Journal
of
Agricultural and Food Chemistry

Volume 23, Number 6 November/December 1975

SYMPOSIUM ON FLAVOR CHEMISTRY OF PROCESSED FOODS

The following papers were among those presented in the Symposium on Flavor Chemistry of Processed Foods, 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1974.

Process Conditions for Improved Flavor Quality of Freeze Dried Foods

James M. Flink

Studies on the retention of flavor during freeze drying, conducted primarily with model systems, have led to the development of mechanisms by which flavor retention phenomena may be explained, and to specification of process conditions to optimize flavor retention. Of greater value is their ability to predict processing conditions giving improved flavor quality for real food materials. Process parameters of greater significance are freezing rate, initial solids content, and conditions which result in maintenance of sample structure. The present paper reviews results of studies in which the flavor retention behavior of real food products, both liquid and solid, has been evaluated. These include coffee, fruit and vegetable juices, and fruits. In most cases, flavor quality for the real food showed the same behavior relative to process conditions as predicted by the mechanisms based on model system studies.

Freeze drying is generally considered to be the dehydration process which will result in the highest quality dehydrated products. This is due to the fact that water is removed without the presence of a free liquid phase, and that heated regions in the dry layer have low moisture contents, while regions of high moisture have low temperatures. One of the crucial quality aspects, maintenance of product flavor, has aroused much interest in the recent past, as it was felt that flavor components, many of which are highly volatile, would be largely lost during the process since the freeze drying is generally conducted at absolute pressures of below 1 Torr.

Most early studies on the retention of flavor during freeze drying have concentrated on simple model systems in which complications due to compositional variations of natural products could be avoided. By means of these studies, in which simple quantitative retention information could be easily evaluated and correlated with changes in process variables, two mechanistic interpretations of flavor retention phenomena during freeze drying were proposed. These were labeled the "selective diffusion" mechanisms (Menting and Hoogstad, 1967; Thijssen and Rulkens, 1968; King and Chandrasekaran, 1973) and the "microregion entrapment" mechanism (Flink and Karel, 1970a) by their respective proponents. These mechanisms have been reviewed recently by King (1971), Thijssen (1973), and Flink (1973). It appears that there is some agreement that these two proposed mechanisms probably are describing the same basic phenomena from two different approaches, namely mathematical or macroscopic vs. morphological or microscopic viewpoints.

Before presenting some of the results obtained with model systems, it might prove valuable to make the fol-

---

Department of Nutrition and Food Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

Table I. Retention of 1-Propanol by PVP^a following Freeze Drying

Initial volatile concn, ppm	Volatile retention, %	Volatile retained, ppm
50	67	33
100	59	59
800	28	224
10,000	26	2600
20,000	25	5000

^{a} Initial PVP concentration = 20%.

lowing observations regarding the use of model systems, since to some this may not seem to be a valid approach to determining what will occur in real foods. It has been noted above that natural foods are subject to compositional variations which lead to an undesirable complication regarding analysis of experimental data. Furthermore, the number of components which would require monitoring, just to be sure which are varying, would greatly increase the experimental burden. Thus, model systems were envisioned as serving as simplified versions of real foods, in which compositions were predetermined and thus well known. The concentrations of all components were independently variable.

In the present era of food processing, model systems may be considered to serve dual roles since besides modeling real foods they are simplified formulated foods. More and more, foods are being produced by mixing a number of individual ingredients together and processing the mixture. This is precisely the method for producing a model system.

It has sometimes been noted that the concentrations of the model flavor compounds present in the model systems are much higher than concentrations generally shown to be present in real foods, a situation arising from considerations of analytical procedures for the large numbers of samples to be evaluated. While it would seem that data at lower volatile component concentrations would be extremely valuable, the information obtained at the higher concentrations is directly applicable to the freeze drying of preconcentrated feeds, or use of freeze drying to prepare encapsulated flavor concentrates.

In the course of developing mechanisms to explain flavor retention phenomena, a sizable body of data has been obtained on the influence of process conditions on retention of model flavor compounds in model systems. Only a small fraction of this information can be presented here; more information is available in the articles listed under Literature Cited.

PROCESS CONDITIONS AND FLAVOR RETENTION IN MODEL SYSTEMS

A number of processing variables have been investigated, and while the listing below may seem exhaustive, it is likely that there exist others which were unfortunately omitted from this listing. Under each processing variable will be given one or more references from which the information was obtained. It should be emphasized that other references listed under Literature Cited will contain information on one or more of the processing variables.

(1) **Solids Composition.** The influence of the type of solid component on volatile retention has been demonstrated in almost all model system studies published, though direct comparison between studies is hazardous due to the variation of other process parameters. Flink and Karel (1970b) presented a tabulation of the retention of various volatile compounds by a variety of mono-, di-, and polysaccharides freeze dried under "identical" conditions. In this case, for most volatiles studied the disaccharides were the most effective, the monosaccharide next, followed by the polymer. In other studies (Chirife and Karel, 1974a) proteins were shown to be effective solids for retention of volatile components.

Studies on binary solid systems at a fixed total solids concentration have shown variable results (Ofcarcik and Burns, 1974; Flink, 1970). For some mixtures retention has improved in a synergistic manner, while in others no effects are noted. It seems likely that this variable behavior is related to the influence of the substituted species on the resultant structural stability of the freeze drying matrix ("collapse"). Thijssen (1972b) has shown how the retention of propanol decreases as glucose is substituted for maltodextrin when freeze drying at an ice front temperature of −25°.

Synergistic effects may result from changes in matrix properties if freezing results in different phase structures of the matrix. Gejl-Hansen (1971) observed freeze dried mixed maltose–maltodextrin systems microscopically. At intermediate levels of maltose substitution, the "dendritic" matrix structure changed to a "cubic cellular" appearance, though eventually, at higher levels of maltose substitution, the dendritic structure reappeared. Unfortunately, volatile retention behavior was not evaluated.

(2) **Solids' Concentrations.** Manipulation of the solids' concentration can be evaluated in two manners, the percentage retention of the initial volatile or as the retention of volatile per unit weight of solid. These two methods, which are of value for different purposes, will give different interpretations. In the discussion which follows, the percentage retention of initial volatile will be used, since that value is most reported in the literature.

Many researchers have noted the importance of the initial solids' concentration on the retention of volatile compounds during freeze drying. Chirife et al. (1973) and Thijssen (1973) have presented information showing that, at low solids' concentrations (below 10–20%), increases in solids' concentration greatly increases volatile retention. When the initial solids' concentration is greater than about 25%, there is little effect of further increases on volatile retention. The initial solids' concentration at which volatile retention attains its asymptotic value appears to depend on the volatile species and solid species present in the model system.

If the above observations are considered on a unit weight of solids basis, it is seen that there exists an optimum solids' concentration at which the volatile retained per unit of solids is a maximum. This optimum will be lower than the solids' concentration at which the volatile retention reaches its asymptote.

(3) **Initial Volatile Concentration.** Similar considerations as noted above relative to the method of evaluation must be made. While it has become customary to present volatile retention as a percentage of the initial volatile content, it should be recognized that, for a fixed solids concentration, it is possible that as the initial volatile concentration increases, the percentage volatile retention can decrease while the absolute amount of volatile retained is increasing (and thus the volatile per unit of solids is also increasing). This is shown in Table I using the data of Chirife et al. (1973). Based on this evaluation, it is difficult to say if the volatile retention has decreased or increased.

Over the range of concentrations most often studied (initial volatile concentration below 1%), it appears that the percentage retention is relatively constant until low concentrations (100–1000 ppm) are reached, at which point the retention increases.

It should be noted that an opposite effect is reported by Voilley et al. (1973) in that increases of initial volatile concentration result in increases in percentage retention.

(4) **Freezing Rate.** The rate of freezing will influence the structure of the freeze dried material as it controls the size of the ice crystals and the degree of solute concentra-

Table II. Retention of Flavor Components of Apple Juice following Partial Freeze Drying

	Flavor retention, %, at solids' content of			
	17%[a]	26%	36%	44%
Ethyl acetate region	78	74	75	80
n-Hexanal region	61	60	73	70
2-Hexenal region	66	65	80	78
n-Hexyl acetate region	50	50	70	70

[a] Only 10% of initial water removed.

Table III. Relative Retention of Coffee Volatiles (Based on Total Peak Area) for Various Freezing and Freeze-Drying Conditions

Freezing conditions[a]	Rel retention, %,[b] at freeze-drying chamber pressure, Torr						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Very slow	92	96	78	77	66	67	34
Slow	100	99	88	82	91	82	35
Foam, slow	67	61	49	53	57	44	63
Quick	47	53	38	38	44	35	36
Foam, quick	48		42	42	43	32	29

[a] Very slow, stepwise to −40°; slow, −40°; quick, spray onto chilled drum at −52°. [b] Relative to slow frozen sample dried at 0.2 Torr, from Ettrup-Petersen et al. (1973).

Table IV. Flavor Loss Tolerances for Heating Coffee Granules during Freeze Drying

Temp, °C	Time at given temp, hr	
	No noticeable flavor loss	No significant flavor loss
40	3.75	7.5
60	2.25	4.5
80	1.5	2.5

tion achieved in the matrix phase. The rate of freezing is one of the most investigated process variables and it can be noted that in all cases reported, slow freezing results in improved retention of the volatile components. The improvements in volatile retention which depend on the retention levels have been reported for the most part to be 2 to 3 times (i.e., if rapid freezing gives 20% retention, slow freezing would give 40–60% retention) (Chirife and Karel, 1974a,b).

(5) **Drying Rate.** The rate of freeze drying can be varied in a number of ways, for example by increasing the ice front temperature to improve mass transfer or by increasing the heating plate temperature to improve heat transfer. These changes can be expected to influence volatile retention by means other than just drying rate. In any case, Thijssen (1972a) calculated the effect of drying rates on volatile retention and showed that higher retentions resulted with rapid drying. This was experimentally demonstrated by Rulkens and Thijssen (1972) by maintaining the ice front temperature constant while heating through the frozen layer and controlling the rate of drying by manipulation of the chamber pressure. As an example, drying at chamber pressures giving a doubling of the drying rate at an ice front temperature of −20° resulted in an increase in 1-propanol retention from 65% (slow drying) to 80% (rapid drying). The observed results are sensitive to volatile species and ice front temperature.

(6) **Sample Dimensions.** The influence of the sample dimensions has been reported for slabs (Chirife et al., 1973) and for layers of granules (Thijssen, 1972b). Sample dimensions which result in improvements in drying rate (thinner slabs or thinner layers of granules) generally will give increased retention of the volatile.

The relationship of diameter of the individual granule to volatile retention is more complex, as there exists for any layer thickness a granule size at which volatile retention is optimum, even though drying rates decrease as the granule size increase (Rulkens and Thijssen, 1972). Since the optimal granule size increases as the freezing rate decreases, it appears that for small particles there is a relationship of total granule dimension and ice crystal dimension which is important relative to volatile retention.

(7) **Frozen Layer Temperature and Collapse.** The influence of frozen layer temperature has already been alluded to above. Thijssen (1972a) and Voilley et al. (1973) have shown that as the ice front temperature increases, the retention of volatile compounds decreases. Increases in ice front temperature which do not result in collapse of the drying matrix will nevertheless result, according to the phase diagram, in a decrease of the matrix solids' concentration due to the melting of some of the ice crystals.

Collapse is a phenomenon in which the matrix undergoes structural degradation due to the onset of viscous flow. Collapse of the freeze drying matrix results in substantial loss of the volatile components, with the loss being directly related to the extent of collapse (Bellows and King, 1973).

(8) **Heat Input Conditions.** Heat input to the sample will influence a number of factors, such as drying rate, temperature gradients, ice front temperature, etc. It has already been shown that drying rate will influence the retention of volatile compounds. Rulkens and Thijssen (1972) have shown that, if the ice front temperature is maintained constant, heating through the dry layer or through the frozen layer results in equal drying rates and equal retention of volatiles. This indicates that the dry layer temperatures attained during the radiant heat transfer through the dry layer have no effect on the retention of volatile compounds. This effect is not unexpected, based on the results presented by Chirife and Karel (1974b) for heat stability of freeze dried carbohydrates.

When considering the effects of heating conditions, in which heat input is not controlled so as to maintain a constant ice front temperature, the possibility for increased loss of volatile occurs, especially if some collapse occurs. The contradictory retention behavior exhibited by various carbohydrates when heated at different heating plate temperatures (ice front temperatures were not monitored), as presented by Flink and Karel (1970b), is presumably due to the increasing extent of collapse in the glucose samples nullifying any improvement due to increased drying rate, while the noncollapsing sample (dextran) shows an increase in volatile.

(9) **Summary of Model System Studies.** Based on the volatile retention behavior observed in freeze drying model systems, it is seen that on a percentage retention basis the most important processing variables are: (1) ice front temperature; (2) freezing rate; (3) solids' concentration.

PROCESSING CONDITIONS AND FLAVOR RETENTION IN "REAL" FOODS

This section will be divided into two parts, one being short summaries of literature articles having flavor retention data for real foods, and the other being a more comprehensive presentation of two studies which have not been previously reported in the technical literature.

Table V. Retention of Volatile Compounds following Freeze Drying of Orange Juice and an Orange Juice Simulating Model Solution

	% retention				
		Dearomatized juice		Model solution	
	Natural juice	100 ppm	1000 ppm	100 ppm	1000 ppm
Ethanol	31	34	29	22	27
Butanol		51	47	27	48
Pentanol		52	56	31	34
Limonene	63	64	63		

Table VI. Retention of Volatile Compounds of Freeze Dried Orange Juice

	Retention, %		
	d-Limonene initial concn, %		
Heating plate temp, °F	0.011	0.046	Water-soluble volatiles
120	26	30	22
110	48	30	28
100	54	26	24
90	26	42	19
80	29	30	24
70	44		24

(1) **Apple Juice (Chandrasekaran and King, 1971).** Apple juice was freeze dried for a period of time which gave partial removal of the initial water (i.e., the material was not dry when the experiments were halted, still containing about 80% of the initial water). They observed that while the eutectic melting point is about −23°, the samples begin to show surface liquid at temperatures of −26°, thus causing termination of the drying. Four major regions of the vapor phase gas chromatogram were evaluated for flavor retention. In all cases, the volatile retention behavior improved as the initial solids content of the apple juice was increased from 17 to 36%. A further increase in solids to 44% showed no improvement over the retention at 36% solids. At the time of termination of the experiments, volatile retentions were determined and are shown in Table II.

(2) **Apple Slices (Saravacos and Moyer, 1968).** Freeze dried apple slices were reconstituted in water containing four volatile organic compounds and then re-freeze dried. The apple slices showed retention behavior very similar to that exhibited by low methoxy pectin gels, with retention levels dependent on the volatile species being considered.

(3) **Apricots (Lee et al., 1966a).** In a comparison of various methods for drying apricots, freeze drying was conducted using either slow (cabinet at −25°) or rapid (liquid nitrogen immersion) methods as the freezing treatment. Retention of flavor did not vary with freezing treatment and was approximately 91% as measured by volatile reducing substances and 93% as measured by volatile carbonyl compounds. Histological comparison of the fresh apricots and the two freeze dried samples showed that the liquid nitrogen frozen and dried samples had a cell structure almost unchanged from the fresh, while the slow frozen sample showed a disrupted cell structure due to ice crystal growth. It appears that this cellular disruption has no effect on flavor retention.

(4) **Banana Puree (Flink, 1970).** The influence of addition of sugar (16%) to banana puree on the retention of volatiles was noted in some preliminary thesis experiments. The results of these experiments showed that the more vol-

Table VII. Generalized Summary of Results Presented by Sauvageot et al. (1969)

Process parameter increased	Units	Values	General trend in retention	Exceptions
Chamber pressure	Torr	0.02 0.12	No change	None
Freezing rate	°C/min	0.5 6.6 16	Decreased retention	A few noted with orange juice
Frozen layer temp	°C	−26 −36	No change	Ethanol shows large decrease
Temp during desorption	°C	28 40 60	Raspberry juice: some loss when compare 28° to 60° Orange juice: no change between 25 and 45°	Acetaldehyde has sizable decrease
Duration of desorption	hr	9 7	Some decrease especially when dry at −36°	Acetaldehyde shows no effect
Thickness of frozen layer	mm	5 10	Slight decrease in retention	
Dry solids content	%	12 18	Retention increased	Acetaldehyde shows no change Ethanol decreased

Table VIII. Retention of Volatile Components of Freeze Dried Peach Slices

Treatment	Soluble solids content, %	Volatile reducing substances	Volatile carbonyls
Fast freezing	11.0	98	92
Slow freezing	11.6	94	92
Partial osmosis + slow freezing	17.0	103	127

Table IX. Retention of Volatile Alcohols during Freeze Drying of Tomato Juice

Freezing conditions	Retention of alcohols, % ethanol–propanol–butanol at thickness, mm			
	3	5	7.5	10
−40° blast	7–11–14			41–57–63
−40° still air	15–23–27	27–40–47	39–58–64	40–53–63
Step program[a]	17–22–22	40–51–56		52–62–62

[a] −8, −20, −30, −40°.

Table X. Retention of Volatile Alcohols during Freeze Drying of Tomato Juice

Initial alcohol concn, %	% retention		
	Ethanol	Propanol	Butanol
0.1	52	62	62
0.01	39	40	41

Table XI. Increase in Solids Concentration due to Osmotic Pretreatment

Fruit	Solids concn, %	
	Before osmosis	After osmosis
Strawberries	9.4	23.0
Honeydew melon	9.6	33.6
Cantaloupe melon	9.6	28.0
Peaches	10.7	29.4
Pears	14.3	28.0
Pineapple	12.1	27.9
Apples	12.8	29.9

atile components were retained to a lower extent, that sugar addition had a greater effect on the less volatile species (2-pentanone and butanol) than on the more volatile species (ethanol, ethyl acetate, isobutyl acetate, and isoamyl acetate), and that flavor retention data were more variable when samples had added sugar.

(5) **Coffee (Ettrup-Petersen et al., 1973).** Influences of various freezing procedures (both rates and gas incorporation) and chamber pressures (ice front temperatures) were investigated for their effect on retention of flavor during freeze drying of coffee granules (Table III). The retention of flavor was improved by slow freezing and by freeze drying at the lowest ice front temperature. The influence of gas addition was dependent on the method used for incorporation. It was further demonstrated that sizable loss of flavor occurs when the ice front temperature is allowed to reach the collapse temperature.

Coffee (Hair and Strang, 1969). The time–temperature tolerance of the dry layer to flavor changes was presented for conditions designed to give "no noticeable flavor loss" or "no significant flavor loss". With an ice front temperature of −25°, the dry layer should not be permitted above 93°. Some examples of maximum times at various temperatures are given in Table IV.

(6) **Onion Juice (Ofcarcik and Burns, 1974).** Pyruvic acid retention was determined for Bermuda onion juice with added carbohydrates, or with added mixtures of carbohydrates. They showed that addition of glucose, sucrose, or lactose gave improved retention up to 10% added solids; addition above this concentration gave very little improvement in pyruvic acid retention. When mixtures of sugars at a total solids concentration of 10% are added to the onion juice, no effect of added sugar composition was noted.

(7) **Orange Juice (Voilley et al., 1973).** Retention of a number of flavor compounds was determined for natural orange juice, dearomatized orange juice with added volatiles, and a model solution with added volatiles. When the added volatiles were present initially at either 1000 or 100 ppm, in the dearomatized juice, the percentage retention was the same. This contrasts with the behavior observed for the model system where they found that the percentage retention decreased as the initial volatile concentration decreased. The natural juice showed retention behavior similar to that observed with the dearomatized juice. Some typical results are shown in Table V.

Orange Juice (Massaldi and King, 1974b). Measurements of *d*-limonene retention for freeze dried orange juice showed an apparent influence of *d*-limonene solubility and subsequent stabilization of the insoluble *d*-limonene droplets by "cloud particles." With increasing initial *d*-limo-

Table XII. Sample Scores for Difference Tests for Taste Acceptability

Sample no.	Fruit	Organoleptic scores[a]			
		IS	IF	NS	NF
1	Cherries	3.18	3.00	3.36	3.29
2	Honeydew	3.63	3.27	3.63	3.13
3	Cantaloupe	4.77	4.08	3.92	4.00
4	Strawberries	3.93	3.79	4.21	3.57
5	Cantaloupe	4.50	3.95	3.84	
6	Strawberries	4.42	4.12	3.79	3.42
7	Cantaloupe (rehydrated)	3.42	2.92	3.29	2.50
8	Pears	4.65	3.60	3.90	3.90
9	Peaches	4.25	3.50	2.83	2.42
10	Pineapple	4.37	3.75	3.50	2.42
11	Pears	3.75	3.10	3.55	4.20
12	Apples	4.58	3.75	2.62	2.58
13	Apples (rehydrated)	4.69	4.00	2.85	

[a] 6 = excellent; 1 = very poor.

Table XIII. Sample Scores from Ranking Tests[a]

Sample no.	Fruit	Rank			
		First	Second	Third	Fourth
1	Cherries	NS 0.190	IS 0.180	IF 0.130	NF −0.140
2	Honeydew	NS 0.300	IS 0.260	NF −0.037	IF −0.530
3	Cantaloupe	IS 0.675	NS 0.023	NF −0.274	IF −0.406
4	Strawberries	IS 0.380	NS 0.095	NF −0.095	IF −0.380
5	Cantaloupe	IS 0.492	NS −0.224	IF −0.268	
6	Strawberries	IS 0.737	NS 0.161	IF −0.211	NF −0.687
7	Cantaloupe (rehydrated)[b]	IS 0.333	NS 0.122	IF 0	NF −0.454
8	Pears	IS 0.678	NF −0.060	NS −0.206	IF −0.412
9	Peaches	IS 0.969	IF −0.001	NS −0.233	NF −0.726
10	Pineapple	IS 0.687	IF 0.172	NS 0.111	NF −0.926
11	Pears	NF 0.618	IS 0.326	NS −0.266	IF −0.678
12	Apples	IS 1.03	IF 0.250	NF −0.518	NS −0.787

[a] The extreme values of ranking ± 1.03; solids content: N, normal; I, increased; freezing rate: S, slow; F, fast. [b] Only three samples giving maximum range of ±0.85 ⟷ 0 ⟷ (−0.85).

nene content, samples with cloud showed improved retention while samples without cloud had sizable decreases in retention.

Orange Juice (Berry and Froscher, 1969). The retention of *d*-limonene and water soluble volatiles was investigated as a function of initial *d*-limonene concentration and freeze dryer heating plate temperature. A summary of their results is presented in Table VI. It appears that for each volatile, there is some optimal heating plate temperature, though in some cases the variation is not too great.

Orange Juice (Sauvageot et al., 1969). The influence of a variety of process variables on the retention of a number of flavor compounds of orange juice and raspberry juice is summarized in Table VII. These results conform with few exceptions to those noted with model systems.

(8) **Peaches (Lee et al., 1966b).** Peach slices were freeze dried following fast freezing (liquid nitrogen immersion), slow freezing (cabinet at −25°), and partial osmosis followed by slow freezing. The retention of volatiles, which was measured as volatile reducing substances and volatile carbonyl compounds, is presented in Table VIII. It can be seen that freezing rate had little effect on retention of the volatile compounds. The authors postulate that the greater than 100% retention with the osmotic treatment may result from fragmentation of reducing sugar during dehydration.

(9) **Raspberry Juice (Sauvageot et al., 1969).** The influence of a variety of process variables on the retention of a number of flavor compounds of raspberry juice is summarized in Table VII (this is the same table as noted in section 7 above).

The remainder of this paper will present results of two previously unpublished studies on flavor retention in tomato juice and fruit slices.

Tomato Juice: Retention of Flavor Compounds in Freeze Dried Tomato Juice. In a study conducted by Mr. Mogens Granborg at the Food Technology Laboratory of the Technical University of Denmark while this author was a Guest Professor at that institution, the influence of a number of process variables on retention of flavor compounds of tomato juice was investigated.

In the first part of the study, three alcohols (ethanol, propanol, and butanol, each at 0.1% w/v) were added to canned tomato juice having a solids' concentration of 7%. The results are presented in Table IX. A number of observations of interest can be noted. The most striking improvement in retention of flavor results from increasing the sample thickness, a finding quite to the contrary of those noted in model system studies. This might, however, be due to slower freezing of the thicker samples. In agreement with model system studies, the slower the freezing rates, the better the retention. Lastly, in almost all cases, the retention increases with an increasing number of carbons in the volatile molecule. In one case, a comparison of retentions in 10 mm thick samples frozen by the step program was conducted for volatiles at initial concentrations of either 0.1 or 0.01% each. The results, shown in Table X, indicate that retention was higher at the higher initial alcohol concentration.

Fruit Slices. In model system studies, it was demonstrated that product flavor quality depended primarily on the initial solids' content and rate of freezing, if freeze drying was conducted so that matrix structural changes were avoided. In recent studies, experiments were conducted to determine if these same processing variables were significant in determining flavor quality of solid foods.

The initial solids' content was increased by an osmotic pretreatment. Sliced fruit was placed in a stirred 60% sucrose solution for a period of up to 6 hr. During this period water was lost by the fruit tissue due to differences in osmotic pressure. Some sugar was taken up by the surfaces of the fruit, but most was removed by a short (30 sec) rinse prior to freezing. The rinse was necessary to prevent sticki-

Table XIV. Summarized Significant Results for Organoleptic Tests of Freeze Dried Fruits[a]

Sample no.	Fruit	Difference test taste, %	Preference test		Ranking test, % (preferred is first)
			Preference[b]	Significance, %	
1	Cherries	NSD	NS/NF 8/14	NSD	NSD
			NS/IS 8/14	NSD	
			IS/IF 10/14	NSD	
2	Honeydew	NSD	IS/IF 13/15	1	IS/IF, 1
			NS/NF 11/15	NSD	NS/IF, 1
			IS/NS 8/15	NSD	
3	Cantaloupe	NS/IS, 1	IS/IF 11/13	5	IS/IF, 1
		IF/NF, 5	IS/NS 11/13	5	IS/NF, 1
		IS/NF, 5	NS/NF 7/13	NSD	IS/NS, 5
4	Strawberries	NSD	IS/IF 10/14	NSD	IS/IF, 5
			NS/NF 8/14	NSD	
			NS/IF 8/14	NSD	
5	Cantaloupe	IS/NS, 5	IS/NS 14/19	NSD	IS/IF, 1
			IS/IF 15/19	5	IS/NS, 1
6	Strawberries	NF/IS, 1	IS/NF 10/12	5	IS/NF, 1
		NF/IF, 1	IS/NS 10/12	5	IS/IF, 1
		NS/IS, 5	NS/NF 9/12	NSD	IS/NF, 1
7	Cantaloupe (rehydrated)	NSD	NS/NF 9/12	NSD	IS/NF, 5
			IS/NS 8/12	NSD	
			IS/IF 8/12	NSD	
8	Pears	IS/IF, 5	IS/NS 7/10	NSD	IS/IF, 1
			NS/NF 5/10	NSD	IS/NS, 1
			IS/IF 8/10	NSD	IS/NF, 5
9	Peaches	IS/NS, 1	IS/IF 11/12	1	IS/IF, 1
		IS/NF, 1	NS/NF 9/12	NSD	IS/NS, 1
		IF/NF, 1	IS/NS 12/12	0.1	IS/NF, 1
		IF/NS, 5			IF/NF, 1
		IS/IF, 5			NS/NF, 5
10	Pineapple	NF/NS, 1	IS/IF 8/12	NSD	IS/NS, 1
		NF/IF, 1	IS/NS 7/12	NSD	IS/NF, 1
		NF/IS, 1	IS/NF 11/12	1	IF/NF, 1
		IS/NS, 5			NS/NF, 1
					IS/IF, 5
11	Pears	NF/IF, 1	NF/NS 8/10	NSD	NF/IF, 1
			IS/NS 8/10	NSD	NF/NS, 1
			IS/IF 9/10	5	IS/IF, 1
					IS/NS, 5
12	Apples	IS/NF, 1	IS/IF 12/12	0.1	IS/NS, 1
		IS/NS, 1	NF/NS 8/12	NSD	IS/IF, 1
		IF/NF, 1	IS/NS 12/12	0.1	IS/NF, 1
		NS/IF, 1			IF/NS, 1
		IS/IF, 1			IF/NF, 1
					NS/NF, 5
13	Apples (rehydrated)	NS/IS, 1	IS/NS 13/13	0.1	
		NS/IF, 1	IS/IF 12/13	1	
		IS/IF, 5			

[a] Normal solids/slow freezing, NS; normal solids/fast freezing, NF; increased solids/slow freezing, IS; increased solids/fast freezing, IF.
[b] Number of judges preferring a given treatment/total number of judges.

ness of the dehydrated product. Table XI gives the increase of initial solids' concentration for a number of the fruits listed. In almost all cases, the contribution of added sugar is about 4%.

Samples were either slowly frozen in a −20° chamber or rapidly frozen by immersion in liquid nitrogen. Samples were freeze dried at ambient plate temperature and chamber pressure below 0.1 Torr.

The four samples produced were encoded as follows: IS, increased solids, slow frozen; IF, increased solids, fast frozen; NS, normal solids, slow frozen; NF, normal solids, fast frozen. Three methods of organoleptic testing were utilized in evaluating the relative quality of the different processing conditions for a number of fruit products.

Products were scored in a difference test for taste and texture using the following scale (together with numerical equivalents): very poor (1), poor (2), fair (3), good (4), very good (5), and excellent (6). By analysis of variance, the differences between samples were evaluated for significance. In addition, the average value of the scores can be used as a measure of product acceptability.

A second test was a paired comparison preference test in which samples were presented in groups of two. In this case, the judge merely expresses a preference for one sam-

Table XV. Summarized Relative Evaluation of Quality

Sample no.	Fruit	Preference tests	Ranking
1	Cherries	NS > NF, IS > IF	NSD
2	Honeydew	IS > NS >(?) IF > NF	NS, IS
3	Cantaloupe	IS > IF, NF, NS	IS
4	Strawberries	IS >(?) NS >(?) NF, IF	IS
5	Cantaloupe	IS > NS > IF	IS
6	Strawberries	IS > NS, IF > NF	IS
7	Cantaloupe (rehydrated)	IS > IF, NS > NF	IS
8	Pears	IS > NS, IF, NF	IS
9	Peaches	IS > NF > IF, NS	IS
10	Pineapple	IS, NS, IF > NF	IS
11	Pears	IS, NF > NS, IF	IS, NF
12	Apples	IS > NF, IF > NS	IS
13	Apples (rehydrated)	IS > IF, NS	

ple over the other. By consideration of the various combinations of paired comparisons, an overall preference can be determined.

In the third organoleptic test, all samples were presented for ranking according to overall quality. By analysis of variance an evaluation of ranking significance can be made. For most tests, when four samples were presented, the degree to which the sample score approaches +1.03 is a measure of its overall acceptance and the difference between values is a measure of the degree of preference.

The results of the organoleptic evaluations are presented in a series of tables (XII–XV).

The scores of the difference tests are presented in Table XII and numerical evaluations of ranking preference tests are given in Table XIII. The highest scores for taste are given in almost all cases to the increased solids, slow frozen (IS) fruits. The notable exception is with cherries where all the samples have a "fair" rating. In most cases, the IS fruits have rated above 4.0 for taste, with a number of samples in the "very good" range (above 4.5). The ranking preference tests (Table XIII) also demonstrate the clear superiority of the IS fruits. Evaluations of statistical significance of the various organoleptic tests are shown in Table XIV, these being summarized in Table XV. These data demonstrate the superiority of the IS fruits.

CONCLUSION

It has been shown through studies using model systems and real foods that the retention of flavor quality during freeze drying is dependent on the process conditions chosen. In most cases, the retention behavior exhibited by the model system studies, and predicted by the currently accepted mechanistic interpretations of freeze drying flavor retention, is also observed with real foods. In particular, the most important process condition appears to be drying so that matrix structure remains unaltered. If this condition is met, the most important process variables are initial solids content and freezing rate. It has been demonstrated that by proper control of the process parameters, retention of flavor compounds can be increased by factors of 2–3.

LITERATURE CITED

Bellows, R. J., King, C. J., *AIChE Symp. Ser. No. 132*, **62,** 33 (1973).
Berry, R. E., Froscher, J. L., *Proc. Fla. State Hortic. Soc.* **82,** 221 (1969).
Chalmers, R. A., Watts, R. W. E., *Analyst* **97,** 224 (1972).
Chandrasekaran, S. K., King, C. J., *Chem. Eng. Prog. Symp. Ser. No. 108*, **67,** 122 (1971).
Chandrasekaran, S. K., King, C. J., *AIChE J.* 18(3), 513 (1972a).
Chandrasekaran, S. K., King, C. J., *AIChE J.* 18(3), 520 (1972b).
Chirife, J., Karel, M., *J. Food Sci.* **38,** 768 (1973a).
Chirife, J., Karel, M., *J. Agric. Food Chem.* **21,** 936 (1973b).
Chirife, J., Karel, M., *Cryobiology* **11,** 107 (1974a).
Chirife, J., Karel, M., *J. Food Technol.* **9,** 13 (1974b).
Chirife, J., Karel, M., Flink, J., *J. Food Sci.* **38,** 671 (1973).
Ettrup-Petersen, E., Lorentzen, J., Flink, J., *J. Food Sci.* **38**(1), 119 (1973).
Flink, J., presented at the 6th International Course on Freeze Drying and Advanced Food Technology, Burgenstock, Switzerland, 1973 (proceedings to be published in 1975).
Flink, J. M., Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1970.
Flink, J., Gejl-Hansen, F., *J. Agric. Food Chem.* **20**(3), 691 (1972).
Flink, J. M., Gejl-Hansen, F., Karel, M., *J. Food Sci.* **38,** 1174 (1973).
Flink, J., Karel, M., *J. Food Technol.* **7,** 199 (1972).
Flink, J. M., Karel, M., *J. Agric. Food Chem.* **18,** 295 (1970a).
Flink, J. M., Karel, M., *J. Food Sci.* **35,** 444 (1970b).
Flink, J. M., Labuza, T. P., *J. Food Sci.* **37,** 617 (1972).
Fritsch, R., Mohr, W., Heiss, R., *Chem.-Ing.-Tech.* **43**(3), 445 (1971).
Gejl-Hansen, F., Technical Chemistry Thesis, Technical University of Denmark, 1971 (in Danish).
Hair, E. R., Strang, D. A., U.S. Patent 3,486,907 (1969).
Karel, M., Flink, J. M., *J. Agric. Food Chem.* **21**(1), 16 (1973).
King, C. J., "Freeze-Drying of Foods", Chemical Rubber Publishing Co., Cleveland, Ohio, 1971.
King, C. J., Chandrasekaran, S. K., *Prog. Refrig. Sci. Technol., Proc. Int. Congr. Refrig., 12th, 1967,* **3,** 649–656 (1973).
Lee, C. Y., Salunke, D. K., Nury, F. S., *J. Sci. Food Agric.* **17,** 393 (1966a).
Lee, C. Y., Salunke, D. K., Watters, G. G., Nury, F. S., *Food Technol.* **20,** 845 (1966b).
Maier, H. G., *Naturwissenschaften* **55**(4), 180 (1968).
Maier, H. G., *Z. Lebensm.-Unters.-Forsch.* **144**(1) (1970).
Maier, H. G., Bauer, A., *Die Starke* **24**(4), 101 (1972).
Massaldi, H. A., King, C. J., *J. Food Sci.* **39,** 438 (1974a).
Massaldi, H. A., King, C. J., *J. Food Sci.* **39,** 445 (1974b).
Menting, L. C., Hoogstad, B., *Experientia* **23**(9), 738 (1967).
Ofcarcik, R. P., Burns, E. E., *J. Food Sci.* **39,** 350 (1974).
Rey, L. R., Bastien, M. C., *Freeze-Drying Foods, Proc. Conf. 1961,* 25–42 (1962).
Rulkens, W. H., Thijssen, H. A. C., *J. Food Technol.* **7**(1), 79 (1972).
Saravacos, G. D., Moyer, J. C., *Chem. Eng. Prog. Symp. Ser. No. 86,* **64,** 37 (1968).
Sauvageot, C., Beley, P., Marchand, A., Simatos, D., Symposium on Surface Reactions in Freeze-Dried Systems, Commission X of the International Institute of Refrigeration, Paris, Dec 11–12, 1969.
Thijssen, H. A. C., *J. Appl. Chem. Biotechnol.* **21**(12), 372 (1972a).
Thijssen, H. A. C., *Proc. Nord. Aroma Symp., 3rd, 1972* (1972b).
Thijssen, H. A. C., presented at the 6th International Course on Freeze Drying and Advanced Food Technology, Burgenstock, Switzerland, 1973 (proceedings to be published in 1975).
Thijssen, H. A. C., Rulkens, W. H., *Ingenieur* **80**(47), 45 (1968).
Thijssen, H. A. C., Rulkens, W. H., "Effect of Freezing Rate on Rate of Sublimation and Aroma Retention in Freeze-Drying", presented at Lausanne, Switzerland, June 5–7, 1969 (1969a).
Thijssen, H. A. C., Rulkens, presented at the CHISA Conference, Marienbad, Czechoslovakia, Sept 15–20, 1969 (1969b).
Voilley, A., Sauvageot, F., Simatos, D., *Prog. Refrig. Sci. Technol., Proc. Int. Congr. Refrig., 13th* **3,** 639–647 (1973).

Received for review January 22, 1975. Accepted April 11, 1975. The studies on fruit slices were supported by Contract No. 9-12485 with NASA/MSC, Houston, Tex. Presented at the Symposium on Flavor Chemistry of Processed Foods, 168th National Meeting of the American Chemical Society, Division of Agricultural and Food Chemistry, Atlantic City, N.J., Sept 1974.