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RECENT RESEARCH AND DEVELOPMENT IN THE FIELD OF LOW-MOISTURE AND INTERMEDIATE-MOISTURE FOODS

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INTRODUCTION

Scope of This Review

The scientific, engineering, economic, and legal aspects of dehydrated and intermediate-moisture (I.M.) foods are too broad to be covered in a single review paper. This review, therefore, will deal only with the *current state of knowledge* and the *most recent research and development* in the following areas:

1. the state of water in foods and its effect on food properties;
2. recent developments in dehydration processes other than freeze-drying, with an emphasis on research and how the physical properties of foods affect dehydration processes;
3. recent developments in freeze dehydration;
4. research progress in mechanisms of flavor retention in dehydrated foods;
5. recent developments in intermediate-moisture foods.

Certain specific aspects of the areas listed above have been well covered by recent comprehensive reviews. Where this is true this author will not

attempt to do more than provide the reader with a critical reference to the particular review and a summary of more recent developments.

The major areas *not* to be covered here include:

1. equipment design and plant operation for producing low-moisture and I.M. foods;
2. economic analysis of various processes;
3. marketing aspects;
4. advanced mathematical descriptions of heat and mass transfer in dehydration processes.

Recent Reviews

For a thorough review of physical principles governing dehydration there is still nothing to match the two-volume classic by Krischer and Kröll (1959; 1963).^{128,129} Unfortunately it is available only in German. For those who read German, two more compact treatments of dehydration are available: Kneule (1959),¹²⁶ and the dehydration chapters in Loncin (1969).¹⁴⁶ Loncin's book is also the best currently available general reference on food engineering.

In English the books by Van Arsdel (1963),²²² by Nonhebel and Moss (1971),¹⁷³ and by Van Arsdel and Copley (1964),²²³ and standard texts on unit operations are the starting point.

The journal *Industrial and Engineering Chemistry* provides periodic reviews of various unit operations, and in one of these, McCormick (1970)¹⁶⁰ noted a serious decline in the quality and quantity of unit operations research in the U.S. He considers this to be a result of the emphasis on mathematical and highly theoretical research in most research centers, which has displaced the search for data and measurement of physical properties. In drying operations it is, however, precisely the lack of numerical values for pertinent properties of solids that limits meaningful process calculation. This author believes that McCormick's views are especially applicable to the drying of foods, where data on properties that would affect design are very scarce indeed. McCormick's review lists recent papers in engineering journals, and notes progress in spray-drying and process control in particular. He also notes lack of progress in practical applications for fluidized bed driers and microwave driers.

Holdsworth¹⁰⁷ reviewed physical aspects of drying and their significance in preservation of organoleptic properties. He offered a simple summary of fundamental aspects of dehydration and reviewed some dehydration processes in detail, particularly the utilization of explosion puffing and recent progress in fluidized bed-drying. Foam-drying was competently reviewed by Hertzendorf and Moshy¹⁰⁵ and will not be treated here. The same is true of applications of microwaves, which were well treated in an article by Decareau,⁴⁹ and are also the subject of a book by Goldblith, soon to be published by M.I.T. Press.

Additional reviews, considered more pertinent to specific topics discussed in subsequent sections, will be mentioned there.

Finally, the compilations of patent literature by Noyes^{174,175} should be noted.

BOUND AND FREE WATER IN FOODS AND THE PROPERTIES OF FOODS

Food preservation processes have certain common characteristics that should be noted.

1. All processes concentrate on prevention of undesirable microbial activity, because deterioration caused by microorganisms is most rapid and also most dangerous. This may be achieved by sterilization (thermal, radiation, etc.) or by

creating an environment unfavorable to microbial growth by drying, freezing, or controlling temperature or pH.

2. Because modern food distribution practices result in substantial separation between producer and consumer, storage stability is required. Storage stability is achieved by minimizing the rate of chemical and physical deterioration, through environmental control (protective packaging, controlled temperature storage) or through chemical additives.

3. Finally, since food is more than just a safe packet of nutrients, food processing is aimed at the often difficult and elusive goal of maximizing eating pleasure.

The concern here is with processes that stabilize foods by reducing the availability of water for microbial growth. This availability of water depends not only on its total amount but also on its state of binding to food components. Water is a highly associated liquid which retains in its liquid state a substantial fraction of the four hydrogen bonds per molecule that exist in ice. The exact nature of the structure of liquid water is, however, still unknown.^{80,81} Water in foods appears even more complicated; in particular it is evident that part of it is "less free" or "more bound" than in the pure liquid. The evidence of water binding by foods and by other hydrophilic substances comes from several types of experimental observations. Some of them shall be mentioned here with an emphasis on recent work.

Unfrozen Water

Unfreezability has been used widely as evidence of water binding. If the total amount of water is known, and the amount of water freezing out during cooling to some arbitrary low temperature is measured, then the remaining water is considered unfrozen or "bound." The experimental difficulty, of course, lies in accurately estimating the amount frozen. Dilatometry, calorimetry, and densitometry have been applied to this end. An example of a relatively simple calorimetric study of bound water in fruit juices appears in the paper by Moy and Chan.¹⁶⁹ The most successful recent investigations have used differential thermal analysis; food samples with different total water contents were cooled to temperatures below -60°C , and then rewarmed in the DTA apparatus. Absence of peaks caused by

absorption of latent heat of fusion indicated that none of the water was frozen. By using a sufficient number of experimental samples with different water contents it was possible to estimate quite accurately the "water bound to freezing" (m_F). Estimates were made by Duckworth,⁵² who found values ranging from 0.13 g water/g of solids for cotton cellulose to 0.43 g for agar and 0.46 for gelatin. Among typical m_F values found by Duckworth were 0.22 for green beans, 0.26 to 0.29 for egg white, and about 0.24 for muscle (beef and cod). Review of other literature values indicates that m_F values reported for foods have ranges most typically between 0.2 and 0.4.

A view has often been expressed that the nonfreezing fraction of water is in a sense already frozen by being ordered, having binding energies as great or greater than those in ice, and by having a low mobility. Recent research, however, with infrared spectroscopy⁶² and nuclear magnetic resonance (e.g., the review by Walter and Hope, 1971)²²⁶ indicates that the water remaining unfrozen does in fact possess substantial mobility and does not show the orderly structure expected of icelike aggregates.

Determination of Water Binding by NMR, and by Measurement of Dielectric Properties

Wide line proton magnetic resonance is used routinely to determine the presence of water (and other liquids having a high proton content) in foods. The basis of its application is as follows: protons of molecules in liquid state, as a result of the more or less random motion of these molecules, experience a similar net magnetic field when placed in a magnet. Therefore, they give sharp and large signals in NMR determination, because they absorb radio energy at about the same frequency. In solids, however, interactions with neighboring atoms change the proton response, and the absorptions by the many protons are spread out over a large frequency. Hence NMR signals are broad and shallow, and within the "window" used to record the signal they may be negligible compared to liquid signal. A portion of the total water in foods shows signals intermediate in character between liquid and solid water, and if the total water content is known, NMR may be used to estimate "bound water content."¹⁹⁸ The amount of water bound to hydrophilic food components is estimated at about 0.1 to 0.3 g of water/g of solids.

The amount of water bound by proteins, polymers, and foods can also be made by dielectric measurements. Dielectric properties of water molecules depend on the molecular environment of these molecules, and "bound" water shows properties intermediate between the rigidly held dipoles of ice and the much more mobile liquid water molecules. The amount of bound water is, however, difficult to estimate by this method. Brey et al.,⁶⁹ working with proteins, report 0.05 to 0.1 g/g solids; Roebuck et al.¹⁹³ reported 0.3 to 0.4 g/g bound in starch.

Water Sorption Isotherms and the Concept of Water Activity

The most successful method for studying properties of water in foods is the determination of water sorption isotherms, that is, curves relating the partial pressure of water in foods to the moisture content. Usually, instead of partial pressure, one actually considers *water activity*, which is defined in Equation 1.

$$a = p/p_o \quad (1)$$

where a = water activity

p = partial pressure of water in food

p_o = vapor pressure of water at the given temperature

The sorption phenomena in foods have been reviewed by Labuza and by Loncin et al.,^{132,147} and the methodology for measurement of sorption properties is the subject of a monograph by Gal.²³⁴ Only the most recent research will be summarized here.

In most polymer-containing foods sigmoid isotherms are found, and a large number of functions have been reported as fitting these isotherms. Several equations reported as fitting water-food isotherms are shown in Table 1. The depression of water activity is due to a combination of factors (listed below), each of which may be predominant in a given range of moisture contents in a given food.

The first is depression of activity due to dissolved solutes. Ideally this depression follows Raoult's Law, and water activity, is numerically equal to the mole fraction of water. In most cases, however, deviations occur for one of the following reasons:

1. Not all of the water in food is capable of

TABLE 1

Some Equations Reported as Describing Food-Water Isotherms

Henderson	$(1-a) = e^{-cm^n}$
Fugassi	$m = \frac{ca}{(ca)(1-a) + ca}$
Kuhn	$m = \frac{c_1}{(\ln a)^n} + C_2$
Oswin	$m = c\left(\frac{a}{1-a}\right)^n$
Mizrahi	$a = \frac{c_1 + m}{c_2 + m}$
Linear isotherm	$m = c_1 a + c_2$

a = water activity
m = water content
C, c = constants
n = exponent

acting as solvent for the solutes. (Some of the water is bound to specific groups of insoluble substances.)

2. Not all of the solute is in solution. (Some may, for instance, be bound to other insoluble food components, as in the case of salts bound to proteins.)

3. Interactions between solute molecules cause deviations from ideal relations.

Water activities of some solutions are shown in Tables 2 and 3. Knowledge of activity depression by solutes is a prerequisite for design of intermediate moisture foods, which will be discussed later.

The second factor is depression due to capillary forces. Ideally this depression is given by Equation 2.

$$\ln(a) = \frac{-2\gamma}{r} \cdot \cos\Theta \cdot c \quad (2)$$

where

γ = surface tension of water
 r = radius of capillary
 Θ = contact angle
 c = constant.

The extent to which capillary forces are operative at very low water activities is not fully understood. Table 4 shows how water activity would vary with capillary radius, assuming a contact angle of zero. It has been reported that capillaries in foods can

TABLE 2

Water Activity of Selected Solutions

Water activity	Molality (moles solute/l. pure H ₂ O)			
	Ideal solute	NaCl	Sucrose	Glycerol
0.90	6.17	2.83	4.11	5.6
0.80	13.9	5.15	—	11.5

TABLE 3

Minimum Activities of Solutions (at room temperature)

Solute	Solubility limit (% w/w)	Minimum activity
Sucrose	67	0.86
Glucose	47	0.915
Invert sugar	63	0.82
Sucrose + invert sugar (Sucrose 37.6% invert sugar 62.4%)	75	0.71
NaCl	27	0.74

be as narrow as 10^{-7} cm. It is doubtful that capillaries with molecular dimensions can be considered to obey the relationships predicted by Equation 2, but Labuza and Rutman^{13,7} in studies of sorption behavior of microcrystalline cellulose found that capillarity contributed to activity depression down to activities of 0.2 to 0.4. More generally, perhaps, one could expect definite capillarity effects above activities of 0.9 since capillaries with a radius of 10^{-6} cm are probably common in foods.

The third factor responsible for water activity depression is the portion of the total water present that is bound to specific polar sites in the food. The most effective methods for estimating the amount held in this manner are the B.E.T. isotherm and estimation of latent heats of adsorption by measuring water activity at several

TABLE 4

Effect of Capillary Radius on Water Activity

Radius (cm)	Activity
1	0.9999999
10^{-2}	0.999895
10^{-4}	0.99895
10^{-6}	~0.90
10^{-7}	0.20

temperatures, at several moisture contents, and then applying the Clausius Clapeyron relation.^{23,4}

A typical B.E.T. isotherm plot is shown in Figure 1, and in Figure 2 is shown the typical

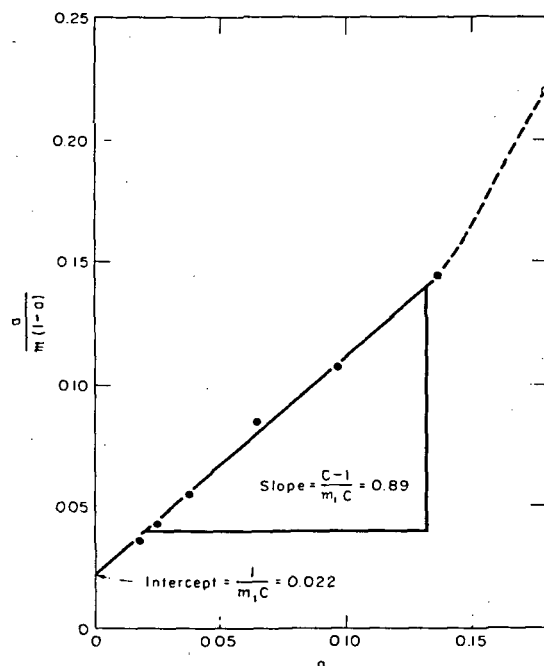


FIGURE 1. B.E.T. plot for water sorption on orange crystals. a = water activity, m_1 = B.E.T. monolayer value, m = moisture content, c = constant.

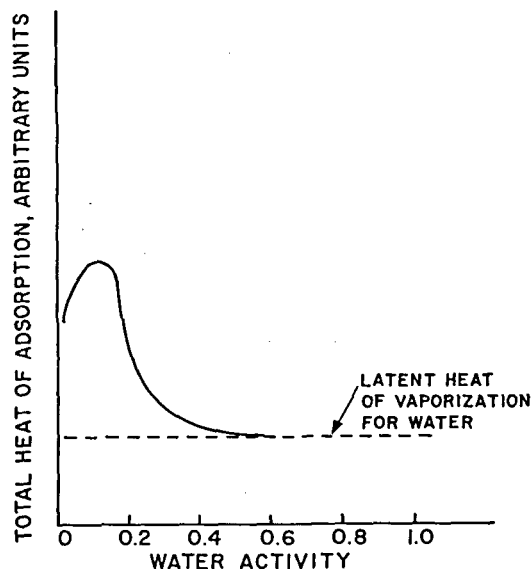


FIGURE 2. Typical dependence of total heat of adsorption on water activity.

behavior of energy of sorption with increasing water content. In general the portion of water that is shown by the B.E.T. analysis to be held bound to specific sites corresponds also to that fraction of water for which the total heat of adsorption is greater than 10.5 kcal/mole, which is the latent heat of vaporization for water. The reported *maximum* latent heats of adsorption for water in foods range from about 11 kcal/mole, to as much as 20 kcal/mole. Polyelectrolytes including proteins and sulfate-group-containing polysaccharides show the highest energies of water binding.²²

Typical monolayer values for selected foods and food components are shown in Table 5, which also presents some maximum energies of binding. The author and co-workers have noted that the B.E.T. monolayer calculation and the estimation of the energy of binding of the adsorbed water offer the most effective way of estimating the water adsorbed on specific polar sites in the food. It must be noted, however, that both of these methods are based on somewhat simplified thermodynamic assumptions, and are certainly *estimates*, rather than exact values. In particular, the assumption inherent in the B.E.T. method that all of the water molecules held in the first adsorption layer have the same binding energy is known to be incorrect. Nevertheless, the B.E.T. monolayer concept is extremely useful, and has been found to be a reasonably correct guide with respect to the following important food properties:

1. Mobility of small molecules in many food systems begins to become apparent at the B.E.T. monolayer.
2. The B.E.T. monolayer correlates with the total number of polar groups binding water.

Capability of Water in Foods to Act as a Solvent and to Impart Mobility to Food Components

Research conducted using radioactive glucose and other substances⁵¹ showed that *some mobility* is imparted to solutes at the B.E.T. monolayer value. Work in this author's laboratory on carbohydrate systems confirmed that some mobility in such systems commences at the B.E.T. monolayer, resulting in freedom for some structural rearrangements. Chemical reaction can in fact proceed, albeit slowly, even below the monolayer value. Until recently, however, there

TABLE 5

B.E.T. Monolayer Values and Maximum Total Heats of Adsorption for Selected Foods and Food Components

Substance	Approximate B.E.T. monolayer (g H ₂ O/g solids)	Maximum ΔH_v (kcal/mole)	Reference
Starch	0.11	~ 14	Duckworth ^{5,3}
Polygalacturonic acid	0.04	~ 20	Bettelheim et al. ^{2,2}
Gelatin	0.11	~ 12	Duckworth ^{5,3}
Lactose, amorphous	0.06	~ 11.6	Flink and Karel ^{7,6}
Dextran	0.09	~ 12	Flink and Karel ^{7,6}
Potato flakes	0.05		Heiss ^{1,0,3}
Spray-dried whole milk	0.03		Heiss ^{1,0,3}
Freeze-dried beef	0.04	~ 12	Kapsalis ^{1,1,8}

has been no accurate way to determine the level at which water in foods begins to act as a true solvent.

Recently, Duckworth^{5,3} used NMR techniques to determine this property. His method is based on the observation that proton-containing solutes such as sugar give different NMR signals in solution than in their precipitated state. He determined that the pertinent property for commencing dissolution of a given solute is water activity, not water content per se, and that this critical water activity depended only on solute and not on polymeric components present in the system. He found for instance that sucrose began to go into solution at an activity of ~ 0.82 in several water-polymer systems. At this activity the water contents of these systems were 0.34 g/g for agar, 0.27 for gelatin, 0.24 for starch, and 0.11 for cellulose. Glucose began to dissolve at an activity of ~ 0.85 and urea at an activity of ~ 0.45 , independent of the polymer studied.

Phase Transformations in Water-sorbing Systems and Their Effects on Water Sorption

Many food components, and in particular low molecular weight carbohydrates and salts, may be present in one of several states: crystalline solids, amorphous solids (bound to other food components), and aqueous solution. Sorption of water in such systems is complicated, and may require consideration of kinetics as well as equilibrium of sorption. The considerations involved are illustrated in Figure 3, which shows the sorption behavior of sucrose in several states. Crystalline sucrose sorbs very little water until water activity reaches approximately 0.8 and the sucrose begins

to dissolve. When the drying procedures are sufficiently rapid to produce amorphous sucrose, however, exposure to increasing humidities results in water uptake, reaching sorption levels far higher than that of crystalline sucrose. This difference in behavior is due to the higher internal area available for water sorption in the amorphous material, and greater ability of water to penetrate into the H-bonded structure, which is less regular than in sucrose crystals. However, the very adsorption of water results in the capability for breaking some H-bonds and imparting a mobility to the sugar molecules; and this mobility results eventually in the sucrose transforming from the metastable amorphous state to the more stable crystalline state. In this process the sugar *loses* water, often as a result of exposure to increasing relative humidity, because the recrystallization that occurred extremely slowly at low humidities sped up with transient water pickup at higher humidities (Figure 3).

All soluble substances have characteristic behavior patterns with respect to water uptake and phase transformations. The phenomena initiated by these transformations are very important to the storage of foods. Their effects will be discussed in spray- and freeze-drying, and in flavor retention of dried products, in subsequent sections of this paper. A general review of the glassy state in foods was given recently by White and Cakebread,^{2,2,8} who discuss graining, stickiness, caking, sandiness, and partial liquefaction defects due to phase changes in various confectionery products. Another recent paper discusses the effects of hydration and crystal formation on the surface area of lactose.^{2,1}

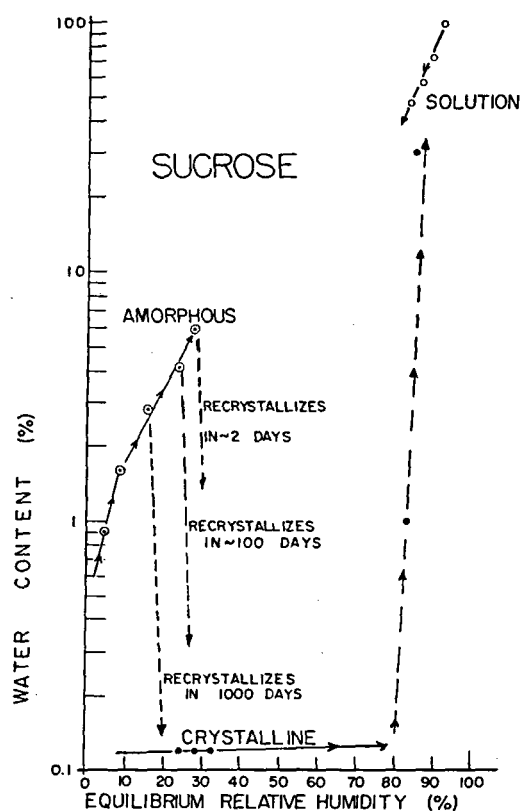


FIGURE 3. Sorption behavior of water in sucrose.

Water Activity and Food Stability

The author has noted that food preservation by dehydration works by reducing the availability of water for *microbial growth*. This is equivalent to requiring that *water activity* be reduced.

Water Activity and Microbial Spoilage

In a classic article published in 1957,¹⁹⁷ Scott summarized the water relationships of microorganisms, and most of the principles he suggested are still held valid. These include:

1. Water activity, rather than water content, determines the lower limit of availability of water to microbial growth. Most bacteria do not grow below a water activity equal to 0.91; most molds cease to grow below an activity equal to 0.8. Some xerophilic fungi were reported to grow at activities of 0.65, but the range of 0.70 to 0.75 is generally considered their lower limit.

2. Environmental factors affect the level of water activity required for microbial growth. The

general principle that seems usually to apply is that the less favorable the other environmental factors (nutritional adequacy, pH, oxygen pressure, temperature) the higher is the *minimum* water activity at which microorganisms will grow.

3. Some adaptation to low activities occurs, and this appears to be particularly true when water activity is depressed by addition of water-soluble substances (principle of intermediate-moisture foods), rather than by water crystallization (frozen foods) or water removal (dehydrated foods).

4. When water activity is depressed by solutes, the solutes themselves may have effects that complicate the effect of water activity per se.

More recent researches, in particular in the area of freeze-dried and intermediate-moisture foods, have resulted in the following major additional findings:

1. Water activity modifies sensitivity of microorganisms to heat, light, and chemicals. In general, organisms are most sensitive at high water activities (i.e., in dilute solution), but the minimum sensitivity occurs in an intermediate-moisture range. A schematic representation of microbial sensitivity to sterilization is shown in Figure 4.

2. Minimum water activities for production of toxins are often lower than for microbial growth. This phenomenon may represent an important safety factor in the distribution of dehydrated and intermediate-moisture foods. However, different toxins from a given microbial species may have different minimum activities.²¹⁷

3. Recently, Labuza et al.¹³⁵ reported that microbial growth depends on the method of adjusting the water activity. Many foods show a *hysteresis effect*, that is, their moisture content in adsorption of water is usually lower, at a given water activity, than in desorption. The extent of hysteresis is often quite substantial.²²⁹ Labuza et al. found that in intermediate-moisture foods the *limiting water activity may be higher during water adsorption than during water desorption*. They claim that growth is controlled not by water activity alone but by water activity *and* total water content.

Effects of Water Activity and Content on the Chemical Deterioration of Foods

The effects of water on chemical reactions in

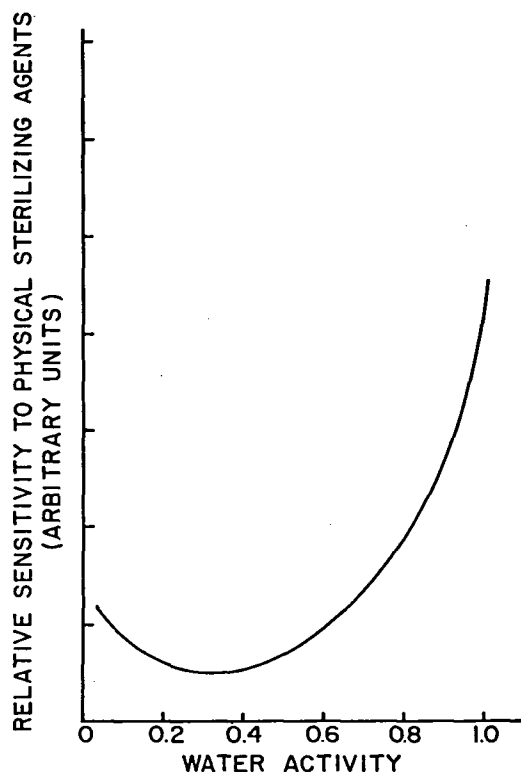


FIGURE 4. Effect of water activity on sensitivity of microorganisms to physical sterilizing agents.

foods are more complicated than are its effects on microbial growth. Water activity is not the only parameter defining the lower limits of chemical activity, and water can act in one or more of the following roles:

1. solvent, for reactants and for products of reaction;
2. reactant (e.g., in hydrolysis reactions);
3. product of reactions (e.g., in condensation reactions such as occur in nonenzymatic browning);
4. modifier of the catalytic or inhibitory activities of other substances (e.g., water inactivates some metallic catalysts of lipid peroxidation). A detailed review of the influence of water on food deterioration is beyond the scope of this review, and only a few general conclusions resulting from recent research will be outlined.

In enzyme-catalyzed reactions in foods, water is most important as a solvent for the substrate, allowing it to diffuse to the active sites of the

enzyme. For a comprehensive recent review by one of the leading authorities in this field see Acker.²

Most dehydrated foods, and practically all intermediate-moisture foods, are subject to non-enzymatic browning. This reaction is water-dependent and invariably shows a maximum rate at intermediate moisture. Recent research by the author and co-workers in this area^{5,8,13,9} indicates that these effects result from water's dual role as solvent and as a product of the reaction, and hence as an inhibitor. At low water activity the limiting factor is inadequate mobility; therefore, addition of water, which adds solvent power, promotes the reaction. At high water contents, however, the dilution of reactants and the product inhibition of condensation by water predominate, and water strongly inhibits browning. The exact position of browning maxima depends on specific products, but generally, concentrated liquids (e.g., unfrozen fruit concentrates) and intermediate-moisture foods (e.g., fillings, and so-called evaporated fruit such as prunes) are in the range of moisture content most susceptible to browning. Typical behavior is shown in Figure 5, which shows

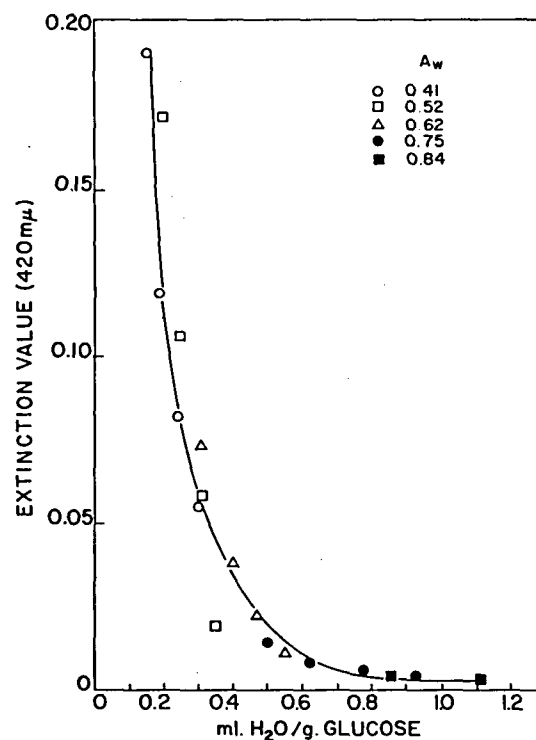


FIGURE 5. Influence of increasing amounts of water in a glucose-glycine-glycerol-water system on the browning rate at constant water activities.

browning in a system containing glucose, glycine and glycerol in aqueous solution.^{5,8} This is particularly important in foods prepared without sulfite, an omission that may receive increased attention with rising interest in additive-free foods.¹⁰

Solvent action of water is required in several other food deterioration reactions.^{13,9}

Water affects oxidation of lipids and other free radical reactions in foods. The effect on oxidation of lipids is very complicated. Table 6 shows the dependence of rate of oxidation of potato chips on water activity and water content. As in many other studies on foods and on model systems,^{102, 133} it was observed that the increasing concentration of water slows the reaction up to a point where the intermediate-moisture range often begins. Peroxide production and oxygen absorption often decrease as the relative humidity is increased above the monolayer of water content (Table 6).

The mechanisms by which water exerts this protective effect include:

1. On the food surfaces, water hydrogen bonds to the hydroperoxides produced during the free radical reaction. This hydrogen-bonding protects the hydroperoxides from decomposing and therefore slows the rate of initiation through peroxide decomposition.

2. Water hydrates trace metal catalysts that accelerate the initiation steps. This hydration reduces or completely stops the catalytic activity.

The extent of the reduction depends on the metal.

3. Water can react with the trace metals to produce insoluble metal hydroxides, taking them out of the reaction phase.

4. The presence of water can also directly affect the free radicals produced during lipid oxidation.

At increasing moisture levels, expected in intermediate-moisture foods, the above mechanisms may give substantial protection against oxidation. At high moisture levels, however, oxidation increases again. This might be explained by the increased diffusion of those metal catalysts that were not inactivated, and possibly also by the swelling of the porous matrix, which allows for faster uptake of atmospheric oxygen. Data on oxidation rates at intermediate-moisture levels, however, are sparse, and more studies are needed. For additional recent papers reviewing some aspects of water-dependent food deterioration, the reader is referred to Heiss,¹⁰³ Kapsalis,¹¹⁸ Labuza et al.,¹³⁶ Quast and Karel,^{187,188} Tamsma and Pallansch,²¹¹ and Tuomy et al.,²¹⁹ in particular.

Figure 6 shows schematically the dependence of oxidation of potato chips on water activity. It may be noted that water has a strong protective effect early in oxidation but offers little protection once oxidation is well advanced.¹⁸⁸

Reactions occurring in the process of drying itself have been studied in model systems by Kluge and Heiss.¹²⁵

TABLE 6
Effects of Water Activity on Oxidation of Potato Chips Stored at 37°C

Water activity	Initial oxygen absorption rate in air ($\mu\text{l O}_2 \times \text{g}^{-1} \times \text{hr}^{-1}$)	Oxidation rate in a closed container ^a ($\mu\text{l O}_2 \times \text{g}^{-1} \times \text{hr}^{-1}$)	Peroxide value after 2000 hrs
0.001	2.7	0.15	70
0.11	0.26	0.13	—
0.20	0.16	—	15
0.32	0.15	0.07	—
0.40	0.16	0.06	5
0.62	—	0.19	—
0.75	—	1.6	—

^aInitial concentration of oxygen 12.2%; rate measured when oxygen content dropped to 10%.

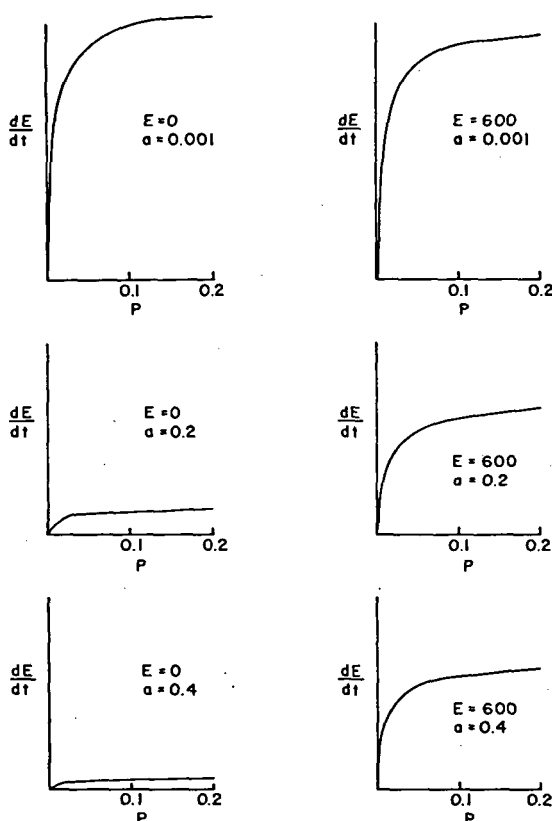


FIGURE 6. Effects of water activity and of oxygen pressure on oxidation of potato chips in an early and an advanced stage of oxidation. p = oxygen pressure, atm., a = water activity, t = time, E = Extent of oxidation expressed as microliters of oxygen absorbed per gram of potato chips. (Rancidity is considered to make the product unacceptable at 1200 $\mu\text{l/g.}$) $\frac{dE}{dt}$ = Rate of oxidation.

DEVELOPMENTS IN FOOD DEHYDRATION PROCESSES OTHER THAN FREEZE-DRYING

Introduction

In 1960, the five products dried in the U.S. in the largest quantities were sugar, 9.3×10^6 tons; coffee, 1.4×10^6 tons; corn starch, 1.1×10^6 tons; milk products, 1.04×10^6 tons; and flour mixes, 9.7×10^5 tons. Other important dehydrated products included breakfast foods, pet foods, pasta products and dried fruits.¹¹³ The situation in recent years has remained essentially unchanged. The dehydration of breakfast foods, of mixes, and of potato and corn chips has shown increases, and according to the 1972/73

Canner/Packer Yearbook, the production of major dehydrated items included the following:

Item	Approx. Amt. (Short tons)	Year
Milk products	1.1×10^6	1971
Breakfast foods and flour mixes	2×10^6	1970
Sugar	10×10^6	1968
Corn starch	1.4×10^6	1968
Dried fruit	0.45×10^6	1970
Dried potatoes	65×10^6	1969

The dehydration of coffee showed a significant change in increasing the share of freeze-drying in the total instant coffee market; this trend will be discussed later. In milk products, a trend towards increased drying of whey is evident (Table 7). In some countries, dehydration, in particular of vegetables and fruit, is a more important segment of the food processing industry than in the U.S.¹⁷⁶

In general, however, the major food products being dehydrated on a large scale continue to include:

sugar
starch and industrial starch products
coffee
milk products (especially nonfat milk and whey)
flour mixes and breakfast foods
snacks (including potato chips)
macaroni and pasta products
fruits
vegetables for soup mixes and as bulk ingredient.

In 1963, Van Arsdel estimated that, of the total U.S. production of dehydrated foods, air-drying accounted for 55%, spray-drying for 40%, and all the remaining methods for less than 5%. All of the major products listed above are dried primarily by air- or by spray-drying, and therefore it is probably still true that these two methods account for most industrial dehydration.

Dehydration of Solids in Air

The most widely used dehydration methods involved exposure of foods to heated air (*direct* dryers), sometimes in combination with heating of surfaces on which the food is placed (*indirect* drying). In these driers the primary mode of heat

TABLE 7

Dry Milk Production (F.A.O. Data) Thousands of Metric Tons

	United States		Canada	Netherlands	France
	1964	1968	1968	1968	1968
Whole dry milk	40	43	4	43	30
Dry skim milk	998	728	169	104	677
Whey solids	169	226	24	34	42

1969 Utilization in the United States after Hammonds and Call⁹⁷

Whole dry milk 23 thousands metric tons

Nonfat dry milk 462 thousands metric tons

transfer is by *convection*, but additional heat may be supplied by *radiation* and/or by *conduction*. The methods include *batch* drying as in the case of *tray driers*, *kiln driers*, and some types of *fluid beds*; and *continuous* drying which may be conducted in *tunnels*, *rotary driers*, various types of *belt* or *band driers* and many other types of equipment. Spray-drying is a type of convection drying, but will be discussed later.

Recent reviews treat the air-drying of foods in adequate detail,^{107,203} and the present review will only mention a few recent trends and developments which seem to be of particular interest.

Increasing sophistication in mathematical formulation of dehydration processes — Loncin,¹⁴⁶ Holdsworth,¹⁰⁷ and Nonhebel and Moss¹⁷³ have reviewed the engineering analysis of dehydration. More recent papers that deserve mention include the analysis of dehydration process regularities by Luikov and Kuts,¹⁵⁰ who have established a relationship between the basic equations for drying kinetics and the Nusselt number; a review of nonstationary temperature and moisture profiles by Valchar,²²¹ and analysis of transport processes in early stages of drying by Bimbenet.²³ Digital computer analysis of dehydration processes can now be used routinely [e.g., Nellist and O'Callaghan,¹⁷¹ Bakker-Arkema,⁶⁵ and two recent papers that contribute ideas on utilization of analog computers for simulation of dehydration processes and related transfer problems (Middlehurst and Parker,¹⁶⁵ Baughman et al.¹⁵)]. For simplified situations it is also possible to use programmable electronic calculators.

Determination of heat and mass transfer properties of foods, and their utilization in process design — Holdsworth's (1971) review gives a good summary of the status of this research,¹⁰⁷ which is also adequately covered in the reviews by King.^{123,124} A compilation of physical properties of foods by Adam also deserves mention.³

Instrumentation, process control and automation — A major thrust of modern industrial practice has been to increase instrumental analysis, feedback control, and automatic operation of process lines. In food processing this development has lagged, primarily because

1. Food materials are complex and difficult to describe in simple engineering properties.
2. When description is possible, measurement of on-line and feedback control is difficult (e.g., it is difficult to measure rapidly the chemical composition, or rheological properties).
3. Where equipment and theoretical knowledge to accomplish 1 and 2 (see above) are available, it is still difficult to find food technologists with adequate engineering background and experience to utilize them.

Nevertheless, progress is being made in this direction. A recent review by Harbert⁹⁸ summarizes the available on-line moisture measurement techniques, which are now quite extensive. Shinsky¹⁹⁹ describes a control scheme for a fluid bed drier based on only three temperature measurements: inlet and outlet air temperatures, and temperature of the air wet bulb. The quantity *K* is maintained at a constant level by adjustment

through a temperature controller of the inlet air temperature T_i .

$$\frac{T_o - T_w}{T_i - T_w} = K \quad (3)$$

where

- T_o is temperature of outlet air
- T_i is temperature of inlet air
- T_w is wet bulb temperature of air.

Other instrument companies have reported feedback controls,^{5,6,9,70} and there is also much automation progress in the food industry that remains unreported in the technical literature.

Modification of solid food products in order to improve their drying rates, and/or their organoleptic properties — A major problem in air dehydration of solid foods is the limitation of drying rate due to the low diffusivity of water as the moisture content decreases. Associated with this problem are shrinkage and organoleptic changes lowering quality; in particular, the following three types of changes are almost always a potential danger in air dehydration:

1. poor rehydration of finished product;
2. browning and flavor deterioration during drying;
3. oxidation of lipids, lipid-soluble pigments, vitamins, and some water-soluble compounds both in drying and in storage.

Most of the research and product development in the dehydration industry is concerned with the above problems, and a full discussion of this aspect could easily warrant another review. Therefore, only some published developments that seem original, typical, or likely to be of future merit will be mentioned here.

A number of ideas have been advanced to counteract the aggregation in the solids during dehydration that limits drying rate and rehydration. Holdsworth's review¹⁰⁷ covers very well the work on *explosion puffing*.

Freezing and thawing of foods prior to drying to increase internal porosity and thus increase mass transport in dehydration and rehydration is relatively old, but a novel idea has recently been patented by Haas in the U.S. and Canada.^{94,95} He proposed freezing foods that have been previously pressurized with 500 to 1500 psig of methane,

nitrogen, CO, air, freon, or ethane (CO₂ and He were not suitable). The pressurized, frozen substances are then air-dried, and retain their shape. The phenomenon was not fully understood by its inventor, who wrote that it is not known why the bubbles of entrapped gas are retained within the solids upon melting and during drying, thus preventing shrinkage.

An interesting method, albeit presently not applicable because of FDA regulations, is the *irradiation* of dried vegetables with ionizing radiations to produce scission of some polysaccharides with resultant improved rehydration and texture. Gardner and Wadsworth⁸⁸ have improved the original process by irradiation with 1 to 100 megarads at very low temperatures (below -100°C), thus preserving flavor as well as improving texture of dehydrated diced potatoes.

A variety of *additives* have been explored in an attempt to improve organoleptic quality. Some of the compounds tried and found partially successful in improving quality were (in addition to sulfite and phenolic antioxidants) various carbohydrates, in particular dextrans; sodium chloride; ascorbic acid; and amino acids.

Some novel or improved ideas for dehydration processes that have been advanced — Fluidized beds have been suggested as rapid and effective driers for solid food pieces. Recent work by Farkas et al.⁶⁴ and Lazar and Farkas¹⁴² is particularly noteworthy. A good review of other work is given by Holdsworth.¹⁰⁷

Acoustic vibrations are claimed to produce improved dehydration rates. A typical recent study is that of Bartolome et al.,¹⁴ who used acoustic vibrations during air-drying of potato cylinders and found improved drying rates with a maximum near 8,100 cps. The authors reviewed previous literature as well as their own research results but were unable to provide an explanation of the observed effects in terms of a definite mechanism. They concluded, however, that the process has commercial possibilities.

Spray-Drying

Spray-drying is the most important method for dehydration of liquid food products. Among the widely recognized applications is drying of milk products, coffee, and eggs. A wide variety of other products have been successfully spray-dried, either in pilot plants or in commercial installations, and a partial list is shown in Table 8. Historically, the

TABLE 8

Some Food Substances That Have Been Spray Dried

Bananas	Proteins from various plant
Blood	sources
Cake mixes	Soy isolates and hydrolyzates
Casein and Caseinates	Starch and derivatives
Cheese	Tea
Citrus juices	Tomato puree
Coffee	Yeast
Corn Hydrolyzates	Cream
Egg	Ice cream
Fish concentrates	Milk replacer
Milk	Yoghurt
Potatoes	

development of spray-drying in the food industry has been closely associated with dehydration of dairy products. Discussions and reviews of milk product dehydration and of applications of spray-drying of foods often coincide. The following recent reviews of spray-drying are noteworthy: Lyne (1971); Masters (1968); Knipschildt (1969).^{127,151,157} There have also been recent reviews and discussions of instantizing and agglomeration, which are closely related to spray-drying. Instantizing will be considered later.

In principle, spray-drying consists of the following steps. A liquid or a paste is atomized into a chamber, where it is contacted with a stream of hot air and dehydrated. The dry particles, suspended in the air stream, flow into separation equipment where they are removed from the air, collected and packaged, or subjected to further treatment such as instantizing. Each of the steps, so simply described, actually constitutes a complicated and delicately balanced engineering operation. Thus the properties of feed, including viscosity, surface tension, and chemical composition, must be controlled; the atomization procedure is extremely important and often imperfectly understood; the flow, heat and mass transfer events in the chamber are complicated; and the separation of the dry material from the air stream is often difficult to achieve with good yield. The characteristics of the product may place additional restraints on the operation. For instance, drying of some types of materials, such as protein hydrolysates, may require that the spray drier walls be cooled to prevent powder from sticking to them. The complicated nature of the flow and heat transfer patterns in the chamber makes this

operation difficult to describe in simple engineering equations; furthermore, and perhaps more significantly, they make pilot plant experience difficult to apply to subsequent commercial scale-up.

Several aspects of recent research in spray-drying will be discussed here, and the reader is referred to the reviews mentioned above for further information.

Advances in Engineering Analysis of Events in Spray-drying

Atomization — Since the atomization determines the size distribution of droplets, it is the most important feature of a spray drier. Reviews of recent developments in atomization theory and practice are given by Masters and by Antonsen.^{12,157} Apparently there have been no drastic new developments in the last few years in theoretical treatment of rotating disc atomizers and pressure nozzles. Recently, attention has been given to sonic and ultrasonic means of droplet production, but no applications to foods have appeared.

Heat and mass transfer in the drying tower — Few details are known about the actual heat and mass transfer processes in the drying tower, primarily because the pertinent variables, such as temperature, humidity, and droplet distribution, are difficult to measure and to estimate. Theoretical analysis of drying processes under conditions approximating the events in a single droplet in a spray drier can, however, be studied readily. Van der Lijn et al.²²⁴ studied droplet heat and mass transfer under spray-drying conditions and concluded that: A history of drying in a single droplet may be constructed; in an initial period, temperature increases to the wet bulb temperature. In the second period, a concentration gradient builds up in the drop, and water activity at the surface drops, thus allowing an increase of the surface temperature above that of the wet bulb. In the third period, internal diffusion is entirely limiting. Van der Lijn et al. consider that there is a critical moisture content that results in a surface impermeable to aroma losses; calculating the effect of inlet and outlet conditions and of airflow patterns on predicted aroma losses, they conclude that *high inlet temperatures* and *perfect cocurrent* patterns tend to minimize flavor losses. They also present calculated moisture and temperature profiles in the droplet and mention

the potential applicability of such data to calculation of damage due to chemical reactions occurring during drying.

The residence time distribution in a tower was studied by Keey.¹²¹ He noted that the evaporation from a single drop is easily understood by theoretical analysis; however, information on behavior of *particle clouds* with a wide range of diameters is lacking. He pulsed a feed solution containing a salt tracer and analyzed concentration as a function of time, position, and conditions of drying. The experiments showed that in the experimental, 200 mm diameter, tall-form spray-drying tower the residence times of the drops within the chamber were only 10% above times calculated for free fall, and the drops were not entrained. If the ancillary cyclone recirculation is substantial, the droplet residence time is an order of magnitude greater than that in the drying chamber.

Advances in Research on Structure and Properties of Spray-dried Materials

One of the most exciting areas of research in spray-drying has been the exploration of the structure and the physical and physicochemical properties of spray-dried materials. The process of spray-drying is greatly affected by the properties of the feed, and the properties of product in turn depend on the process conditions.

Viscosity and surface tension are the properties of feed that are most important at the atomizer. Viscosity may be influenced by composition and preconcentration. Knipschildt¹²⁷ notes the tendency to feed highly preconcentrated milk products into the spray drier, in an attempt to minimize the cost of the overall process. He warns of potential viscosity-related problems at too high a concentration combined with the low temperature required in handling heat-sensitive fluids. Surface tensions of various food liquids have recently been measured and reported by Labuza and Simon.¹³⁸

The effect of drying itself on the properties of the product has been studied recently; the scanning electron microscope has been particularly valuable. Buma³⁴ has used scanning electron microscopy and other methods to study structure of spray-dried milk particles and the distribution of free fat in them. He showed that spray-drying results in hollow particles in the shell of which a glassy structure, primarily of amorphous lactose,

entraps a part of the total fat, with other portions of the fat being "free" in the sense of either being located directly on the surface, or being accessible to the solvents used for fat determination. Buma and Henstra³⁶ compared scanning electron microscope pictures of spray-dried caseinate with those of spray-dried lactose, and were able to confirm that lactose gave spherical particles with no dents or folds, but caseinate, like spray-dried skim milk, gave folded particles. They attribute the folds in dried skim milk to the presence of casein, which, unlike amorphous lactose, shrinks unevenly during drying.

In his most recent paper, Buma³⁵ studied the influence of drying and storage conditions on porosity of dried milk by a method in which the permeability of the powder to gas was measured. He concluded that spray-drying increases porosity, because of mechanical damage to the particles in the drier and the thermal stresses occurring in drying and cooling. Small particles are more porous than larger particles, though whole milk, whey, and skim milk behave somewhat differently in this respect. During storage, Buma observed decreases in porosity, possibly due to flow in the amorphous matrix of the powder relieving stresses and eliminating some cracks and pores.

Tamsma et al.²¹⁰ studied the effects of drying techniques and feed composition on the properties of nonfat dried milk. The major properties studied were bulk density, particle density, sinkability, and dispersibility. The treatments studied included spray-drying, vacuum-puff-drying, and foam-drying; all powders were compared against commercial instantized milk powder. They found that foam spray-drying, under conditions producing aggregation, and vacuum-puff-drying gave powders with low bulk densities and good dispersibility. Since an excellent review of foam-drying was published recently (Hertzendorf, 1970),¹⁰⁵ the process will not be discussed here. Rather, Tamsma et al. are mentioned, because their evaluations included spray-drying, in a 2.74 m Swenson spray drier, of skim milk concentrate containing 0.1% of four different surface-active agents; they found that the powder containing these agents had improved sinkability characteristics and good dispersibility, but its bulk density was unchanged from control powder. (Powder instantized by agglomeration, on the other hand, had a lowered bulk density as well as improved sinkability and dispersibility.) Micro-

photographs showing how different atomization procedures affect the size and agglomeration, and hence bulk density, are shown by Antonsen.¹²

It has been noted previously that phase transformations of carbohydrates affect their water binding characteristics, and that in spray-dried milk the matrix of the shells of the hollow particles is based on amorphous lactose. In many other spray-dried products, such as juices and extracts, various amorphous soluble substances compose the spray-dried particle matrix. Recrystallization in storage, or partial crystallization in the drying process itself, may have important effects such as changes in water absorption, caking, color and texture changes, and release of entrapped flavors. Lactose has long been known to undergo recrystallization in powdered milk when exposed to humidities in excess of 50% R.H. Recently a thorough study of water absorption and x-ray diffraction patterns in spray-dried and freeze-dried milk has been reported by Bushill et al.,^{3,7} who noted that dried lactose is usually in an amorphous state, but occasionally contains some crystalline α -monohydrate. After absorption of water, lactose recrystallizes into α -monohydrate, or a mixture of α -monohydrate and β -anhydride. The effects of water-initiated crystallization in dried milk powders were also studied by Berlin et al.²⁰ They reported lactose recrystallization in various milk products at a water activity of about 0.5. They showed that most of the water adsorbed initially is held by protein, and that the contribution of lactose to water binding increases as the critical activity of ~ 0.5 is approached. They also observed that the critical activity depended somewhat on the method of drying.

Selected Developments in Product and Process Innovations and Improvements

Spray-drying is a well-established method, and as such not likely to undergo frequent drastic changes and innovations. Knipschildt¹²⁷ reviewed spray-drying of milk products and noted the following major developments:

1. Large plants with a capacity of 6000 to 7000 gal/hr are becoming common, and these plants tend to use automatic control of air temperatures.

2. Automatization of other components of the plant is also progressing, including automatic filter replacement.

3. More drying chambers are installed in the open, thus reducing building costs.

4. Concern about air pollution, and attendant legislation, require improved separation of the powder; this area needs more work.

5. Filled milk and other specialty products require modified drying procedures. In addition, in some countries drying of filled milk in the same plant where milk is processed is prohibited by law.

Nonfat milk, whey, and casein have received some attention with respect to spray-drying improvements. Caseinate spray-drying has been discussed recently by Bergmann¹⁸ and whey powder by Keay.¹²⁰

Spray-drying of eggs continues its importance, and Plummer and Geddes¹⁸⁴ reported the installation of the largest egg-drying facility in the world in Riverside, California. The drying chamber is 14 ft in diameter, and has a water removal capacity of 4,000 lbs/hr. The clean-in-place system used in the plant allows it to convert from an eggwhite- to a yolk-drying operation in 2 1/2 hr. Another feature of the drier is the air flow pattern which is controlled so as to prevent product adherence to drier walls. Automatic product transfer is included in the control features of the process. Properties of spray-dried eggs as components of various food products, including bakery products, were investigated along with work on freeze-dried and frozen egg in a series of papers by Zabik and co-workers. One of the latest papers in this series dealt with coagulation patterns of eggs from different processing methods.⁸⁷

Dehydration of *coffee* by spray-drying remains the major method for producing instant coffee, but most recently published research and development has been in agglomeration and freeze-drying, which will be discussed later.

Spray-drying of *fruit* and of *tomato products* remains much discussed in the literature. These products, which contain a high percentage of sugars and other soluble solids, yield amorphous thermoplastic glasses on dehydration and tend to adhere to walls of the drying chamber. Various modifications have been suggested, and Holdsworth¹⁰⁷ has reported on tomato-drying with tall drying towers and low air temperatures. A 250 ft tower has been reported by *Food Processing* for paste powder.⁷⁹ This process uses air at a temperature below 125°F that has been dehumidified by passing it through a silica gel bed. The capacity of

this plant, located in Burgdorf, Switzerland, is reported to be 450 lb of powder/hr. Low-temperature towers of the BIRS process type are reported to have been installed elsewhere in Europe, but the cost of these procedures is considered to be high.

The other major approach to drying of fruit juices has been the incorporation of additives reducing the tendency of the powder to stick. Mizrahi et al.¹⁶⁷ reported using isolated soybean protein as an aid to the spray-drying of banana puree. They found that soybean protein improved the drying behavior of banana puree; sodium proteinate is more effective than isoelectric protein. Addition of up to 20% of protein (on a dry basis) did not affect flavor, and as little as 4% protein substantially improved resistance to caking. They concluded that 4 to 20% protein could be used to produce a satisfactory and nutritious banana-based beverage. Brennan et al.²⁷ studied the addition of carboxymethyl cellulose, gum Acacia, and liquid glucose as spray-drying aids for orange juice. They found that addition of liquid glucose to produce a feed solution of 29.8% orange juice solids and 23.6% glucose gave the best performance, when the wall temperatures were kept below 105°F. Coulter and Breene⁴⁷ used skimmed milk as an additive in the spray-drying of a wide variety of fruits and vegetables. They found that the amount of skimmed milk required to achieve efficient dehydration ranged from 0% for peas to 60% for tomatoes and apples. The air temperatures in their operations were kept high to give high efficiency; undoubtedly lower percentages of skimmed milk than the 60% noted for tomatoes could be used at lower temperatures.

Spray-drying of fruit-milk protein combinations may be of substantial importance in the future, since fruit-flavored dairy products including milk shakes, yoghurt products and flavored dairy drinks are currently popular consumer items.

Another interesting concept in spray-drying is the dual drier developed by Meade^{162,163} in which liquid products are atomized at the top of a spray-drying chamber, then mixed with heated air and directed onto a screen-mesh conveyor belt. The partially dried particles form a mat, and are dried by through circulation drying. The porous aggregated mat can be reduced by being passed through rollers. The inventor claims to have been successful with calf starter, whey, and cheese. This author visited the plant in Albert Lea, Minnesota,

and observed the drying of calf starter in an apparently satisfactory operation. Other innovations in spray-drying are primarily in the fields of control, automated plant operation, and nozzle development.^{1,59}

The continuous spray-drying process offers both quality and economic advantages and is likely to continue to dominate the processing of liquid food. Spray-drying also has the advantage of allowing the production of spherical particles, yielding a product with desirable flow properties without any need for grinding, milling, and size separation. Furthermore, spray-drying allows the coating of particles with another substance. The major disadvantages are a higher cost than in other air-drying techniques, and a greater thermal damage potential than with freeze-dehydration.

Instantized Powders

Much recent work has been devoted to processes for production of "instant" powders of various food substances prepared by spray-drying. "Instant" is usually taken to imply relatively rapid and complete dispersion in the dehydration liquid, which is almost invariably water or an aqueous solution and is often specified as *cold* water.

Mechanism of Dispersion of Powders, and Its Dependence on Powder Properties

The mechanism of reconstitution of powders is complex and not entirely understood. The following properties, however, are essential:

1. A large wettable surface;
2. Sinkability, of the powder to counteract its tendency to float on the rehydration liquid;
3. Dispersibility in small particles throughout the liquid.

In addition, it may be desirable to have resistance to sedimentation once dispersion is achieved.

The wettability depends on the total surface area of the powder and on surface properties of the powder particles. Figure 7 is a schematic representation of forces acting on a drop of liquid resting on the surface of a solid. The balance of forces results in the establishment of the contact angle shown in Figure 7; Equation 4 gives the ideal dependence of this angle on surface properties:

$$\cos\theta = \frac{\gamma_s - \gamma_{s-L}}{\gamma_L} \quad (4)$$

where

- Θ is contact angle
- γ_s is free surface energy of the solid (in contact with air) ergs/cm²
- γ_L is free surface energy of the liquid (in contact with air)
- γ_{s-L} is interfacial free surface energy between solid and liquid.

Wetting of a solid by a liquid as shown in Figure 8 will occur when the spreading coefficient S shown in Equation 5 is positive:

$$S = \gamma_s - \gamma_{s-L} - \gamma_L \quad (5)$$

Spreading coefficient S is related to the contact angle by Equation 6:

$$S = \gamma_L (\cos \Theta - 1) \quad (6)$$

and is positive only when $\Theta = 0^\circ$. Hence, one of the requirements for wetting is a zero contact angle. Inspection of Equation 5 shows that the spreading coefficient can be increased by increasing γ_s , which in practical terms means increasing the *polarity* of the particle surfaces.

In real food materials, inadequate surface polarity normally results from free fat located on these surfaces. The counteracting measures involve the addition of surfactants such as *emulsifiers*, and the usual materials used in food powders are *lecithin* and synthetic emulsifiers, when permissible. Pintauro¹⁸¹ has prepared a compilation of patents for instantized food processes, including addition of surface active agents and emulsifiers. The other possibility evident from Equation 5 is to lower γ_L , the surface tension of the rehydration liquid. Addition of wetting agents to the powder

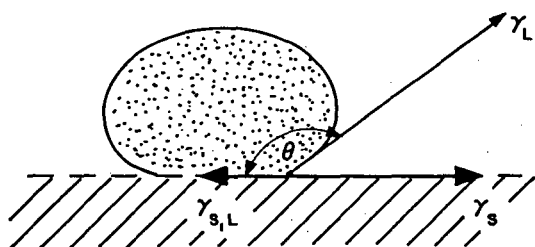


FIGURE 7. Contact angle of a liquid drop on a solid surface.

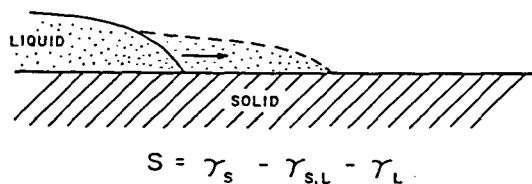


FIGURE 8. Spreading of a liquid on a solid surface.

may accomplish this aim if they rapidly dissolve in the rehydration medium and do not otherwise impair the powder properties. We have noted previously the work of Tamsma et al.²¹⁰ who observed improved dispersibility of spray-dried powder containing 0.1% of added surface active agents.

Assuming that the polarity of the powder surface is as high as possible, the other obvious course would be to increase the internal surface area by making the particles small. However, this does not work. When particles become very small, wetting is greatly impaired and the particles tend to clump together. Sticky clumps, wet outside and dry inside, are created by this system of incompletely wetted powder and entrapped air. This problem can be minimized by sinkability, a tendency for the particles to penetrate into the liquid, and to stay there.

In practice, the industry has achieved instantizing by a combination of surface treatment mentioned above (e.g., addition of lecithin) and *agglomeration*.

In agglomerated products, the individual, very small particles are fused into much larger aggregates in which the points of contact between the particles are so few that practically all of their surface area is available for wetting; they are stable enough, however, to assure that the particles will not clump on exposure to the rehydration liquid, but will break only after each particle is well surrounded by the rehydration medium. Samhammer¹⁹⁶ presents good macro- and micro-photographs of the structure of agglomerated *milk* and of the process of reconstitution in agglomerated milk powders.

Pisecky and Westergaard¹⁸² reviewed the manufacture of instant *whole milk* by agglomeration and addition of lecithin to improve wettability. They concluded that instant milk powders should form agglomerates of 100 to 250 μm with

few if any unagglomerated particles. The desired density of the particle is 1.2 g/cm^3 .

Properties of instantized *flour* are reviewed by Miller et al.¹⁶⁶ They show scanning electron micrographs of instantized flour, and discuss results of physical measurements. The agglomerate size in the instantized flour is predominantly 100 to 250 μm , compared to the original flour with most particles measuring less than 150 μm . The wettability, flowability, and oil-binding characteristics of the instant are superior to those of untreated flour.

Ulrich²²⁰ discusses instantized *sugar* and other instant powders and notes the poor "wettability" of particles smaller than 50 μm ; he notes also that the internal surface area of agglomerated (instant) sugar is high (bulk density of 450 kg/m^3 compared with 850 to 900 kg/m^3 for normal sugar).

The technology and properties of agglomerated *instant coffee* are discussed by Wuellenweber.²³² Properties of other products are mentioned in the patents compiled by Pintauro.¹⁸¹

Technology of Instantizing

Instant powders can be produced by one of the following types of processes:

1. incorporation of surface-active materials in the feed to improve wettability. This procedure, usually only partially effective, has been discussed previously.

2. increase in the porosity of individual particles produced by dehydration, rather than agglomeration of dense particles produced by spray-drying. The two major processes in this respect are freeze-drying, which is discussed in a subsequent section, and foam-drying, which has recently been covered thoroughly by Hertzendorf and Moshy.¹⁰⁵ It will not be reviewed here, except for noting that the process for the foam-drying of whole milk, developed by Eastern Regional Labs, is continuing to be evaluated by that group with encouraging results.²⁰¹

3. coating of particles with additives that increase wettability. These procedures often are combined with agglomeration and require close control of conditions under which the wetting agent is added to the dry or partially rewetted particles.¹⁸¹

4. primary particles may be imbedded in a substrate that is soluble in rehydration liquid but keeps individual particles separated during the

initial contact with water, thus achieving good rehydration.²²⁰

5. agglomeration. Agglomeration, the effect of which is discussed above, is the major method for preparation of instant powders. The agglomeration has been accomplished in some systems by a single step, that is, the conditions of dehydration in the spray drier could be varied to produce spontaneous agglomeration of the particles.¹⁸¹ In the most common processes, however, spray-dried powder is rewetted, the degree of this rewetting being carefully controlled; the particles are brought into contact and allowed to grow into aggregates; the aggregates are then redried, cooled, and separated by size.

The processes for the instantizing of milk powders have been developed in the U.S. by several different companies, and have been well treated in other reviews.²²⁰ They vary primarily in the type of equipment used in each step of the general process. For instance, the humidification necessary for surface rewetting may be conducted on free-falling particles by exposure to low pressure steam jets, or the particles may be air blown into a chamber and exposed to a controlled amount of steam there, or slightly superheated steam or an air-steam mixture may be allowed to pass through a fluidized bed. Subsequent drying, and the period of time during which the particles are contacted with each other in the turbulent air stream, may also vary from process to process. Most of the processes developed for milk can also be applied to other spray-dried particles, including sugar-containing mixtures.²²⁰ Each product, however, may require specific modification of equipment and procedures. Thus, in a recent review of agglomeration technology in processing of instant coffee, Wuellenweber²³² points out the difficulties in agglomeration. Coffee powder contains solubles that form a matrix that reaches a sticky point at 50°C when relatively dry. However, the sticky point of all amorphous food substances depends on moisture content, as shown diagrammatically in Figure 9; when rewetting takes place, it is essential that the moisture content be high enough so that the particles form a strong agglomerate, and yet not so high that extensive particle fusion and caking occurs. According to Wuellenweber, the process developed by his company produces a highly satisfactory coffee agglomerate by fulfilling the following criteria: it

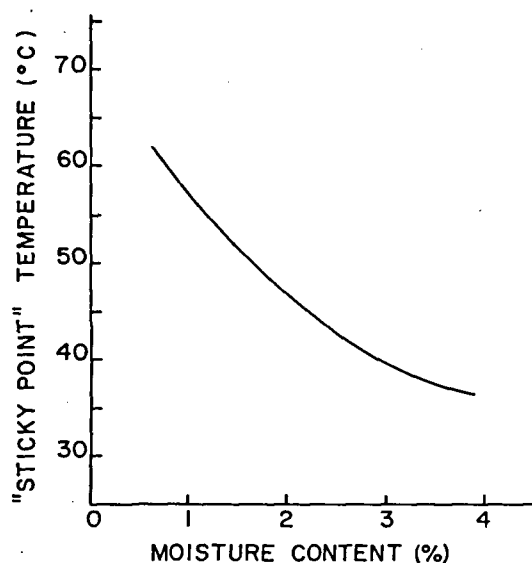


FIGURE 9. Dependence of the sticky point on moisture content in a typical dehydrated fruit powder.

operates at low temperatures, and involves gentle redrying; the time of contact between the rewetted particles is carefully controlled at levels above free-fall times; the amount of added moisture is maintained at the optimal level, so over-setting is avoided; and the procedure is designed to avoid contact between moisture and wall surfaces.²³²

The "agglomeration bloom" in the coffee industry is a controversial subject. Some industry critics believe that there are no good technical reasons for agglomeration of spray-dried coffee, and that the trend to agglomeration is a large-scale "sales gimmick" that is prompted by "a race to imitate the excellent flavored freeze-dried coffee with a particle size of the same appearance in order to fool the public."²³⁰ Others feel that conversion to agglomeration procedures is feasible only for the large processors, and that the advertising push for the agglomerates is in fact an attempt to "force the small processor out of business."²³⁰ The freeze-drying of coffee will be discussed later, but it may be noted here that doubts have also been expressed concerning real technical advantages of commercial freeze-dried coffees, in spite of a substantial consensus among experts that freeze-dried instant has superior flavor.

Drum-Drying

In drum driers, a layer of wet material is deposited on the surface of one or more revolving, steam-heated drums. Drum driers are characterized by the capability for very high rates of heat transfer, with overall heat transfer coefficients greater than $300 \text{ BTU} \times \text{hr}^{-1} \times \text{ft}^{-2} \times ^\circ\text{F}^{-1}$ for low-viscosity fluids, permitting dehydration at high temperatures. For most foods the achievable drying rates are much lower, but still can exceed the rates attainable in other equipment. A disadvantage of drum-drying is the potential for heat damage to food products, although short residence times and operation at reduced pressure can lessen this danger.

Spadaro et al.²⁰⁵ provided an excellent review of fundamentals of drum-drying and of the status of development of applications in the U.S. Fritze⁸⁶ has provided a good review of applications with examples referring to starchy materials, and with an emphasis on European industrial literature. The following features characterize progress in drum-drying:

1. The dependence of drying rate on operational characteristics and on properties of the drying material is now reasonably well understood, and the operation can be optimized. The production rate has been found to be proportional to the ratio of initial to final solids contents and inversely proportional to the film thickness raised to the 0.3 power. Since retention time on the drum is proportional to film thickness raised to the 1.3 power, drying rate decreases rapidly as retention time increases. However, other conditions being constant, the final moisture content decreases with increasing retention time. A high rate of production combined with a low moisture content can be achieved by operating at a high temperature. The maximum drying rate is often limited by the temperature tolerance of the specific product.

2. Relatively high drying rates can be achieved; Spadaro et al.²⁰⁵ note drying rates ranging up to $2 \text{ to } 3 \text{ lbs H}_2\text{O} \times \text{hr}^{-1} \times \text{ft}^{-2}$ for sweet potatoes dried to moisture contents as low as 1 to 2%.

Fritze⁸⁶ shows examples of how operational variables can be adjusted to minimize damage to the drying material and still maintain a good drying rate. For instance, in the case of milk concentrate, the solubility of the resulting powder

was only 80% when the drum drier was operating at a steam pressure of 4 kg/cm² (56 psi) and feed temperature of 40°C (104°F); solubility increased to 98%, however, when the feed temperature was decreased to 10°C and steam pressure to 3.5 kg/cm² (49.7 psi). In both cases the production rate was 4 lbs/ft²/hr, corresponding to almost 5 lbs of water removed/ft²/hr. Commercial drum-drying equipment with controlled temperature air flow directed at specific zones of the drum is available.¹⁷

The present applications of drum-drying in the food industry are limited. Milk products are no longer dried this way, primarily because spray-drying yields a more acceptable product. Some potato flakes are being drum-dried in the U.S. as well as in several other countries, and they are considered highly acceptable. The largest food application at present is the production of readily rehydratable cereal products for use in baby cereals and other so-called "instant" products. Applications to various vegetables and fruit have been suggested, and processes have been developed by various laboratories here and abroad but commercial realization is still lacking.²⁰⁵

Fritze⁸⁶ considers drum-drying the method of choice for yeast grown on industrial waste streams. The author's colleagues at M.I.T. have evaluated processing of single-cell protein grown on petroleum and on other sources, and they consider drum-drying the most likely method for dehydration of these cells.

The major advantages of the process are still its low cost (Spadaro et al. estimated it at 0.8¢/lb water removed), high throughput, and ability to operate continuously; the major disadvantage is the potential heat damage.

Other Developments

Most of the other significant developments in dehydration methods other than freeze-drying have been covered in recent reviews. Foam-drying and puff-drying were covered by Hertzendorf and Moshy.¹⁰⁵ Fluidized bed drying was discussed by Holdsworth,¹⁰⁷ and in recent monographs Bergougnou et al.,¹⁹ Vanecek et al.,²²⁵ and most recently Brown et al.³² published a comprehensive report on their studies using a centrifugal fluid bed. Microwave-drying is well reviewed by Decareau.⁴⁹ We shall discuss osmotic dehydration and related developments later, along with intermediate-moisture foods.

Vacudry Company in Emeryville, California, obtained patents on vacuum dehydration of foods, with heat transfer through a liquid medium, preferably edible oils.⁵⁰ At present, however, this process has not reached large-scale utilization.

Some attention has been given in the literature to solvent-drying of foods, in combination with vacuum. Ethyl acetate has been suggested by Sun Oil Co.,⁶ and two-stage drying using hydrocarbon is the subject of the patent by Toussaint.²¹⁶ Recently, other solvent systems were investigated.¹⁰⁶

Isopropanol extraction of fish with subsequent solvent removal forms the basis of the Bureau of Commercial Fisheries, Fish Protein Concentrate Process and apparently has the potential for preparation of satisfactory food grade powder.⁶⁷

FREEZE-DEHYDRATION

The critical review by King¹²³ continues to be recognized as the definitive review of heat and mass transfer aspects of water removal, and volatile retention in freeze-dehydration. The present section is based on the assumption that the interested reader will consult the work of King as well as the present article. This review will therefore concentrate on recent developments and on presentation of points of view that are most likely to further amplify King's paper.

Partial Pressure of Water over Frozen Systems

In freeze-dehydration, water is removed from foods by transfer from solid state (ice) to gaseous state (water vapor); it can only be accomplished when the vapor pressure and temperature of the ice surface at which the sublimation takes place are below those at the triple point (4.58 torr and a temperature of approximately 32°F). The relationship between the vapor pressure of ice and its temperature below the triple point is shown in Figure 10. Partial pressure of all water in foods containing ice crystals must, in theory, be equal to the vapor pressure of this ice, if an equilibrium exists; the diagram in Figure 10 then represents the vapor pressure of water in frozen foods as a function of temperature, given the existence of an ice phase. Actual measurements of vapor pressure over frozen cod, conducted by Storey and Stainsby,²⁰⁸ agreed with this rule, but Dyer et al.⁵⁵ reported lowered pressures in frozen beef, attributing this phenomenon to interactions with

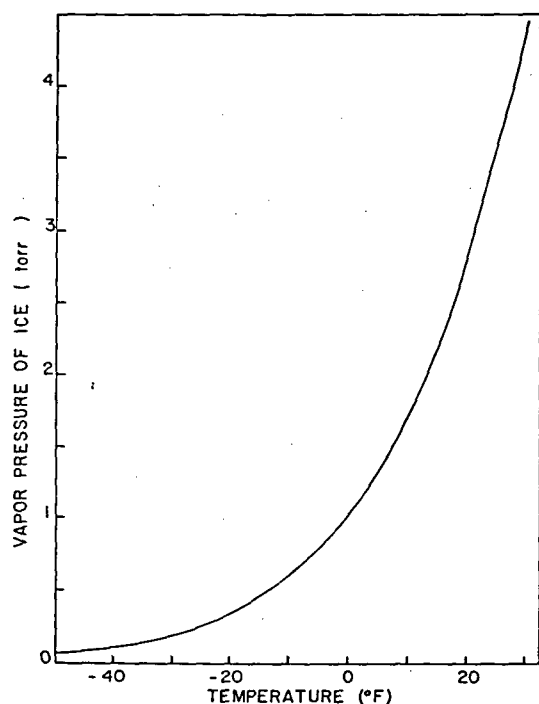


FIGURE 10. Vapor pressure of ice.

proteins. Recently this author visited several European laboratories conducting research in this field and was informed of recent research that indicates that the partial pressure over partially frozen solution and frozen foods is indeed lower than the vapor pressure of ice at the same temperature. In a convincing experimental demonstration, two tubes, one containing water and the other a physiological salt solution, were placed in the same constant-temperature enclosure and allowed to freeze and equilibrate. The headspaces over each substance were then connected, and a *continuing* transfer of vapor from the ice to the frozen salt solution was observed, indicating a pressure difference between the two tubes.¹⁹⁴ In conversations the author held with several leading researchers in the field of freeze-drying systems, no good theoretical explanation could be advanced. If the attempted explanation is based on inclusion of vapor pressure-depressing solute within the ice crystal structure, then the amount required would be quite high, and this contradicts the experimentally observed separation of quite pure ice crystals by freeze concentration.²¹² Recent results^{119,140} obtained by the author and co-workers with a system of water and 1% butanol indicate that the alcohol is entrapped in

ice in interdendritic spaces, and in pores and cracks; but this type of entrapment should not influence the vapor pressure of the ice.

Mass and Heat Transfer in Freeze-Drying

General Considerations

Every pound of water being sublimed at the ice surface must be transported away from this surface, and will require the supply of energy corresponding to its latent heat of sublimation (ΔH_s). Hence, freeze-drying involves both mass transfer and heat transfer, and the rate of drying depends on the magnitude of resistances to these transfers. Figure 11 shows a schematic representation of the process and of the resistances to mass and heat transfer. Thus, the rate of sublimation is given by:

$$G = \frac{A(p_i - p_c)}{R_d + R_s + K} \quad (7)$$

where

G = rate of sublimation

R_d = resistance of the "dry" layer in the food

R_s = resistance of space between food and condenser

K = constant

p_i = partial pressure of water at the ice interface

p_c = partial pressure of water in the condenser

A = drying area.

The ideal distribution of moisture during sublimation appears in Figure 12A. There is an interface at which the moisture content drops from the initial level (m_0) in the frozen layer to

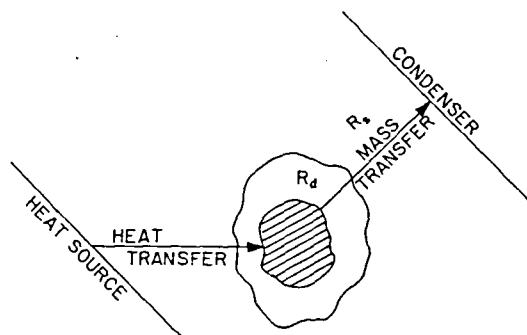


FIGURE 11. Schematic representation of heat and mass transfer resistances in freeze-drying.

the final level of the dry layer (m_f), which in turn is determined by equilibrium with partial pressure of water (p_s) in the space surrounding the dry layer. The actual process is represented more accurately by Figure 12B which shows the existence of some gradients in the "dry layer." The figure shows the presence of a "transition region" in which there is no longer any ice, but in which the moisture content is still substantially higher than that of the dry layer (m_f). Recent

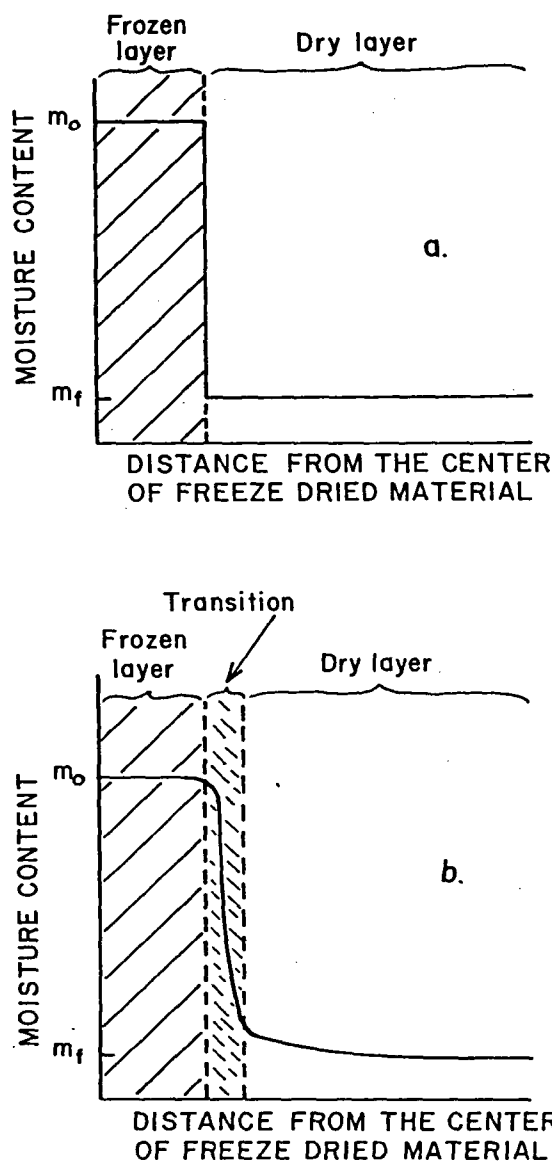


FIGURE 12. Schematic representation of the moisture gradient in freeze-drying material: a. idealized gradient, b. probable gradients occurring in freeze-drying.

detailed studies on this transition layer show it to be relatively narrow, and the assumption of uniformly receding interface of zero thickness does not lead to large errors in the engineering analysis of sublimation.^{1,2,3}

The temperature and moisture gradients in the food being freeze-dried depend strongly on the drying layer's properties, which are partially "set" during freezing. For instance, if solute migration is possible during freezing, an impermeable film that substantially lowers drying rate can form at the surface.^{2,3,5} Such a film may be removed mechanically, or it can be prevented by slush freezing. Slow freezing produces bigger crystals, hence usually bigger pores and better mass flow during drying and reconstitution if solute migration and film formation are prevented. The beneficial effect of slow freezing on mass transfer rates is often offset by the structure's collapse if the frozen layer temperature is too high.

Ideally, the vapor flows through the pores and channels left by ice crystals. If freezing produces isolated ice crystals surrounded by a solid matrix, however, the vapor must diffuse through the solids (Figure 13). A similar situation results if the matrix collapses at the ice front and seals the channels. However, the matrix can be cracked, particularly in rapidly frozen systems.

Collapse often occurs at a fixed temperature close to recrystallization temperature,^{1,6,11,15,3} when the matrix is sufficiently mobile to allow flow under the influence of various forces. Collapse temperatures for several solutes are shown in Table 9. Freezing causes a separation of the aqueous solutions into a two-phase mixture of ice crystals and concentrated aqueous solution.

TABLE 9

Collapse Temperatures for Different Solutes

Solute	Collapse Temperature (°C)		
Sucrose	-25 ^a	-32 ^b	-22 ^c
Glucose	-40	-40	-40.5
Lactose	-19	-31	-21
Dextran	-2	-10	—
Orange juice	—	—	-20
NaCl	-22	—	—
Coffee	—	—	-20

^aIto (1971).^{1,11}

^bMacKenzie (1966).^{1,5,3}

^cBellows (1972).^{1,6}

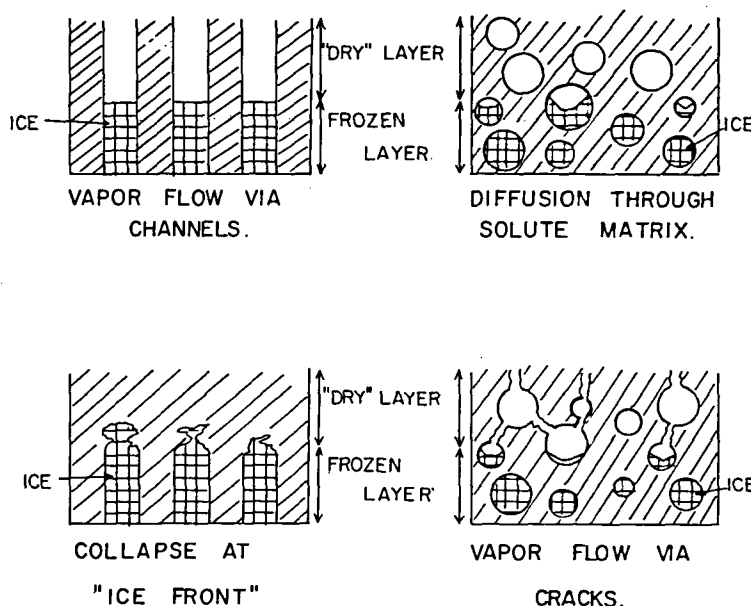


FIGURE 13. Representation of types of vapor flow in freeze-drying.

The properties of the concentrated solution depend on temperature, concentration, and composition. If drying is conducted at a very low temperature, then mobility in the extremely viscous concentrated phase is so low that no structural changes occur, and the final structure consists of pores in the locations that contained ice crystals, surrounded by dry matrix of insoluble components and precipitate compounds originally in solution. If, on the other hand, the temperature is above a critical level, mobility in the concentrated aqueous solution may be sufficient to result in flow and loss of the original separation and structure. Some typical temperatures of the frozen layer occurring in freeze-drying processes are shown in Table 10.

Both temperature and moisture gradients exist in the drying materials during freeze-drying and the mobility, and therefore collapse, of the concentrated solutions forming the matrix may vary from location to location. Mobility of an amorphous matrix depends on moisture content as well as temperature; hence collapse can occur at areas other than the ice surface (Figure 14).

Analysis of Heat and Mass Transfer Processes during Freeze-drying

The process of heat and mass transfer through the dry layer is thoroughly reviewed by King,¹²³

and additional recent studies have confirmed his analysis. Hatcher et al.¹⁰⁰ measured moisture and temperature distribution in freeze-drying beef at 1 torr. They confirmed the existence of a sharp transition layer. Solutions for rate of sublimation drying with heat supplied by radiation were recently presented by Cho and Sunderland,⁴³ Dyer and Sunderland,⁵⁶ and McCulloch and Sunderland,¹⁵⁹ and extended to the mixed radiation and conduction heating by Hatcher and Sunderland.⁹⁹

Mellor and Greenfield⁶⁴ analyzed cyclic-pressure freeze-drying in a product whose heat and mass transport occurred via the dry layer. They used simulation of cyclic-pressure drying by numerical solution of the pertinent equations for pressure distribution in the "dry" layer and for temperature distribution in both the "dry" and the frozen layer; they concluded that: cyclic pressure drying gives increased rates of sublimation, and condenser design for cyclic processes requires special consideration.

Freeze-dehydration of liquids, and of solids capable of intimate contact with a heating surface, can be accomplished with heat transfer through the frozen layer. Practical systems include the tubular drier invented by Seffinga, as well as several other patented procedures.¹⁷⁴

TABLE 10

Frozen Layer and Maximum Dry Surface Temperatures in Typical Freeze-drying Operations Conducted with Heat Input Through the Dry Layer

Food material	Chamber pressure (torr)	Maximum surface temperature (°F)	Frozen layer temperature (°F)
Chicken dice	0.95	140	-4
Strawberry slices	0.45	158	5
Orange juice	0.05-0.1	120	-45
Guava juice	0.05-0.1	110	-35
Shrimp	0.1	125	-20
Shrimp	0.1	175	0
Salmon steaks	0.1	175	-20
Beef, quick frozen	0.5	140	7
Beef, slow frozen	0.5	140	1

POTENTIAL "COLLAPSE" IN THE "DRY" LAYER.

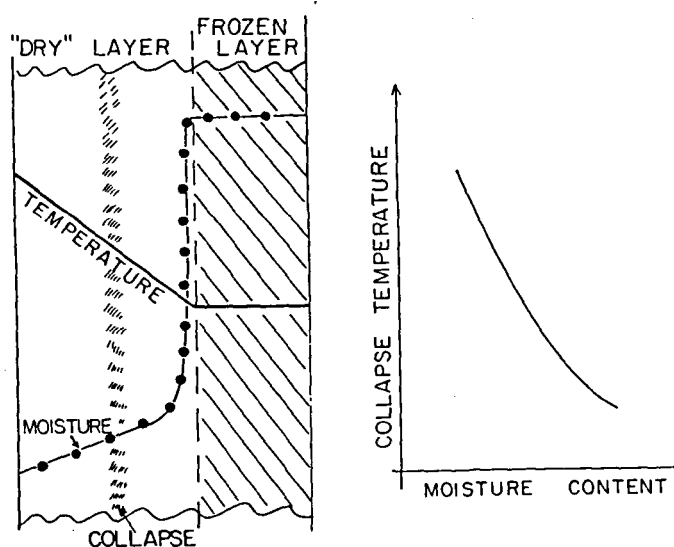


FIGURE 14. Potential collapse of structure in the partially dry layer of freeze-drying materials.

When heat transfer occurs through the frozen layer, the balance between ease of heat transfer and ease of mass transfer changes continuously, with mass transfer becoming more difficult as drying progresses (longer path through the dry layer) and heat transfer becoming easier (shorter path through the frozen layer). The resistance of the frozen layer to the transport of heat is, in any case, not formidable, with the thermal conductivities often as high as $1.0 \text{ BTU} \times \text{ft}^{-1} \times \text{hr}^{-1} \times ^\circ\text{F}^{-1}$, and therefore as much as two orders of

magnitude higher than the thermal conductivities of the dry layer. As a consequence, theoretically calculated averaged drying rates with heat input through the frozen layer often exceed those attained with heat transfer through the dry layer. The drying rate of materials dried with heat transfer to the frozen layer surface could be greatly increased by continuously removing most of the dry layer, perhaps with a rotating knife or other scraping device (as suggested by Greaves).⁹¹ The improvement theoretically achievable by this

method of minimizing mass transfer resistance is evident from the calculated drying rates of a

hypothetical slab of one inch thickness, with the following properties and drying conditions:

dry layer permeability = $2 \times 10^{-2} \text{ lb} \times \text{hr}^{-1} \times \text{ft}^{-1} \times \text{torr}^{-1}$
 chamber pressure = 0.05 torr
 dry layer thermal conductivity = $5 \times 10^{-2} \text{ BTU} \times \text{hr}^{-1} \times \text{ft}^{-1} \times \text{torr}^{-1}$
 frozen layer thermal conductivity, $k_f = 1.0 \text{ BTU} \times \text{hr}^{-1} \times \text{ft}^{-1} \times \text{torr}^{-1}$
 dry bulk density = 20 lb/ft^3
 initial moisture = 2.5 lb water/lb solids
 final moisture = 0.05 lb water/lb solids
 latent heat of sublimation = 1200 BTU/lb
 maximum permissible surface temperature = 125°F.

Data calculated for this slab are shown in Figure 15 which compares drying rates for heat transfer by conduction through the dry layer (from two faces of the slab) with three different cases of conduction through the frozen layer. It should be noted that drying is complete when the dry layer thickness reaches 0.5 inches in the case of conduction through the dry layer, but the dry layer thickness must equal 1 in. for heat to

transfer from the "backface." In the particular example chosen here, the drying times would be as follows:

1. Heat transfer by radiation = 8.75 hr
2. Heat transfer by conduction to backface of slab with wall at 10°F = 13.5 hr
3. Same as 2 (above) but wall at 28°F = 7.2 hr
4. Same as 2 (above) but dry layer removed continuously = 4.0 hr.

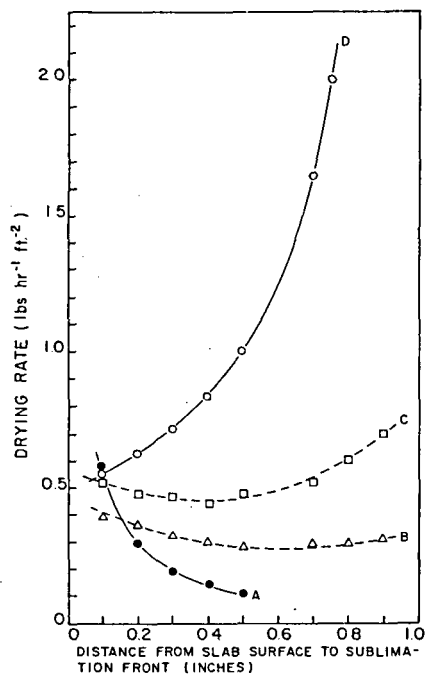


FIGURE 15. Drying rate for hypothetical slab with properties specified in text: A. Heat transfer by radiation to two faces of slab. B. Heat transfer by conduction to "backface" of slab. Wall at 10°F. C. Heat transfer by conduction to "backface" of slab. Wall at 28°F. D. Heat transfer by conduction to "backface" of slab. Wall at 10°F, dry layer removed continuously.

The limitations on heat transfer rates in conventionally conducted freeze-drying operations have led early to the attempt to provide *internal heat generation* through microwave power.

Theoretically, the use of microwaves should result in a highly accelerated drying rate, because the heat transfer does not require internal temperature gradients, and the temperature of ice could be maintained close to the maximum permissible for the frozen layer, without the need for excessive surface temperatures. If, for instance, it is permissible to maintain the frozen layer at 10°F, then the drying time for the 1 in. slab described in the preceding section would be 1.37 hr for an ideal process using microwaves.

It should be noted that this drying time compares very favorably with the 8.75 hr required when heat input was through the dry layer, 13.5 hr when heat input was through the frozen layer, and even with the relatively short drying time of 4 hr when the dry layer was continuously removed. In laboratory tests a 1 in. thick slab of beef was freeze-dried in slightly more than 2 hr, compared with about 15 hr for conventionally dried slabs.¹⁰⁸

In spite of these apparent advantages, the application of microwaves to freeze-drying has not

been successful. The major reasons for the failures are the following:

1. Energy in the form of microwaves is very expensive. A recent review estimates that one BTU supplied from microwaves may cost 10 to 20 times more than one BTU supplied from steam.⁹²

2. A major problem in application of microwaves is the tendency to glow discharge, which can cause ionization of gases in the chamber and deleterious changes in the food, as well as loss of power. The tendency to glow discharge is greatest in the pressure range of 0.1 to 5 torr and can be minimized by operating the freeze driers at pressures below 50 microns. Operation at these low pressures, however, has a double drawback. First, it is expensive, primarily because of the need for condensers operating at a very low temperature, and second, the drying rate at these low pressures is much slower.

3. Microwave freeze-drying is very difficult to control. Since water has an inherently higher dielectric loss factor than ice, any localized melting produces a rapid chain reaction that results in "runaway" overheating.

4. Economical microwave equipment suitable for freeze-drying on a large continuous scale has not yet been made available.

In view of all of the above limitations, microwave freeze-drying is at present only a potential development.

Research on Mass and Heat Transfer Properties and on Structure of Freeze-dried Materials

A major area of research in the area of freeze-drying is the laboratory study of the structure and properties of freeze-drying materials. Several important lines of inquiry should be mentioned here.

The rate of drying depends strongly on the heat and mass transfer properties of dry and partially dry food materials. Recent work has contributed additional data and correlations. Among recent studies on heat transfer properties of food materials are those of Fito et al.⁶⁸ who studied thermal diffusivities of food-related materials, that of Leric¹⁴⁵ who determined heat transfer in freeze-drying food gels, and that of Petree and Sunderland¹⁸⁰ who studied thermal radiation properties of freeze-dried meats. Several laboratories have investigated relationships between

mass transfer properties and methods of pretreatment of freeze-dried materials. King¹²³ reviewed the influence of muscle fiber orientation (in poultry), of freezing rate, and of other process variables on the water diffusivity in freeze-dried foods.

Among the more recent work on mass transport in freeze-drying, the paper of Massey and Sunderland¹⁵⁶ deals with fundamental analysis of mass flow in specific geometries of freeze-drying materials. Several laboratories continue research in the relations between the internal structure of materials and their mass transfer properties. At the University of Dijon in France, for instance, studies are progressing on relations between microscopically determined internal structure and porosity,²⁴ and at the Technical University of Karlsruhe, Germany, and in Massy, France, Professor Loncin is supervising research on fundamental aspects of diffusion in porous solids. The Nestle research group recently published some of its fundamental studies on vapor transfer during freeze-drying and internal surface areas of freeze-dried substances.^{26,93} Researchers at M.I.T. and others have been concerned with water transport and volatile transfer in drying, and this last aspect will be discussed later.

A particularly exciting aspect of research on the structure of freeze-dried materials is the use of microscopic techniques — light microscopy, electron microscopy, and scanning electron microscopy. The author and co-workers have used microscopy to study freeze-dried carbohydrate solutions^{73,119} and recently have begun extensive research using a freeze-drying microscope in which events during drying itself can be observed, filmed, or displayed on a TV screen. The technique of freeze-drying microscopy that was pioneered by MacKenzie¹⁵² and Rey¹⁹⁰ has been adapted by several laboratories in the U.S. and abroad. Recently Chauffard⁴⁰ published photographs obtained with the Nestle's freeze-drying microscope in Vevey, Switzerland, and an improved temperature gradient microscope stage is described by Freedman et al.⁸⁴

Atmospheric freeze-drying

Freeze-drying can be conducted at atmospheric or other pressures in excess of 4.5 torr provided that the partial pressure of water remains low enough. The King review¹²³ covers work done in the 1960's on this process. A more recent paper is

that of Heldman and Hohner,¹⁰⁴ who analyzed atmospheric processes for foods and developed mathematical models describing atmospheric freeze-drying. Investigating the influence of various factors on the drying process, they found that in beef the transport of heat was primarily by conduction through the solid matrix, and that the process could best be speeded up by reducing the size of the particles and by increasing the surface mass transfer coefficient. The drying of food solids in atmospheric freeze driers is currently limited by the very small piece size that allows an economic drying rate, and by heat sensitivity of the frozen layer of many products (in atmospheric freeze-drying, in contrast to most vacuum freeze-drying, the limiting temperature is not the surface temperature, but the collapse temperature of the frozen layer). An interesting application recently presented at a meeting of the A.I.Ch.E. is atmospheric freeze-drying of cigarette tobacco.¹ The purpose of the process is to decrease bulk density.⁷

Sonic wave improvement of a nonvacuum freeze-drying process was reported by Moy and Dimarco,¹⁷⁰ and combined freeze-drying, and air-drying was the process used for dehydration of potatoes in a recent patent.²⁰⁴

Process Developments in Freeze-Drying *Status of Industrial Applications*

During the 1960's several industrial organizations explored freeze-drying for a variety of uses. Modifications and improvements have been described in patents and in scientific literature. Practically all plants of that period operated on the batch principle, and involved prefreezing followed by vacuum-drying with radiant heat transfer, breaking of vacuum with nitrogen, and packaging in rooms whose humidity was maintained at a low level.

Of the various freeze-dried products that have been tried in markets of the U.S., Europe, and some other areas, freeze-dried coffee has certainly been the most successful, accounting for about 20% of the total instant coffee market in the U.S. in 1969 and 28% in 1970. It has been suggested that traditional spray-dried instant coffee will be replaced entirely by that prepared by freeze-drying and by agglomerated instant coffee, which resembles freeze-dried in density and particle size.²³¹

The major barriers to large-scale applications of freeze-drying have been cost, problems in the

storage stability of foods that are susceptible to oxidation, and losses of juiciness in foods derived from animal tissues. Another potential problem is loss of flavor components during drying. The first three problems were relatively less important to soluble coffee than to other foods. The raw material involved is sufficiently expensive to bear process costs, and the consumer accepts the relatively slight loss of quality incurred in storage. Improved processing overcame the problem of flavor losses, and a superior freeze-dried instant coffee is now enjoying a spectacular rise in popularity. This increased popularity has occurred in spite of an increased cost which can range up to 30% more per unit weight of dried coffee at the retail level.⁸

Application of freeze-drying to other products has been relatively slow. The following developments, however, merit recognition.

Eggs are being freeze-dried on a large scale by Affined Foods in Great Britain, and smaller quantities of vegetables, dairy products, and soup ingredients are freeze-dried elsewhere (Spicer, 1969).²⁰⁶ In the Far East, mushrooms are dried successfully. In Europe and Latin America, new plants are on stream for production of orange juice, as well as coffee.

In the United States, besides the expanding freeze-dried coffee markets, some activity is evident in the area of freeze-drying of components for the institutional market, and for governmental agencies, including the military. Although small in scale, a spectacular development in terms of publicity has been the application of freeze-dried items to space diets. The majority of entrees used on the Apollo flights were freeze-dried. These foods were selected for Apollo primarily because of their high nutritional quality, and good taste. An additional advantage of using freeze-dried foods in space flight is the reduction in weight of the food system whenever water is available from other sources. On Apollo, ample potable water was produced as a by-product of fuel cell operation.

The menu for the Skylab Space Research Program utilizes 68 foods of which 22 are freeze-dried. These include such diverse items as asparagus, salmon salad, strawberries, shrimp cocktail, chicken and rice, beef hash, peach ambrosia with pecans, spaghetti and meat sauce, and macaroni and cheese.¹⁸⁹ The forthcoming Space Shuttle Program will have ample quantities of potable water available from fuel cell opera-

tions. This program is, therefore, planning for extensive use of freeze dried food items. The Shuttle will have the capacity for carrying up to 10 passengers/scientists in a shirt-sleeve environment much like today's aircraft with first class food service. Work on high quality dehydrated and intermediate-moisture space foods for the Shuttle Program is now underway in several laboratories, including the author's.

The use of freeze-dried foods in military and space rations is paralleled by the limited, but growing, market for "backpack rations" for hikers, mountain climbers, and other civilian consumers desiring the "instant reconstitution" and stability of freeze-dried foods. A recent survey of such foods was published by Labrenz.¹³¹ Although it emphasized the menu planning aspects for the backpacker with diabetes, this extensive report on composition of various commercial items has a much broader significance. The items surveyed were marketed by the following companies: Wilson and Company, Recreation Equipment, Inc., Trail Chef, Oregon Freeze Dried Foods, Rich Moor Corporation, and Chuck Wagon Foods. The list of available foods included various meat and fish items (beef, chicken, pork, tuna, turkey); a variety of salads; vegetables including beans, corn, and mushrooms; soups, and fruit.

Other commercial items appear from time to time, still with quite limited applications. Thus freeze-dried orange juice has been advertised;¹⁸³ freeze-dried peas continue to be packed by Erin Foods and marketed by H. J. Heinz Ltd.¹⁴¹

A completely different application pioneered by Flink and Hoyer⁷⁷ and Flink,⁷¹ the preservation by freeze-drying of water-damaged books and documents, received recent publicity in *Newsweek*.¹⁷²

Continuous Processing of Liquid Foods

The fact that production of freeze-dried foods is concentrated on a few items produced in relatively large volume has allowed the development of processes specifically tailored to the products being dried, with great improvements in economy and quality. Warman and Reichel have recently reviewed problems of adjusting specific steps to specific products.²²⁷

The present review will present only a few examples of such process modifications.

Processing of liquids prior to freezing — Solid food products may require various preparatory

steps such as cleaning, cutting, or grinding. Liquid products are equally demanding. The first consideration is the concentration to be used. Since freeze-drying is expensive, removal of a portion of the water by other methods may improve the economy. On the other hand, concentrated solutions may have a lower permeability of the dry layer, and may also have a different quality after drying. In addition, the concentration of solids in the feed also affects the bulk density of the freeze-dried product.

Where a low bulk density is desirable, but a concentrated feed is desired for reasons of economy, foaming prior to freezing may be practiced.

Preconcentration may be achieved by any of the usual methods, but where a very high quality level is to be maintained, freeze-concentration is best. Thijssen recently reviewed concentration processes for foods.²¹²

Prefreezing — Freezing of materials to be dried affects the quality very strongly indeed. As has been discussed, permeability of the dry layer depends on freezing rate; furthermore, an impermeable film may form at the surface of frozen liquids if solute is concentrated at the surface. This last effect can be eliminated either by slush freezing, or by mechanical disruption of the surface layer prior to drying; both practices are mentioned in patents and other industrial literature. Prefreezing greatly affects flavor retention and color of coffee.^{59,60}

An increasingly important method for prefreezing is the production of frozen granulate. The liquid is frozen to a consistency of soft ice or flakes, or of sheets of desired size, then hardened in a belt-, blast- or other kind of freezer. It is then reduced to the desired size by milling and sieving at a very low temperature.

Dehydration process — The most recent developments in industry show a trend toward continuous methods of drying. These methods are labor saving and therefore are economically superior; they are usually, however, designed with a specific product in mind and require a high initial investment. They are therefore employed when a specific type of application has been firmly established.

Not much information is available about continuous freeze-drying processes, especially those used in coffee production, since most successful installations have been custom built, or custom

modified, and operators are reluctant to publish details of their commercial installations. Equipment builders, however, are obviously interested in publication of features of their designs, and most published technical descriptions of continuous systems originate with specific equipment manufacturers. An excellent recent review is that of Pyle and Eilenberg,¹⁸⁶ who cover principles as well as some of the practice of continuous freeze-drying. Additional notable articles include: Lorentzen¹⁴⁸ on the Atlas continuous freeze-drier; Oetjen, Betterman and Eilenberg¹⁷⁸ who discuss continuous freeze-drying of plastics; Oetjen,¹⁷⁷ and Kessler¹²² who discuss the heat and mass transfer in beds of moving particles.

In the following, the author will discuss only the basic types of freeze-drying equipment being developed and applied; the reader is referred for details of available commercial units to the articles cited above.

There are two basic types of continuous driers: *tray driers*, in which the product is placed on trays that are continuously moved through the drier, and *dynamic* or *trayless* driers, in which particles of the product are moved through the drier.

Figure 16 shows a schematic diagram of a tray drier with semicontinuous operation. A bank of trays containing prefrozen product passes into an entry lock where the initial evacuation takes place. The trays are then moved to the next section of the drier, the first of two drying tunnels. It then passes in several discrete movements through the two tunnels, and into the exit lock where the vacuum is broken with inert gas. The entry lock and the two drying tunnels are equipped with heating platens, and the temperature program in

each section may be adjusted. The entry lock and the two drying tunnels are connected to two condensers each; only one condenser is used at a time, while the other is being defrosted; thus shutting down the operation for defrosting is avoided. A continuously operating vapor removal system is also possible.¹³⁰

Tray driers — Only some of the possible arrangements of tray driers can be mentioned here.

1. A single drying tunnel may be used with entry and exit locks accommodating only a single tray. The semicontinuous operation consists, then, of a series of discrete movements in which individual trays are moved in a predetermined pattern.

2. Individual sections of a multisection drying tunnel (as shown in Figure 16) may be operated at different pressures.

3. Condensers may be located within the drying tunnels with some arrangements allowing continuous or periodic defrosting of some of them. This arrangement is claimed to offer economical construction and operation.

4. The movement of the trays through the driers may be accomplished by any of several mechanical devices including rail carts, belts, and chains.

5. The continuous or semicontinuous operation may include the freezing and packaging steps, and even an associated continuous tray cleaning cycle.

6. The trays may be ribbed, pocketed, or otherwise structured to optimize heat transfer and material handling.

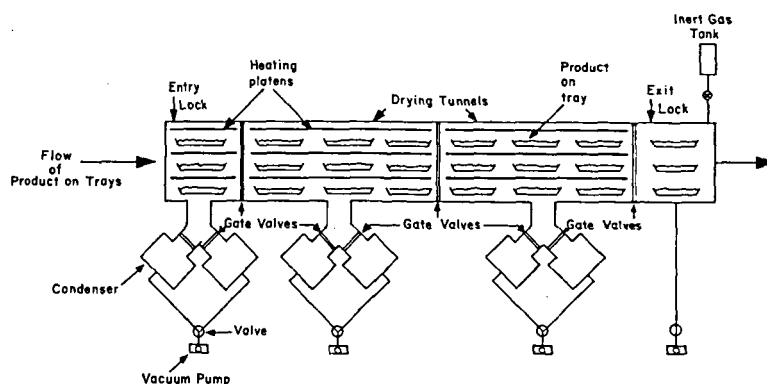


FIGURE 16. Schematic diagram of one type of continuous tray freeze-drier.

Finally, it should be noted that the continuous tray driers are closely related in their design to batch driers, and may, in fact, be composed simply of several modules, each of which is essentially equivalent to a batch drying unit.

Dynamic driers — There are many types of dynamic or trayless driers, including:

1. Belt freeze-drier (Figure 17).
2. Circular plate drier in which circular heater plates are arranged above each other with a rotating shaft in the center. The shaft has attached to it blades that gently move the product from one edge of the plate to the other edge, from which it falls to the plate below. By the time the product traverses the stack of plates, it is dry (Figure 18).

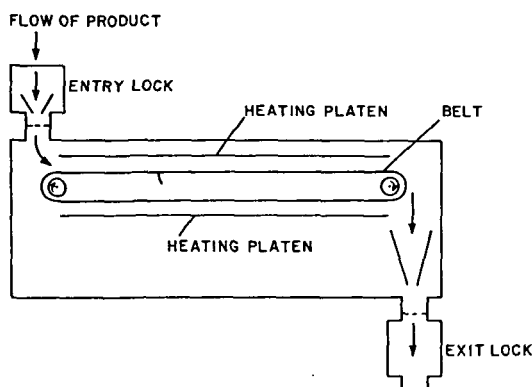


FIGURE 17. Schematic diagram of continuous belt freeze-drier.

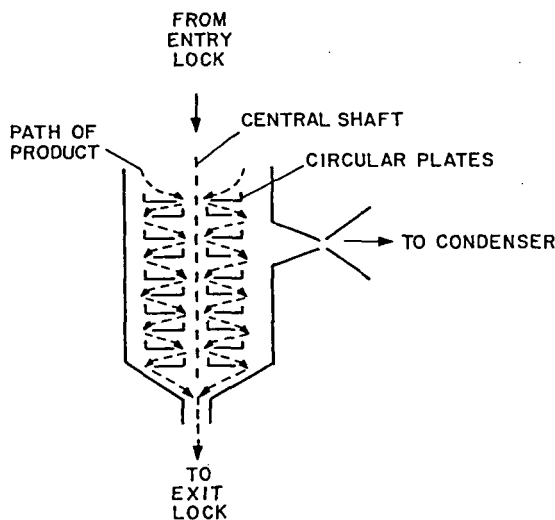


FIGURE 18. Schematic diagram of continuous circular plate freeze-drier.

3. Vibratory driers. The product is moved from plate to plate by oscillations of these plates, which may be horizontal or somewhat inclined to facilitate the transport. In some driers the vibrating plates are replaced by a spiral chute or by disc-shaped heaters. Since the residence time, rate of heat and mass transfer, and temperature and moisture profiles of the product all depend highly on the type of flow the product experiences, the design of vibratory driers is a very demanding subject, and has usually been undertaken with a specific product in mind.

4. Fluidized bed-drying and spray freeze-drying. With small particles, it is possible to conduct the drying operation while the particle is suspended in another fluid, which is usually air, nitrogen, and other gases. Industrial applications of these processes for freeze-drying in vacuum seem less likely than for high pressure dehydration.

In all continuous systems in which the particles of the product are subject to movement, the danger of excessive abrasion must be avoided. Process design and control is another aspect of current development. Simulation of continuous freeze-drying of egg was recently reported by Flink and Fosbol.⁷²

Other Freeze-dehydration Developments

Among the variety of developments reported in recent years, the following seem also to merit mention: freeze-drying of organic solutions and from nonaqueous solvents; compressed freeze-dehydrated foods; freeze-drying from nonaqueous solvents. Many materials, including vitamins and drugs, are partially or completely insoluble in water. Their preservation in a dry, readily dispersible state can, however, be achieved by freeze-drying from organic solvents. This technique was pioneered by Rey and co-workers,¹⁹¹ who claim several advantages for this process and for a further development that they call complex freeze-drying which results in interesting structures with intermingled impregnated compounds. Some of these structures exhibit new properties such as selective absorption and retention of volatile aromas. For example, the following complex system was described.¹⁹¹

A 5% solution of dextran in water was prepared and freeze-dried.

The porous cake was then impregnated by a 2% solution of polystyrene in benzol. The system was frozen and benzol sublimated away under vacuum.

The system was once more dipped into a solution of maltose in diethylamine. The whole was frozen and the solvent extracted by sublimation.

The result was a porous material having a main structure of dextran fibers enclosing substructures of polyethylene and maltose. This complex filter will retain certain substances and act as a selective screen. According to Rey,¹⁹¹ Nestlé patents cover these applications.

Freeze-drying of nonaqueous solvents and solvent mixtures opens large possibilities in the chemical industry for the preparation of fine chemicals, dyes and catalyzers. Interesting applications have already been found in the nuclear field, where controlled drying of low- and medium-activity radioactive wastes can provide adequate means to rid nuclear plants of the main stream of effluents.

Other applications include sublimation from liquid ammonia and carbon dioxide.

Compressed freeze-dried foods — The desire to minimize bulk and weight of military rations resulted in extensive research on compression of dehydrated food. U.S. Army Natick Labs have produced highly acceptable compressed food items. They have developed criteria for proper plasticizing of various items during compression, and techniques that allow the food components to spontaneously return to their normal appearance. Bars of compressed vegetables with a bulk density of 50 lbs/ft³ have been achieved.²⁹

Formulated compressed dehydrated foods have also been reported by the Australian military.⁶¹

RETENTION OF ORGANIC VOLATILES IN DEHYDRATED FOODS

The substantial retention of organic volatiles is often desirable (as in the case of flavor retention), but sometimes highly undesirable (as when solvents or other unwanted chemicals are entrapped). Thorough reviews on retention mechanisms have been recently presented by Thijssen²¹³ and King.¹²⁴ This review shall therefore be limited to describing the most recent work in this field, particularly in the area of retention mechanisms in freeze-dried foods.

The retention of selected compounds in dehydrate materials is often much higher than

expected from relative volatility. Table 11 compares the retention of pyridine in dehydrated coffee with retention predicted by various models. It is evident that all models underestimate retention.

Freeze-dried foods are generally dehydrated in a high-vacuum environment. Contrary to what one might expect, compounds of different vapor pressures do not have different volatile retentions. The retention of the organic volatiles is based largely on the properties of the solute that forms the amorphous matrix of the freeze-dried solid.

The retention of organic volatiles has been considered to result from surface adsorption of the volatile on the dry layer of the freeze-drying sample¹⁹² or from an entrapment mechanism that immobilizes the volatile compounds within the amorphous solute matrix.^{39,76,195,214} A simple experiment shows that the retention phenomena depend on local entrapment rather than adsorption.^{74,75} Maltose solutions were frozen in layers, some of which were volatile-containing, others, volatile-free. After freeze-drying, the layers were separated and analyzed separately for the volatile. The results (Table 12) show that volatile is retained in those areas where it was initially present. This experiment demonstrates that adsorption is not the major retention mechanism since volatile escaping from the lowest layer of

TABLE 11

Retention of Pyridine in Coffee Powder

	Retention (%)
A. Predicted from Theoretical Relations	
Raoult's Law	7.5
Volatility in infinitely dilute solutions, data of Thijssen ^a	0.01
Relation suggested by Sivetz ^b	5.0
Calculated using volatility determined experimentally for 0.01% aqueous solution at -20°C ^c	<10 ⁻⁵
B. Observed Retention	
Coffee powder ^b	50
Freeze-dried model (1% glucose) ^c	85
Freeze-dried model (1% starch) ^c	50

^aThijssen²¹³

^bSivetz and Foote²⁰⁷

^cFritsch et al.⁸⁵

TABLE 12

Results of "Layering" Experiments

	2-Propanol content after freezing		(g/100 g maltose) drying in layers	
	Before drying	After drying	Before drying	After drying
Top layer	0	0	4	2.52
Middle layer	0	0.05	0	0.05
Bottom layer	4	2.73	0	0.02

Sample A was not retained in large amounts on the upper dry layers. Furthermore, volatile retention is unaffected by the passage of water vapor through the volatile-free maltose layers, as shown for Sample B. In a companion experiment, sections of the freeze-dried cake were cut from a sample perpendicular to the mass transfer axis. Essentially uniform retention was observed for the whole sample, supporting observations that volatile retention is determined locally in the food and not by surface adsorption. The gross structure of the freeze-dried material is freely permeable to the flow of volatile from the lower freeze-drying levels, and the retained volatile is not located on the surface of the dry layer but within the amorphous solute matrix.

The physical aspects by which the volatile is entrapped within the amorphous solute matrix are only partially understood. Perhaps two mechanisms, selective diffusion²¹⁴ and micro-regions,⁷⁴ represent macro- and micro-views of the same basic phenomenon. The size of the entrapments is small since grinding and evacuation of the dry material do not release any volatile. Recently the size of the microregions has been shown to vary with, among other things, the solubility of the organic volatile in the aqueous solution. Retained hexanal (about 1 g hexanal per 100 g maltodextrin) freeze-dried from an aqueous 20% maltodextrin solution appeared under the optical microscope within the amorphous solute matrix as 2 to 6 μm droplets.⁷³ Concurring evaluations have been made with a scanning electron microscope. The numbers and sizes of droplets observed in the optical microscope for a series of *n*-alcohols qualitatively indicated that droplet size and number increased with alcohol molecular weight.

The addition of sufficient water to the dry material will cause volatile loss, the extent of which depends on the amount of water added and

the particular solute matrix, since water can disrupt and/or plasticize various hydrophilic substances composing food solids.

The importance of maintaining matrix structure has been further demonstrated by humidifying at reduced temperature; even after equilibration to high moisture contents, only an observable collapse of the solute matrix will cause volatile loss. Maintenance of the solute structure *during* freeze-drying is equally important to volatile retention.

The influence of frozen layer temperature on volatile retention during freeze-drying has been demonstrated recently by Thijssen,²¹³ Bellows,¹⁶ and Ettrup-Petersen et al.⁶⁰ They showed that if the ice-front temperature rises above the collapse temperature for the solute matrix, a sizable volatile loss occurs. This is due to the viscous flow of the solute matrix ("collapse") which results in the degradation of the matrix structure.

The influence of the freezing conditions has been noted by virtually every researcher studying volatile retention. Differences in solute phase separation and concentration, matrix pore size, and concentrated solute phase thickness, which are thought to be important in controlling volatile retention, result from variations in the freezing rate and final sample temperature. Slow freezing results in up to tenfold improvement of volatile retention compared to results from very rapid freezing.⁷⁸

Some recent investigations of the volatile-retaining properties of frozen materials have yielded results of different treatments of frozen aqueous maltodextrin solutions.^{119,207} Of particular interest was the partial hexanal loss resulting from exposure of the frozen solutions to activated charcoal under vacuum. This observation indicates that the volatile can be trapped in the frozen matrix as well as in the dry state.

Most recently Lambert, working with Flink and Karel, has studied 1-butanol loss from the frozen aqueous solution.¹¹⁹ When equilibrated at -10°C over activated charcoal in the presence of ice (to prevent water loss from the samples), only 25% of the butanol was lost. The remaining 75% was not removed even when samples were transferred to a desiccator that contained fresh activated charcoal. While the mechanisms for this retention in the absence of a solute phase are not fully understood, apparently ice crystals are fully capable of entrapping organic volatiles, though this entrapment cannot persist through any freeze-drying process.

Retention of organic volatile compounds in the freeze-drying process depends on the control of processing steps. The first step is the formation of the concentrated solute phase during freezing; control of this step gives a solute matrix structure capable of retaining volatile. To maintain this structural arrangement in the frozen sample at high moisture contents, the temperature must be kept below the collapse temperature during freeze-drying. After drying, the volatile-containing sample will be stable over a wide range of temperatures, but the sample moisture content must still be controlled.

Most of the research conducted by the author's group and Thijssen's group has been concerned with interactions between carbohydrates and various volatiles in which these carbohydrates are insoluble. Recently, the author and co-workers have initiated research using polyvinylpyrrolidone (PVP) solutions containing C^{14} -labeled 1-propanol. PVP is a polymer soluble in propanol, and the retention of this alcohol shows some similarities and some differences when compared with retention of alcohols in carbohydrates.^{41,42} Carbohydrate systems and PVP show similar effects of freezing rate (Table 13). Table 13 presents a comparison of propanol retained in freeze-dried PVP systems and retentions observed previously with freeze-dried carbohydrates. In both types of systems, slow freezing results in higher retention. The fraction retained was considerably higher at low absolute concentrations of the alcohol. Finally, the results show that both polymeric systems, namely PVP and dextran, retain less alcohol than the low-molecular-weight carbohydrates. All of the above findings are compatible with the microregion concept. Slow freezing, which allows diffusion of solute from the freezing front, results in fewer, large, more con-

centrated microregions. These microregions have a lower permeability.⁷⁵ The reduced molility of the polymers, as compared to the low-molecular-weight carbohydrates, also retards formation of impermeable microregions that entrap volatiles; this explains why Dextran-10 and PVP retain less alcohol under the conditions of the author's experiments.

Similarities between PVP and carbohydrates in effects of alcohol concentration have also been observed. When solids content is kept approximately constant, relative retention decreases with increasing alcohol concentration. The use of C^{14} -labeled 1-propanol allowed the use of a wide range of concentrations and the results obtained previously with carbohydrates; retention expressed in *absolute* amounts (as weight of volatile per weight of solid) increases nonlinearly with concentration, resulting in the *relative* decreased retention noted above (Figure 19). This behavior reflects a saturation of microregion entrapment capacity. The microregions theory predicts that increasing the solid concentration increases volatile retention, up to a limiting concentration that depends on type of solid, with type and amount of volatile. Results obtained with the PVP-1-propanol system were compared with results published for other systems, and the curves were generally similar.⁴²

The most convincing evidence for the existence of water-sensitive volatile-entrapping microregions in carbohydrate systems was obtained through humidification experiments in which water vapor sorption above a critical moisture level resulted in structural changes and consequent volatile release.^{76,119} Figure 20 presents results of a humidification experiment using PVP. PVP solutions (20% solids, 1% 1-propanol) were freeze-dried under standard conditions (slow freezing in ambient temperature), resulting in the retention of 1.2 g 1-propanol/100 g PVP. The freeze-dried systems were then exposed to different relative humidities, and water uptake and volatile loss were measured as a function of time. At 11% R.H. an apparent loss of propanol was noted. Although small, this loss may be real, perhaps representing surface-adsorbed propanol or propanol in imperfect microregions. Even in the case of exposure to higher humidity, sizable volatile loss does not commence until the absorbed water is sufficient to disrupt the PVP structure. Thus, in the case of exposure to 32% relative humidity, complete

TABLE 13

Effect of Freezing Rate on Retention of Propanol by Model Systems

Solid	Initial concentration (%)	Volatile	Initial concentration (%)	Retention of volatile (%)	
				fast freezing	slow freezing
PVP	20.0	1-propanol	1.0	9.8	24.0
PVP	20.0	1-propanol	0.01	—	58.0
Glucose	18.8	1-propanol	0.75	47.8	
Glucose	18.8	2-propanol	0.75	52.8	
Maltose	18.8	2-propanol	0.75	67.6	87.5
Dextran-10	18.8	1-propanol	0.75	4.2	
Dextran-10	18.8	2-propanol	0.75	7.5	
Dextran-10	20.0	2-propanol	0.01	56	88

humidification is achieved in about four hours, and the volatile loss appears to become significant at about the same time. Extensive tests have confirmed that the B.E.T. monolayer value, which for PVP is about 12.5 g water/100 g solids occurring at an equilibrium relative humidity of about 30%, seems to mark the initiation of volatile release due to microregion disruption.

It appears, therefore, that *most* of the alcohol entrapped in PVP systems is held in microregions. However, because the propanol-PVP interactions are strong, adsorption also contributes to the total retention. Some evidence of such adsorption appears in Figure 21, which shows the desorption of propanol from PVP after exposure to saturated vapor of propanol, in absence of water. Unlike carbohydrates, PVP in the dry state does sorb alcohols that are then entrapped in the matrix of the polymer which has been opened up by the adsorbed alcohol. Similar experiments using vapors

in which PVP is insoluble showed rapid desorption of the originally adsorbed vapor. The author and co-workers are currently preparing a paper summarizing the evidence that adsorption contributes to total retention of vapors.⁴² Through "layering" experiments, similar to those shown for maltose in Table 12, it was estimated that the amount adsorbed by passing through a dry layer originally containing no alcohol was less than 2% of the retention by entrapment. Similar experiments with PVP showed the amount adsorbed to be about 10% of the total retention. Similar results might be expected in other situations where the nonvolatile solids comprising the freeze-dried matrix interact strongly with the volatile.

Among recent workers investigating the adsorption contribution to retention is Le Maguer,¹⁴⁴ who used frontal analysis gas chromatography to study water-organic volatile interactions during sorption on cellulose. Maier¹⁵⁴ studied sorption of aliphatic amines by various food components and observed strong bond formation. Salts were formed with acids and acid carbohydrates, amides with pectic acid and pectin, and condensation products with reducing sugars. In neutral polysaccharides the sorption was reversible, but in acidic polysaccharides Maillard reaction-type binding caused formation of irreversible bonds. Maier noted that, unlike alcohols, the amines can penetrate into aggregates formed by polymeric carbohydrates. We would expect, therefore, that the effects we observed in the PVP-propanol system⁴² would also occur in the polysaccharides-amines system.

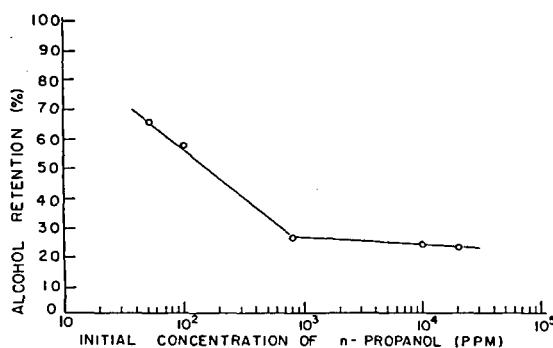


FIGURE 19. Effect of initial concentration on retention of 1-propanol in a freeze-dried PVP system.

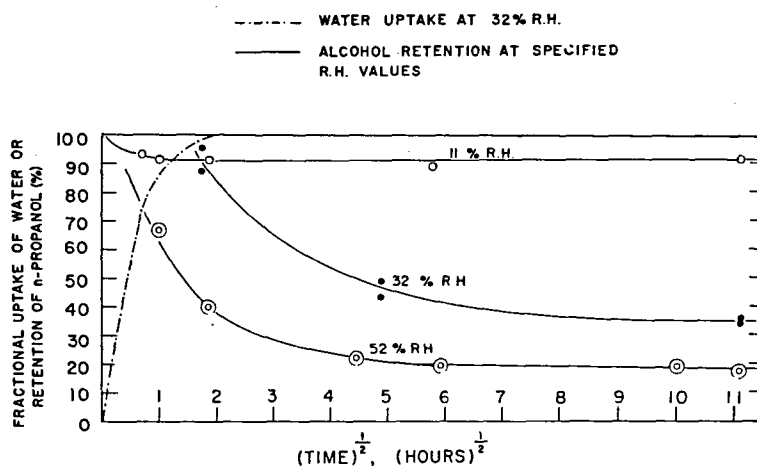


FIGURE 20. Effect of humidification on fractional uptake of water and retention of 1-propanol in a freeze-dried PVP system.

In 1972 Maier reported on sorption of ketones in dry and humidified substrates, including coffee, milk, potato flakes, fruit powders, zein, cellulosic materials, pectins, starches, alginic acid, casein and agar, and egg albumin.¹⁵⁵ He observed that the sorption increased with the water content of the macromolecular solid components of foods. The sorption in dry foods and in dry polymeric substrates was low, except in the presence of fat (which apparently dissolved the ketones). In most cases, hydrogen-bonding of the carbonyl group with the polar groups in the solids studied seemed responsible for sorption. The sorption was fully reversible in the dry state, except for some ketones held by *entrapment* in agar and in cellophane, and for diethyl-ketone which was similarly entrapped in starch. In casein and in egg albumin some acetone was held irreversible by unspecified mechanisms.

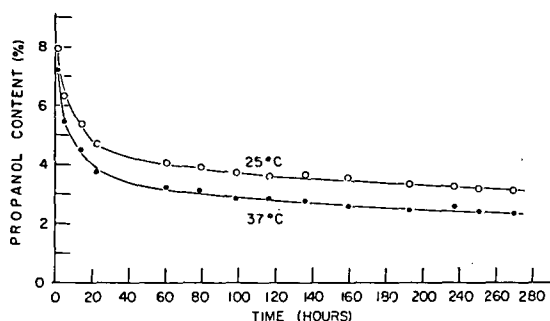


FIGURE 21. Desorption of 1-propanol from freeze-dried PVP after exposure of the dry PVP to 1-propanol vapor.

Sorption and desorption of various organic volatiles were studied by Gray and Roberts,⁹⁰ who also determined heats of sorption with a microcalorimeter. They found strong sorption of amines on pectin. Triethylamine was adsorbed very strongly; heat of sorption was 2.6 kcal/mole, and ethylamine yielded 0.65 kcal/mole. Other adsorbates yielded substantial heats of sorption on silica gel, but not on polysaccharides.

Some other recent developments in the area of flavor retention deserve mention.

1. A patent has been issued for preparation of acetaldehyde, fixed in a carbohydrate matrix, to be added to rehydratable foods as a flavoring agent.⁶⁶
2. A Japanese patent has been issued for freeze-drying of sake under conditions assuring retention of alcohol and flavor.²⁰⁹
3. Zabik and Dugan²³³ have reported entrapment of pesticides in freeze-dried eggs.

INTERMEDIATE-MOISTURE FOODS AND OSMOTIC DEHYDRATION OF FOODS

In the present section the author will deal with intermediate-moisture foods, with osmotic dehydration, and with some related processes. The common principle is the use of agents with high osmotic pressure for lowering the water activity of the foods [in the case of intermediate-moisture foods (IMF)], or for removal of water from the

food into a solution with high osmotic pressure (in the case of osmotic dehydration).

Some other treatments involving the addition of additives to food will also be mentioned.

Principles of IMF

Intermediate-moisture foods are characterized by a water activity low enough to prevent the growth of bacteria, and by conditions minimizing the potential for growth of other microorganisms. Definitions of such foods are therefore not rigorous at all. "Dried fruits," also known in the industry as "evaporated fruits," such as prunes and apricots, certainly belong in this category, as do jams, some types of sausage, and some pie fillings.

Water activities and associated moisture contents vary widely among these well-known foods; they range generally from 0.7 to 0.9 water activity, and 20 to 50% water by weight.^{30,185} The margin of safety against attack by organisms resistant to low water activities has usually been provided by chemical additives (e.g., sulfite in fruit; nitrite in meat products; preservatives of various kinds in jams). Pasteurization and/or low temperature storage also may be used to extend life of products with water activities near the critical level. Leistner and Wirth¹⁴³ have reported the water activity of various meat products and the limits of resistance to attack by various organisms; some semistable sausage products have water activities of 0.83 to 0.97 and the *lactobacilli* and *streptococci* which are likely to grow in meat products have minimum activity requirement of 0.89 to 0.94. Sausages of the type described by Leistner and Wirth, therefore, are at the upper limit of activities still to be considered as pertaining to IMF.

IMF have received new attention since the development of new products based on the following technological principles: lowering of water activity by addition of a solute such as glycerol, sucrose, glucose, or salt; retardation of microbial growth by addition of antimicrobial, and primarily antimycotic, agents such as propylene glycol, and/or sorbic acid.

The following optional steps may be taken: Water activity may be depressed below the potential offered by addition of solutes through lowering of total water present, via dehydration or evaporation. Stability may be enhanced by pasteurization. Antioxidants and other chemical preservatives may be added to counteract chemical

deterioration. Potential for enzymatic deterioration may be minimized by blanching.

Technology of IMF

The technological renaissance of IMF produced its initial impact in the area of pet foods. The pet IMF, known in the trade as "soft-moist," are based on a combination of meat byproducts with soyflakes and sugar (glucose or sucrose) to give a product with a moisture content of about 25% and a water activity of about 0.83.¹¹⁴ Propylene glycol (about 2%) and potassium sorbate (0.3%) provide antimycotic activity, and the glycol also serves as a plasticizer. Emulsifiers, salt, nutritive supplements, and other functional components are also present. The soft-moist pet foods are considered a success; their sales in 1969 were estimated at about 100 million dollars, corresponding to about 10% of the total pet food sales.⁴⁴ Recent studies at M.I.T. indicated that soft-moist dog food was a good source of nutrition for growing beagles.⁸⁹

Development of IMF for human consumption has been encouraged by the U.S. military and NASA because of logistic advantages of such food.³⁰ The major problem in developing such foods has been the inadequate range of safe, effective, and palatable osmotic agents, and/or preservatives. Melpar, Inc., under contract with U.S. Army Natick Labs, surveyed several additives and the U.S. Army had other contracts for development of IMF, especially with General Foods Corp.³⁰ The U.S. Air Force had similar contracts with Swift and Co.,¹⁷⁹ and considerable work is also underway in other industrial and academic organizations, and in laboratories run by the military and NASA.

The principal method of IMF preparation developed in these studies has been to combine glycerol with other food constituents to give products with glycerol contents of 10 to 50% and water contents of 15 to 40%, and with water activities of 0.80 to 0.85.^{114,185} Two major methods were used for preparation: Solid food pieces were freeze-dried and then soaked or infused with a solution containing the osmotic agents. Solid food pieces were cooked in an appropriate solution to bring the final water content to the desired level.

A recent article,¹¹ reviewing development of IMF at Swift and Co., reports good results with the cooking methods, which included cooking in

cans at 6 psi of steam pressure; cooking in cans at 77°C; water-cooking in an open steam kettle; oven-roasting; cooking with glycerine and salt in the can; cooking in infusion solutions followed by equilibration; and braising.

Fourteen products, including seven meat items, halibut, fruits, vegetables, pancakes and french omelette, were prepared with an activity of about 0.70 to 0.86 and different moisture contents. Conclusions drawn were that products with high glycerol and water contents were made unacceptable by the bittersweet taste of glycerol. Partially dried products, on the other hand, were unacceptably tough. Some of the products were acceptable, however, since the scores on all products ranged from 2 to 8 on a 9-point hedonic scale.

Glycerol-based intermediate-moisture foods were the subject of several patents issued to industrial concerns. General Foods obtained patents for a variety of products. Kaplow and Halik¹¹⁵ report a process for IMF products, including diced chicken pieces, carrot dices, and apple slices. Their process involves infusion of predried food with a solution containing polyhydric alcohols including one or more of the following: glycerol, sorbitol, mannitol and propylene glycol; and adjustment of water content to 20 to 40%. All the examples specify glycerol (14 to 50%) and addition of 0.3 to 2% of propylene glycol and 0.2 to 0.3% of potassium sorbate. Processes were patented for preparation of eggs with an activity of 0.65 to 0.8; examples had about 30% each of glycerol and of water.¹¹⁶ A pressure infusion method for preparation of IMF with a glycerol content giving water activities between 0.75 and 0.9 and with water contents of 15 to 50% is patented by Mauge.¹⁵⁸ Examples include pork, celery, pickles, and olives.

Other IMF items, patented by General Foods and based on addition of glycerol, propylene glycol, and sorbate included rice⁴⁸ and pasta.⁹⁶ Other General Foods patents covered use of sugars and partial starch hydrolyzates in combination with alcohols and preservatives.^{33,54}

Glycerol-containing deep-fried fish with an ultimate water activity of 0.82 to 0.87 and water contents of 28 to 40%, along with ~20% glycerol and ~4% salt, 1% propylene glycol, and 0.5% potassium sorbate were developed by Collins et al.⁴⁵

Since all IMF items with high glycerol contents

have an objectionable taste, other approaches to IMF production are being sought.

Dymsza et al.⁵⁷ reported on preservation of fish, shrimp, and tomatoes by immersion in aqueous solutions of propylene glycol or of 1,3-butylene glycol. Frankenfeld et al.^{82,83} patented use of 1,3-butylene glycol and other diols and diol esters to extend the shelf life of baked products.

Agarwal et al.⁴ reported a process for stabilization of fish based on combination of the following treatments: cooking in 20% brine containing 0.1% paraben; dehydration to 35 to 40% water; irradiation with 0.5 megarad of ionizing radiation.

Pasteurization, plus reduction of water activity to levels between 0.85 and 0.98 by dehydration, is the process patented by Unilever (examples include partially dried steak, fish, and carrot dice).²¹⁵ Borochoff et al.²⁵ of General Mills were issued a patent for a process that converts starch to glucose within a starchy material; it was to be used in producing a pet food. An intermediate-moisture banana product was developed by blanching and partial dehydration.¹⁴⁹

Stability of IMF in Storage

Intermediate-moisture foods are in an activity range likely to allow rapid chemical deterioration due to both nonenzymatic browning and lipid oxidation. Some potential also exists for enzymatic reactions and microbial growth. Studies on this aspect of IMF are few,^{110,112,135,136} and it is not yet clearly established what combinations of antioxidants, chelators, preservatives, packaging, and storage conditions will be needed for adequate stability in commercial distribution channels.

Osmotic Drying

Dehydration of foods by immersion in liquids with a water activity lower than that of the food forms the essence of osmotic drying. Solutions of sugars or of salt are usually employed, giving rise to two simultaneous counter-current flows: solute diffuses from solution into food; and water diffuses out of the food into the solution. Unfortunately, the processes are complex and no correlations between effective diffusivities and process conditions have been published. Most studies report only penetration under selected conditions, with no attempt made to analyze the mass transfer in terms of engineering properties.

Data for cure diffusion in pork are given by Arganosa and Hendrickson,¹³ and some information on the extent of simultaneous extraction of water and infusion of sugar in *osmotic dehydration* appears in a study by Farkas and Lazar.⁶³ An interesting mass transfer situation arises in osmotic dehydration of fruit pieces by immersion in concentrated sugar solution. Diffusivity of sugars is much lower than that of water, making it possible to design processes which result in substantial water removal with only marginal sugar pickup. Slow processes, on the other hand, approach equilibrium for both sugar and water resulting in production of "candied" sugar-rich fruits. One would expect also that disruption of structural barriers within the fruit pieces would increase diffusivities of both water and of sugar, but would tend to allow a faster approach to equilibrium, and thus favor "candying" as opposed to dehydration. And, indeed, an improved candying process incorporating presoftening of the fruit with enzymes produced by the mold *Aspergillus niger* was recently patented.¹⁶⁸

Where osmotic dehydration rather than candying is desired, the best results are obtained in stirred baths at elevated temperatures. Farkas and Lazar⁶³ found that Golden Delicious apples cut into wedges and half rings could be osmotically treated in 70° Bx sucrose at 50°C to reduce their weight by 50%. In the author's laboratories similar results with apples, melons, and peaches have been obtained, and the Hawaii Experimental Station has reported satisfactory production of osmotically treated bananas.⁹ Coltart⁴⁶ patented a process for producing osmotically dehydrated fruit by immersion in a rotating drum containing a 40 to 90% sugar solution at a temperature of 70° to 180°F. Hope and Vitale¹⁰⁹ reported that osmotic dehydration of mangoes, bananas, and plantains could be satisfactorily effected by treatment in sucrose or in salt.

Quantitative information on the amounts of sugar picked up during dehydration under different conditions is scarce. Farkas and Lazar⁶³ indicate that the soluble solids of osmotic apples are about 40% of total solids, compared to 25% of air-dehydrated apples; thus, the sugar pickup is about 25% on total solids basis. Work by the

author and co-workers conducted on thin slices resulted in somewhat higher sugar uptakes.

An interesting procedure was proposed by Camirand et al.³⁸ for foods that cannot tolerate solute pickup. They coated foods with a solute-impermeable coating of low-methoxy, calcium pectate. They then immersed the coated food pieces in a solution of invert sugar and sucrose. Because the coating slows down the process, Camirand et al.³⁸ found drying times to range up to 144 hr at 25°C. They dried a variety of items including fruit, olives, meat balls, pieces of fish, and whole prawns, and claim that the coated items were satisfactory, while the uncoated were excessively sweet. The very long drying times at a temperature permitting microbial growth, however, appear to this author to be unsatisfactory.

Miscellaneous Processes

The following dehydration processes, like IMF and osmotic processes, involve addition to dehydrated food of selected components:

1. U.S. Army Natick Labs have developed a process for texture improvement of dehydrated celery by glycerol treatment.²⁰⁰
2. Truckenbrodt and Sapers,²¹⁸ of Corn Products Co., have a patent on improving dehydrated foods by treatment with sodium chloride.
3. Addition of hydrophilic colloids, including gelatin, to gravies and soup mixes results in instantized products in which the colloid provides networks or paths for penetration of the rehydration fluid.¹⁶¹

STORAGE STABILITY AND PACKAGING OF DEHYDRATED FOODS

An extremely important aspect of dehydrated and intermediate-moisture foods is their protection in storage. The subject is, however, entirely too broad for the present review. A general review of packaging of foods has recently been published by Brody,³¹ a recent article by Labuza¹³⁴ discusses nutrient losses in storage, and this author has reviewed work on quantitative analysis of food packaging requirements.¹¹⁷ These articles should provide a starting point for further research.

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