974; CFR Title 21, 1977, revised).

Table 1. Comparison of recommended daily allowances

Nutrient	U.S. RDA	1974 NAS/NRC RDA (23-50)	
		Male	Female
Vitamin A	5000 IU	5000 IU	4000 IU
Vitamin C	60 mg	45 mg	45 mg
Thiamine	1.5 mg	1.4 mg	1.0 mg
Riboflavin	1.7 mg	1.6 mg	1.2 mg
Niacin	20 mg	18 mg	13 mg
Calcium	1000 mg	800 mg	800 mg
Iron	18 mg	10 mg	18 mg

In addition to the specific nutrients that must be labeled, there are also specific rules as to the numbers that can appear on the label. Table 2 outlines the general requirements. As seen, if the amount falls below 2% of the U.S. RDA it must be labeled either as 0% or asterisked with a note below that it contains less than 2%. From 2 to 10% the value can only be in increments of 2%; from 10 to 50% in increments of 5%; and from 50 to 150% in 10% increments. Thus, a value of 7% is reported as either 6 or 8%; 13 as 10 or 15%; and 54 as 50 or 60%. The decision to use the higher or lower number depends on the type of food. If the product is a natural type food (for example — canned peas) 80% of a sample lot must show nutrient levels above 80% of the label declaration. If nutrients are added to the product, then the label must be at 100% or more. The analyses are to be performed on foods picked up at point of sale. To be sure of compliance most manufacturers usually use the lower values.

Protein labeling, as shown in Table 3, is based in part on the PER. If the PER of the protein in the food is equal to or better than that of casein with a PER of 2.5, then the percent U.S. RDA is based on 45 g. If the PER is less than 2.5, the label is based on 65 g. If the PER is less than 0.5, then the percent U.S. RDA must be labeled as zero with a statement that the food is "not a significant source of protein."

Given this as a background, one must then look at nutrient losses that could occur during distribution and storage of the food, since the labeling is based on values at point of sale or consumption, not on an "as manufactured" basis. Table 4 lists those nutrients for which signifi-

Table 2. Percent nutrient labeling rules

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0— 2%	Label either as 0% or * with "less than 20%" printed below label
2—10%	Label as 2, 4, 6, 8, 10%
10—50%	Label as 10, 15, 20, etc. up to 50%
50—150%	Label as 50, 60, 70, etc. up to 150%

Examples

7% is labeled as 6 or 8%

13% is labeled as 10 or 15%

54% is labeled as 50 or 60%

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Table 3. Protein labeling

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If food protein has a PER = 2.5 then basis is 45 g

If food protein has a PER  $\leq 2.5 < 0.5$  then basis is 65 g

If food protein has a PER  $< 0.5$  then it cannot be labeled as a significant source of protein

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Table 4. Relative stability of nutrients for label

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<u>Very labile</u>
Vitamin C
Protein quality
<u>Moderate stability</u>
Thiamine
Riboflavin
Niacin
Vitamin A
(Vitamin D, E) <sup>1</sup>
<u>Stable</u>
Iron
Calcium
(Zn, iodine, magnesium, phosphorus, copper) <sup>1</sup>

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<sup>1</sup> Not required but optional

cant losses could occur and those for which there is less of a problem. As seen, the minerals would show no change; thus, they can be labeled as the amount at time of manufacture.

Vitamin C is the most labile of the vitamins as has been noted by several researchers (Lee and Labuza 1974; Kirk *et al.* 1977; Harris and

Karmas 1976). It is subject to anaerobic as well as aerobic oxidation, the rates of which increase with increasing water activity ( $a_w$ ) and temperature. The rate increase for a  $10^\circ\text{C}$  increase in temperature called the  $Q_{10}$  is about 2 to 3 for vitamin C. The rate increase for an increase in  $a_w$  depends very much on the product but is about 1.5 times for a 0.1  $a_w$  increase. In general, a plot of the log of the rate constant versus  $a_w$  follows a straight line. Very little information is available for the kinetics of destruction of the other water soluble vitamins (Labuza 1972). With respect to the fat soluble vitamins, again very little information is available, especially with respect to the rates of destruction as a function of  $a_w$ , temperature and oxygen.

The loss of protein quality through a non-enzymatic browning reaction is the other important nutrient loss occurring during distribution and storage of the food (Labuza *et al.* 1977). In this reaction, reducing compounds react with the essential amino acid lysine, and thus reduce the nutritional value. The rate increases between 4 to 6 times for a  $10^\circ\text{C}$  temperature increase and about 2 times for a 0.1  $a_w$  increase up to an  $a_w$  maximum. Thus moisture gain by a dry food could cause significant losses in protein quality as well as in vitamin C.

Given the foregoing as a general basis for the possible nutrient losses that could occur for dehydrated foods, as well as other foods, certain decision rules can be made in order to estimate the possible extent of loss that might occur.

#### Rule 1

In order for a good prediction of losses, knowledge of the distribution cycle must be made available. Unfortunately there are no good data in the current literature as to time/temperature/relative humidity conditions during food distribution. Old data from the 1940's exist, but transportation methods have changed. Thus, a food processor should collect specific information on minimum, average, and maximum temperatures, as well as times spent at those temperatures, along each distribution channel. This undertaking can be a long and expensive one but can result in identification of portions of the distribution channel that result in significant losses in the food. One should also identify the percent of product going through each leg of the distribution channel.

#### Rule 2

As noted previously, moisture gain can lead to increased rates of nutrient losses. Thus, if the food is a dehydrated product in a semi-permeable pouch, information as to average, minimum and maximum relative humidities along the distribution channel must also be collected, since moisture gain is a function of the outside vapor pressure as seen in equation 1:

$$\frac{dw}{d\theta} = \frac{k}{x} A (p_{out} - p_{in}) \quad (1)$$

where:

$\frac{dw}{d\theta}$  = rate of moisture gain

$\frac{k}{x}$  = package permeance in g H<sub>2</sub>O per (day) (meter)<sup>2</sup> (mm Hg)

A = package area

$p_{out}$  = outside water vapor pressure

$p_{in}$  = vapor pressure of water in the food

Moisture loss would not be important with respect to nutrient losses since the rates decrease with decreasing  $a_w$ .

### Rule 3

The best way to estimate nutrient losses in a food would be to do experiments directly on the food held under steady state conditions as has been done by Waletzko and Labuza (1976). The food is prepared to 2 or 3  $a_w$ 's and then is held at 3 temperatures (20, 30 and 40°C), and the level of the nutrient is measured during storage. From this the kinetic equations are applied to the data to determine whether the reaction follows a zero order reaction as in equation 2:

$$-\frac{dA}{d\theta} = k_o \quad (2)$$

where:

$\frac{dA}{d\theta}$  = rate of loss of nutrient in amt/unit weight/day

$k_o$  = rate constant in amt/unit weight/day

A = amount of nutrient/unit weight

or first order as in equation 3 where the rate is concentration dependent:

$$-\frac{dA}{d\theta} = k_1 A \quad (3)$$

where:

$k_1$  = rate constant in (day)<sup>-1</sup>

The loss data follow a straight line on linear graph paper for a zero

order reaction and on semilog paper for first order. Care should be taken in deciding what the order is, but in many cases it is difficult to do this from much of the literature. If it is impossible to carry out the experiments, then the only alternative is reliance on published reaction rate data. Care should be taken in accepting published rate constants, especially if very few data points were taken to establish the value. In some cases only one value (an endpoint) is known. Thus, it is impossible to decide the reaction order. Table 5 shows the problems that would occur if only one value of degradation is known. The calculated half life is compared for first and zero order. As seen in Table 5, below 50% loss the difference is small so that the prediction error may not be large. Labuza (1978) also reported the same findings for the error with fluctuating temperature. It should be pointed out that the rate constants are only empirical and may not describe the reaction mechanism exactly.

Table 5. Half life prediction based on a single data point

Condition	Half Life (days)	
	Zero Order	First Order <sup>1</sup>
10% destruction in 3 days	17	20
30% destruction in 10 days	17	20
50% destruction in 20 days	20	20
60% destruction in 25 days	22	20
90% destruction in 68 days	38	20

<sup>1</sup>Based on a true half life of 20 days

#### Rule 4

Some decision must be made as to the maximum amount of loss that would be tolerated. For added vitamin C this could be simply based on the fact that the level at the end must meet the label value. Thus, once the label value is chosen, the extra amount added is based on cost and the effects on product organoleptic and textural qualities. For a natural food product it would be based on a maximum of 20% loss per FDA regulations. For protein it would be based on the amount of lysine destruction that would lead to a PER of less than 2.5 for a high quality product.

#### Rule 5

Using the above data and the methods published by Labuza and Karel groups (Labuza 1978; Reimer and Karel 1977; Labuza *et al.* 1972; Mizrahi *et al.* 1970a, b), prediction of the losses that would occur

are made for both zero and first order reactions, especially if the reaction order is not known. For zero order the general equation is:

$$A = A_o - \Sigma (k_i \theta_i)$$

where:

- A = amount at time  $\theta$
- $A_o$  = initial value
- $k_i$  = the specific rate constant for time period  $\theta_i$  at temperature  $T_i$  and water activity  $a_i$

For first order the equation is:

$$A = A_o e^{-\Sigma (k_i \theta_i)}$$

If it is a dehydrated food in a semi-permeable pouch, then a separate prediction of the moisture gain as a function of external conditions must be made first. This equation is:

$$\ln \frac{m_o - m_e}{m_o - m} = \frac{k}{x} \frac{A}{w_s} \frac{p_o}{b} \theta$$

where:

- $m_o$  = initial moisture content
- $m_e$  = moisture content of the product that would be in equilibrium with the external temperature and humidity that occurs during period  $\theta_i$
- $m$  = moisture content at the time  $\theta$  in period  $\theta_i$
- $\frac{k}{x}$  = the film permeance
- $w_s$  = the weight of dry solids contained in the package
- $p_o$  = the vapor pressure of pure water at temperature  $T_i$  during period  $\theta_i$
- $b$  = the slope of the isotherm of the food
- $\theta$  = the time during period  $\theta_i$

Rule 6

If the calculated value is less than 50% destruction based on the initial value and it is not known whether the reaction is zero or first order, then the difference as seen in Table 6 is small, so either value can be used. If the calculated value is greater than 50%, then experimental

data must be collected to get a true estimate of the reaction order.

Table 6. Effect of sine wave temperature sequence (20 to 40°C) on nutrient loss<sup>1</sup>

Value in Table represents A (the amount left)

$\theta$ Days	Zero Order (fluctuating)				First Order (fluctuating)			
	Constant T = 30°C	Q <sub>10</sub>			Constant T = 30°C	Q <sub>10</sub>		
		2	5	10		2	5	10
20	90	88.8	82.4	71.6	87	85.6	78.4	67.4
40	80	77.6	64.8	43.2	77	73.3	61.4	45.5
60	70	66.5	47.2	14.8	66	62.8	58.1	30.7
80	60	55.3	29.7	0	58	53.8	37.7	20.7
100	50	44.1	12.1	0	50	46.1	29.6	14.0
120	40	32.9	0	0	44	39.4	23.2	9.4
140	30	21.7	0	0	38	33.8	18.2	6.4

<sup>1</sup> Initial value 100 at  $\theta = 0$ , 50 at  $\theta = 100$  period of sine wave 20 days.

Presently in our laboratory we are testing these rules in a shelf life study of the nutrient losses occurring in two foods. For pasta we are following thiamine, riboflavin and lysine loss, and for several whey powders we are following lysine loss. The product is being studied both at steady state and fluctuating (sine wave) temperature conditions.

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# EFFECT OF FREEZING AND MONOGLYCERIDES ON STALING OF BREAD

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## ABSTRACT

*The increase in firmness of frozen and thawed and of nonfrozen breads with and without added monoglyceride was followed during storage at room temperature. Freezing retarded the increase in firmness after thawing, the effect being more pronounced the longer the time of frozen storage. This effect was cumulative with that of glyceryl monostearate. Electron micrographs indicated that the breaking of bread structure during compression occurs predominantly at the starch-protein interface. This breakage was lowest in breads with added monoglyceride which had been stored frozen and subsequently thawed.*

## INTRODUCTION

Freezing is currently used in the baking industry mainly for balancing weekly peaks in production and demand. Certain items are also marketed frozen. At the temperatures of frozen storage, the retrogradation of starch is minimal, but some earlier results also indicate that even after thawing the firmness of frozen breads develops slightly more slowly than that of non-frozen breads (Pence & Standridge, 1955; Mälkki *et al.* 1974). This effect has been found to be significantly greater for breads stored frozen for longer times and for fat-containing dough breads (Mälkki *et al.* 1974). The increase in firmness during aging can be effectively counteracted by adding monoglycerides, but this causes a tendency to crumbling. The aim of the present study was to find out whether the above effect of freezing could be effectively used for retarding staling, in combination with monoglycerides.

## EXPERIMENTAL

The basic recipe for the test loaves was 100 parts wheat flour, 52

parts water, 10 of sugar, 12 of 50% yeast suspension, and 2 of salt. To some of the loaves monoglyceride preparations were added in the hydrated state (Krog and Nybo Jensen 1970), at a level of 1% of the weight of flour. The monodiglyceride preparation used contained 43% each of glyceryl mono- and distearates and the monoglyceride preparation 90% glyceryl monostearate. After baking and initial cooling, the test loaves were packed in polyethylene bags and frozen 100 min after baking in an air blast of  $-40^{\circ}\text{C}$  until the center of the loaves had reached a temperature of  $-20^{\circ}\text{C}$ . The loaves were stored at  $-20^{\circ}\text{C}$  from 1 to 7 days, subsequently thawed at  $50^{\circ}\text{C}$  for 2 hr, and further stored at  $20^{\circ}\text{C}$ . Control breads of the same formulations and from the same batch were aged at  $20^{\circ}\text{C}$  without freezing and thawing treatments.

The firmness of the breads was tested by compressing slices of 30 mm in thickness, with crust removed, to a deformation of 3 mm, in an Instron Universal Testing Machine with a crosshead speed of 0.33 mm/s. To balance the inhomogeneity of the loaves, four slices were tested from each loaf. To avoid drying of the surface, the slices were tested while loosely packed in polyethylene bags. The deformation used was sufficiently small not to cause visible breaking of the structure, and the force-distance curves showed that it was in the elastic range of compression.

For calculation of Young's modulus, the deviation of the slices from parallelity was balanced by extrapolating the linear part of the force-distance curve to the axis to obtain a point interpreted as the beginning of compression.

For electron microscopic examination, samples were taken both from non-compressed slices and from slices compressed to 70% of the original thickness and allowed to recover. The samples were lyophilized, cut in rectangular pieces in a microtome, gold coated, and examined in a scanning electron microscope. All electron micrographs presented are from the bottoms of bread pores, and thus from non-cutted surfaces and have the same magnification.

## RESULTS AND DISCUSSION

In the breads with no added monoglyceride (Fig. 1), the freezing itself caused only a minute change in the elastic modulus, and 10 hr after baking or thawing, no difference was measurable between frozen and non-frozen breads. However, the breads stored frozen for 7 days had a distinctly slower increase in firmness after thawing, as compared to the non-frozen breads.

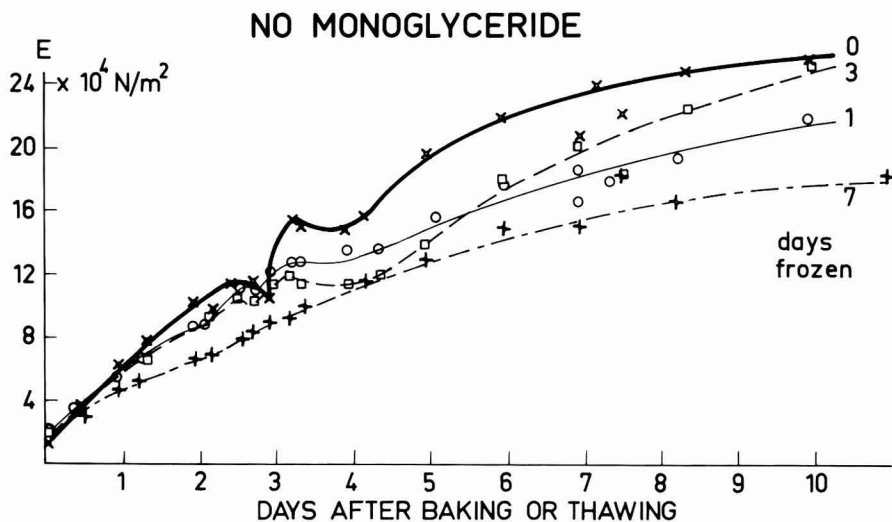


FIG. 1. INCREASE IN FIRMNESS OF FROZEN AND NON-FROZEN BREADS WITH NO ADDED MONOGLYCERIDE

Around 3 days after baking or thawing, a discontinuity phase was repeatedly observed in the elastic modulus versus storage time pattern. This phase has not previously been reported, probably partly due to greater time intervals between observations and partly to less sensitive measurement techniques in earlier experiments. This phase tends to move towards the beginning of the thawed storage when the time of frozen storage is increased.

To determine whether the general theories of crystallization could explain the observed phenomenon, the modified Avrami equation (Cornford *et al.* 1964) was applied:

$$\theta = e^{-k t^n}$$

where:

- $\theta$  = uncrystallized material fraction
- $k$  = velocity constant for nucleation and growth
- $t$  = time
- $n$  = a whole number (1...4), "mode of nucleation and growth"

If  $E$  is regarded as a linear measure of the degree of crystallization, the uncrystallized fraction is obtained from the equation:

$$\theta = \frac{E_{\infty} - E_t}{E_{\infty} - E_0}$$

in which the indices refer to the time of storage. Because of the discontinuity phase, the values were calculated separately for the first three days after baking or thawing and for the rest of the observations. The results showed that during the first 3 days a value of 1 was obtained for  $n$ , reflecting a linear growth of crystals from predetermined nuclei. After 3 days of storage above freezing point,  $n$  had a value of 1 for non-frozen samples and for those stored frozen one day, but a value of 2 when the frozen storage was 3 or 7 days. If the crystallization alone controlled the firmness, this would indicate either a plate-like growth of crystals or a continuous formation of new nuclei. Another explanation, however, is alteration in the protein structure of the breads.

According to the electron micrographs, the starch granules in non-frozen bread with no added monoglyceride and stored for one day are well embedded in the protein matrix (Fig. 2) and the compression causes only slight breaking of the structure. After 3 days' storage, (Fig. 3) cracks are more abundant, and after 6 days (Fig. 4) advanced breakage of the protein structure is observed, especially at the interface of starch and protein.

In frozen and thawed bread with no added monoglyceride (Fig. 5, 6, 7) the results are nearly similar, with the exception that the one-day old sample tends to break more than the corresponding non-frozen sample.

In the breads with added monoglyceride, the same phenomenon was observed, but at a lower level of elastic modulus (Fig. 8). The breads stored frozen for one day did not deviate noticeably from the non-frozen controls during the first three days, and even later the differences were small. The breads stored frozen for 3 or 7 days had significantly slower increase in firmness, and the discontinuity phase occurred earlier.

The electron micrographs show that a typical feature for all breads with added monoglyceride is that starch granules are less embedded in the protein matrix.

In the non-frozen bread one day after baking (Fig. 9) compression caused severe breaks in the structure and a nearly complete separation of larger starch granules from the protein. The structure seems to be most fragile at the point where the discontinuity is observed in the elastic modulus versus time curves, i.e. at age 3 days. The starch granules are separated from the protein before compression, evidently by the stress caused by slicing (Fig. 10). At the age of 6 days, the structure is again firmer. This could be explained by a more rigid structure when slicing or by the multitude of minute cracks in the structure.

Frozen breads with added monoglyceride (Fig. 12, 13, 14) were found to keep their structure best when aging. Again, however, the

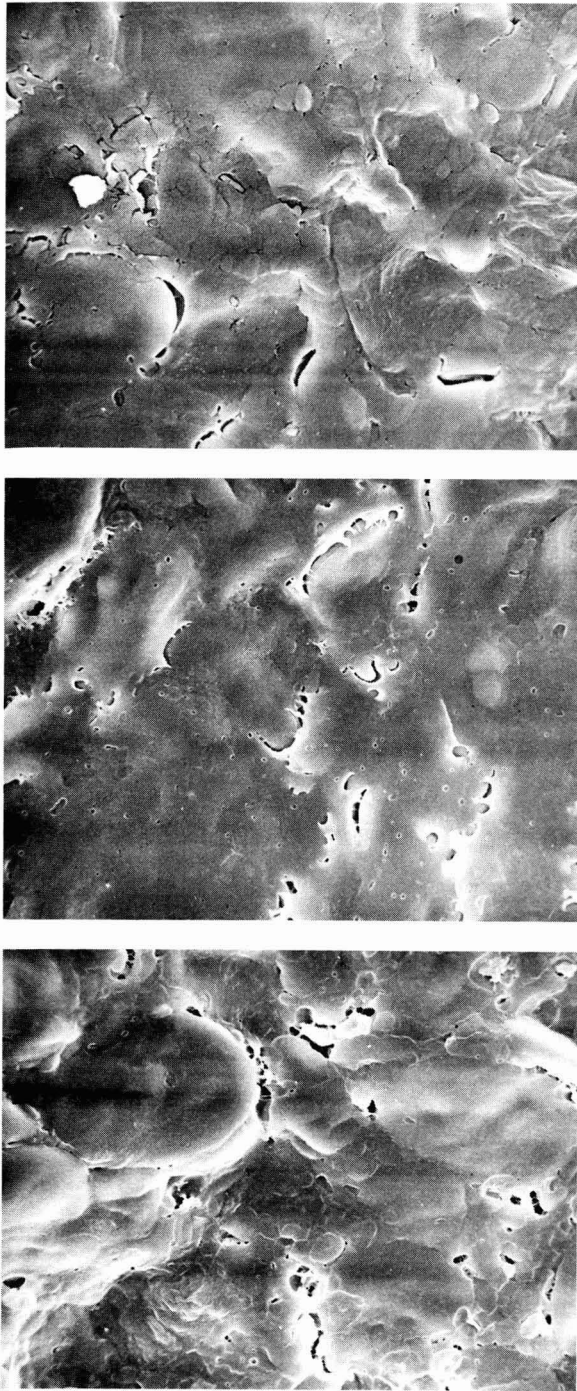


FIG. 5, 6 & 7. BREADS WITH NO ADDED MONOGLYCERIDE, STORED FROZEN FOR 4 DAYS, 1,3 AND 7 DAYS AFTER THAWING, RESPECTIVELY

Fig. 5 and 6 from compressed samples, Fig. 7 from a non-compressed sample ( $\times 640$ ).

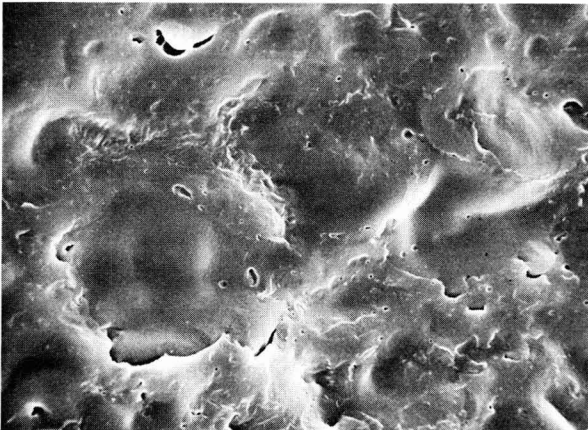
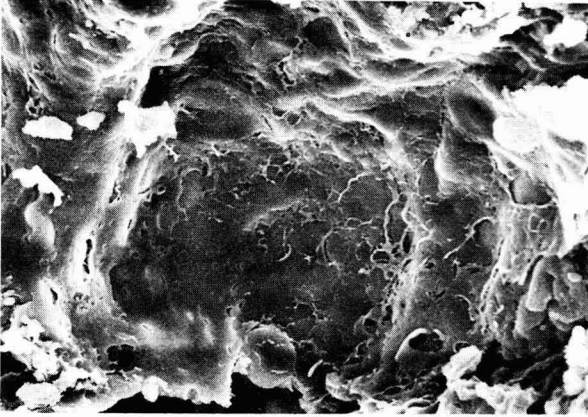


FIG. 2, 3 & 4. NON-FROZEN BREADS WITH NO ADDED MONOGLYCERIDE, 1, 3 AND 6 DAYS AFTER BAKING, RESPECTIVELY

Each picture is of the bottom of a pore, after compression to 70% of the original height of the sample ( $\times 640$ ).

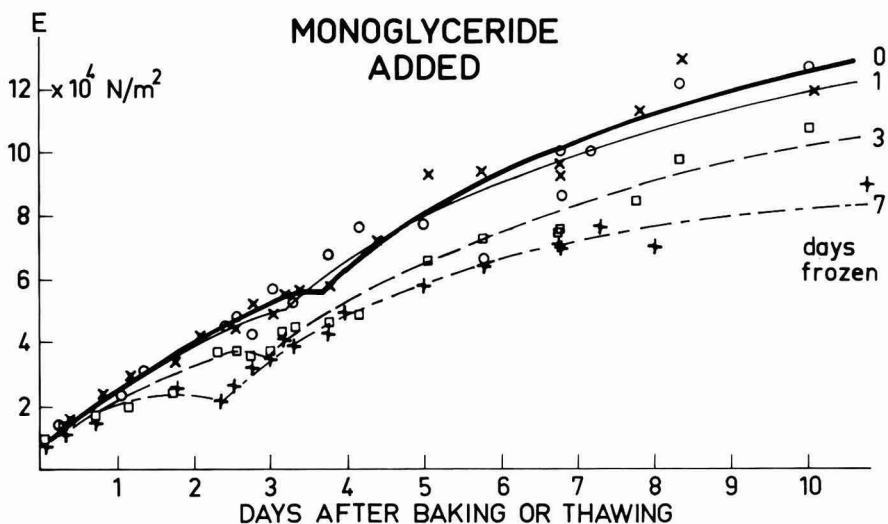


FIG. 8. INCREASE OF FIRMNESS OF FROZEN AND NON-FROZEN BREADS WITH MONO-DIGLYCERIDE ADDED (1% OF FLOUR WEIGHT)

bread sample 3 days after thawing (Fig. 13) had the weakest structure. The present results do not reveal any clear-cut explanation for this difference from non-frozen samples. Possible causes could be changes in the volume of starch granules and in the water content of the protein. The slight difference in the outer appearance of the protein layer on the starch granules indicates the latter possibility.

When the two sets of loaves are compared, it can be noticed that glyceryl monostearate and frozen storage have cumulative effects on retarding staling. Since the retardation of staling by freezing was also observed in loaves with no added fat or monoglyceride, the effect is evidently not due to an increase in the effective concentration on monoglyceride during freezing. By combining the use of monoglycerides and freezing, it is possible to keep the freshness, as judged by the firmness, a longer time than by either of these means alone, especially when the time of frozen storage is longer than one day. The breads containing monoglyceride and stored frozen for 7 days reached the same elastic modulus 7 days after thawing which the non-frozen breads with no added monoglyceride had already reached 28 hr after baking.

According to the electron micrographs, freezing and frozen storage diminish the tendency towards cracking and thus could diminish the tendency towards crumbling the monoglyceride-containing bread.



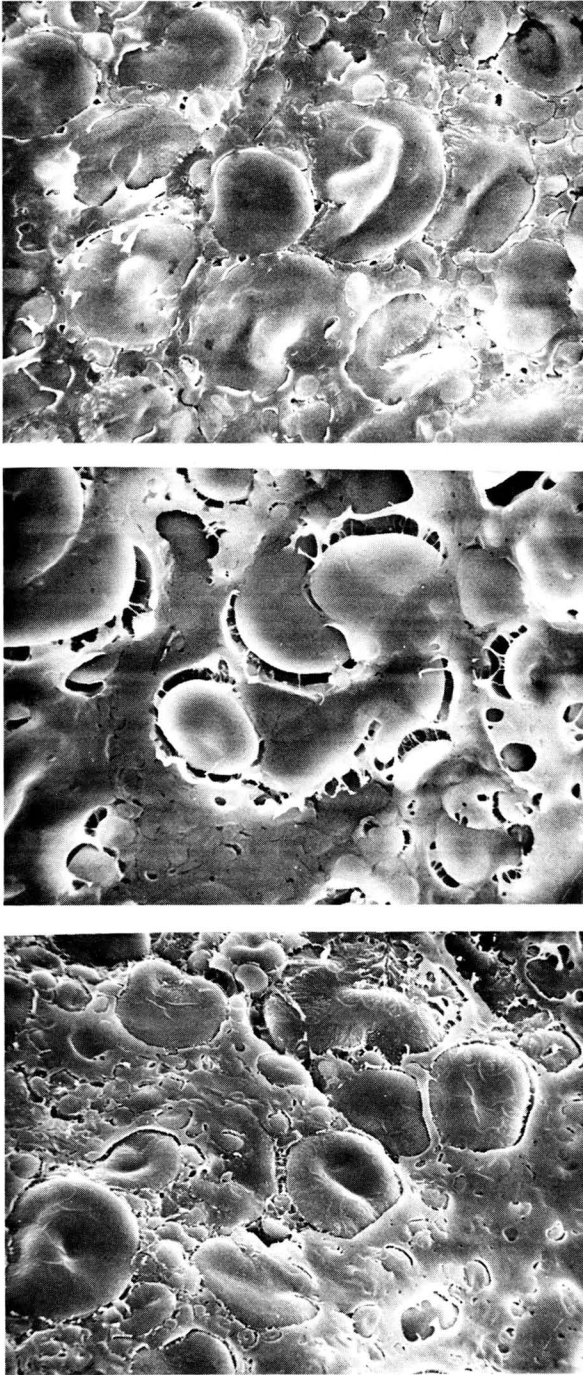


FIG. 9, 10 & 11. BREADS WITH GLYCERYL MONOSTEARATE ADDED (1% OF FLOUR WEIGHT), 1, 3 and 6 DAYS AFTER BAKING, RESPECTIVELY

Fig. 9 is a compressed sample, Fig. 10 and 11 non-compressed samples (X 640).



FIG. 12, 13 & 14. BREADS WITH ADDED MONOGLYCERIDE, STORED FROZEN FOR 4 DAYS, 1, 3 AND 6 DAYS AFTER THAWING, RESPECTIVELY

Fig. 12 is a compressed sample, Fig. 13 and 14 non-compressed samples ( $\times 640$ ).

## ACKNOWLEDGMENTS

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# THE EFFECT OF DIALYSIS ON HEAT-INDUCED GELATION OF WHEY PROTEIN CONCENTRATE<sup>1</sup>

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## ABSTRACT

*Time required for gelation of 10% protein dispersions of commercial whey protein concentrate (WPC) heated at 100°C was influenced by preparation technique. Gel times ranged from 1.25 to greater than 30 min. Dialysis of a rapid gelling WPC resulted in the formation of stronger, more cohesive, less springy, more gummy, more chewy and more translucent gels with heating (100°C for 15 min) at 10% protein than did non-dialyzed WPC. Addition of CaCl<sub>2</sub> or NaCl to the dialyzed WPC increased gel strength more dramatically than did salt addition to non-dialyzed WPC. Resistance to penetration and hardness of dialyzed whey protein gels maximized with CaCl<sub>2</sub> addition from 5.0 to 20 mM and decreased with 25 mM CaCl<sub>2</sub> addition. In non-dialyzed whey protein gels, resistance to penetration maximized at 25 mM added CaCl<sub>2</sub> while hardness values maximized at 5.0 mM CaCl<sub>2</sub>. Addition of 0.2 to 0.5 M NaCl increased resistance to penetration of both whey protein gel systems. Hardness values for dialyzed WPC gels maximized at 0.1 to 0.3 M NaCl and decreased at 0.4 M or greater added NaCl. Hardness values of non-dialyzed WPC were only slightly affected by NaCl addition. Addition of CaCl<sub>2</sub> at 5 mM or greater or NaCl at 0.1 M or greater decreased cohesiveness and springiness of dialyzed WPC gels. Cohesiveness of non-dialyzed WPC gel systems was maximal at 10 mM CaCl<sub>2</sub> or 0.2 M*

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*NaCl. Salt had no apparent effect on springiness of the non-dialyzed WPC gels. Gumminess data followed similar trends to those observed for hardness with respect to salt effects in WPC gel systems. Maximum chewiness values for both WPC gel systems were apparent with addition of 5.0 to 10 mM CaCl<sub>2</sub> or with addition of 0.1 to 0.3 M NaCl.*

## INTRODUCTION

Excellent nutritional values and unique functional properties have resulted in considerable interest in the recovery and utilization of cheese whey proteins in food systems (Morr 1976). Because of processing variations, a wide variety of commercial whey protein concentrates (WPC) are available. Differences in composition and functional properties have been observed for WPC's prepared by differing separation methods (Morr *et al.* 1973; McDonough *et al.* 1974).

An important functional property of whey proteins is their ability to form gel structures capable of immobilizing large amounts of water with heating in food systems (Hermansson 1972, 1973; Hermansson and Akesson 1975a,b). Visual characteristics of whey protein gels may vary from that of a firm elastic gel to a curd-like gel structure depending on preparation technique. Differences in gels formed from WPC prepared by diafiltration and ultrafiltration could be related to lactose and ash concentration in the preparation (Haggett 1976). Sternberg *et al.* (1976), reported on a WPC with low lactose content isolated by polyacrylic acid precipitation which possessed heat-induced gelation characteristics at 10% protein similar to those of egg white at 15% protein. These workers also observed that lipid content interfered with heat-induced whey protein gelation.

The mechanism of whey protein gel formation is still not completely understood. A complex set of conditions optimal for disulfide and ionic bridging are apparently required since gelation properties can be altered by addition of salts and sulfhydryl reducing agents (Illingworth 1977; Schmidt *et al.* 1978).

In the present investigation several commercial WPC's were compared for their gelation ability. A WPC forming strong gels with heating was then further purified by dialysis to provide a model system to study effects of salt addition on gel characteristics.

## MATERIALS AND METHODS

### Protein Preparation

Source, method of preparation and compositional data for WPCs

investigated are presented in Table 1. Ten percent protein dispersions of WPC in deionized water were adjusted to pH 9.0 with 1.0 N NaOH and were allowed to equilibrate with stirring for 30 min at 35°C. The dispersions were then cooled to 25°C and the pH was adjusted to 7.0 with 1.0 N HCl.

Table 1. Method of preparation, compositional and qualitative gelation characteristics for commercial whey protein concentrates (WPC)

Protein Concentrate	Method of Preparation	Composition			Gel Time <sup>2</sup>
			%	Ratio <sup>1</sup>	
WPC-A <sup>3</sup>	gel filtration	protein	53.6	—	1.25
		lactose	26.5	2.02	
		fat	2.5	21.44	
		ash	10.2	5.26	
WPC-B <sup>4</sup>	electrodialysis	protein	29.0	—	13.00
		lactose	57.0	0.51	
		fat	2.5	11.60	
		ash	11.0	2.64	
WPC-C <sup>5</sup>	electrodialysis	protein	35.2	—	17.00
		lactose	53.8	0.65	
		fat	3.2	11.00	
		ash	3.0	11.73	
WPC-D <sup>6</sup>	ultrafiltration	protein	50.0	—	30.00+
		lactose	40.0	1.25	
		fat	3.0	16.67	
		ash	2.8	17.86	
WPC-E <sup>7</sup>	ultrafiltration	protein	34.4	—	30.00+
		lactose	51.8	0.66	
		fat	3.5	9.83	
		ash	6.6	5.21	

<sup>1</sup> Ratio: protein/non protein component

<sup>2</sup> Time (min) at 100°C required to produce a gel with a rating of 4.0 to 5.0 (Schmidt 1978)

<sup>3</sup> Enpro 50, Stauffer Chemical Co., Westport, CT

<sup>4</sup> Puretein 29, Purity Cheese Co., Mayville, WI

<sup>5</sup> Foretein 35, Foremost Foods Co., San Francisco, CA

<sup>6</sup> Hiprotal 50, Tetroid Co., Inc., Hamilton, NY

<sup>7</sup> Meloskim WP34, Dairyland Products, Inc., Savage, MN

Dialysis was performed at 25°C in an Amicon DC-2 hollow fiber apparatus (Amicon Corp., Lexington, MA) in concentration mode with a continuous feed external dialysate reservoir. The dialysate was deionized water to which 0.01% sodium azide was added as a preservative. Dialysis was terminated when eight volumes of dialysate had passed through the system. The final dialyzed WPC solution was adjusted to pH 7.0 and diluted to 10% protein concentration.

### Addition of Salts

Sodium chloride was added to the WPC dispersions at final concentrations ranging from 0 to 0.5 M. Calcium chloride was added at concentrations ranging from 0 to 25 mM. The dispersions were allowed to equilibrate with stirring for 30 min at 25°C after salt addition.

### Gel Formation

For qualitative determination of gelation ability, 3-ml aliquots of the WPC dispersions were dispensed in screw capped test tubes and heated in an oil bath at 100°C. Tubes were removed from the bath at 30-s intervals and placed into an ice bath. Gel strength was evaluated on a visual rating scale of 0 to 5.0 as previously described (Schmidt 1978). The time required at 100°C for the formation of a gel with a rating of 4.0 or higher was reported as gel time. Tabulated data represent means of four replicate trials.

Gels for quantitating gel characteristics were prepared in screw capped centrifuge tubes (22 × 100 mm) by heating at 100°C for 15 min as previously discussed (Schmidt *et al.* 1978). Gel strength was determined by a penetration technique using the Instron fitted with a disk probe (6.0 mm diameter) (Schmidt *et al.* 1978). Additional gel characteristics were determined by texture profile analysis on the Instron (Bourne *et al.* 1966). Cylindrical plugs of 1.5-cm diameter were removed from gel centers with a cork borer and were sliced with a razor cutting device into 1.0-cm segments. Each segment was compressed a distance of 5.0 mm with a 5.5-cm crosshead at 2.0 cm/min. The calculated texture profile parameters were hardness, cohesiveness, springiness, chewiness and gumminess. Data presented are means of five trials ± standard deviation.

### Chemical Analyses

The protein preparations were analyzed for lactose (Dubois *et al.* 1956); protein (Lowry *et al.* 1951), fat and ash (A.O.A.C. 1970). Specific mineral analyses were by atomic absorption spectroscopy.

## RESULTS AND DISCUSSION

### Gelation of Commercial Whey Protein Concentrates

From the data presented in Table 1, gelling ability of the WPC's was affected by preparation method. WPC-A prepared by gel filtration, re-

quired the least time (1.25 min) to gel at 100°C while WPC-D & E, manufactured by ultrafiltration, did not form gels after 30 min heating at 100°C. Similar visual characteristics were noted for the WPC's which did form gels with heating at 100°C (A, B and C). The whey protein gels were characterized as strong, opaque-white and curd-like.

Differences in gelling time, in general, could not be explained by compositional differences. The most rapidly gelling WPC did have higher protein/lactose and protein /fat ratio than other WPC's. The protein/ash ratio, however, was intermediate. WPC-B (prepared by electro dialysis) with lowest protein/ash ratio gelled more rapidly than did WPC-C with similar protein/lactose and protein/lipid ratio. Lack of gel formation in WPC-D & E cannot be predicted from compositional data suggesting involvement of other factors such as specific protein composition and denaturation.

The most rapidly gelling WPC (A) was chosen to serve as a model system to further investigate effects of dialysis and salt addition on gelation. Compositional data for dialyzed (D-WPC) and non-dialyzed (ND-WPC) 10% protein dispersions of WPC-A are compared in Table 2.

Table 2. Compositional data for dialyzed and nondialyzed 10% protein solutions of whey protein concentrate (WCP-A)

Sample	Proximate Composition (%)		Mineral Concentration (mM)	
Non-dialyzed	protein	10.0	sodium	152.1
	lactose	4.9	potassium	79.5
	fat	0.5	calcium	52.5
	ash	1.9	phosphate	18.0
Dialyzed			magnesium	16.5
	protein	10.0	sodium	56.5
	lactose	0.1	potassium	0.4
	fat	0.1	calcium	5.8
	ash	0.7	phosphate	0.7
		magnesium	2.0	

### Dialysis Effect on Gelation

Dialysis generally increased the gel strength of the WPC gels as indicated by increased penetration resistance and hardness values (Fig. 1). Gels from D-WPC were also more translucent in visual appearance indicating less light scattering than observed in the more opaque gels from ND-WPC. Light scattering is generally related to particle size,



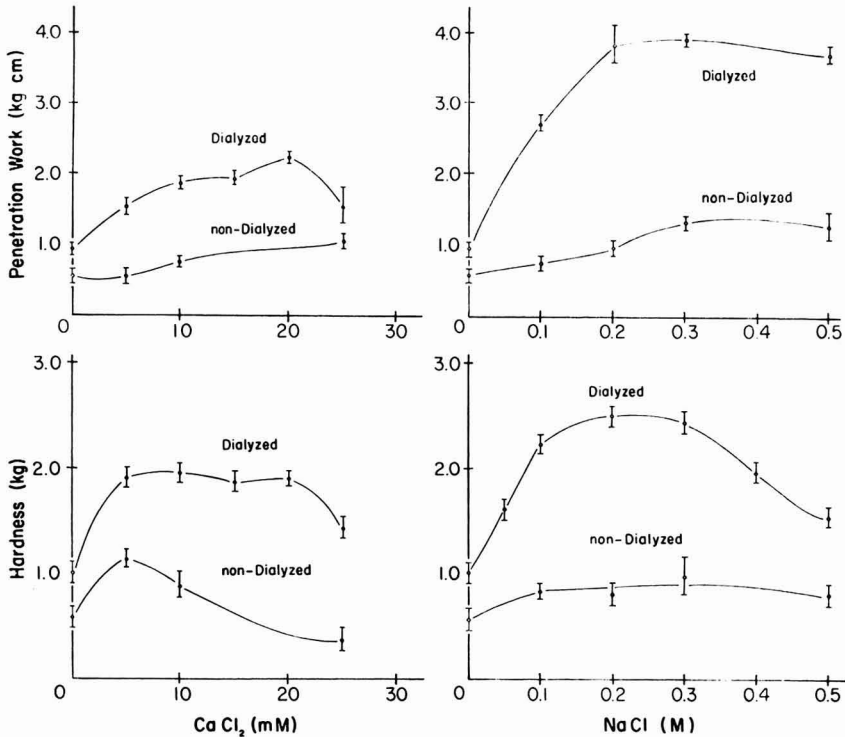


FIG. 1. EFFECT OF SALT ADDITION TO 10% PROTEIN DISPERSIONS OF DIALYZED AND NON-DIALYZED WHEY PROTEIN CONCENTRATE ON THE STRENGTH OF GELS FORMED BY HEATING AT 100°C FOR 15 MIN

Penetration work (Kgcm) from penetration to 3 cm with 6.0 mm probe at 2 cm/min (Schmidt *et al.* 1978). Hardness (Kg) from texture profile analysis (Bourne *et al.* 1966).

to refractive indices of both particle and medium, and to the dielectric constant of the particles and medium (Kerker 1969). Therefore, lower light scattering in protein gels probably indicates lower particle size and lower hydration. A translucent appearance in gels has also been related to less intermolecular bridging and a more compact gel structure with shorter interchain distance (Ferry 1948).

Gels formed from D-WPC were more cohesive than were those from the ND-WPC system (Fig. 2). Higher cohesiveness (or stickiness to itself) also suggests that dialysis resulted in a more tightly packed structure.

Lower springiness values were observed in D-WPC gels than for those

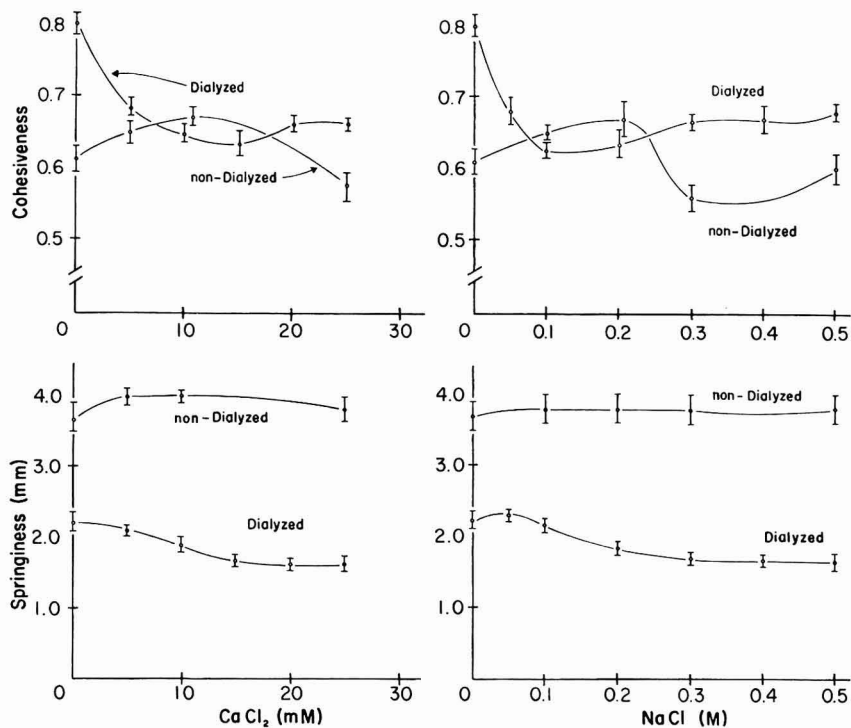


FIG. 2. EFFECT OF SALT ADDITION TO 10% PROTEIN DISPERSIONS OF DIALYZED AND NON-DIALYZED WHEY PROTEIN CONCENTRATES ON THE COHESIVENESS AND SPRINGINESS OF GELS FORMED BY HEATING AT 100°C FOR 15 MIN

Cohesiveness and springiness (mm) from texture profile analysis (Bourne *et al.* 1966).

from ND-WPC. Since springiness, as determined herein, is a measure of gel elasticity, it should vary inversely with the degree of crosslinking in the gel structure (Huggins 1946).

The secondary parameters (gumminess and chewiness) were calculated from the three primary parameters (Bourne *et al.* 1966). Dialysis increased the gumminess value (defined as hardness  $\times$  cohesiveness) and chewiness values (gumminess  $\times$  springiness) as shown in Fig. 3.

#### Effect of Salt Addition on Gelation

While ionic bonding in protein gels probably plays its most important role in protein-solvent interactions, a subtle role may be ascribed to opening the protein structure at specific salt concentrations, thereby

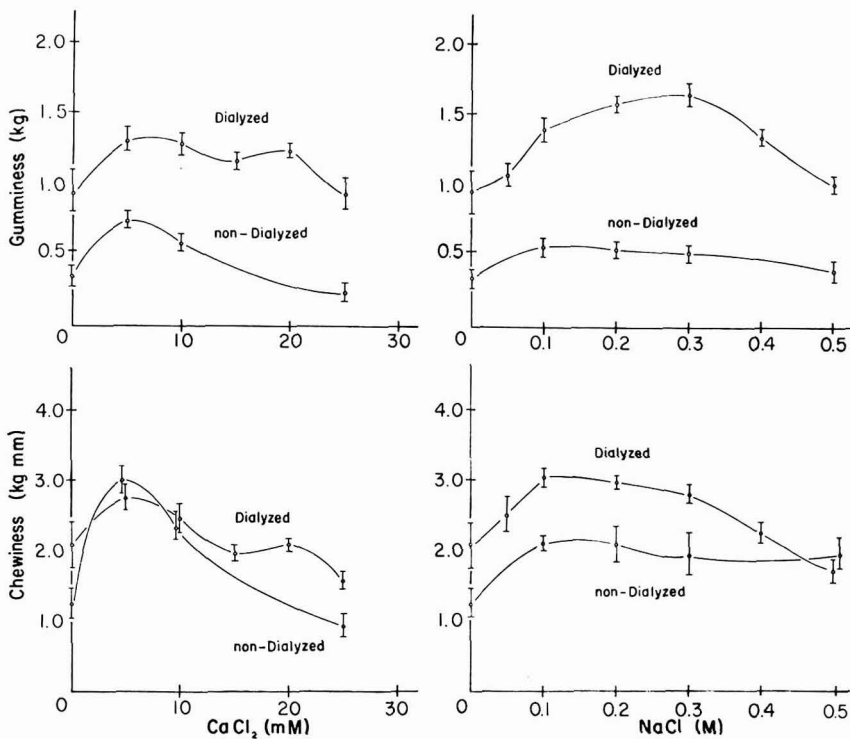


FIG. 3. EFFECT OF SALT ADDITION TO 10% PROTEIN DISPERSION OF DIALYZED AND NON-DIALYZED WHEY PROTEIN CONCENTRATE ON THE GUMMINESS AND CHEWINESS OF GELS FORMED BY HEATING AT 100°C FOR 15 MIN

Chewiness (Kg mm) and gumminess (Kg) calculated from texture profile analysis (Bourne *et al.* 1966).

enhancing the gelation phenomenon (Florey and Rehner 1943), Moreover, ionic bonding at specific loci in the protein (especially calcium) may provide stability to the gel structure.

A more dramatic increase in gel strength was noted with CaCl<sub>2</sub> or NaCl addition to the dialyzed system than for the ND-WPC (Fig. 1). These data indicate that occlusion or interaction with lactose and fat interferes with the salt effects on gelation.

Differing trends were observed for effects of salt addition on hardness and penetration values (Fig. 1). Hardness and penetration maximized in the D-WPC gels with CaCl<sub>2</sub> addition from 5.0 to 20 mM and decreased at 25 mM CaCl<sub>2</sub>. Decreased gel strength at higher levels of Ca<sup>+2</sup> could indicate intra-chain calcium bridging. For the ND-WPC gel

system, penetration values increased slightly with  $\text{CaCl}_2$  addition to 25 mM while hardness values were maximal at addition of 5.0 mM  $\text{CaCl}_2$ . NaCl addition to 0.2 M or above maximized penetration values for D-WPC gels while hardness values reached a maximum at 0.1 to 0.3 M NaCl and decreased at 0.4 M NaCl or above. Since hardness is essentially a compression test while penetration is a measure of combined resistance to compression and shear (Bourne 1966), differences in data would not be unexpected and may suggest subtle differences in the gels. Higher penetration values at high ionic strength may indicate loosely associated ionic bridging resistant to shear. The breaking of this bridging with solvent expulsion during compression is reflected by lowered hardness values. These phenomena should be further investigated.

Salt addition to the D-WPC system initially decreased gel cohesiveness values followed by a slight increasing trend at higher salt concentrations. Cohesiveness was apparently minimal at 10 to 20 mM  $\text{CaCl}_2$  or at 0.1 to 0.2 M NaCl for the D-WPC gels. The decreased cohesiveness probably resulted from the formation of a more open structure in the presence of  $\text{CaCl}_2$  or NaCl. Opacity or whiteness also increased with salt addition suggesting more intermolecular bonding or more solvent occlusion in the structure. The slight increase in cohesiveness at high-salt levels may be a result of intramolecular salt bridges in the protein (especially with calcium). The cohesiveness of the ND-WPC gels followed differing trends with salt addition than did D-WPC gels. Maximal cohesiveness for ND-WPC gels was apparent with addition of 5.0 to 10 mM  $\text{CaCl}_2$  or 0.1 to 0.2 M NaCl.

Springiness of the D-WPC gels decreased slightly with  $\text{CaCl}_2$  addition above 10 mM or with NaCl above 0.1 M. If, indeed, springiness (or elasticity) varies inversely with degree of crosslinking in the gel (Huggins 1946), we can only conclude that the increased gel strength and decreased cohesiveness noted with salt addition resulted from a more swollen structure imbibing more solvent than from a dramatically increased crosslinking effect. It is also conceivable that ionic crosslinking does not necessarily inversely relate to springiness. No apparent differences in springiness were noted in the ND-WPC gels with salt addition.

Gumminess values followed general trends similar to those observed for hardness with respect to salt addition. Maximal gumminess for both gel systems was apparent with  $\text{CaCl}_2$  addition of 5.0 mM. Addition of 25 mM  $\text{CaCl}_2$  decreased gumminess values. Chewiness for both gel systems maximized to a similar level at 5.0 mM  $\text{CaCl}_2$ . The D-WPC gels however decreased in chewiness at 0.4 M NaCl or above while that of the ND-WPC gels increased and leveled off with NaCl addition.

### SUMMARY AND CONCLUSIONS

The results presented clearly indicate differences in gelling ability for commercial WPC's. Differences should not, however, be construed as a measure of quality since gelling is not necessarily desirable in all food applications. The results merely suggest the need for testing specific WPC's in specific food applications for optimal utilization.

Dialysis of WPC resulted in the formation of stronger, more cohesive, less springy, more gummy, more chewy and more translucent gels with heating than did the ND-WPC system. Moreover, the D-WPC gel system was more responsive to salt addition than was the ND-WPC gel system and provided a more adequate model system for studying the whey protein gelation phenomenon.

Increased gel strength and decreased cohesiveness were observed with the addition of NaCl or CaCl<sub>2</sub> to the D-WPC gel system. This suggests that the ionic involvement in whey protein gel formation is by forming a less tightly packed structure with the possibility of more crosslinking and stability. Salt addition, however, decreased gel springiness suggesting that the amount of crosslinking did not increase or that the effects were more complex than could be measured by this parameter.

Additional research is necessary to more clearly understand the effects of heat treatment and reagent combinations on the textural attributes of whey protein gels.

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# INSECT RESISTANCE OF FOOD PACKAGES — A REVIEW<sup>1</sup>

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## ABSTRACT

*Food processors can protect their products from insect infestation, despite worldwide substandard distribution facilities, by the use of insect-resistant packages. Insect-resistant packages must exclude insect species that enter through existing openings (invaders) and species that bore through the package wall (penetrators). In the United States, treatment of packages for insect resistance is restricted to pyrethrins synergized with piperonyl butoxide (alpha-[2-(2-butoxyethoxy)ethoxy]-4,5-(methylenedioxy)-2-propyltoluene) on multiwall paper or cotton shipping bags or on laminated cellophane-polyethylene for small fruit packages. The chemical treatment can migrate from the package into the commodity; therefore, physical barriers or appropriate treatment formulations must be employed.*

*Packaging materials vary in resistance to penetration by insects, although some species of insects can penetrate most flexible films, foils, papers, and combinations of these. Polycarbonate film is the most resistant polymer film; polyester and polyester urethane films also resist insect penetration. Cellophane and paper are the least resistant commonly used flexible packaging materials.*

*Shipping containers can be made insect resistant by the use of appropriate chemical treatment or physical barriers. Treated shipping bags with insect-tight seals, polyethylene-overwrapped or fully taped corrugated cases and heat-shrunk film overwraps on pallet loads of bags or cases provide protection from infestation.*

*Consumer-sized packages such as overwrapped cartons, cartons with fully sealed flaps, and polyethylene-coated cartons with heat-sealed*

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<sup>1</sup> Mention of a pesticide in this paper does not constitute a recommendation for use by the USDA nor does it imply registration under FIFRA as amended. Mention of a proprietary product does not constitute an endorsement by the USDA.



*flaps provide varying degrees of protection from insects. Composite cans are very resistant to both invading and penetrating insects.*

## INTRODUCTION

Sanitation standards and handling techniques vary greatly in food warehousing and distribution systems throughout the world. On the one hand, there are temperature- and humidity-controlled warehouses that are maintained according to excellent standards of sanitation. At the other extreme, there are warehouses in which there is no control of temperature, humidity, insects, rodents, birds, weather, or even cattle and dogs. Between these two extremes there are the greater number of warehouses and transportation facilities in which sanitation measures receive varying degrees of attention. It is these facilities which handle most of the packaged food shipped internationally or in domestic trade and in governmental programs.

Although the food processor may take all possible precautions to package an insect-free commodity, he often has little or no control over the shipping and storage facilities once the packaged commodity leaves his plant. This is especially true of products packaged for international trade or foreign aid programs. Such lack of control over distribution facilities becomes critical when the packaged food is destined for developing countries where sanitation standards and handling techniques have not been developed sufficiently to provide good protection to the sorely needed food.

Loss or deterioration of food after it is received at the overseas warehouse not only reduces the available food supply but also contributes to higher total food costs because the food has incurred all costs of growing, harvesting, processing, packaging, shipping and warehousing. In these situations the cost-benefit ratio of protective packaging changes, especially when one is faced with the necessity of conserving as much food as possible.

The insects that attack packaged, insect-susceptible food in the United States today are generally the same species that attack these stored products around the world. World trade has disseminated these stored-product insects to all areas with similar climates. Wherever these species are found, they destroy and contaminate large quantities of stored products. The problem is two-fold: Some species (penetrators) such as *Rhyzopertha dominica* (F.) (lesser grain borer), *Tenebroides mauritanicus* (L.) (cadelle), *Lasioderma serricorne* (F.) (cigarette beetle), *Trogoderma variabile* Ballion, *Dinoderus minutus* (F.) and

*Corcyra cephalonica* (Stainton) (rice moth) can bore through nearly all flexible packaging materials in use today. Other common species (invaders) usually cannot enter packages unless there is an existing opening; however, they can easily enter the small openings in most packages as currently designed and manufactured.

#### CHEMICAL TREATMENTS

The invading and penetrating capabilities of insects set prerequisites for the manufacturer of insect-resistant packages. First, the package must be constructed so as to be insect tight, and secondly, all packages (except composite cans) must be chemically treated to prevent penetrators from making holes in the package. As a corollary, the chemical treatment helps repel invading insects.

In the United States only pyrethrins synergized with piperonyl butoxide (*alpha*-[2-(2-butoxyethoxy)ethoxy]-4,5-(methylenedioxy)-2-propyltoluene) are registered for use as an insect-resistant package treatment. This combination must not exceed 6 mg of pyrethrins and 60 mg of piperonyl butoxide per square foot on the outer surface of multiwall paper bags. (Anon. 1966) or 5.5 mg of pyrethrins and 55 mg of piperonyl butoxide per square foot on the outer surface of cotton bags (Anon. 1968). The bags must contain at least 50 lb of dry food. Treated cotton bags must have an inner waxed paper liner, and the product in these bags must contain no more than 4% fat.

The Environmental Protection Agency (EPA) has also approved (Anon. 1974) the use of a treated cellophane-polyethylene laminate (Yerington 1974) to protect prunes, raisins, and other dried fruits from infestation. In this case the pyrethrins and piperonyl butoxide are incorporated into the laminating adhesive at the rate of 10 and 50 mg per square foot, respectively. The official tolerance is 1 and 10 ppm, respectively, of pyrethrins and piperonyl butoxide in the fruit. To ensure that excessive residues cannot occur in the fruit the packaging material must contain no more than 0.31 mg of pyrethrins and 3.12 mg of piperonyl butoxide per ounce of fruit.

Insect-resistant spunbonded polypropylene (Typar®) shipping bags have also been developed (Highland 1975a), though they have not been registered for use by EPA. These bags were made of Typar laminated to saran-coated paper with an adhesive of ethylene vinyl acetate, wax, and synergized pyrethrins, the first instance of an insect inhibitor being applied in laminating adhesive.

Other extensive investigations at the Stored-Product Insects Research

and Development Laboratory have led to the development of insect-resistant pouches for such products as cocoa powder and dried soup mixes (Highland *et al.* 1977). These heat-sealed pouches are made of a laminate consisting of an exterior ply of greaseproof paper laminated to polyethylene-coated foil with an adhesive containing synergized pyrethrins. The greaseproof paper prevents transfer of the synergized pyrethrins to the interior surface of the laminate during storage in roll form; the foil prevents migration of the synergized pyrethrins into the contents of the pouch after filling. At this writing these pouches have not been approved by the EPA.

One reason for the caution in using chemical repellents on food packages is the possibility that the product could be contaminated by the repellent migrating from the treated surface through the package walls and into the commodity. This migration can be reduced or prevented by the use of barrier plies between the chemically treated ply and the package contents. Four plies of kraft paper prevented the occurrence of unacceptable residues of piperonyl butoxide in cornmeal, flour, rice, or beans stored in treated shipping bags (Highland *et al.* 1966). Saran-coated paper and some greaseproof papers also provide effective and economically feasible barriers to the migration of piperonyl butoxide (Highland and Secreast 1973). Paper treatments such as copolymer ethylene vinyl acetate in a paper coating that contained synergized pyrethrins reduced the movement of piperonyl butoxide into packaged food (Highland *et al.* 1968a).

### PACKAGING MATERIALS

Paper and cellophane are probably the least resistant to penetrating insects of all the flexible packaging materials in use today. Some insects, depending on environmental conditions, storage practices, and species, can penetrate kraft paper in less than a day, and multi-ply construction adds little to the resistance.

Also, most flexible polymer films, combinations of films, and aluminum foil can be penetrated by one or more species of insects though Highland and Jay (1965) found polycarbonate to resist penetration. Rao *et al.* (1972), using small pouches in a beaker, found that penetrating insects and some invaders could penetrate one or more of 18 films and laminates including cellophane, polyethylene, cellophane/polyethylene, polyethylene/paper, saran/cellophane, polyethylene/jute, paper/foil/polyethylene, and aluminum/vinyl. However, no penetrations were found in polyester/polyethylene, polyethylene/canvas, foil/

polyethylene, or paper/foil/polyethylene which was twice as thick as the foil in the penetrated paper/foil/polyethylene. Gerhardt and Lindgren (1954, 1955) found that insects easily penetrated single thicknesses of polyethylene, cellophane, saran, cellophane laminates, and saran/pliofilm, but laminates of saran plus polyester, with the polyester exposed to the insects, were not penetrated. The larvae as well as the adults of several species can penetrate the common packaging materials including aluminum foil (Cline, In press).

Yerington (1975) showed that polypropylene-polyethylene combination films tested as pouches against mixed populations of invaders and penetrators were generally more resistant than were other combination films. Also, coextruded polypropylene-ethylene vinyl acetate and coextruded polypropylene-polyethylene films showed more resistance to penetration than other saran-coated polypropylene- and polyethylene-coated cellophane films. Oriented polypropylene films were more resistant than nonoriented polypropylene films. Highland *et al.* (1968b) showed that biaxially oriented polypropylene film had excellent insect-resistant properties when used as an overwrap on paperboard cartons, but was ineffective as a pouch.

Other tests at the Stored-Product Insects Research and Development Laboratory have indicated that films of polyethylene terephthalate (the polyester, Mylar® or polyester urethane (Tuftane®) are more resistant to penetration than are most other films. However, saran, ionomer (Surlyn®), cellophane, and polyvinyl chloride films exhibited very low levels of resistance to penetration by lesser grain borers.

Tests have clearly demonstrated that aluminum foil can also be penetrated, although foil packages are generally more resistant to penetration than are film or paper packages. Indeed, Batth (1970) reported that dried soup mix pouches of 4-mil foil were penetrated within 4 days by *Tenebroides mauritanicus* (L.) and within 2 weeks by *Trogoderma inclusum* LeConte but not by *Oryzaephilus surinamensis* (L.). Also, at Savannah (unpublished data), paper/foil/polyethylene pouches that had not been treated with synergized pyrethrins were penetrated within 1 month of exposure in an infested simulated warehouse.

Thicker films are more resistant to penetration than are thinner films made of the same polymer resin. For instance, polyethylene film is not notably resistant to penetration, but in unpublished tests conducted at Savannah polyethylene films of 5-mil or greater thickness showed some resistance. Thus films vary in susceptibility to penetration, depending on thickness, on the basic resin from which the film is made, on the combination of materials, and on the package structure and configuration.

## TYPES OF PACKAGES

### Shipping Containers

Although packaging materials can be carefully chosen and chemically treated to make them resistant to insect penetration, no treatment is effective if the package is not insect tight. For example, bags treated with methoxychlor (1,1,1-trichloro-2,2-bis-(*p*-methoxyphenyl)ethane) that had tight, permanent seals remained insect-free during 24 months of exposure to heavy insect populations, but similarly treated bags with sewn, untaped closures were infested within 3 months (Highland *et al.* 1964).

The corrugated paper case is a major type of shipping container in the U.S. and in most other developed countries, but it is difficult to make these cases resistant to infestation. Well sealed tape can be placed over all flap junctures, or the case can be overwrapped with a heat-shrunk, polyethylene film overwrap. However, neither method protects from penetrating insects because both the film and the paper can be penetrated.

Heat-shrunk polyethylene film overwraps on pallet loads of bags or cases provide protection from invading insects providing a polyethylene deck sheet is placed between the load and pallet. During the heat-shrink process this sheet is partially sealed to the film overwrap. Use of a black deck sheet and an infrared heat source can provide an insect-tight heat-seal of the deck sheet to the overwrap.

### Consumer-Sized Packages

Although it is more economical to make the outer shipping container insect resistant, it is often more desirable to insect-proof the consumer-sized package. This process protects the package from infestation throughout the distribution channel, including retail outlets, until the package is opened. The paperboard carton is widely used for consumer packaging in developed countries and in developing countries where food is imported. These cartons can be made insect resistant by the use of tight, well sealed overwraps such as polypropylene film (Highland *et al.* 1968b). Also, Collins (1963) showed that fully adhered paper-foil laminated overwraps are quite resistant to insect invasion.

In the absence of an insect-tight overwrap, the flaps of cartons must be sealed so they are insectproof, which is difficult in modern high-speed packaging operations. However, beads of adhesive along the folds and edges of the end flaps and extended folded-down tabs at the sides of the end flaps (the "Van Buren ear") do provide some insect

resistance. Yerington (1971) described a polyethylene-coated carton with heat-sealed flaps that protects raisins from infestation.

More recent tests (Highland 1975b) have shown that composite cans are extremely resistant to both invading and penetrating insects. These cans have rigid paperboard walls that can be covered by laminations of paper, polymer films, and foil. The ends are metal and can be applied in high-speed operations. These cans resisted insect penetration during 29 months of exposure to heavy populations of both penetrating and invading insects.

Current investigations at the Stored-Product Insects Research and Development Laboratory reflect current needs for insect-resistant packaging and include (1) evaluation and development of chemical repellents as insect-resistant package treatments, (2) laboratory evaluation of promising chemical flour beetle repellents as penetration deterrents to lesser grain borers, (3) tests to determine the resistance to infestation provided by insecticide-treated deck sheets on shrink-wrapped pallets, and (4) the development of insect resistant, woven polypropylene shipping bags.

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# EFFECTS OF SUCROSE AND ACIDS ON OSMOVAC-DEHYDRATION OF TROPICAL FRUITS<sup>1</sup>

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## ABSTRACT

*A determination of the relationship of acidity and sucrose concentrations to rate of osmotic dehydration of papaya and mango was made. Dehydration by the osmotic step was found to increase with increasing sucrose concentration and contact time. Mango weight loss was directly proportional to sucrose concentration while it was non-linear for papaya, apparently due to reversal of pectin gelation. Acidification of concentrated sucrose syrups with organic acids increased the osmotic rate for dehydration of papaya but not mango. Combining acid and sucrose was found to increase moisture removal from papaya by inhibiting gelation.*

## INTRODUCTION

Osmovac-dehydration of foods involves a two-step process of osmotic and vacuum dehydration (Ponting *et al.* 1960; Farkas *et al.* 1969). Depending on thickness, initial moisture content and structural characteristics of the fruit slices, as well as other factors, immersing fruit slices in concentrated syrup for 5–6 h can remove at least 50% of the moisture. The remaining moisture can be removed by vacuum drying. A higher osmotic rate would make the process more efficient and practical. The present studies have determined the relationships of acidity and sucrose concentrations to the rate of osmotic dehydration of the tropical fruits papaya and mango.



### METHOD AND MATERIALS

Papaya (var. Solo) and mango (var. Haden),  $\frac{3}{4}$ -ripe, were peeled, deseeded, cut into  $\frac{1}{4}$  in.-thick slices, and weighed into sucrose syrups of 0–60% concentration with or without acidification by addition of acetic, citric, lactic or hydrochloric acids at concentrations of less than 3.5%. The weight ratio of fresh fruit to syrup was varied in the range 1:3 to 1:6 but mostly 1:4. Syrups were constantly stirred to maintain good circulation. Osmotic dehydration was carried out at 21°C for 1 to 12 h, after which the samples were drained, lightly blotted, weighed, and placed on trays for vacuum drying at 60°C and 1–2 mm Hg. Samples after vacuum drying were weighed and their qualities evaluated. For rehydration, weighed dried pieces were immersed in water or syrups of 15 or 30% sucrose.

### RESULTS AND DISCUSSION

The effect of sucrose concentration (0 to 60 weight %) on the osmotic dehydration rates of papaya and mango slices is shown in Fig. 1. The amount of water removed by the osmotic step increased with increasing sucrose concentration and with contact time. The optimum contact time was about 6 h at 21°C. After 6 h the dehydration rate decreased as an equilibrium was established. For mango, the weight loss was directly proportional to sucrose concentration while it was non-linear for papaya. The apparent increased osmotic rate for papaya attained at higher sucrose concentrations was probably due to reversal of pectin gelation by diffusion of sucrose into the papaya flesh. Mango does not exhibit this problem of gelation allowing ready diffusion of solute (Kuprianoff 1960; Moy *et al.* 1971). At sucrose concentrations of less than 20% the osmotic gradient favored movement of soluble solids from the fruit to the solution and consequent increase in moisture content of the fruit.

Acidification of concentrated sucrose syrups (60%) effectively increased the osmotic rate for papaya slices. Adjusted to isomolar final concentration, the 5 media (sucrose, and sucrose plus 4 acids) gave various osmotic rates in a 6-h period, as shown in Table 1. Hydrochloric acid increased the dehydration rate more than did organic acids but caused darkening and quality deterioration during subsequent vacuum drying and storage. Lactic acid was the most effective organic acid in the osmotic dehydration step, followed in order by acetic and citric acid in a 60% sucrose solution. In osmotic dehydration of  $\frac{1}{4}$ -in. mango

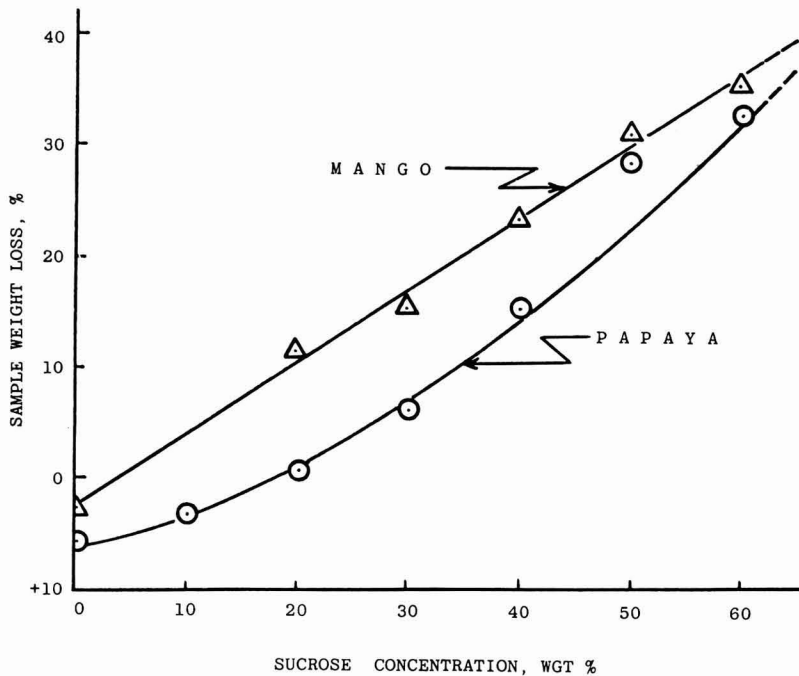


FIG. 1. OSMOTIC DEHYDRATION OF  $\frac{1}{4}$  IN. PAPAYA AND MANGO SLICES IN SUCROSE SYRUPS FOR 6 H

Table 1. Water removal by osmotic dehydration of papaya slices ( $\frac{1}{4}$ " thick) in sucrose syrup with and without acidification in 6 h

Sucrose Conc. %	Percent of Available Water Removed			
	No Acid	Acetic (1.0%)	Lactic (1.5%)	Citric (3.5%)
0	1.6	8.4	11.6	15.6
20	18.0	20.4	23.1	27.9
60	55.8	61.7	68.9	52.6

slices, moisture loss after 6 h was 42, 44 and 38% in 60% syrup and syrups acidified with 3% citric and 1.0% acetic, respectively. In contrast to the results observed for papaya there were no significant differences between the three organic acids on the osmotic dehydration rates for mango slices.

Sensory evaluation of osmotic-dehydrated papaya slices showed that samples having been immersed in 1% acidified 20% syrup for 6 h and then vacuum dried had better flavor and texture than those immersed

in acidified 60% syrup. Among the four acids tested, lactic and acetic acids appeared more useful in terms of osmotic effectiveness and retention of relative flavor and texture. Hydrochloric acid seriously damaged the products.

Rehydration of osmovac-dehydrated fruits was evaluated by placing weighed pieces in water, 15% sucrose or 30% sucrose solutions. The samples' weight, texture, flavor and appearance were determined at 10, 40 and 60 min intervals. The weight gained was expressed as a ratio of rehydrated weight to original fresh fruit weight. The maximum rehydration was about 60% of the original weight. Rehydration rates were decreased with increasing concentration of sucrose in the original osmotic dehydration step. The texture was firmer for the higher sucrose dehydrated fruits. All fruit pieces had a sweet and acceptable flavor regardless of treatment (Table 2).

Table 2. The relationship of sucrose concentration in acidified syrup to the rehydration for 40 min of osmovac-dehydrated papaya slices ( $\frac{1}{4}$ " thick) expressed as relative firmness<sup>2</sup>

Rehydration in	Syrup for Dehydration	Sucrose conc. in osmotic dehydration	0%	20%	60%
Water	No acid	—	—	++	+++
	Acetic <sup>1</sup>	—	—	++	+++
	Lactic	—	+	+	+++
	Citric	—	—	+	+++
15% Sucrose	No acid	—	—	+++	++++
	Acetic <sup>1</sup>	—	—	++	++++
	Lactic	—	—	++	++++
	Citric	—	—	++	++++
30%	No acid	—	—	++++	++++
	Acetic <sup>1</sup>	—	—	++++	++++
	Lactic	—	+	+	++++
	Citric	—	—	+	++++

<sup>1</sup>Concentrations of added acids were: acetic, 1.0%; lactic, 1.5%; citric, 3.5%.

<sup>2</sup>Relative firmness are subjective ratings of very firm: + + + + to least firm: + to soft: —.

## CONCLUSIONS

The rate of moisture removal in osmovac-dehydration of papaya and mango slices was directly related to the concentration of the sucrose syrup and immersion time. Acidifying syrups with organic acids increased the osmotic rate for dehydration of papaya but not mango.

Combining acid and sucrose increases moisture removal from papaya by inhibiting gelation. Osmovac-dehydration of tropical fruits using sucrose syrups could be promising as a means of producing quality dehydrated fruit pieces. Work is continuing to optimize the process, to study the economics of reusing the syrup and to determine shelf stability.

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# ELECTRICAL PROPERTIES OF GRAIN AND OTHER FOOD MATERIALS

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## ABSTRACT

*The electrical properties of usual interest for quality measurement and in high-frequency and microwave dielectric heating of agricultural products and food materials are defined, and basic principles of dielectric dispersion theory are presented. Curves for grain, insects, and seed are shown that illustrate the dependence of dielectric properties upon such factors as frequency, moisture content and density. The temperature dependence of the dielectric properties is also discussed. Sources of information on the dielectric properties of agricultural products and food materials are cited, and a general discussion is included on the dielectric behavior to be expected from food materials.*

## INTRODUCTION

Electrical properties of agricultural products and food materials are of interest for two principal reasons. First, they are useful for some rapid quality determinations, such as the measurement of moisture content in grain and other food products. Secondly, they determine to a large extent the absorption of energy in high-frequency dielectric heating and microwave heating applications that are useful in the processing of food materials.

The electrical properties of interest have been defined in detail previously, both from electromagnetic field concepts (Nelson 1973a) and from the electrical-circuit point of view (Nelson 1965). The electrical properties of usual interest are the conductivity,  $\sigma$ , the dielectric constant,  $\epsilon_r'$ , the dielectric loss factor,  $\epsilon_r''$ , and the loss tangent,  $\tan \delta$ . D-C conductivity results from the motion of free charges and ions, and this type of conduction contributes to the total conductivity at low fre-

quencies. Alternating electric fields produce an additional component of conductivity that is predominant at frequencies too high for the ionic conductivity to constitute the major contribution.

Basically, the dielectric constant of a material is related to its capability for storing energy in an electric field in the material, whereas the loss factor is related to the material's capability for absorbing energy from the field. The dielectric constant of a material is frequently considered to be the ratio of the capacitance of a capacitor, with the material as its dielectric, to the capacitance of the same capacitor with air, or, more properly, with vacuum as its dielectric. The loss factor is an index of the material's energy dissipation characteristics when the material is exposed to alternating electric fields. The loss tangent value is also indicative of a material's energy dissipation characteristics. The conductivity is the reciprocal of the specific volume resistivity, which is the resistance between opposite faces of a cube of unit dimensions of the material.

In general, the electromagnetic properties of matter are described by three complex constitutive parameters,  $\sigma$ ,  $\epsilon$ , and  $\mu$ , respectively, the conductivity, permittivity, and permeability. In most biological materials, however, the magnetic permeability is the same as that of free space,  $\mu_0$ , and the loss component of the complex conductivity is included in the dielectric loss component of the complex permittivity,  $\epsilon = \epsilon' - j\epsilon''$ , so the complex nature of the electromagnetic parameters for food materials is important only for  $\epsilon$ .

In practical applications, the permittivity of materials relative to the free-space permittivity,  $\epsilon_0$ , is the parameter customarily used. The complex relative permittivity is, therefore,  $\epsilon_r = \epsilon_r' - j\epsilon_r'' = \epsilon/\epsilon_0 = \epsilon'/\epsilon_0 - j\epsilon''/\epsilon_0$ , where the real component is the dielectric constant, and the imaginary component is the dielectric loss factor. The loss tangent (tangent of the loss angle of the dielectric), also called the dissipation factor, is related to the dielectric constant and loss factor as  $\tan \delta = \epsilon_r''/\epsilon_r'$ . The a-c conductivity of a material is given as  $\sigma = \omega\epsilon_0 \epsilon_r''$ , where  $\omega = 2\pi f$  is the angular frequency of the alternating fields. The dielectric constant, loss factor, and loss tangent are dimensionless quantities, but the conductivity can be expressed as  $\sigma = 0.556 f\epsilon_r''$  nmhos per cm when  $f$  is in KHz, in  $\mu$ mhos per cm when  $f$  is in MHz, and in mmhos per cm when  $f$  is in GHz (one mho per cm is equivalent to 0.01 siemens per meter).

### DIELECTRIC DISPERSION

The conductivity is obviously dependent upon frequency, but  $\epsilon_r'$  and

$\epsilon_r''$  are also frequency dependent for most biological materials. Debye (1929) described mathematically the nature of dielectric dispersion (variation in dielectric constant with changing frequency) and absorption for polar materials of a single relaxation time,

$$\epsilon_r = \epsilon_{r\infty}' + (\epsilon_{rs}' - \epsilon_{r\infty}') / (1 + j\omega\tau) \quad (1)$$

where  $\epsilon_{rs}'$  is the low-frequency or static value of the dielectric constant,  $\epsilon_{r\infty}'$  is the value of the dielectric constant at a frequency infinitely high with respect to the dispersion phenomenon, and  $\tau$  is the relaxation time, i.e., the period which characterizes the time required for the dipoles to revert to random orientation when the polarizing potential is removed. Debye's formulation can be more easily seen when Equation 1 is separated into its real and imaginary parts.

$$\epsilon_r' = \epsilon_{r\infty}' + (\epsilon_{rs}' - \epsilon_{r\infty}') / (1 + \omega^2\tau^2) \quad (2)$$

$$\epsilon_r'' = (\epsilon_{rs}' - \epsilon_{r\infty}') \omega\tau / (1 + \omega^2\tau^2) \quad (3)$$

and one refers to the graphical representation of Fig. 1. The loss factor,  $\epsilon_r''$ , peaks where  $\omega = 2\pi f = 1/\tau$ . At this frequency, viz., the relaxation frequency,  $\epsilon_r''$  has the value  $(\epsilon_{rs}' - \epsilon_{r\infty}')/2$ , and  $\epsilon_r'$  has the value  $(\epsilon_{rs}' + \epsilon_{r\infty}')/2$ . Since the loss decreases to zero at the frequency extremes,  $\epsilon_{rs}' = \epsilon_{rs}$  and  $\epsilon_{r\infty}' = \epsilon_{r\infty}$ ; so Equations 1, 2, and 3 are usually written without the prime marks on  $\epsilon_{rs}$  and  $\epsilon_{r\infty}$ .

The dispersion of some pure liquids closely follows the Debye equations (Buckley and Maryott 1958), but where there is a distribution of relaxation times in materials, a modification by Cole and Cole (1941) describes the dispersion more satisfactorily. They noted that a semi-circle is obtained (Fig. 2) when values for  $\epsilon_r'$  and  $\epsilon_r''$  from the Debye relation (Equations 2 and 3) are plotted in the complex plane (Argand diagram). Equations 2 and 3 are parametric equations of a circle, and combining the 2 equations and eliminating  $\omega\tau$  provides the following Cole-Cole relation:

$$\left( \epsilon_r' - \frac{\epsilon_{rs} + \epsilon_{r\infty}}{2} \right)^2 + (\epsilon_r'')^2 = \left( \frac{\epsilon_{rs} - \epsilon_{r\infty}}{2} \right)^2 \quad (4)$$

Equation 4 describes a circle of radius  $(\epsilon_{rs} - \epsilon_{r\infty})/2$  with its center on the  $\epsilon_r'$  axis at coordinates  $(\epsilon_{rs} + \epsilon_{r\infty})/2, 0$ . The modified equation presented by Cole and Cole (1941),



$$\epsilon_r = \epsilon_{r\infty} + \frac{\epsilon_{rs} - \epsilon_{r\infty}}{1 + (j\omega\tau)^{1-\alpha}} \quad (5)$$

results in a Cole-Cole plot which is an arc of a circle with its center below the  $\epsilon_r'' = 0$  axis (Fig. 3). The empirical relaxation-time distribution parameter,  $\alpha$ , takes on values between 0 and 1 and is an index of the spread in the relaxation times. Several other models have been developed to explain the behavior of certain types of materials. One known as the Cole-Davidson representation results in a skewed arc (Fig. 4), rather than the symmetrical Cole-Cole circular arc (Davidson and Cole 1951). The Cole-Davidson representation is mathematically defined as

$$\epsilon_r = \epsilon_{r\infty} + \frac{\epsilon_{rs} - \epsilon_{r\infty}}{(1 + j\omega\tau)^\beta} \quad (6)$$

where  $\beta$  is restricted to values between 0 and 1. For  $\beta = 1$  the arc is the Debye semicircle, but for values of  $\beta < 1$  the arc is skewed to the right, i.e., the value of  $\epsilon_r''$  peaks to the right of the center line for the Cole-Cole arc. The Cole-Davidson representation is useful for materials exhibiting a nonsymmetrical distribution of relaxation times with polarization processes of decreasing significance extending into the higher frequency region. The Cole-Cole relation (Equation 3) has been found to describe reasonably well the frequency dependence of some biological substances (Schwan 1957; Grant 1969).

The dielectric behavior of a material with a distribution of relaxation times can be described more generally (Hill *et al.* 1969) as

$$\epsilon_r' = \epsilon_{r\infty} + (\epsilon_{rs} - \epsilon_{r\infty}) \int_0^\infty \frac{f(\tau)d(\ln\tau)}{1 + \omega^2\tau^2} \quad (7)$$

$$\epsilon_r'' = (\epsilon_{rs} - \epsilon_{r\infty}) \int_0^\infty \frac{f(\tau)\omega\tau d(\ln\tau)}{1 + \omega^2\tau^2}$$

Use of Equation 7, however, usually leads to complicated expressions for  $\epsilon_r'$  and  $\epsilon_r''$  or for  $f(\tau)$ .

Another absorption process is found in biological and food materials. The Maxwell-Wagner absorption, which results from polarizations at interfacial boundaries, occurs in nonhomogeneous materials and is fre-

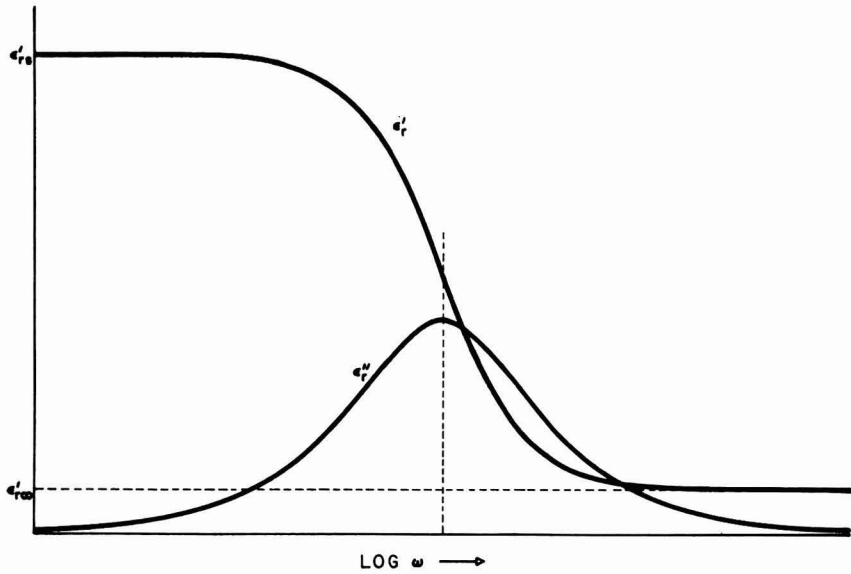


FIG. 1. DISPERSION AND ABSORPTION CURVES REPRESENTING THE DEBYE MODEL

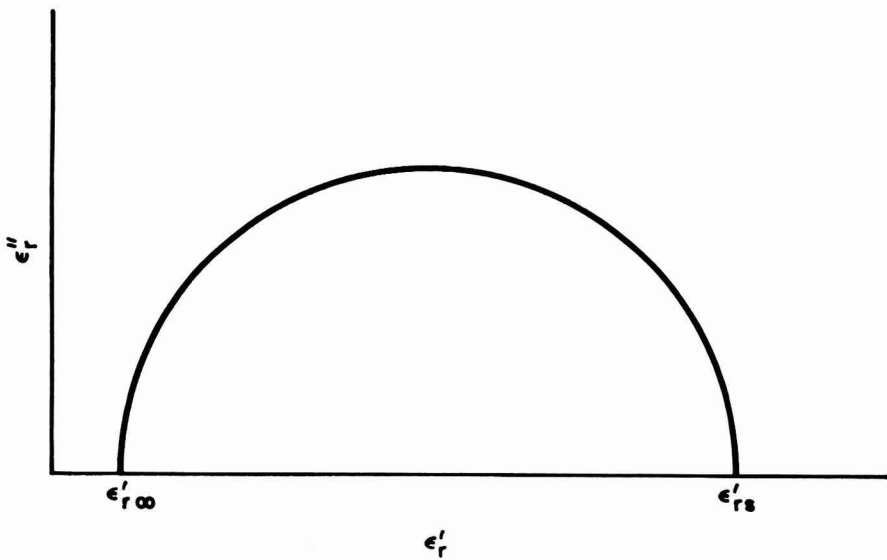


FIG. 2. THE COLE-COLE PLOT FOR THE DEBYE MODEL

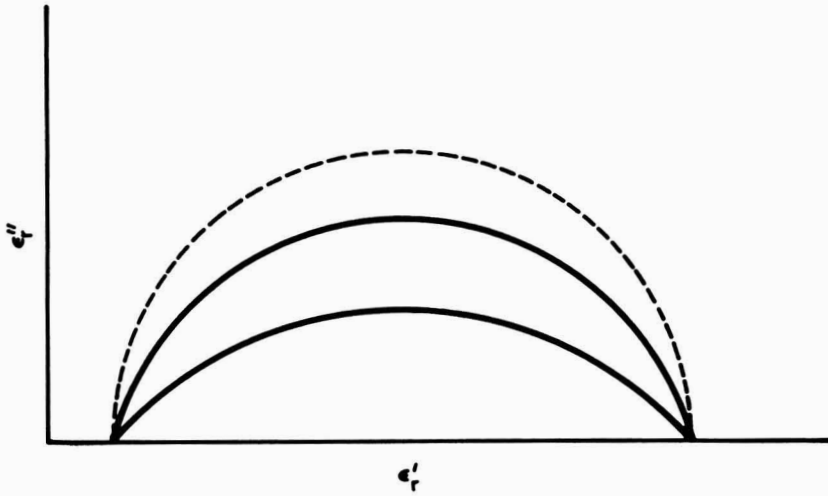


FIG. 3. COLE-COLE-MODEL CIRCULAR ARCS

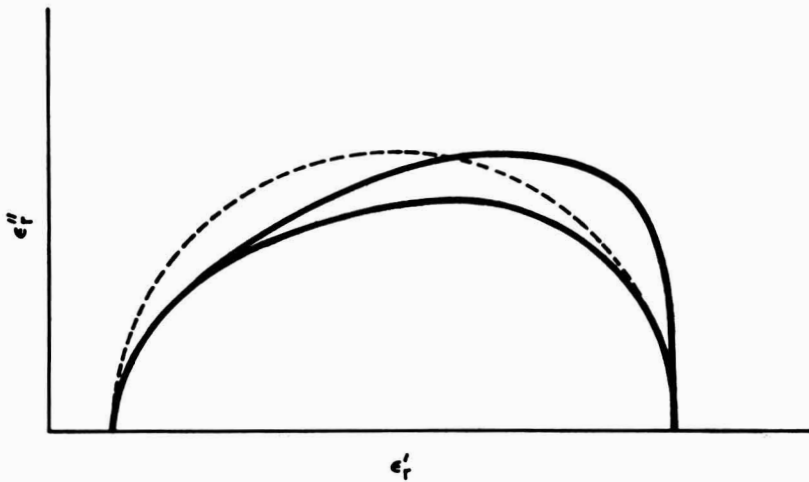


FIG. 4. COLE-DAVIDSON-MODEL SKEWED ARCS

quently seen in biological materials (Davies 1969; Schwan 1957, 1959). Frequency dependence of the Maxwell-Wagner absorption is similar in nature to that of the Debye dipolar absorption, but it occurs at lower frequencies.

Dielectric properties of materials are also temperature dependent. In polar materials, the relaxation time decreases as temperature increases,

and examination of Equation 2 reveals that the dielectric constant will, therefore, increase with temperature in the region of dispersion or dielectric loss. In the absence of dielectric loss, the dielectric constant for such materials decreases with increasing temperature (Böttcher 1952).

## DIELECTRIC PROPERTIES OF MATERIALS

Dielectric properties of some agricultural products and food materials have been measured at certain frequencies and under certain conditions. Values for the dielectric constant, loss factor, loss tangent, and conductivity were tabulated for many of these materials (animal tissues, foods, plant materials, fruits and vegetables, grain and seed, wood, and textiles) from data available in the literature (Nelson 1973a). Generally, however, data are not available over a sufficiently wide frequency range to provide a very complete picture of the dielectric behavior of these materials. Gaps in our knowledge of their dielectric properties, with respect to frequency, are even more evident in a retabulation of these data by frequency ranges, supplemented by data on dielectric properties of additional materials (Tinga and Nelson 1973).

Data were selected for presentation here to illustrate the dependence of the dielectric properties upon some of the important factors. The region of dispersion is illustrated in Fig. 5 for the dielectric properties of hard red winter wheat and adult rice weevils (Nelson and Charity 1972). The dispersion and absorption were found to be similar to the Debye relaxation process, but do not fit the Debye or Cole-Cole models well. The relaxation frequencies for the rice weevils and for the wheat lie in the range where bound forms of water are expected to contribute to this type of frequency-dependent behavior (de Loor 1968).

Frequency dependence data over a wide frequency range for several kinds of grain and seed are shown in Fig. 6 (Nelson and Stetson 1975) and similar data for wheat at different moisture contents are presented in Fig. 7 (Nelson and Stetson 1976).

Moisture content is a very important factor that influences dielectric properties of materials. The dependence of the dielectric constant and loss factor on moisture content is shown for 2 different frequency ranges, 5.1 MHz (Nelson and Stetson 1976) and at microwave frequencies of 1, 2.44, and 5.54 GHz (Nelson 1973b) in Fig. 8 and 9.

Interesting relationships between dielectric properties and both frequency and moisture content have been observed at audiofrequencies (Stetson and Nelson 1972). Evidence of some absorption phenomenon

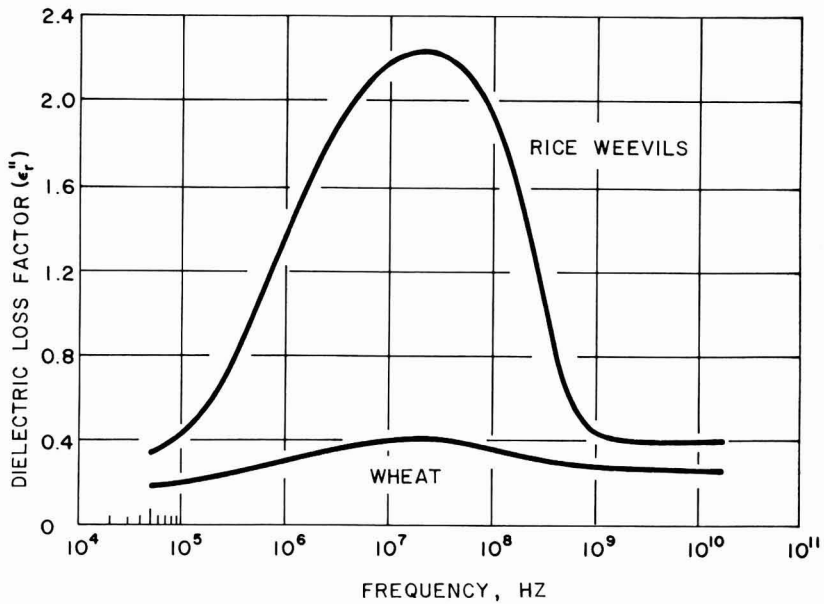
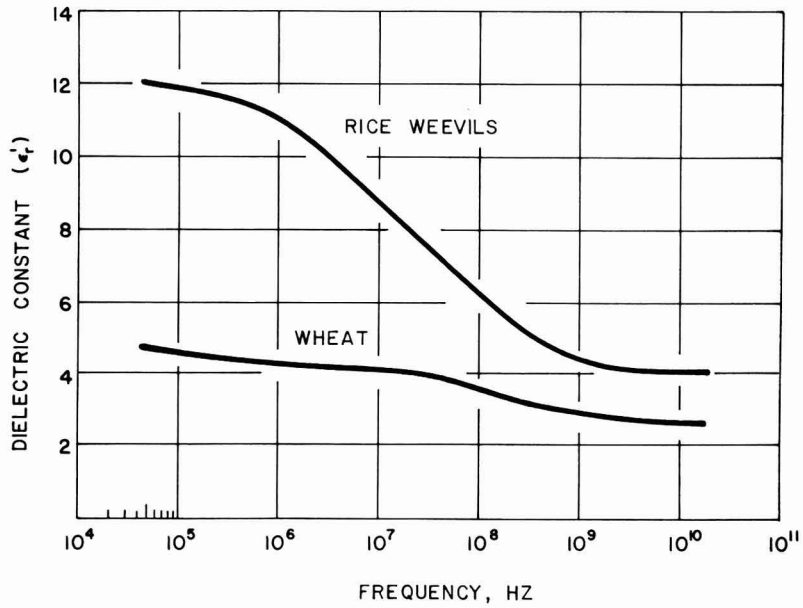


FIG. 5. DIELECTRIC DISPERSION AND ABSORPTION AT 24°C FOR BULK SAMPLES OF ADULT RICE WEEVILS AND HARD RED WINTER WHEAT (10.6% MOISTURE, w.b.)

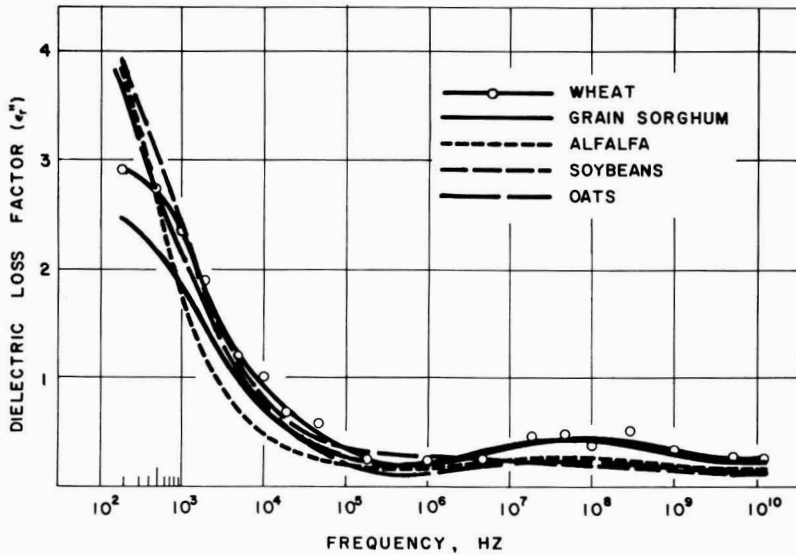
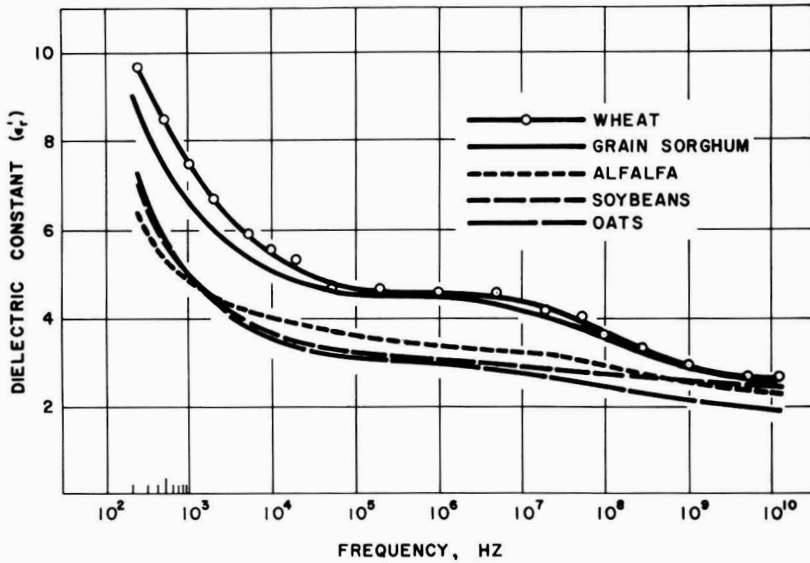


FIG. 6. FREQUENCY DEPENDENCE OF THE DIELECTRIC PROPERTIES AT  $24^\circ\text{C}$  OF GRAIN AND SEED OF MOISTURE CONTENT CONDITIONED TO EQUILIBRIUM AT  $5^\circ\text{C}$  AND 40% r.h.

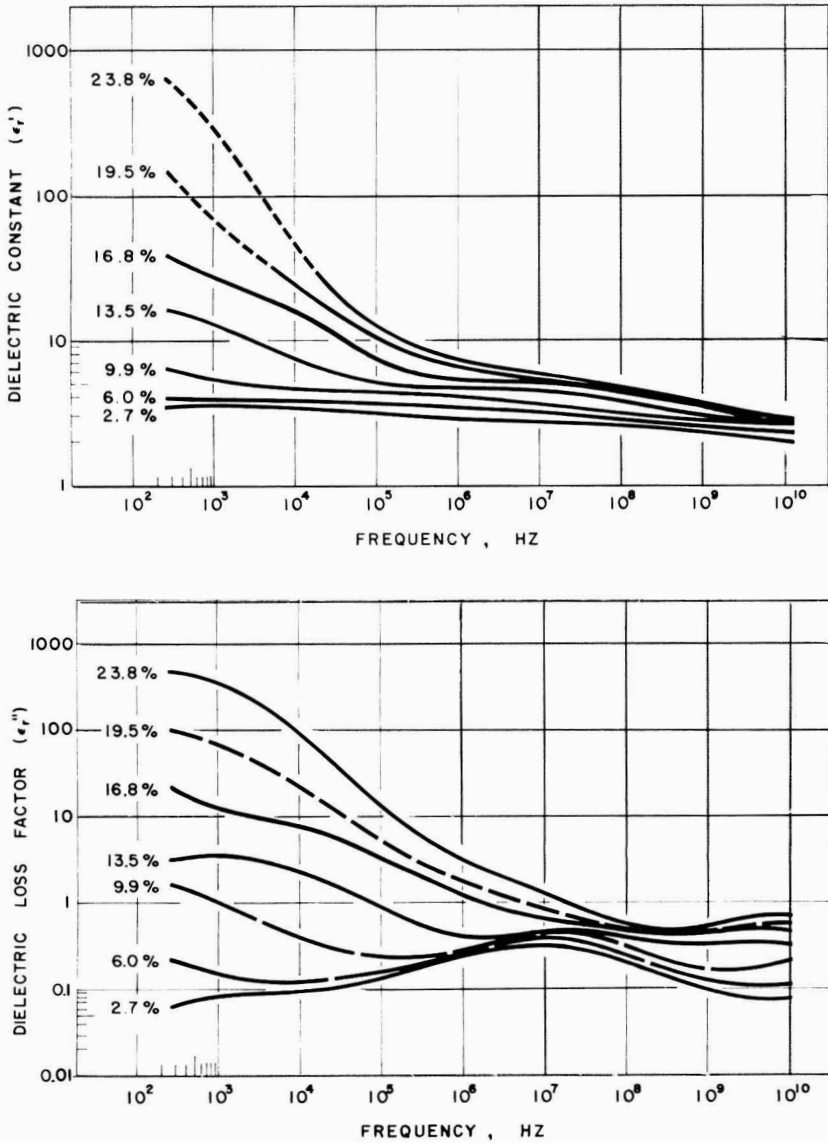


FIG. 7. FREQUENCY DEPENDENCE OF THE DIELECTRIC PROPERTIES OF HARD RED WINTER WHEAT AT 24°C AND INDICATED MOISTURE CONTENTS (w.b.)

was indicated at these frequencies (Fig. 10), and the relaxation frequency shifted to higher frequencies as moisture content increased.

Density is another factor that influences the dielectric properties of materials. The variation in dielectric constant and loss factor with the

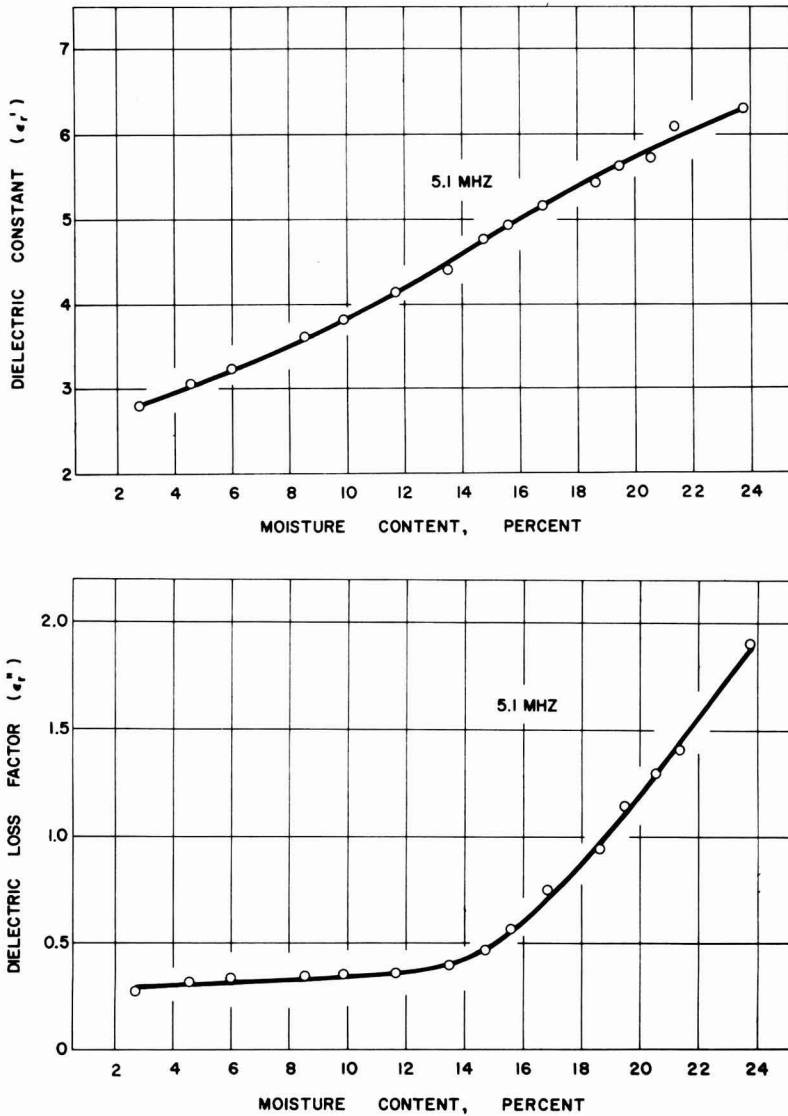


FIG. 8. MOISTURE DEPENDENCE OF THE DIELECTRIC PROPERTIES OF HARD RED WINTER WHEAT AT 24°C AND 5.1 MHz

degree of packing, measured as bulk density, is shown for oats in Fig. 11.

Since the review and tabulation mentioned (Nelson 1973a) was prepared in 1971, additional data on dielectric properties of food materials have been reported, especially for microwave frequencies used in microwave cooking. Some of these reports are identified here briefly.



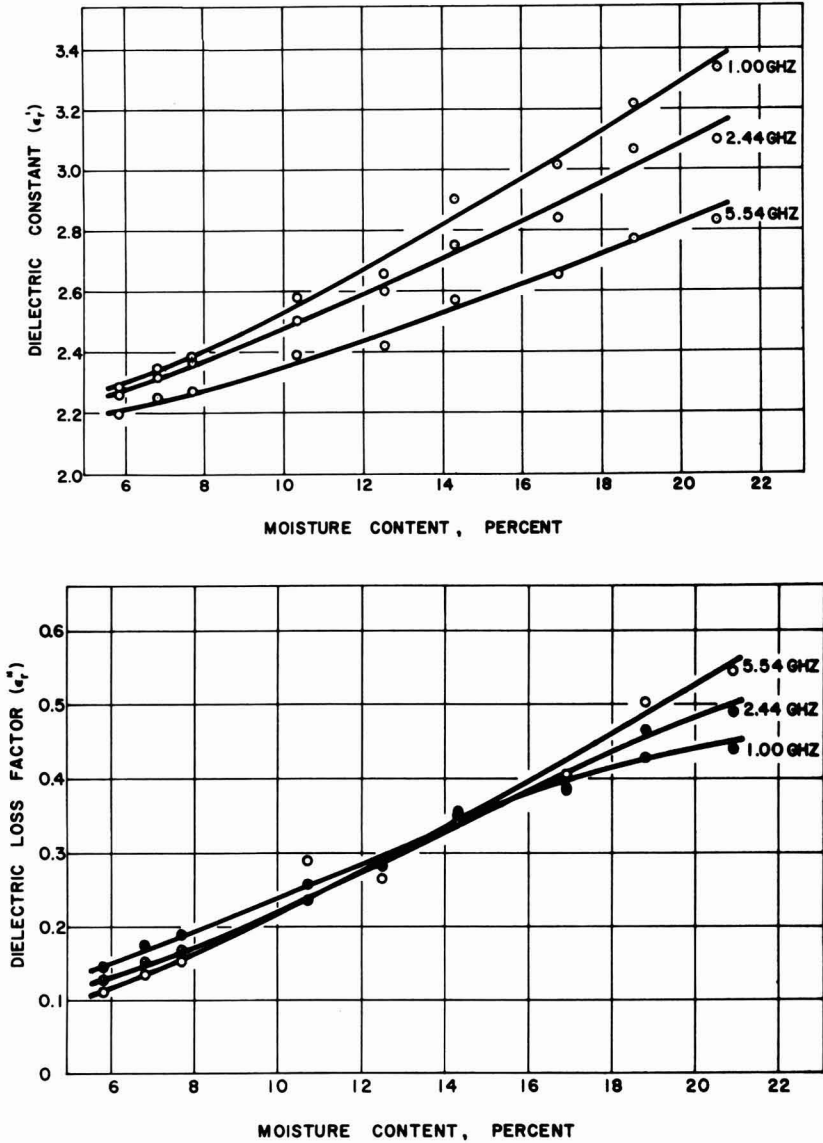


FIG. 9. MOISTURE DEPENDENCE OF THE DIELECTRIC PROPERTIES OF HARD RED WINTER WHEAT AT 24°C AT INDICATED MICROWAVE FREQUENCIES

Mudgett *et al.* (1971) reported studies on the dielectric loss factors at 3 GHz of aqueous solutions of nonfat dried milk and chemically simulated dried milk solutions based on proximate analysis. Studies of the complex permittivity of fishmeal were reported by Kent (1970, 1972a,

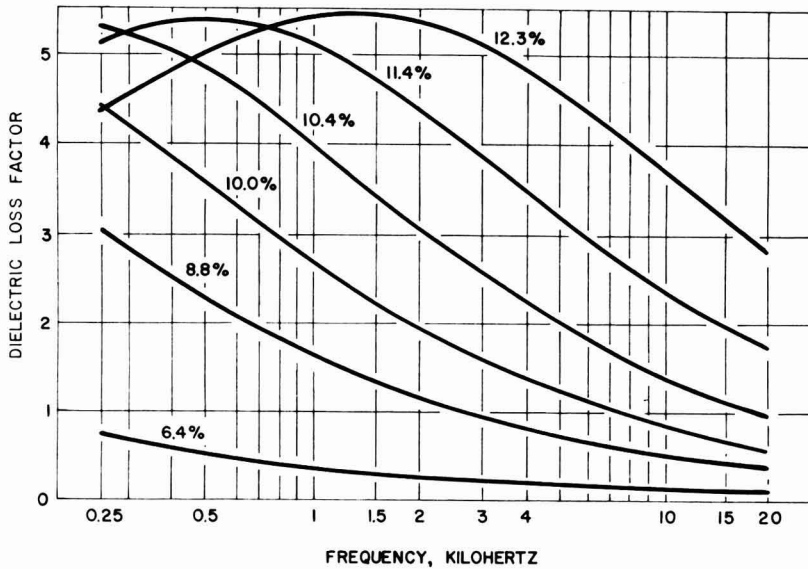
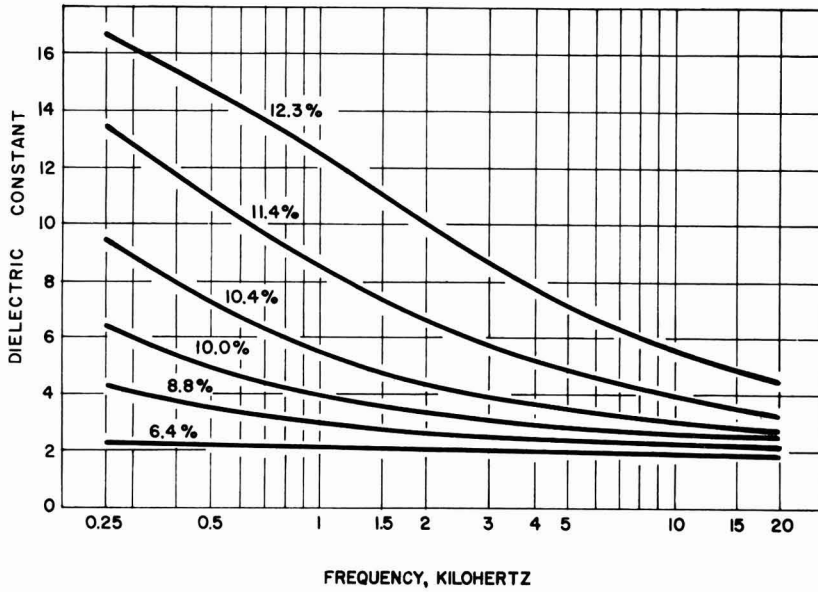


FIG. 10. FREQUENCY DEPENDENCE OF THE DIELECTRIC PROPERTIES OF KENTUCKY BLUEGRASS SEED AT 24°C AND INDICATED MOISTURE CONTENTS (w.b.)

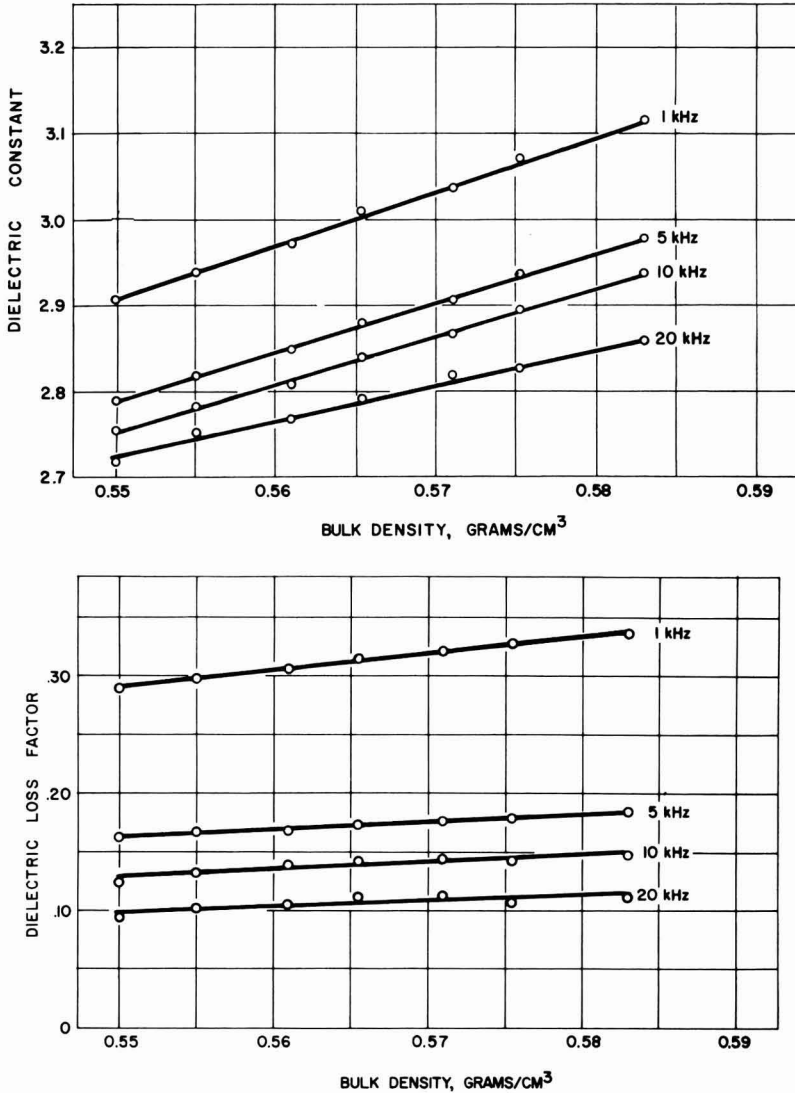


FIG. 11. DEPENDENCE ON BULK DENSITY OF THE DIELECTRIC PROPERTIES OF OATS AT 8% MOISTURE AND INDICATED FREQUENCIES AT 24°C

b) in relation to both moisture content and temperature at 9.4 and 10 GHz. Broader frequency range data (3 to 100 MHz) on dielectric properties of frozen fish were obtained utilizing time-domain spectroscopy measurements (Kent 1975). Data on the loss tangent of fresh fish, as a function of time in storage in ice, was presented by Jason and Richards (1975) for frequencies from 20 Hz to 20 kHz.

Dielectric properties data at 2450 MHz were obtained for nonfat milk powder, whey powder, and commercial butter over the temperature range from  $-10$  to  $70^{\circ}\text{C}$  and also as a function of moisture content at about  $20^{\circ}\text{C}$  (Rzepecka and Pereira 1974). Data were also reported on the loss factor of rehydrated nonfat dry milk at 300 MHz, 1 GHz, and 3 GHz between temperatures of 25 and  $55^{\circ}\text{C}$  (To *et al.* 1974). Values for the dielectric constants and loss factors of raw and cooked beef and turkey and their cooked juices were also reported by To *et al.* at frequencies of 300 and 915 MHz and 2.45 GHz over the temperature range from 5 to  $65^{\circ}\text{C}$ .

A considerable amount of data on the dielectric properties of foods at 2.8 GHz were reported by Bengtsson and Risman (1971) and Risman and Ohlsson (1973) and at 450 and 900 MHz by Ohlsson *et al.* (1974) over the temperature range from  $-20$  to  $60^{\circ}\text{C}$ . These measurements included several raw and cooked meats and vegetables, and extended temperature range data ( $60$  to  $140^{\circ}\text{C}$ ) were recently reported for these and several additional industrially prepared foods at the same 3 frequencies (Ohlsson and Bengtsson 1975).

## DISCUSSION

Electrical properties of biological and food products vary widely and are dependent upon many factors. Frequency is one of the basic factors that influence values of electrical properties, and an understanding of the nature of the frequency dependence can be helpful in predicting the dielectric behavior of food materials. When all other conditions are held constant, the dielectric constant of a material either decreases or remains constant as frequency increases. Only with resonance conditions at optical frequencies does the dielectric constant increase with frequency just before a sharp decrease in value. The loss tangent and the dielectric loss factor may either increase or decrease with frequency, depending upon the frequency range and the nature of the absorption process. Conductivity generally increases with increasing frequency, but is also dependent upon the loss factor.

Temperature is also an important factor. Temperature dependence and frequency dependence are closely related in theories of dielectric dispersion, and the nature of the dispersion can be explored by varying either of these factors. In a region of polar dispersion (Fig. 1), the relaxation frequency increases as temperature increases, as a consequence of the decrease in relaxation time. Therefore in the dispersion region, the dielectric constant increases with increasing temperature, whereas outside such a region it decreases with increasing temperature.

The loss factor, in the region of dispersion, may either increase or decrease with temperature, depending upon whether one is operating above or below the relaxation frequency. Temperature coefficients for electrical properties may, therefore, be either positive or negative, depending upon the temperature and frequency range. Also, the dielectric properties of water change drastically as it changes from the liquid to the solid phase. Therefore, the dielectric constant and loss factor of foods increase markedly as they go from the frozen to the unfrozen state. As temperature increases above the 0°C region, the microwave dielectric constant of many food materials gradually decreases and the loss factor gradually increases or decreases, depending upon the frequency and the composition of the product.

The electrical properties of hygroscopic materials are strongly dependent upon moisture content. Furthermore, the way in which water is held in the structure of the materials has an important influence on the degree to which electrical properties depend on moisture content. Chemically bound water has less influence on the dielectric properties of the materials than does free water in which the polar molecules can orient freely with an applied electric field. The dielectric constant of most materials increases rather regularly with moisture content. The loss factor usually increases with moisture content, but since the moisture content can influence the dielectric relaxation frequency of the material, it is also possible, in some frequency ranges, to observe decreases in loss factor with increasing moisture content.

The density of materials also influences their electrical properties. For some materials, within limited ranges of density, the dielectric properties appear to be almost linearly related to density. Any anisotropic nature in the structure of materials is another factor which must be taken into account. Nothing has been said here about dielectric mixture theory, but there is such a body of information that is very useful in explaining dielectric behavior of nonhomogeneous materials (de Loor 1968).

From the information available in the literature on dielectric properties of materials that have been measured, reasonably good estimates can be made for the dielectric properties of many materials. However, precise values for any particular food material under a particular set of conditions can probably be obtained only by careful measurement.

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Page one should contain: the title, which should be concise and informative; the complete name(s) of the author(s); affiliation of the author(s); a running title of 40 characters or less; and the name and mail address to whom correspondence should be sent.

Page two should contain an abstract of not more than 150 words. This abstract should be intelligible by itself.

The main text should begin on page three and will ordinarily have the following arrangement:

**Introduction:** This should be brief and state the reason for the work in relation to the field. It should indicate what new contribution is made by the work described.

**Materials and Methods:** Enough information should be provided to allow other investigators to repeat the work. Avoid repeating the details of procedures which have already been published elsewhere.

**Results:** The results should be presented as concisely as possible. Do not use tables and figures for presentation of the same data.

**Discussion:** The discussion section should be used for the interpretation of results. The results should not be repeated.

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DEWALD, B., DULANEY, J. T. and TOUSTER, O. 1974. Solubilization and polyacrylamide gel electrophoresis of membrane enzymes with detergents. In *Methods in Enzymology*, Vol. xxxii, (S. Fleischer and L. Packer, eds.) pp. 82-91, Academic Press, New York.

HASSON, E. P. and LATIES, G. G. 1976. Separation and characterization of potato lipid acylhydrolases. *Plant Physiol.* 57, 142-147.

ZABORSKY, O. 1973. *Immobilized Enzymes*, pp. 28-46, CRC Press, Cleveland, Ohio.

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Tables should be numbered consecutively with Arabic numerals. The title of the table should appear as below:

Table 1. Activity of potato acyl-hydrolases on neutral lipids, galactolipids, and phospholipids

Description of experimental work or explanation of symbols should go below the table proper.

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**Acknowledgments:** Acknowledgments should be listed on a separate page.

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