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ACADEMIC
PRESS

Advances in Food and Nutrition Research

Volume 48

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WATER AND SOLIDS MOBILITY IN FOODS

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I. INTRODUCTION

"*Water—blood of the earth*"
From *Life's Matrix*, by Philip Ball (2001)

Water is the most abundant, unique, and necessary substance on the face of the earth. It is one of the earth's most precious resources and, along with oxygen, is more important for sustaining life, in the short term, than even the consumption of food.

ADVANCES IN FOOD AND NUTRITION RESEARCH VOL 48
ISSN: 1043-4526

Because of its vast and vital importance to life, water has been the focus of at least two and a half millennia of philosophical and scientific inquiry. However, there still remains much about water that we do not yet know and/or understand (Angell, 2001; Ball, 2001). The quest to identify the chemical and physical nature of water dates back at least as far as Thales, who lived from seventh to sixth century B.C. Thales, a citizen of the Greek colony of Miletus in Ionia, proposed that all of reality originated from a single material substance and that substance was water (O'Grady, 2001). The Greek philosopher Empedocles of Acragas in fifth century B.C. is credited with popularizing the classic four-element natural philosophy of Greece. Water was then considered one of four primary elements or "roots" of the universe, along with fire, air, and earth (O'Grady, 2001). Despite continuous investigation, it was not until several centuries later that the true elemental composition and proportions of water were uncovered. In 1781, the British chemist Henry Cavendish, extending the studies of others, demonstrated that the igniting of hydrogen and oxygen produces water. Two years later, the French chemist Antoine Lavoisier proved that water was not an element, but rather a compound composed of oxygen and hydrogen. In 1805,[1] the French chemist Joseph Gay-Lussac, collaborating with the German naturalist Alexander von Humboldt, determined that water consists of two volumes of hydrogen to one volume of oxygen (Green and Peterson, 1992). A few years later, Avogadro (1811) stated "...since we know that the ratio of the volumes of hydrogen and oxygen in the formation of water is 2 to 1, it follows that water results from the union of each molecule of oxygen with two molecules of hydrogen." In 1814 Berzelius proposed that compounds be described by chemical signs (which evolved into the modern-day chemical formula) based on their elemental substance—the sign for water being $2H + O$ (Berzelius, 1814), thereby approaching the modern-day chemical composition and formula for water—H_2O.

In addition to its philosophical and scientific importance, water has also been the subject of multitudinous authors, artists, and musicians. Many are familiar with the saying "Water, water everywhere and not a drop to drink"[2]

[1]Some sources give the date as 1804. Gay-Lussac read these now famous results before the Philomathic Society in 1808, which were published in 1809, in Gay Lussac, J.L., Memoir on the Combination of Gaseous Substances with Each Other. Mémoires de la Société d'Arcueil 2, 207–34. An English translation of this document, published by Henry A. Boorse and Lloyd Motz, eds., The World of the Atom, Vol. 1. New York: Basic Books, 1966 (translation: Alembic Club Reprint No. 4), can be found at http://webserver.lemoyne.edu/faculty/giunta/gaylussac.html.

[2]The exact quote from The Rime of the Ancient Mariner by Coleridge (1798) is: "Water, water, everywhere, And all the boards did shrink; Water, water, everywhere, Nor any drop to drink."

(Coleridge, 1798), the 1906 *Water Lilies*[3] painting by Claude Monet, and the 1717 work *Water Music*[4] by George Frideric Handel. Water has also served as a bridge connecting science and art, as expressed by the research and photos of Nagel studying "the cascade of structure in a drop of water falling from a faucet[5]" (Shi *et al*., 1994) and the photographs of Wick (1997) in his book entitled "*A Drop of Water*." Finally, water in substance and symbol has been profoundly woven into the theology of the world's religions. For the interested reader, a comprehensive biography of water has been published by Ball (2001), exploring the central secret of water's nature as the matrix of life. In addition, a multidisciplinary examination of the significance and role of water in the life and culture of planet earth is currently under construction on the World Wide Web by Witcombe and Hwang (2004).

The importance of water in foods begins with the hydrological cycle and concludes with the consumption of safe, wholesome, and plentiful foods. In between, water is a vital component in the various stages of food production and preservation. Water in the final food product, whether fresh or processed, profoundly influences the chemistry, microbiological safety, nutritional value, texture, appearance, and taste of the food. Because of this intimate relationship between water and food quality and safety, a more complete understanding of water and its properties, behavior, and influence, alone and in foods, is of prime importance.

The objectives of this review are to discuss the fundamental and more recently discovered properties of water alone and to critically examine the system properties and measurement methods used to measure the mobility of water and solids in foods—specifically water activity, nuclear magnetic resonance (NMR), and the glass transition.

II. WATER

A. WATER MOLECULE STRUCTURE

As traced historically in the introduction, water has the molecular formula H_2O. However, it is important to mention that the hydrogen atoms are not

[3]More about Claude Monet and his *Water Lilies* painting can be found at Pioch, N. WebMuseum, Paris. http://www.ibiblio.org/wm/paint/auth/monet 19 September 2002 (Accessed 12 January 2004).

[4]More about George Frideric Handel and his *Water Music* can be found at Boynick, M. *Classical Music Pages*. http://w3.rz-berlin.mpg.de/cmp/handel.html 10 October (Accessed 12 January 2004).

[5]For the interested reader, the image and movie of the Cascade of Structure in a Drop Falling from a Faucet, by Nagel and co-workers, can be viewed at http://mrsec.uchicago.edu/Nuggets/NagelDrop/index.html 8 July 1995 (Accessed 12 January 2004).

permanently attached to each oxygen; rather, the hydrogen atoms are constantly exchanging due to protonation–deprotonation processes (also called proton exchange) (Chaplin, 2004). This exchange process is catalyzed by both acids and bases (i.e., the exchange rate is slowest near neutral pH and faster under acidic or basic pH conditions). The influence of proton exchange on oxygen-17 (^{17}O) NMR relaxation in water and other systems has been investigated by several researchers (Glasel, 1972; Richardson, 1989). The average residence time for a hydrogen atom at pH 7 is about a millisecond (Chaplin, 2004). Despite the dynamic effects of the proton exchange process on the structure of water, water is usually regarded as having a permanent structure.

The electronic structure of an isolated water molecule is often described as being composed of four sp^3-hybridized electron pairs—two associated with the hydrogen atoms and two as lone-pair orbitals of the oxygen atom—with an overall nearly tetrahedral geometry (Figure 1). The common "two lone-pair orbitals on the oxygen atom" description of water (referred to as "rabbit ears") is actually controversial (Chaplin, 2004; Finney, 2001). Based on ultraviolet absorption or photoelectron spectra or ionization energy of water, only one lone-pair orbital is invoked, the other orbital being at a much lower energy (Laing, 1987). Nevertheless, based on the localized molecular orbital procedure, it is appropriate and useful to describe water as having two equivalent lone-pair orbitals on the oxygen atoms; however, Martin (1988) suggested that they may be better described as "squirrel ears."

Regardless of which orbital description is selected, the four localized regions of excess charge appearing in a tetrahedral arrangement around

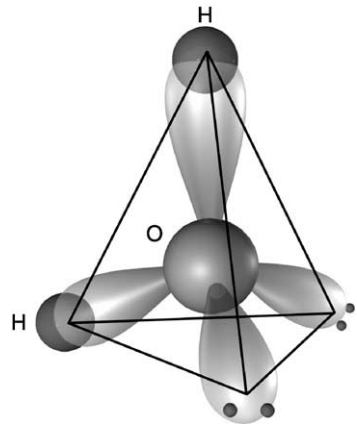

FIG. 1 Schematic orbital model of a water molecule.

the central oxygen atom provide a useful qualitative description of the electron distribution in the water molecule. Overall, the water molecule is electrically neutral, but the positive and negative charges are distributed unsymmetrically. The oxygen atom has a higher electron density than the two hydrogen atoms. This is represented as a partial negative charge on the oxygen atom and a partial positive charge on each hydrogen atom (Figure 2). The hydrogen atom is bonded covalently to the oxygen atom (called a polar covalent bond because of the unequal sharing of the electrons), with an energy of 492 $kJmol^{-1}$ (Ruscic, 2002). For an isolated water molecule (Figure 2), the calculated O–H bond length is 0.9584 Å and the H–O–H angle is 104.45° (Kern and Karplus, 1972). The experimental values vary somewhat, depending on the phase of water being investigated and the measurement method employed (Chaplin, 2004; Wallqvist and Mountain, 1999). The average van der Waals diameter for the water molecule has been reported as 2.82 Å by Franks (2000) and 3.3 Å by Fennema (1996). Molecular model values and intermediate peak radial distribution data indicate that the value is around 3.2 Å (Chaplin, 2004). Evidence discussed by Finney (2001) suggests that the van der Waals radius around a water molecule oxygen atom exhibits a small (about ±5%) but significant degree of nonsphericity, ranging between 1.6 and 1.8 Å, depending on which axis is selected (Savage, 1986).

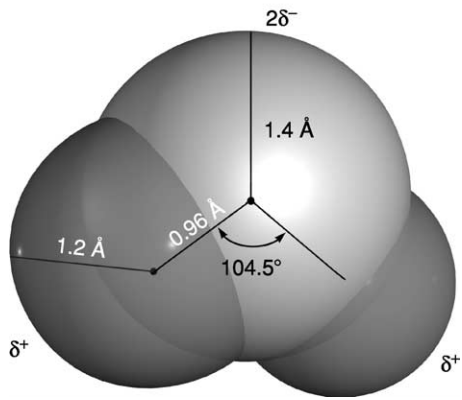

FIG. 2 Space-filling model of an isolated water molecule, in the vapor state, with associated van der Waals radii and rounded values for the O–H bond length and the H–O–H angle. Each hydrogen atom has a slight positive charge (δ^+), and each lone-pair oxygen orbital has a slight negative charge (for a total of $2\delta^-$).

B. HYDROGEN-BONDING ASSOCIATIONS

In addition to its two O–H polar covalent bonds, water molecules participate in hydrogen bonding—an intermolecular attraction between the hydrogen atom of one water molecule and an oxygen lone pair of another water molecule. The hydrogen bond is thought to be approximately 90% electrostatic and 10% covalent in nature (Chaplin, 2004). Hydrogen bonding is a dominant interaction between water molecules and pervasively affects the structure and behavior of water. The most basic hydrogen-bonding situation occurs in the water dimer (Figure 3), where one hydrogen bond exists between two water molecules in the vapor phase. The measured hydrogen-bond length [R(O···O)] in the vapor phase water dimer is about 2.98 Å, which is significantly longer than the lengths in both liquid water (2.85 Å) and regular ice (2.74 Å) (Ludwig, 2001). The shortening of the R(O···O) distance in liquid water and regular ice (i.e., stronger hydrogen bonding networks) is due to the cooperative nature of hydrogen bonding discussed later. Details of hydrogen-bond geometry in liquid water have been investigated by Modig *et al.* (2003) from 0 to 80 °C by combining measurements of the proton magnetic shielding tensor with *ab initio* density functional calculations. Their results suggest a substantial hydrogen-bond distortion, which increases in nonlinearity and distance with increasing temperature.

The hydrogen-bonded water pentamer is illustrated in Figure 4. Using natural bond orbital (NBO) terminology, the two hydrogen–oxygen-bonding orbitals of the central water molecule can act as charge acceptors, and the two oxygen lone-pair orbitals of the central water molecule can act as charge donors (Ludwig, 2001). Another terminology convention present in the

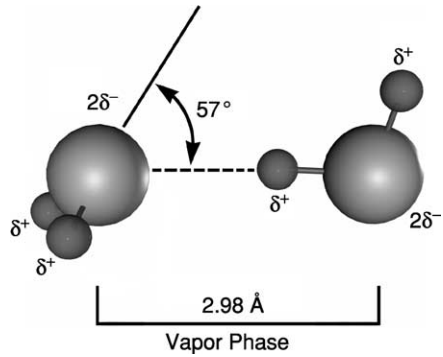

FIG. 3 The vapor phase water dimer structure. Polar covalent bonds are shown as solid lines and the hydrogen bond as a dashed line (adapted from Ludwig, 2001).

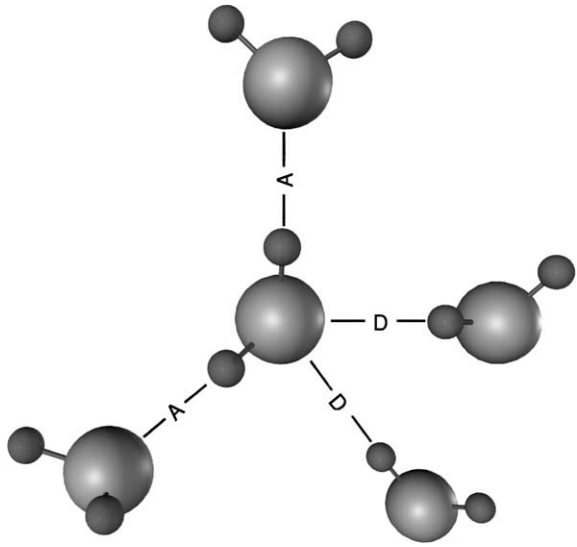

FIG. 4 The hydrogen-bonded water pentamer, using natural bond orbital (NBO) terminology, the two hydrogen-oxygen bonding orbitals of the central water molecule can act as charge acceptors (A), and the two oxygen lone-pair orbitals of the central water molecule can act as charge donors (D).

literature (e.g., Fennema, 1996; Franks, 2000) refers to the two hydrogen–oxygen-bonding orbitals as proton (or hydrogen-bond) donors and the two oxygen lone-pair orbitals as proton (or hydrogen-bond) acceptors. The difference in the two approaches is what is being accepted and donated—the charge or the proton. Regardless of the terminology used, each water molecule has the potential of forming up to four hydrogen bonds with four other water molecules, resulting in a three-dimensional hydrogen-bonding structure. The actual number, strength, and duration of the hydrogen bonds that form depend on the phase of water being investigated. In ice, each water molecule is involved in four hydrogen bonds, each about 3 $kJmol^{-1}$ stronger than the energy per hydrogen bond in liquid water (23.3 $kJmol^{-1}$ — energy required for breaking and completely separating the hydrogen bond) (Chaplin, 2004; Suresh and Naik, 2000). In liquid water, the number of hydrogen bonds per liquid water molecule has been difficult to quantify. An average value of approximately 3.4 hydrogen bonds per liquid water molecule is given in Stryer (1995). Based on computer simulations, most water molecules have two or three instantaneous hydrogen bonds per liquid water molecule, some have four, and very few have five (one more hydrogen bond than the maximum of four proposed earlier) (Ball, 2001).

The number of hydrogen bonds per molecule in liquid water depends on the balance between the favorable energetic aspect of optimal hydrogen bonding and the unfavorable entropy considerations resulting from restrictions in water molecule location (Wallqvist and Mountain, 1999).

An important feature of hydrogen bonds in water is that they act co-operatively—in other words, there is interdependence among the bonds. The formation of a first hydrogen bond between two water molecules enhances the ability of both molecules to form even stronger second hydrogen bonds because of the existence of the first hydrogen bond (Ludwig, 2001). This cooperative hydrogen bonding results in highly transient combinations of bonds among molecules, which makes elucidating the structure of liquid water immensely more complicated than for a substance that forms stable, well-defined bonds.

C. ANOMALOUS PROPERTIES

Compared to other molecules of similar molecular weight and atomic composition, water exhibits an intriguing array of anomalous physical and chemical properties, such as large values for melting and boiling points, phase transition enthalpies, surface tension, heat capacity, and thermal conductivity (Table I). Many of the unusual properties of water are related to its ability to engage in extensive, three-dimensional hydrogen bonding, which was discussed in the previous section. The cooperative and extensive hydrogen bonding in water serves to alter the properties of water compared to compounds of similar molecular structure. For example, the melting point at atmospheric pressure of water is over 100 °C higher, the boiling point at atmospheric pressure of water is over 150 °C higher, and the critical point of

TABLE I
SUMMARY OF SOME OF THE ANOMALOUS PROPERTIES OF WATER[a]

Property	Value and units
Melting point at 1 atm	0.0 °C
Boiling point at 1 atm	100.0 °C
Enthalpy of fusion at 0 °C (ΔH_{fus})	6.012 kJmol^{-1}
Enthalpy of vaporization at 100 °C (ΔH_{vap})	40.657 kJmol^{-1}
Enthalpy of sublimation at 0 °C	50.91 kJmol^{-1}
Surface tension at 20 °C	72.75×10^{-3} Nm^{-1}
Heat capacity at 20 °C	4.1818 J/g^{-1} K^{-1}
Thermal conductivity at 20 °C	0.5984 Wm^{-1} K^{-1}

[a]From Fennema (1996).

water is over 250 °C higher than expected by extrapolation of the melting, boiling, and critical points, respectively, of other group 6A hydrides—H_2S, H_2Se, H_2Te, and H_2Po (Chaplin, 2004). Explanations for the anomalous behavior of water are rooted in the ability of water to hydrogen bond and are elucidated in detail by Chaplin (2004). For example, in the case of the boiling point, the extensive hydrogen bonding in liquid water prevents water molecules from being released easily from the surface of the water. This reduces the vapor pressure of the system. Because boiling occurs when the vapor pressure equals the external pressure, a higher temperature is required to boil water compared to the nonhydrogen bonding molecules of similar structure.

Two of water's most prominent anomalies are the liquid-phase density maximum (Figure 5) and the increase in volume upon freezing (Figure 6) (Ludwig, 2001). The density of liquid water ($^1H_2\ ^{16}O$) at atmospheric pressure increases as temperature decreases to 3.984 °C, where it exhibits a maximum density value of 0.999972 gcm^{-3} (Franks, 2000). Below 3.984 °C, the density decreases with decreasing temperature to the freezing point. If the water is kept from freezing, the density continues to decrease into the supercooled liquid region (Figure 5). If the water freezes, there is a discontinuous (i.e., step change) decrease in density (Figure 5), which corresponds

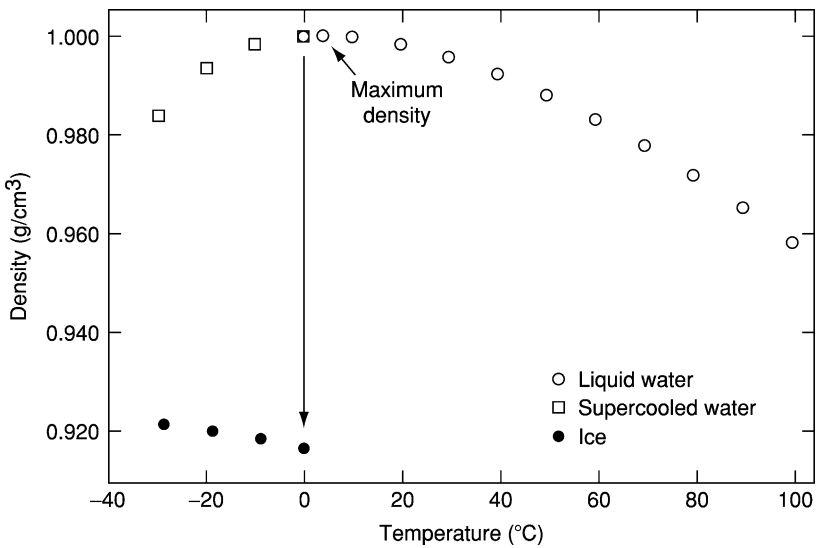

FIG. 5 The density of liquid and supercooled water as a function of temperature, illustrating the anomalous liquid phase density maximum of water (data from Lide, 2002–2003).

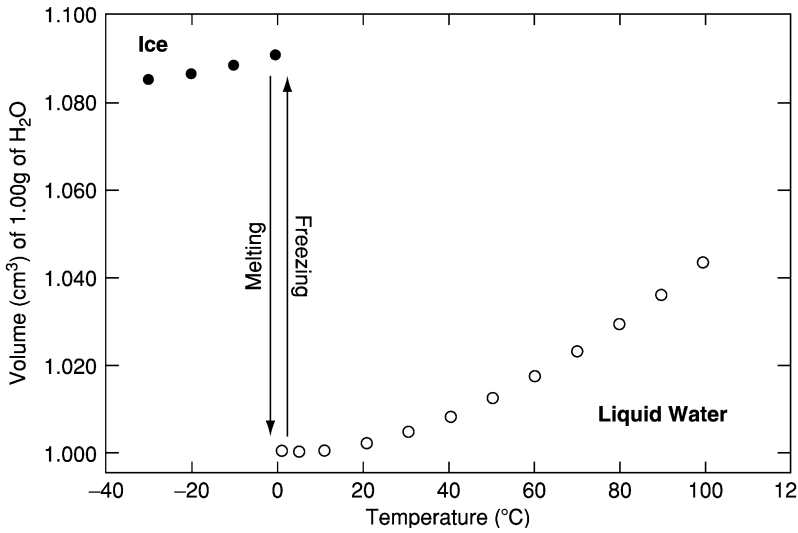

FIG. 6 The volume per 1 g of liquid and solid (ice) water as a function of temperature, illustrating the anomalous increase in the volume (or decrease in density), when liquid water freezes (data from Lide, 2002–2003).

to a discontinuous increase in volume (Figure 6). Most liquids are denser in the solid state than in the liquid state. Water, however, is unique—the solid form of water is less dense than the liquid. As can be observed in Figure 6, an increase in volume of approximately 9% accompanies the liquid-to-solid transition (freezing) of water at 0 °C and 1 atmosphere (~0.1 MPa) pressure (Kalichevsky *et al.*, 1995).

The anomalous properties of water remain an important subject of inquiry (Errington and Debenedetti, 2001; Mishima and Stanley, 1998). Chaplin (2004) gives a comprehensive overview of 40 anomalous properties of water and suggested explanations. Chaplin (2004) aptly pointed out that whether the properties of water are viewed as anomalous depends on what materials water is compared to and the interpretation of the term "anomalous." For example, Angell (2001) included a section on the nonuniqueness of water, stating that "...water is not unique, as is often supposed, but rather water is an intermediate member of a series of substances that form tetrahedral networks of different degrees of flexibility, and that, accordingly, show systematic differences of behavior." Additional references that discuss the properties of water as nonanomalous are Franks (2000), Kivelson and Tarjus (2001), and Netz *et al.* (2002).

D. ISOTOPIC COMPOSITION

Water is a mixture of varying isotopic composition (Franks, 2000). In addition to the two most common isotopes, ^{16}O and ^{1}H, there are two stable oxygen isotopes (^{17}O, ^{18}O), one stable hydrogen isotope (^{2}H, deuterium), and one radioactive hydrogen isotope (^{3}H, tritium, half-life = 12.6 years). Water also contains low concentrations of hydronium (H_3O^+) and hydroxide ions (OH^-) and their isotopic variants. In total, water consists of more than 33 chemical variants of HOH; however, these variants occur in relatively minor amounts (Fennema, 1996). Table II gives the natural abundance isotopic composition of the four major water species.

E. PHASES AND FORMS OF WATER

"*I am one thing. I am many things. I am water.*"
From *Water Dance*, by Thomas Locker (1997)

Water is a very structurally versatile molecule. Water exists in all three physical states: solid, liquid, and gas. Under extremely high temperature and pressure conditions, water can also become a supercritical fluid. Liquid water can be cooled carefully to below its freezing point without solidifying to ice, resulting in two possible forms of supercooled water. In the solid state, 13 different crystalline phases (polymorphous) and 3 amorphous forms (polyamorphous) of water are currently known. These fascinating "faces" of water are explored in detail in this section.

Water is the only form of matter occurring abundantly in all three phases (or states): solid, liquid, and gas (or vapor) (Fennema, 1996). Temperature and pressure determine the phase of water, as well as the type(s) and velocity(ies) of water molecule motion. A basic phase diagram (moderate pressure–temperature range) for pure water is shown in Figure 7. Given the

TABLE II
NATURAL ABUNDANCE ISOTOPIC COMPOSITION AND MOLECULAR WEIGHT OF THE FOUR MAJOR SPECIES IN WATER[a]

Characteristic	$^{1}H_2{}^{16}O$	$^{1}H_2{}^{18}O$	$^{1}H_2{}^{17}O$	$^{1}H^{2}H^{16}O$
Natural abundance isotopic composition (%)	99.7280%	0.2000%	0.0400%	0.0320%
Molecular weight (g/mol)	18.01056	20.01481	19.01478	19.01684

[a]Based on Franks (2000).

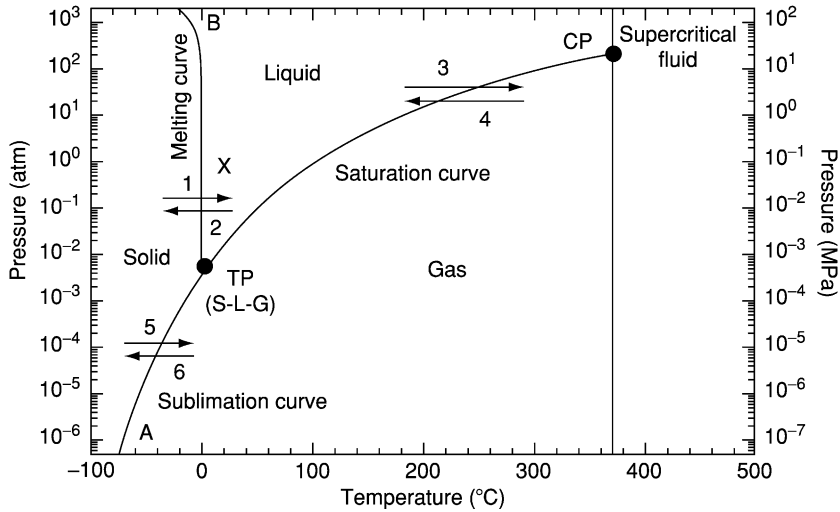

FIG. 7 Phase diagram for pure water showing the preferred physical state of water at various temperatures and pressures. The phase transitions indicated by the numbered arrows are (1) melting, (2) freezing, (3) boiling (or evaporation), (4) condensation, (5) sublimation, and (6) deposition (or ablimation). "X" marks the location on the phase diagram for water at typical room temperature (20 °C) and pressure (1 atm) conditions. TP is the triple point, where solid–liquid and gas (S-L-G) phases coexist in dynamic equilibrium. CP is the supercritical point. A and B are labels that have been added to facilitate the discussion of the sublimation and melting curves, respectively. This phase diagram was drawn using the international equations for pressure values along the phase boundary curves (melting, evaporating, and sublimation) for water (Wagner and Pruss, 1993; Wagner *et al.*, 1994).

importance of water in foods and food processing (i.e., concentration, dehydration, freezing, and freeze-drying), a thorough understanding of the phase diagram for water is of critical importance.

The phase diagram features four phase regions, three phase boundaries, and two points of particular interest: the triple point (TP) and the supercritical point (CP). Values for TP and CP from The International Association for the Properties of Water and Steam[6] (IAPWS) are 273.16 K and 611.657 Pa (IAPWS, 2002) and 647.096 K and 22.064 MPa (IAPWS, 2002), respectively. Three of the phases (solid, liquid, and gas) are bounded by equilibrium

[6]The International Association for the Properties of Water and Steam (IAPWS) provides internationally accepted values and formulations for the properties of light and heavy steam, water, and selected aqueous solutions for scientific and industrial applications. IAPWS Releases and Guidelines can be obtained online at http://www.iapws.org.

curves (sublimation curve [A to TP], melting curve [TP to B], and saturation curve [TP to CP]) that indicate the combination of pressure and temperature values at which the three reversible phase transitions occur. The liquid–gas boundary terminates at the supercritical point, and the fourth (pseudo) phase, supercritical fluid, begins. At and above the supercritical point the density of the gas becomes the same as the density of the liquid (Jones and Atkins, 2000). A liquid phase is no longer identifiable because there is no longer a dividing liquid–gas interface. Thus, by definition, what remains is a gas (a substance that fills any container it occupies) that cannot be condensed to a liquid at and above the supercritical point. A review of the properties and usefulness of supercritical water is given by Shaw *et al.* (1991).

The triple point is the location at which all three phases' boundaries intersect. At the triple point (and only at the triple point), all three phases (solid, liquid, and gas) coexist in dynamic equilibrium. Below the triple point, the solid and gas phases are next-door neighbors, and the solid-to-gas phase transition occurs directly.

One of the major differences among the phases of water at the molecular level is the motions of the water molecules. Using the phase diagram (Figure 7), we can follow the effects of temperature and pressure on the molecular mobility of water. For example, if we hold pressure constant (say at 1 atm) and increase temperature, molecular mobility increases as we move from the solid to the liquid to the gas phase regions. Conversely, if we hold temperature constant (say at 100 °C) and increase pressure, molecular mobility decreases as we move from the gas to the liquid phase region.

The temperature at which a phase transition occurs is dependent on pressure (Figure 7). At atmospheric pressure (1 atm) the solid-to-liquid phase transition occurs at 0 °C and the liquid-to-gas phase transition occurs at 100 °C. If we increase the pressure, say to 100 atm, the solid-to-liquid phase transition occurs at a temperature slightly less than 0 °C (−0.74 °C); however, the liquid-to-gas phase transition occurs at a much greater temperature (312 °C). If we decrease the pressure, say to 0.1 atm, the solid-to-liquid phase transition occurs at a temperature slightly greater than 0 °C (0.004 °C) and the liquid-to-gas phase transition occurs at a lower temperature (46 °C). If we decrease the pressure further to below the triple point, there is no solid-to-liquid phase transition; rather, the solid-to-gas phase transition occurs directly. At a pressure of 0.001 atm, the sublimation temperature is −20.16 °C.

If the phase diagram is viewed as a map (as suggested by Ball, 2000), similar to a map of the United States, with the different water phases (solid, liquid, gas) comparable to different states (i.e., Iowa, Illinois, and Wisconsin) and the phase boundaries as the state borders, we can envision

water as "traveling about" in the phase diagram. For water to do this "traveling about" in the phase diagram, changes in temperature (i.e., energy needs to be added or removed) and/or pressure are required. The amount of sensible or latent heat required to change the temperature or phase of the water (respectively) depends on the pressure. Figure 8 illustrates the steps in the phase diagram and the energy required for ice starting at −20 °C to become superheated gas (steam) at 120 °C at atmospheric pressure (1 atm). The enthalpy of fusion (ΔH_{fus}) and vaporization (ΔH_{vap}) are also given in Table I in units of $kJmol^{-1}$.

Careful cooling of pure water at atmospheric pressure can result in water that is able to remain liquid to at least 38 °C below its normal freezing point (0 °C) without crystallizing. This supercooled water is metastable and will crystallize rapidly upon being disturbed. The lower the temperature of the supercooled water, the more likely that ice will nucleate. Bulk water can be supercooled to about −38 °C (Ball, 2001; Chaplin, 2004). By increasing the pressure to about 210 MPa, liquid water may be supercooled to −92 °C (Chaplin, 2004). A second critical point (C′) has been hypothesized (Tc′ = 220 K and Pc′ = 100 MPa), below which the supercooled liquid phase separates into two distinct liquid phases: a low-density liquid (LDL) phase and a high-density liquid (HDL) phase (Mishima and Stanley, 1998; Poole *et al.*, 1992; Stanley *et al.*, 2000). Water near the hypothesized second critical point is a fluctuating mixture of LDL and HDL phases.

The effects of pressure on the phase transition of liquid water to ice (and within the ice phase itself) are complicated by the formation of several pressure-dependent ice polymorphs (Chaplin, 2004; Franks, 1984, 2000; Kalichevsky *et al.*, 1995; Ludwig, 2001). Thirteen crystalline forms of ice have been reported to date: I_h (hexagonal or normal or regular ice), I_c (cubic

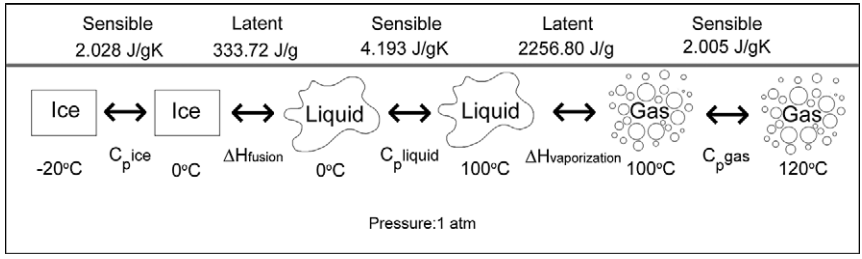

FIG. 8 Schematic illustration of the steps in the phase diagram and the energy required for ice starting at −20 °C to become superheated gas (steam) at 120 °C at atmospheric pressure (1 atm). The type and amount of heat (sensible or latent) required to change the temperature or phase are given, where C_p is the specific heat and ΔH is the change in enthalpy.

ice), and ices II–XII. Only regular ice (I_h), which is the normal form of ice and snow, is shown in Figure 7 because the other ice polymorphs occur at higher pressures and/or lower temperatures than those in Figure 7. A comprehensive phase diagram with a 0 to 800 K temperature range and a 0.1 to 10^{12} Pa pressure range, showing several of the ice polymorphs, as well as the liquid, gas, and supercritical regions, is given by Chaplin (2004). All of the ice polymorphs involve the water molecules being hydrogen bonded to four neighboring water molecules. These hydrogen bonds, however, are able to bend, stretch, and shorten under high pressure and low temperature conditions to form the various ice polymorphs. For ice I_h, application of pressure initially decreases the solid–liquid phase transition temperature, reaching a minimum of −22 °C at 207.5 MPa (2048.4 atm) (Kalichevsky *et al.*, 1995). After this minimum is reached, additional pressure results in an increase in the solid–liquid phase transition temperature and formation of different ice polymorphs. For example, the solid–liquid phase transition temperature (for ice VI to liquid water) increases to 20 °C with an increase in pressure to 882.9 MPa (Kalichevsky *et al.*, 1995). For the interested reader, Kalichevsky *et al.* (1995) and Knorr *et al.* (1998) discuss the potential application of high-pressure freezing and thawing for use in foods.

Amorphous water (also called glassy water or amorphous ice) can form when the temperature is decreased extremely rapidly below the glass transition temperature (T_g) of water (about 130 K at 0.1 MPa) (Mishima and Stanley, 1998). There are three types of amorphous ice: low-density amorphous ice (LDA), high-density amorphous ice (HDA), and very high-density amorphous ice (VHDA), with VHDA being discovered most recently (Finney *et al.*, 2002).

F. WATER MOBILITY

Water molecules exhibit three types of molecular motions: vibrational, rotational, and translational. For a nonlinear polyatomic molecule (such as water) containing N atoms, there are $3N$ coordinates needed to specify the locations of the atoms (a set of x, y, and z Cartesian coordinates for each atom). This corresponds to a total of $3N$ degrees of freedom for vibrational, rotational, and translational motions. Three degrees of freedom account for the translational energy of the molecule, three involve rotational energy, and the remaining degrees of freedom pertain to the vibrational energy $(3N - 6)$. For water with $N = 3$ atoms, there are nine total degrees of freedom (3×3): three for translational energy, three for rotational energy, and three for vibrational energy $(=[3 \times 3] - 6)$.

The water molecule can vibrate in a number of ways. In the gas phase, vibrational motion involves changes in the size and shape of the molecule

through stretching, bending, and rotation of bonds. It is intramolecular motion, i.e., motion within the molecule. As calculated earlier, water in the gas phase exhibits three vibrational modes: symmetric and asymmetric stretching of the H–O–H bonds and bending of the H–O–H bond angle (Figure 9). However, in liquid water and ice phases, vibrational motions are much more complex, mainly because they involve additional water molecules through hydrogen bonding. Chaplin (2004) gave a detailed explanation of the vibrational modes in liquid water and ice phases. Vibrational motion can be measured using infrared and Raman spectroscopy (Conway, 1981).

Rotational motion is spinning of the entire molecule around an axis in three-dimensional space. Figure 10 illustrates the rotational motion of a water molecule. Rotational motion occurs in liquid and gas phases of water and, to a limited extent, through defects in the solid phase (ice). Rotational motion of water molecules can be measured using NMR and dielectric spectroscopy (Belton, 1994).

Translational motion is the change in location of the entire molecule in three-dimensional space. Figure 11 illustrates the translational motion of a few water molecules. Translational motion is also referred to as self-diffusion or Brownian motion. Translational diffusion of a molecule can be described by a random walk, in which x is the net distance traveled by the molecule in time Δt (Figure 12). The mean-square displacement ($\overline{x^2}$) covered by a molecule in a given direction follows the Einstein-derived relationship (Eisenberg and Crothers, 1979):

$$\overline{x^2} = 2D\Delta t \tag{1}$$

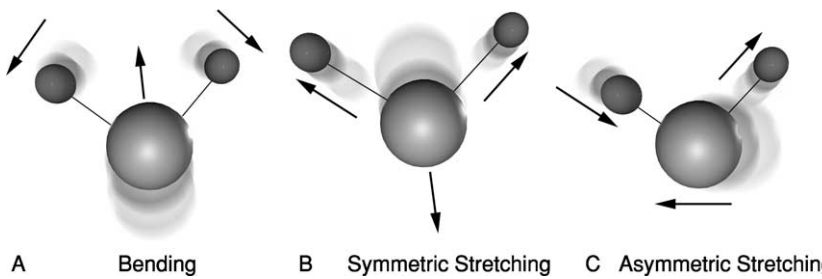

FIG. 9 Diagram illustrating the three vibrational modes ($3N-6$) of water in the gas phase. (A) The first mode is called bending, in which the water molecule moves in a scissors-like manner. (B) The second is the symmetric stretch, where the hydrogen atoms move away from (or toward) the central oxygen atom simultaneously—i.e., in-phase motion. (C) The third is the asymmetric stretch, in which one hydrogen atom approaches the central oxygen atom, while the other moves away—i.e., out-of-phase motion.

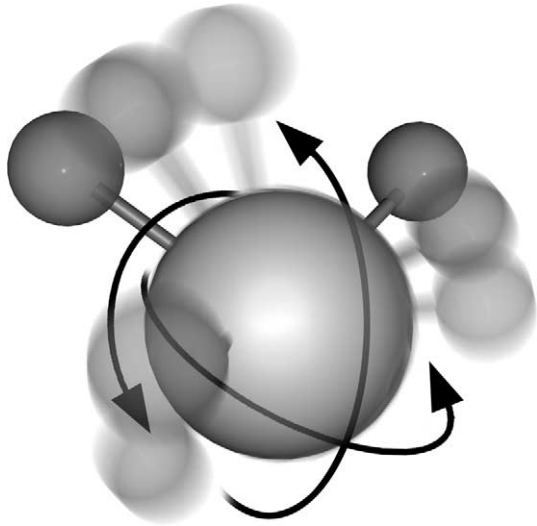

FIG. 10 Schematic illustration of the rotational motion of a water molecule. The water molecule can rotate in all three dimensions, but does not change locations.

where D is the proportionality constant referred to as the self-diffusion coefficient (m^2s^{-1}). In addition, Einstein showed that $D = k_B T/f$, and in conjunction with the Stokes expression for the friction factor f for spheres, the so-called Stokes–Einstein relationship becomes

$$D = \frac{k_B T}{6\pi\eta_s r} \tag{2}$$

where k_B is the Boltzmann constant (1.381×10^{-23} JK^{-1}), T is temperature, η_s is the dynamic viscosity of the solvent, and r is the molecular radius. For a temperature of 298 K, a viscosity of 0.8904×10^{-3} Ns/m^2, and a radius of 1.41×10^{-10} m, the D value for water in water, calculated using Eq. (2), is 1.74×10^{-9} m^2s^{-1}, which is similar in magnitude to the average experimentally determined D value, reported by Franks (1984) for water, of 2.5×10^{-9} m^2s^{-1} at 298 K.

Translational motion occurs in liquid and gas phases of water, but is virtually eliminated in the solid phase (ice). Translational motion of water molecules can be measured using NMR and magnetic resonance imaging (MRI) spectroscopy (Sun and Schmidt, 1995).

Despite the care taken to depict the three types of water motion in Figures 9 through 11, it is difficult to illustrate the dynamic three-dimensional motion of water in a static figure. A basic, but very well-done narrated

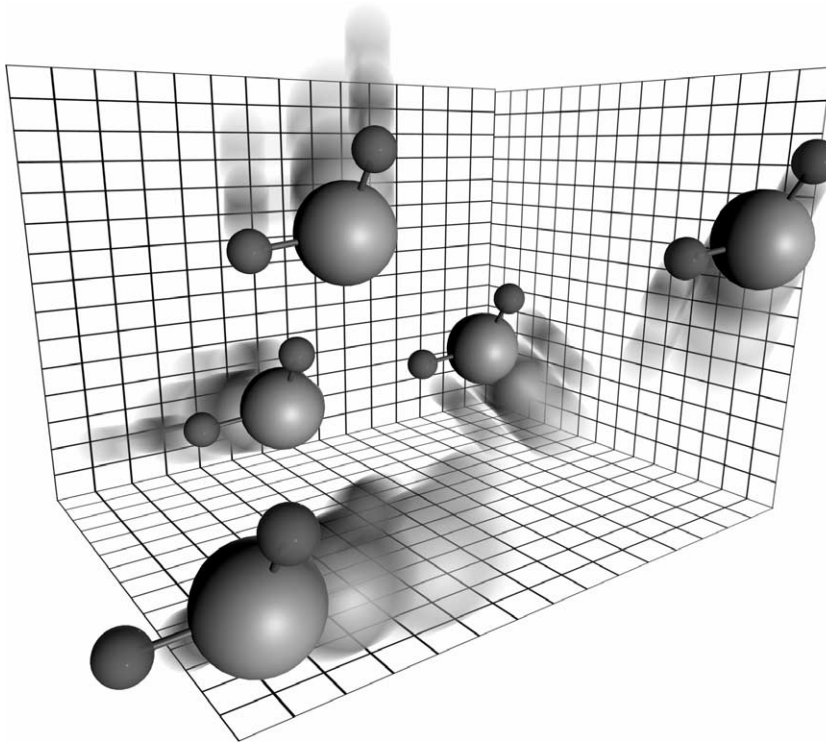

FIG. 11 Schematic illustration of the translational motion of a few water molecules. The water molecule changes locations, but does not rotate.

molecular animation of the motions of water molecules, developed originally by Tasker *et al.* (1996a,b), is available on videotape through the Films for the Humanities and Sciences; it is called "Water: A Molecular Substance" (FFH #7749).

G. WATER MODELS

Over the years, a large number of models of water structure have been developed in an attempt to reconcile all the known physical properties of water and to arrive at a molecular description of water that accounts correctly for its behavior over a large range of thermodynamic conditions. Early models of water structure have been categorized by Fennema (1996) and Ball (2001) into three general types: mixture, uniformist, and interstitial. Mixture models are based on the concept of intermolecular hydrogen bonds

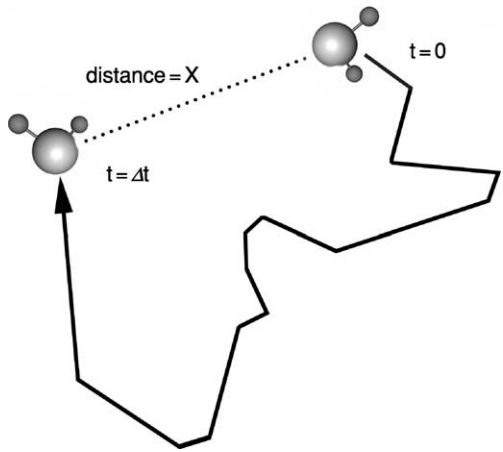

FIG. 12 Translational diffusion (also called Brownian motion) of a water molecule can be described by a random walk starting at $t = 0$ and ending at $t = \Delta t$, where x is the net distance traveled during Δt and t is time.

being momentarily ($\sim 10^{-11}$ s) concentrated in bulky clusters of water molecules that are in dynamic equilibrium with other, more dense clusters of water molecules, containing less than their full complement of hydrogen bonds (Fennema, 1996; Luck, 1981). Uniformist (also called continuum) models are based on the concept that liquid water consists of a random network of intermolecular hydrogen bonds, with frequent strains and broken bonds, that are continually undergoing topological reformation (Stillinger, 1980). Interstitial models are based on the concept that upon melting, some of the water molecules remain in place in the ice lattice and others that break loose, moving around in the empty (or interstitial) spaces (Ball, 2001; Fennema, 1996).

Reviews on water structure models include Mishima and Stanley (1998), Wallqvist and Mountain (1999), and Ludwig (2001). Mishima and Stanley (1998) concentrated their review on three relatively recent water structure hypotheses: (1) the stability limit hypothesis (Speedy, 1982), (2) the singularity-free hypothesis (Sastry *et al.*, 1996), and (3) the liquid–liquid phase transition hypothesis (Poole *et al.*, 1992).

Wallqvist and Mountain (1999) explored molecular models of water, beginning with the precomputer-era models, but mainly focused on the computer-era models. Computer simulations, which have been available since the 1960s, have contributed the missing dimension of time to the picture (or should we say movie) of the molecular structure of water. Computer simulations are powerful additions to the previous combination

of experimental and theoretical approaches to the elucidation of water structure (Wiggins, 1995). The limiting factors are the computing power and time needed for multiwater molecule simulations; thus, simulations are often limited to a few hundred water molecules in boxes with 2.5-nm edges for times equivalent to a few picoseconds (Chaplin, 2004). One of the major advances from simulated studies has been to quantify the development of the hydrogen-bond network with the thermodynamic conditions from the supercooled state to the supercritical region in passing by the ices (Guillot, 2002). Although simulations have contributed significant progress toward a self-consistent molecular model of water, much work remains to be accomplished. For a review on the progress of using computer simulation for determining water structure, see Guillot (2002).

Ludwig's (2001) review discusses water clusters and water cluster models. One of the water clusters discussed by Ludwig is the icosahedral cluster developed by Chaplin (1999). A fluctuating network of water molecules, with local icosahedral symmetry, was proposed by Chaplin (1999); it contains, when complete, 280 fully hydrogen-bonded water molecules. This structure allows explanation of a number of the anomalous properties of water, including its temperature-density and pressure-viscosity behaviors, the radial distribution pattern, the change in water properties on supercooling, and the solvation properties of ions, hydrophobic molecules, carbohydrates, and macromolecules (Chaplin, 1999, 2001, 2004).

Despite the efforts of a large number of scientists from a wide array of disciplines, to date, no single model successfully accounts for all the properties of real water. However, with each passing year, experimental and theoretical studies continue to contribute important pieces to the puzzle of the unusual properties of water, forming an increasingly coherent picture of the true nature of water.

III. WATER AND SOLIDS IN FOODS

Now we turn our attention to the water and the solids that compose the myriad of fresh and processed foods we consume. When a component is added to water (or coexists with water, as in a fresh food), the overall mobility of the water decreases, compared to that of pure water. The magnitude of the decrease depends on the number, amount, and nature of the component(s) added, as well as the effect of any processing methods used. In the past, researchers focused their attention on the relationship between water (activity, availability, mobility) and food stability. Based on the introduction of the polymer science approach to food stability by Slade and Levine (1985, 1988, 1991), the focus has shifted to the relationship

between solids (via the glass transition) and food stability. A combined approach of probing both the water and solids mobility and their individual and combined relationships to food stability is most desirable and is the approach recommended in this review. It is important to remember that the water and solids mobility values obtained are dependent on the property and measurement method selected to probe the system. This is discussed in greater detail in subsequent sections.

Before we proceed to explore the mobility of water and solids in foods, as examined by water activity, nuclear magnetic resonance, and the glass transition, we need to pause and appreciate the complex nature of the systems that we are attempting to investigate.

A. COMPLEX NATURE OF FOODS

Foods are complex, dynamically heterogeneous mixtures of macromolecules, solutes, and solvents (including water). Eads (1999) classified the complexity of food materials into three main dimensions or types: (1) compositional, (2) structural, and (3) dynamical complexity. Compositional complexity of foods ranges from a few simple compounds, such as sucrose and flavors in beverages, to hundreds of compounds in systems such as coffee (Lindsay, 1996) and aged cheeses (Eads, 1999). Structural components and structures in foods range in size from subatomic particles (10^{-15} m) to molecules to molecular assemblies to networks and composites to whole foods such as peas (0.5 cm), apples (8 cm), steaks (20 cm), and watermelon (50 cm). Structures also range in complexity from single atoms to assemblies containing thousands of molecular units, such as amino acids in the case of proteins and glucose units in the case of starch. Identifiable structures also include domains or phases in foods (Eads, 1999). Dynamical complexity in foods refers to both the changes that occur over time, because most food systems are not in equilibrium (Slade and Levine, 1991), and to the distribution of molecular motions. The characteristic duration for dynamical processes in food materials spans about 15 orders of magnitude, from femtoseconds (10^{-15} s) for absorption of light to years for recrystallization of sugars (Eads, 1999).

Ice cream serves as a wonderful (and tasty) example of a complex, dynamically heterogeneous food system. A typical ice cream mix contains milk or cream (water, lactose, casein and whey proteins, lipids, vitamins, and minerals), sucrose, stabilizers and emulsifiers, and some type of flavor (e.g., vanilla). After the ingredients are combined, the mix is pasteurized and homogenized. Homogenization creates an oil-in-water emulsion, consisting of millions of tiny droplets of milk fat dispersed in the water phase, each surrounded by a layer of proteins and emulsifiers. The sucrose is dissolved in

the water phase. The ice cream mix is whipped and frozen, which creates two more discrete structural phases—millions of tiny ice crystals and air bubbles—dispersed in the concentrated, unfrozen mix. The water undergoes a phase transition to form ice, and the dissolved sucrose becomes increasingly concentrated in the unfrozen phase, as ice continues to form. The resultant frozen ice cream contains four microscopic structures: ice crystals, air bubbles, fat droplets, and the unfrozen material (Goff, 1998). Ice cream comprises a solution, suspension, foam, and emulsion and contains extensive air/liquid, fat/liquid, and ice/liquid interfaces (Charley and Weaver, 1998). The water in ice cream may coexist in as many as four different forms: ice, glass, viscous liquid, and hydration layers on macromolecular surfaces (Eads, 1995). Over time, changes in ice cream take place. Ice crystals increase in size (ripen), yielding a coarse, undesirable texture, and lactose crystallizes, resulting in the so-called "sandiness" texture defect. For the interested reader, Hartel (1998) provides an excellent discussion of the various phase transitions important in the manufacturing and storage of ice cream.

As we proceed with discussing the various system properties and measurement methods that can be used to investigate water and solids mobility, it is important to keep in mind the influence the complexity of food systems, such as in the ice cream example just discussed, can have on our ability to measure, interpret, understand, and predict food quality, stability, and safety.

B. WATER ACTIVITY

1. Development of the water activity concept

The concept of substance "activity" was derived by Gilbert N. Lewis in 1907 from the laws of equilibrium thermodynamics and is described in detail in the text entitled "Thermodynamics and the Free Energy of Chemical Substances" by Lewis and Randell (1923). In a homogeneous mixture, each component has a chemical potential (μ), which describes how much the free energy changes per mole of substance added to the system. The chemical potential of water (μ_w) in a solution is given by

$$\mu_w = \mu_w^o + RT \ln a_w \tag{3}$$

where μ_w^o is the chemical potential of pure water in a standard state ($a_w = 1$), R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$), T is temperature, and a_w is water activity. For an ideal solution, a_w equals the mole fraction of water (x_w) and varies between 0 and 1:

$$a_w = x_w = \frac{m_w}{m_w + \Sigma m_{s,i}} \tag{4}$$

where m_w is the molar concentration of water and $m_{s,i}$ is the molar concentration of each of the solutes. Equation (4) is commonly referred to as Raoult's law. Equation (4) is obeyed for ideal solutions, such as dilute sucrose solutions ($x_{sucrose} \leq 0.01$), but is poorly obeyed for concentrated solutions. Most foods exhibit marked nonideality, and calculation of a_w from composition is difficult for real food systems (Walstra, 2003). The main causes of this nonideality, as discussed by Walstra (2003), are (1) dissociation of the solute, such as in the case of NaCl, (2) solute molecule size, and (3) solvent–solute interactions. Rahman (1995) has reviewed extensively several models for predicting a_w based on composition, such as the Norrish (1966) and Ross (1975) models, which have shown moderate success for some model food systems. In general, water activity for foods is best determined experimentally.

Because the chemical potentials of water distributed in two phases (i.e., solution and vapor) must be equal, the water activity of a food can be measured by bringing the food into "equilibrium" with the air above it. At equilibrium, under conditions of constant temperature and pressure, the a_w values of the aqueous phase of a food ($a_{w,f}$) and of the air ($a_{w,v}$) are equal and can be estimated from the ratio of the partial vapor pressure of water above the food (p_v) to the vapor pressure of pure water (p_v^o) at the same temperature (Walstra, 2003):

$$a_{w,f} = a_{w,v} = \frac{p_v}{p_v^o} \tag{5}$$

Thus, the water activity of a food is equal to the relative vapor pressure p_v/p_v^o. The relative vapor pressure is also related to percentage relative humidity (%RH) divided by 100. It is critical to bear in mind the assumptions underlying the development and thus the use of Eq. (5) for determining the a_w of a food. These assumptions are examined in detail in the next section.

Before proceeding, it is worth noting that at temperatures below freezing (i.e., below the freezing point of food, in the presence of an ice phase), the definition of a_w changes to (Fennema, 1996)

$$a_w = \frac{p_{ice}}{p_{SCW}^o} \tag{6}$$

where p_{ice} is the vapor pressure of pure ice and p_{SCW}^o is the vapor pressure of pure supercooled water at a specified temperature and pressure. Because both of these vapor pressure values have been measured and/or calculated for several temperatures below freezing, a_w below freezing can be calculated using Eq. (6) (Table III). Thus, below freezing, a_w is independent of sample composition and is determined by the temperature of the system. So, below freezing pure ice and food containing ice have the same a_w at the same

TABLE III
WATER (LIQUID OR SUPERCOOLED) AND ICE VAPOR PRESSURES AND THEIR RATIO (WATER ACTIVITY BELOW FREEZING) AT 0 °C AND SEVERAL SUBFREEZING TEMPERATURES

Temperature (°C)	Vapor pressure (mmHg)		$\frac{p_{ice}}{p^o_{SCW}}$
	Liquid or supercooled water[a]	Ice[b] or food containing ice	
0	4.579	4.579	1.00
−5	3.163	3.013	0.95
−10	2.149	1.950	0.91
−15	1.436	1.241	0.86
−20	0.9406	0.776	0.83
−25	0.6053	0.476	0.79
−30	0.3816	0.2859	0.75
−35	0.2354	0.1675	0.71
−40	0.1418	0.0966	0.68

[a]Supercooled at all temperatures except 0 °C. Measured values for −15 °C and warmer (Weast, 1975). Calculated values for −20 °C and colder (Mason, 1957).
[b]Measured values from Weast (1975), except −35 °C from Mason (1957).

temperature. Consequently, below freezing a_w is not a useful concept for predicting the stability of different food systems (Fennema, 1996).

2. *Assumptions underlying the water activity concept*

The two main assumptions underlying the derivation of Eq. (5) are (1) thermodynamic equilibrium and (2) conditions of constant temperature and pressure. These assumptions, especially assumption number 1, however, are often violated in food systems. Most foods are nonequilibrium systems. The complex nature of food systems (i.e., multicomponent and multiphase) lends itself readily to conditions of nonequilibrium. Many food systems, such as baked products, are not in equilibrium because they experience various physical, chemical, and microbiological changes over time. Other food products, such as butter (a water-in-oil emulsion) and mayonnaise (an oil-in-water emulsion), are produced as nonequilibrium systems, stabilized by the use of emulsifying agents. Some food products violate the assumption of equilibrium because they exhibit hysteresis (the final a_w value is dependent on the path taken, e.g., desorption or adsorption) or delayed crystallization (i.e., lactose crystallization in ice cream and powdered milk). In the case of hysteresis, the final a_w value should be independent of the path taken and should only be dependent on temperature, pressure, and composition (i.e.,

chemical potential is a state function) (Franks, 1991). Regardless of the cause of a nonequilibrium state, a_w values in foods can change as a function of time, thus violating the assumption of thermodynamic equilibrium listed earlier.

In addition to conditions of thermodynamic equilibrium, water activity is also temperature and pressure dependent (Bell and Labuza, 2000; Kapsalis, 1987). The effect of temperature on a_w can be significant. For many food systems, at constant moisture content, water activity increases as temperature increases (Figure 13A). However, the opposite occurs for several small molecular weight solutes, such as crystalline sugars and salts. For these molecules, at constant moisture content, as temperature increases, water activity decreases (Figure 13B) (Audu *et al.*, 1978; Kapsalis, 1987; Mathlouthi and Roge, 2003). This temperature effect can also be observed for the saturated salt solutions used in constructing sorption isotherms. For example, the water activity of a saturated magnesium nitrate solution is 0.544 at 20 °C, but decreases to 0.514 at 30 °C (Greenspan, 1977). A combination of the temperature–a_w shifts illustrated in Figure 13A and B is observed for foods containing a large amount of solutes (e.g., dried fruits). At low a_w values (~0.55 to 0.75) (at constant moisture content), an increase in temperature results in an increase in a_w, after which an a_w inversion point is reached, and an increase in temperature (at constant moisture content) results in a decrease in a_w (Figure 13C). The specific location of the inversion point depends on the composition of the food and the solubility of the solutes present (Rahman, 1995).

The Clausius–Clapeyron equation can be used to predict the change in a_w with a change in temperature (Kapsalis, 1987):

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{\Delta H_{st}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{7}$$

where a_{w1} and a_{w2} are water activity values at temperatures T_1 and T_2 (absolute temperature, K), respectively, ΔH_{st} is the net isosteric heat of sorption at the moisture content of the sample (cal/mol), and R is the universal gas constant (1.987 cal/mol K). ΔH_{st} is defined as the difference between the total molar enthalpy change and the molar enthalpy of vaporization of pure water. The assumptions underlying Eq. (7) are that moisture content is constant and ΔH_{st} is constant over the a_w and temperature ranges considered (Kapsalis, 1987; Rahman, 1995) for each system under study.

A food system can experience rather large fluctuations in temperature during its lifetime, depending on a variety of factors, such as the location and time of year the product is manufactured and the conditions of distribution, storage, and display. For example, if a food product, such as an intermediate moisture cheese, is manufactured and packaged with an a_{w1} equal to 0.66 at

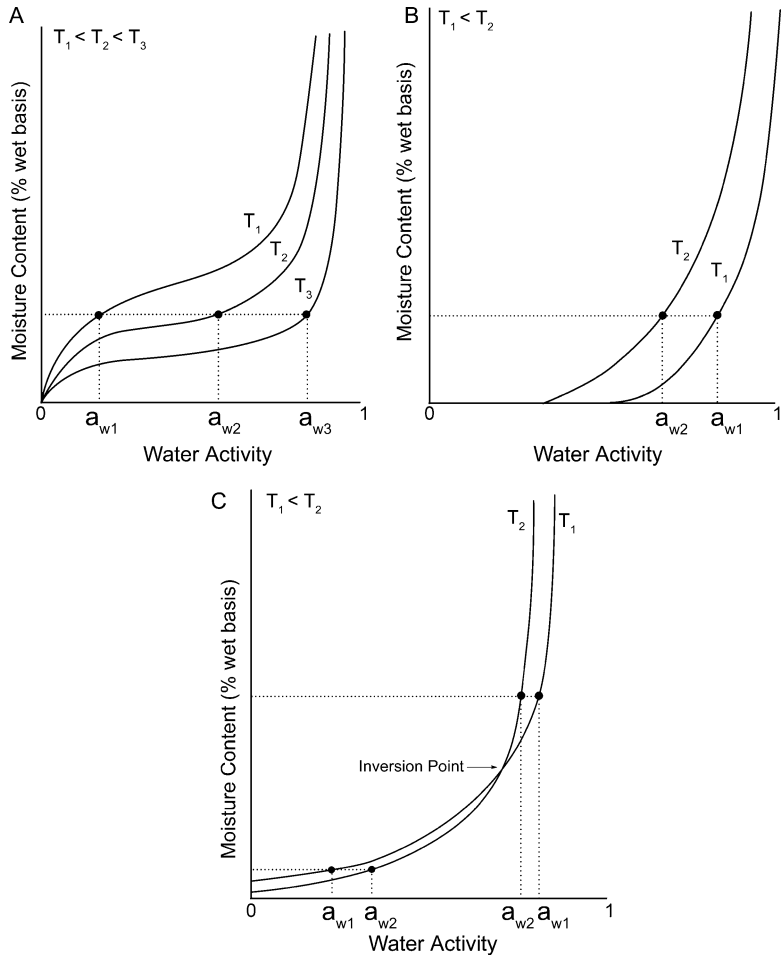

FIG. 13 Illustration of the effect of temperature (T) on a_w for (A) a complex food system, (B) a small molecular weight solute, such as fructose, and (C) foods containing large amounts of solutes, such as raisins. In all case, $T_1 < T_2 < T_3$.

25 °C (298 K) in Wisconsin and is then shipped by railroad car to Illinois in August, temperatures could increase during transport to 45 °C (318 K). Using Eq. (7) and a ΔH_{st} for cheese of 1573 cal/mol (Okos *et al.*, 1992) and assuming no moisture gain or loss, the a_{w2} of the cheese in the railcar would equal 0.78. This 0.12 increase in a_w could result in new microbiological problems and an increase in deleterious chemical reactions, such as Maillard browning. Depending on the characteristics of the product, a 10 °C change in temperature can result in a 0.03 to 0.20 change in a_w (Fennema, 1996).

Before leaving the effect of temperature on a_w topic, it is important to note that when monitoring the effect of temperature on a_w careful control and measurement of the temperature in the regions occupied by the sample and the sensor are needed. The temperature for both sample and sensor must be equal. If the temperature experienced by the sample is different than the temperature experienced by the sensor, data collected are not valid.

In contrast to the effects of temperature, the effect of pressure on a_w is relatively small and can be neglected for reasonable pressure differences. Based on thermodynamics, a change in total pressure of a system affects the vapor pressure. The change in water activity with pressure, at constant moisture content, can be calculated using Eq (8) (Bell and Labuza, 2000):

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{\overline{V}_L}{RT}[P_2 - P_1] \tag{8}$$

where a_{w1} and a_{w2} are water activity values at total pressures P_1 and P_2 (in atm), respectively, $\overline{V}_L$ is the molar volume of water (18 cm^3/mol), R is the gas constant (82.06 cm^3 atm/Kmol), and T is temperature (in K). The atmospheric pressure range in the United States varies from about 1 atm in New Orleans (near sea level) to about 0.82 atm in Denver (the "mile-high" city). Using this atmospheric pressure range, a product with an a_{w1} of 0.60 at 25 °C in New Orleans would have an a_{w2} of 0.5999 at 25 °C in Denver, a negligible difference in a_w.

Strictly speaking, given the violations of the assumptions underlying Eq. (5) discussed earlier, the concept of a_w should not be applied to food systems. However, the concept of a_w has proven to be an extremely useful and practical tool in both the food industry and in food science research (Franks, 1991). Rather than discarding the use of a_w in foods, perhaps it would be more prudent at this point for one to stress the time-dependent nature (i.e., kinetics) of a_w measurements and perhaps, as suggested by Slade and Levine (1991) and Fennema (1996), to use the term relative vapor pressure (RVP, the measured term) in place of a_w (the theoretical term). To avoid confusion, the term a_w will continue to be used in this review, with the understanding that what is most often being measured is RVP.

The continued use of a_w in foods does not preclude the use of other concepts or measurement methods, such as the "food polymer science" approach proposed by Slade and Levine (1991) or rotational and translation mobility as measured by NMR. Rather, it may be most useful to combine these various approaches, recognizing the strengths, perspective (i.e., distance and time scales), and limitations of each. Then, each approach can be utilized where it is most applicable so as to build a multilevel understanding of the workings of specific food systems.

3. *Distance and timescales involved in the water activity concept*

An illustration to help conceptualize the physical meaning of the a_w parameter is given in Figure 14. Water activity is defined [Eq. (5)] as the ratio of the vapor pressure of water above a food (p_v) divided by the vapor pressure of pure water (p_v^o), measured in separate small closed containers (with a small head space) at constant temperature and atmospheric pressure. The vapor pressure in both containers is established by the macroscopic diffusion of water out of the water and out of the food. When equilibrium is reached, the vapor pressure in each container can be measured using a manometer. Thus, the a_w measurement involves water traveling over macroscopic distance scales. In addition to the manometer used in Figure 14, a_w measurements can be made using a variety of techniques, such as hygrometric instruments (i.e., resistance, capacitance, and dew point), hygroscopicity of salts, and isotherm and isopiestic methods (Rahman, 1995), each of which involves water traveling over macroscopic distance scales.

"When is equilibrium reached?" is an important follow-up, timescale question. The water activity measurement involves two interrelated timescales. The first timescale is related to the nonequilibrium nature of most

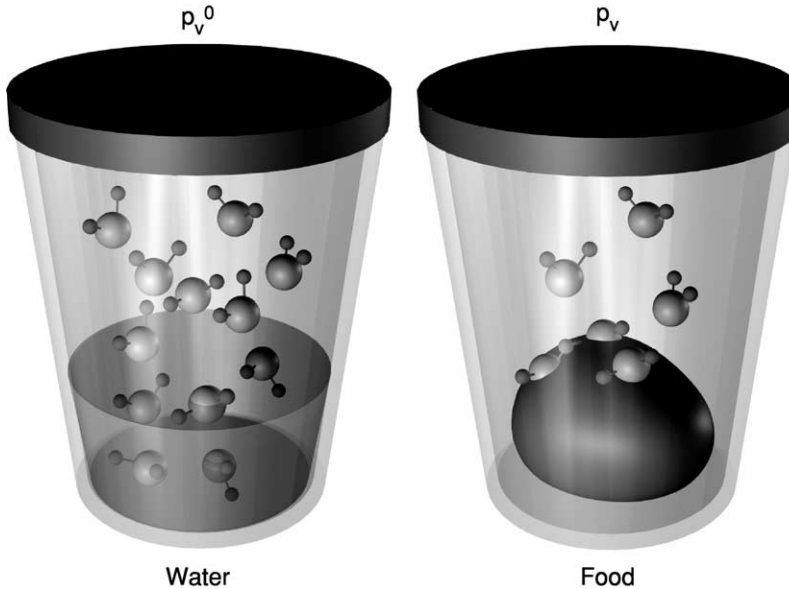

FIG. 14 Illustration of the vapor pressures measured in an a_w measurement. The vapor pressure in both the water and the food containers is established by macroscopic diffusion of water out of the sample (pure water or food).

foods, i.e., the nonequilibrium conditions within a food sample itself (discussed previously). The measured a_w value obtained would depend on the current conditions of the sample being measured (i.e., sample age, moisture content, moisture distribution among components, occurrence of any phase transitions, pH). For many foods, the change in a_w with time is relatively small and of little consequence within the shelf life of the food. Some foods change as a function of time in an attempt to reach equilibrium. For example, it is well documented that if an amorphous (noncrystalline) material, such as a sugar-based candy glass, is held at a high enough relative humidity and temperature for a sufficient length of time, the amorphous material will release the water it gained, and perhaps the water it originally contained, and crystallize (to a thermodynamically more stable state). This amorphous-to-crystalline transformation results in a dramatic change in the measured sample water activity (and the isotherm of the sample). The length of time required for water release and subsequent crystallization depends on the type of amorphous sugar (e.g., glucose versus sucrose) and the specific relative humidity (Makower and Dye, 1956). Some foods, such as butter, a water-in-oil emulsion, and mayonnaise, an oil-in-water emulsion, may never reach equilibrium. For butter, the continuous lipid phase surrounding the water has an a_w of zero, whereas the dispersed water droplets have an a_w of around 0.98 in unsalted butter and 0.91 in salted butter (25 °C). Despite the internal nonequilibrium nature of a butter sample, the a_w of butter can still be measured. However, measurement using an electronic a_w instrument takes a longer time (~30 min) compared to that for a typical food sample (~10 min) because the continuous lipid phase greatly inhibits the macroscopic diffusion of water into the head space of the measurement chamber of the instrument.

The second timescale involves equilibration of a food sample with the air or known relative humidity environment (e.g., saturated salt solutions, in the case of obtaining an isotherm). In this case, equilibration depends on the size of a sample, the measurement method used, and the nature of the sample being measured (this factor is related to the first timescale discussed previously, as illustrated with butter). For example, measuring the a_w of 2 g of corn starch at 25 °C can be done in less than 5 min using, for example, a Decagon AquaLab (Decagon, Pullman, WA) chilled-mirror a_w instrument. Measuring the isotherm for corn starch (2 g), using desiccators containing various saturated salt solutions (0.33 to 0.95 a_w at 22 °C), can take weeks to months (depending on the specific a_w), whereas measuring the isotherm for the same amount of corn starch over the same a_w values using individual proximity equilibration cells (PEC) takes from days to weeks (Lang *et al.*, 1981).

Depending on the food item, only pseudo-equilibrium (or a stationary state) may be reached in the time frame of a measurement, as a very long

time may be required for a sufficient number of water molecules to escape from the food and establish a true equilibrium. However, for many foods, this pseudo-equilibrium state may be close enough to true equilibrium, and the resultant a_w measurement is likely to fall within the uncertainties typically associated with its measurement (± 0.005 to ± 0.02 a_w; Chirife and Buera, 1996; Fennema, 1996, respectively). Chirife and Buera (1996) discussed the establishment of equilibrium in the case of sorption isotherms using a maximum tolerable weight change as the criterion and suggested that sorption determinations performed carefully using this criterion are likely to be close to equilibrium.

Automated water sorption instruments, with ultrasensitive microbalances capable of generating specific %RH values at selected temperatures, are now available, facilitating the production of isotherms in a shorter period of time, from several hours to a few days. Commercially available instruments include the dynamic vapor sorption (DVS) instrument from Surface Measurement Systems Ltd., the IGA*sorp* from Hiden Analytical, and the SGA-100 symmetric gravimetric analyzer from VTI Corporation. Literature concerning the DVS method for isotherm measurements includes Teoh *et al.* (2001), who investigated the sorption behavior of cornmeal components, and Arabosse *et al.* (2003), who compared the DVS method to the saturated salt solution method. Accuracy and repeatability of these new automated water sorption instruments, compared to standard saturated salt solution methods, are currently being investigated in the author's laboratory.

4. Usefulness of the water activity concept in foods

The modern-day study of water activity in foods began taking shape when Scott (1953, 1957; see also Christian and Scott, 1953), applied the thermodynamic concept of water activity to predict the growth of food spoilage microorganisms (van den Berg and Bruin, 1981). Since that time, the concept of water activity has been thoroughly incorporated into academic, industrial, and governmental food science and technology sectors. For example, a_w limits are currently used in the U.S. Federal Regulations on Good Manufacturing Practices and in the food industry as quality assurance specifications. However, the usefulness of a_w as an indicator of food stability and quality has been questioned over the last two decades (Franks, 1982, 1991; Slade and Levine, 1991) and remains a topic of great controversy (Chirife and Buera, 1996; Le Meste *et al.*, 2002). The approach offered here on the usefulness of a_w is based on its practical value, not its absolute theoretical correctness, which has already been investigated and discussed earlier. The compilation of ideas presented in this section on the usefulness of a_w was influenced by the following sources: Rahman (1995), Chirife and

Buera (1996), Fennema (1996), Champion *et al.* (2000), Labuza *et al.* (2001), and Le Meste *et al.* (2002).

a. Assessment of moisture content as a function of relative humidity. Water activity can be useful in determining the moisture content of a food system as a function of relative humidity at the same temperature (i.e., moisture sorption isotherms). Despite the possibility of inadequate conditions for equilibrium, an isotherm is still a useful indicator of moisture content and moisture content changes as a function of relative humidity. Moisture sorption isotherms are useful for a variety of processing and product stability applications, as discussed further later.

b. Prediction of moisture transfer. Water activity can be useful for determining the direction of possible water migration between food components or between a food and its environment. If two components with unequal water activities (e.g., crisp component 1 with an $a_w = 0.25$ and soft component 2 with an $a_w = 0.60$) are placed together in a closed chamber (e.g., a food package), they will over time equilibrate to a single a_w, with component 1 gaining water and becoming soggy and component 2 losing water and becoming hard. This concept of equalizing water activities is at the heart of the development of shelf-stable, dual-texture products, such as raisin-and-flake cereals and cake-and-filling desserts (e.g., Twinkies). This same principle of equalizing water activities applies to the interaction of a food material with its environment, as influenced by the packaging material selected. If a food is packed in moisture-impermeable packaging, such as glass or aluminum foil (>0.001 in. thick), no significant transfer of moisture with the environment will occur. However, if a food is packed in moisture-permeable (e.g., paper) or semipermeable (e.g., plastic films) packaging, the food will gain moisture if the a_w of the food is less than the relative humidity of the air or lose moisture if the a_w of the food is greater than the relative humidity of the air. Moisture sorption isotherms can be used to predict the moisture transfer rate through packaging materials or edible food coatings, and thus predict the shelf life of a food (Rahman, 1995).

c. Development of new products. Water activity and moisture sorption isotherms can be useful in the development of new or reformulated products. The water activity concept is useful in the development of foods in which reduced water contents are desired, such as in the case of intermediate-moisture foods, or in which equal water activities are required, such as in the case of dual-textured foods discussed previously. Effective selection of solutes (e.g., sugars, salts, sugar alcohols) to decrease the water activity is important when formulating a product to a desired or reduced water

activity. For example, in the reformulation of a model granola bar, the substitution of crystalline fructose for honey and brown sugar reduced a_w from 0.56 to 0.48, while maintaining the moisture content of the bar at 4.8% (wet basis) (from A.E. Staley, Krystar Application Bulletin, Number 4:88M504).

d. Determination of product stability and shelf life. Despite its thermodynamic limitations, water activity can be used for product stability and shelf life determinations. As introduced by Labuza *et al.* (1970), a water activity "map" can be used to predict what types of reactions (i.e., chemical, biochemical, physical, and microbial growth and toxin production) will occur in foods. Only a relative reaction rate is plotted versus a_w, as the actual rate is based on a kinetic phenomenon dependent on the specific food system and reaction being investigated. The combined water activity map (Figure 15) and (Table IV) provide a comprehensive and holistic way of

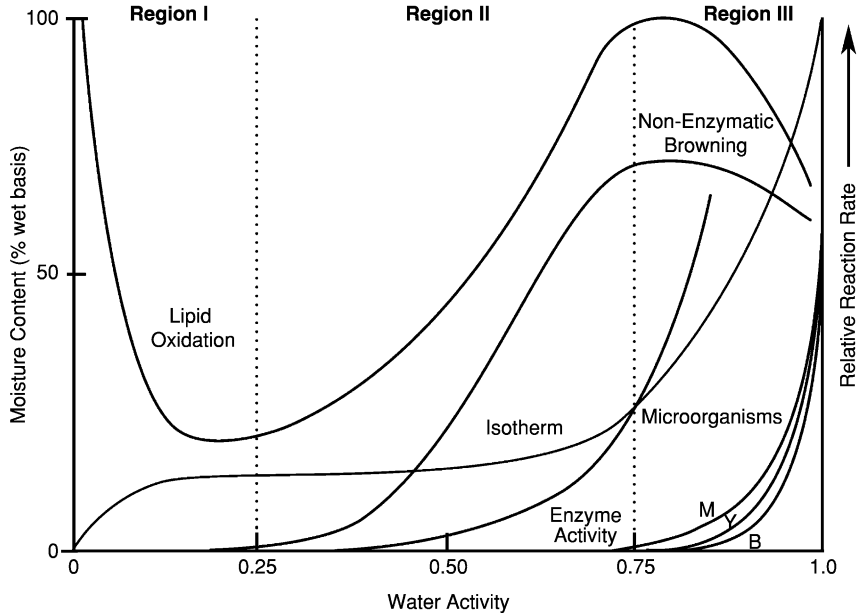

FIG. 15 A comprehensive "stability map" illustrating the general relationship between the occurrence of various reactions important in foods, as a function of water activity, superimposed on a sorption isotherm. M, mold; Y, yeast; B, bacteria. The isotherm is plotted as moisture content (left y axis) versus water activity, whereas all other curves are plotted as relative reaction rate (right *y* axis) versus water activity. Additional information corresponding to regions I, II, and III is given in Table IV.

TABLE IV
WATER ACTIVITY, MOISTURE CONTENT, RELATIVE STABILITY LEVEL, EXAMPLE PROCESSING, PRESERVATION AND PACKAGING TECHNOLOGIES, TEXTURAL ATTRIBUTES, AND EXAMPLE FOOD PRODUCTS CORRESPONDING TO EACH OF REGIONS I, II, AND III IN FIGURE 15

Characteristic	Region I	Region II	Region III
Water activity	0.0 to 0.25	0.25 to 0.75	0.75 to 1.0
Moisture content (%wb)[a]	Low (0 to 2.6%)	Intermediate (2.6 to 18%)	High (18 to 100%)
Relative stability level	High	Intermediate	Low to high, depending on technologies employed
Example processing, preservation, and packaging technologies	Dehydration, drying, extrusion	Concentration, chemical methods	Refrigeration, freezing, modified or controlled atmosphere packaging, pasteurization, canning, aseptic processing, fermentation, chemical methods
Textural attributes	Dry, hard, crisp, shrunken	Chewy, firm, flexible	Soft, juicy, moist, swollen
Example food products[b]	Snack foods, crisp cookies, some breakfast cereals	Some breakfast cereals, granola bars, soft cookies, raisins, some candy bars, IMF pet foods	Fresh fruits and vegetables, fresh meat, poultry, and fish, refrigerated dairy products, canned products

[a]Moisture content values estimated from the composite food isotherm (Figure 17) for 0.25 and 0.75 a_w values.
[b]See Figure 17 for additional product examples.

viewing the pervasive role water plays in foods, from relative stability levels to food processing techniques to textural attributes to example food products. Since its introduction in 1970, the a_w stability map has been referenced and/or reproduced in various forms thousands of times. However, the a_w stability map is not without its limitations. As pointed out by Karel *et al.* (1993), such maps do not always take into consideration the occurrence of phase transitions and time-dependent, nonequilibrium phenomena. Roos (1995) introduced a modified version of the a_w stability map, which is discussed in the glass transition section of this review.

Labuza *et al.* (1970) originally partitioned the stability map into three zones: zone I ranged from 0.0 to 0.25 a_w, zone II ranged from 0.25 to 0.80 a_w,

and zone III ranged from 0.80 to 1.0 a_w. Different reproductions of the map have subsequently used slightly different a_w partitioning values ($\pm$ 0.05) and some have included small range bars between the zones (e.g., Fennema, 1996; Rockland, 1987). Labuza (1984) also introduced an alternative isotherm partition scheme: dry foods 0.0 to 0.6 a_w, intermediate-moisture foods 0.60 to 0.92 a_w, and tissue foods greater than 0.92 a_w. Labuza pointed out that a_w does not begin to decrease much below 0.99 until the moisture content is reduced to about 1 g water/g solid or about 50% moisture content (wb).

Virtually all water containing foods can be categorized using the stability map/table scheme presented in Figure 15 and Table IV. For example, fresh meat (e.g., ground beef, chicken, pork) is located in zone III of the stability map, with an average moisture content of 73% and a_w of 0.98. Refrigeration and freezing are used to extend the shelf life of meat to days and months, respectively. Baked products, such as bread, are a bit more complicated. Bread can typically have a moisture content of approximately 36% and an a_w of 0.96 and is located in region III of the stability map. Baking, used to produce bread, decreases the moisture content of a bread dough, while chemical preservatives methods, such as the use of potassium sorbate as a mold inhibitor, are used to extend the shelf life of the bread from days to weeks.

Chirife and Buera (1996) have extensively reviewed the concerns about using water activity as a predictor of microbial viability and growth. One of those often-cited concerns is that the microbial response can differ at a particular a_w value, depending on the type of solute used (solute-specific effects). Such a solute-specific effect on the growth of *Staphylococcus aureus* is illustrated in Figure 16, where it can be seen that the minimum a_w value for growth is dependent on the solute system used to adjust water activity. However, as noted by Chirife (1994), although the minimum a_w value for growth is clearly dependent on the solute system used, *S. aureus* does not grow below the widely accepted minimum a_w value of 0.86. For different solutes, the variation in minimum a_w value for growth is related to two main effects: (1) the ability of the solute to decrease the a_w of the food medium and/or (2) the ability of the solute to exhibit specific antibacterial activities, including the ability to permeate the bacterial cell membrane (Chirife and Buera, 1996).

Chirife and Buera (1996) likened the solute-specific effect on a_w to that on pH. The solute effect on pH has not precluded the widespread usage of pH in food preservation. Rather, it is important to understand and quantify its limitations, but not discontinue its usage. For example, it is important to quantify the specific inhibitory effects of various food grade acids and to establish safe pH limits corresponding to the less inhibitory ones rather than

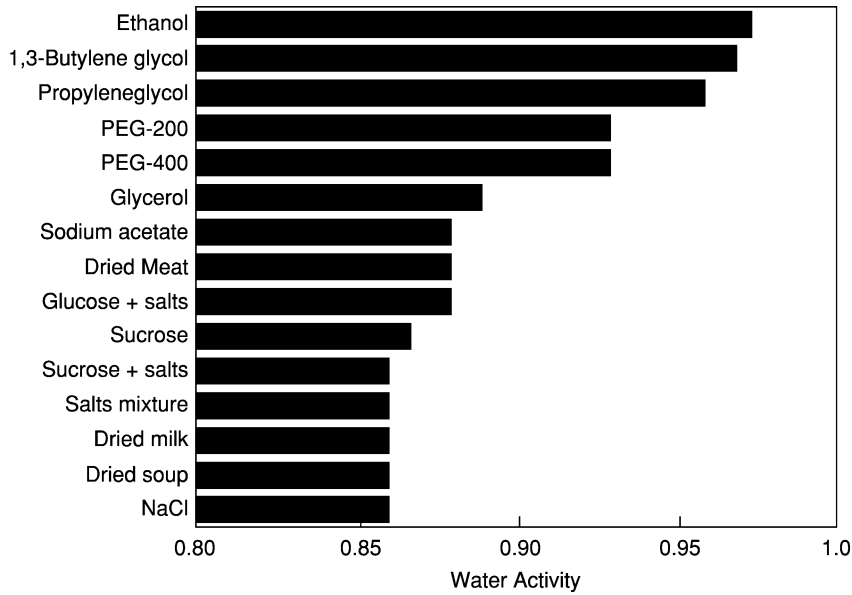

FIG. 16 Minimum a_w for growth of *Staphylococcus aureus* in specific solute systems at 30 to 37 °C (data from Chirife and Buera, 1996).

the most inhibitory ones. Chirife and Buera (1996) recommended the same approach used for pH for use with a_w values in foods. Another often-cited concern about using water activity for the prediction of microbial viability involves the nonequilibrium nature of the water activity parameter. However, Chirife and Buera (1996) argued that nonequilibrium effects are in many cases slow, i.e., slower than the shelf life of a food, and/or so small that they do not seriously detract from the use of the a_w concept as a predictor of microbial stability. Both concerns discussed earlier, regarding the validity of the a_w concept for use as a predictor of microbial viability, should not be overlooked, but rather carefully taken into account, along with other factors that affect viability (e.g., temperature, pH, oxygen level, and sample preparation and history). The cumulative effect of factors such as these on microbial viability is the basis of Hurdle technology proposed by Leistner (1987). Also, the use of other possible stability-predicting parameters, such as molecular mobility, should continue to be investigated.

e. Process design and control. Water activity and moisture sorption isotherms play important roles in the design, operation, and control of water-management unit operations, such as concentration, drying, osmotic

dehydration, freezing, freeze-concentration, freeze-drying, and reverse osmosis. For example, in drying by diffusion operations (e.g., air drying), the driving force for water removal is the difference between the vapor pressure of water at the surface of a food and the partial vapor pressure of water in the air. Thus, the drying rate depends on the a_w of a food throughout a drying process (Rahman, 1995).

5. *Measurement of water activity in foods*

A variety of measurement methods have been developed for determining the water activity of food materials and are well described in texts such as Rahman (1995), Wiederhold (1997), and Bell and Labuza (2000). In general, water activity is a relatively easy parameter to measure, which can be an advantage, especially for use in the food industry. Depending on the technique selected, the water activity of a food material can be measured in a time frame of minutes (e.g., electronic instrument). In addition, individuals can be trained, with a limited amount of instruction, to make water activity measurements. Consequently, when appropriate, water activity measurements can be made relatively quickly by personnel overseeing a manufacturing line for quality assurance purposes. Measurement protocols, such as calibration procedures and proper temperature control, should be implemented to assure the accuracy of online a_w measurements.

Two important, but often under emphasized, aspects of measuring a_w values and isotherms in foods are accuracy and repeatability. Variation in a_w and isotherm values can be due to inherent variation in biological materials, as well as differences in measurement methods, protocols, and equipment employed. Wolf *et al*. (1985) presented the results of a COST 90 Project on the standardization of saturated salt solution isotherm measurement methodology and Lewicki and Pomaranska-Lazuka (2003) discussed errors in the static desiccator method.

6. *Composite food sorption isotherm*

Typically, sorption isotherms are constructed for a single food ingredient or food system. An alternative approach is to plot the moisture content versus water activity (or relative vapor pressure) values for a variety of "as is" food ingredients and food systems. The result is a composite food isotherm (Figure 17). The composite isotherm fits the typical shape observed for a sorption isotherm for an individual food system, with a few products falling above or below the isotherm curve (chewing gum, honey, raisins, bread, and colby and cheddar cheeses). Slade and Levine (1991) were the first to construct such a plot using moisture content and a_w values from van den

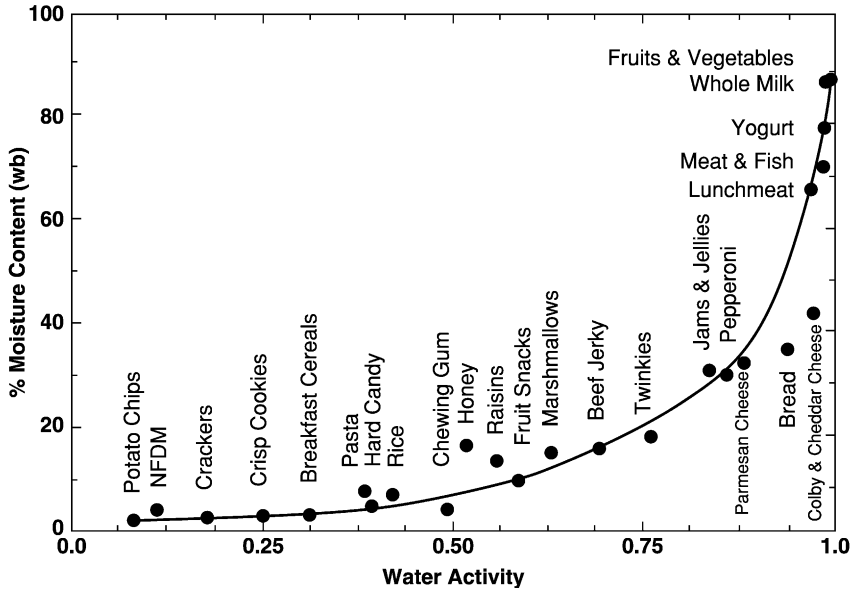

FIG. 17 Water activity (or relative vapor pressure) and moisture content (%, wb) values plotted for a variety of food materials (“as is”), resulting in a composite (or universal) food isotherm. Potato chip and nonfat dry milk (NFDM) data are from van den Berg (1986). All other data are from the author’s laboratory (at 20 or 25 ± 1 °C). Water activity and moisture content values for the breakfast cereal and fruit and vegetable categories had the largest ranges (expressed here as standard deviation): 0.311 ± 0.073 a_w and $2.94 \pm 1.55\%$ mc (wb) and 0.995 ± 0.004 a_w and $89.8 \pm 3.90\%$ mc (wb), respectively. The curve is to guide the eye—it is not a fitted line.

Berg (1986). An advanced version of the Slade and Levine (1991) plot is given later in this review (see Figure 35). Slade and Levine (1991) noted that the overall shape of the resulting curve resembled that of a typical sorption isotherm for a single food material, with a few exceptions (raisin, bread, and cheese; similar results are observed in Figure 17, with the addition of honey). Slade and Levine (1991) noted that raisins exhibit a lower a_w than expected for their moisture content. They attributed this anomalous behavior to desorption hysteresis, as raisins are produced by the dehydration of grapes. However, bread and cheese are produced by thermosetting processes, resulting in a relatively high a_w with a relatively low moisture content. Slade and Levine have subsequently published their isotherm, referring to it as a “universal sorption isotherm” (Slade and Levine, 1998, 2002). A similar plot is included in Walstra (2003), who used a log scale for the a_w axis. Walstra noted two exceptions in his plot. The first is a brine solution

(described as almost saturated with NaCl), and the second is high fat content foods such as cream and margarine. Skim milk and cream have the same aqueous phase, resulting in the same a_w, but different amounts of water. Thus, skim milk and cream have the same a_w, but cream has a lower moisture content compared to skim milk (e.g., 58% moisture content, wb, for heavy whipping cream and 91% moisture content, wb, for nonfat milk).

C. NUCLEAR MAGNETIC RESONANCE

Since the simultaneous discovery of nuclear magnetic resonance by Bloch at Stanford and Purcell at Harvard in 1946, NMR has been applied to countless problems and has benefited virtually every branch of science. Such a wide array of NMR methods exists that it is not possible to adequately describe or even mention all of them in this review. Thus, the approach taken here is to provide a brief section explaining basic NMR principles and to focus on the usefulness of NMR by providing selected examples of NMR techniques used to characterize the mobility of water and solids in food systems. In addition, some NMR techniques useful for determining the glass transition temperature are included in the glass transition section of this review. An excellent comprehensive overview of how to apply selected NMR methods to investigate specific food properties is given by Eads (1999). Eads (1999) links magnetic resonance observables to food analytical quantities, discusses the influence of sample complexity on magnetic resonance observables, and provides the reader with numerous spectroscopic strategies for defeating or embracing the effects of sample complexity. A more specific review by Schmidt (1999) focuses on the usefulness of various NMR techniques to examine the physical and sensory properties of food systems.

1. Principles of NMR

Anomalous to its low-frequency, long wavelength position in the electromagnetic spectrum (radio wave region; 10^9- to 10^3-Hz frequency range and 10^- to 3×10^7-cm wavelength range), NMR is associated with nuclear spin transitions (Belton, 1995). Atomic nuclei with an odd number of protons or neutrons possess a nonzero spin value (I), which can be thought of as being similar to the rotation of a charged nucleus. The strength and direction of the magnetic field surrounding each spinning nucleus can be described by a vector quantity known as the magnetic moment (μ_n), which can interact with a magnetic field. Thus, the first step common to all types of NMR experiments is that the sample to be analyzed is placed in a probe (containing a radio frequency coil), which is located in a strong externally applied magnetic field (B_0, in units of Tesla or T) (Figure 18). The torque exerted by B_0 on the

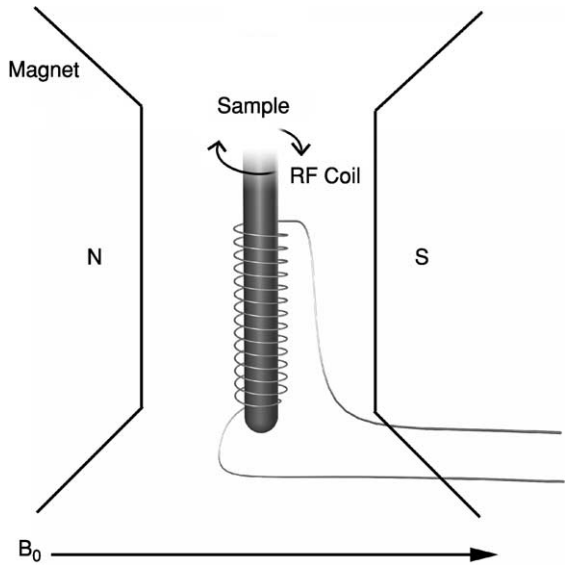

FIG. 18 Schematic representation of an NMR experiment. A sample is placed in a probe containing a radio frequency coil, which is located in a strong applied magnetic field, B_0. The coil is tuned to resonate at the frequency of the applied radio frequency field, B_1.

spinning nucleus causes precession of the magnetic moment (Figure 19), where the frequency of precession is proportional to the strength of B_0:

$$\omega_0 = \gamma B_0 \tag{9}$$

where ω_0 is the angular frequency in radians per second (also called the Larmor or resonance frequency) and γ is the magnetogyric ratio (rad $\text{Tesla}^{-1}\text{s}^{-1}$), which is a unique constant for each nucleus. The angular frequency can also be expressed in frequency units (s^{-1}, Hz), as $\nu = \omega_0/2\pi$:

$$\nu = \frac{\gamma B_0}{2\pi} \tag{10}$$

In the presence of B_0, nonzero spin nuclei adopt a specific number of orientations. The number of allowed orientations is dependent on the spin value and is equal to $(2\text{I} + 1)$. For the simplest case of $\text{I} = 1/2$, two orientations are allowed: one aligned parallel to B_0 and one antiparallel. Nuclei with $\text{I} > 1/2$ have a quadrupole moment (called quadrupolar nuclei) that allows them to interact with electric fields produced by neighboring nuclei and electrons.

Water has three stable nuclei that possess nonzero spin values: proton (^{1}H), deuterium (^{2}H), and oxygen-17 (^{17}O). The spin values and number of

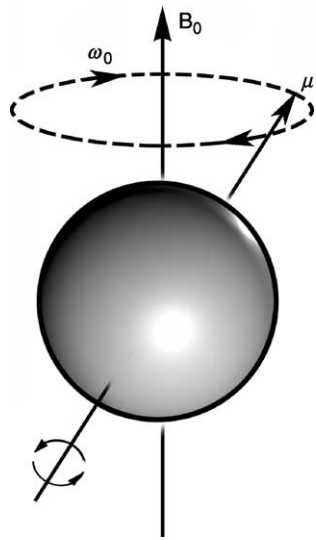

FIG. 19 An external magnetic field (B_0) applied to a nucleus causes the nucleus to precess at a frequency (ω_0) proportional to the strength of the magnetic field [Eq. (9)].

allowed orientations, as well as other NMR parameters, for the three NMR-active water nuclei are given in Table V. Each orientation has a different energy level, with the magnetic moments parallel to the applied magnetic field having slightly lower energy than those that are antiparallel, Figure 20 illustrates the energy difference, in the absence and presence of B_0, for ^{1}H nuclei, where I = 1/2. In the absence of B_0, magnetic nuclei are oriented randomly and all have the same energy level. In the presence of B_0, an excess of magnetic nuclei align parallel to B_0 and have a lower energy level than those that align antiparallel to B_0. The number of nuclei in the parallel and antiparallel positions is determined by the Boltzmann distribution [Eq. (11)]:

$$\frac{N_\alpha}{N_\beta} = e^{\Delta E/kT} \tag{11}$$

where N_α and N_β are the numbers of nuclei in the α (lower energy) and β (higher energy) positions, respectively, ΔE is the energy difference between the states and is equal to $h\nu$ (h is Planck's constant, 6.6×10^{-34} Js), k is the Boltzmann constant (1.38×10^{-23} JK^{-1}), and T is temperature (in K). There is a slight excess of parallel nuclei (N_α), which results in the creation of sample magnetization. The NMR spectrum is a measure of the energy required to cause a transition between energy levels and depends on the strength of B_0 (Belton, 1995). Typical NMR magnetic field strengths (0.2 to

TABLE V
PARAMETERS FOR THREE STABLE NMR-ACTIVE WATER NUCLEI[a]

Isotope	Spin value (I)	Natural abundance (%)	Number of allowed orientations	Gyromagnetic ratio (γ) (10^7 rad $T^{-1}s^{-1}$)	Relative sensitivity[b]	Frequency at 2.35 T (MHz)
^1H	1/2	99.98	2	26.75	1.00	300.000
^2H	1	1.5×10^{-2}	3	4.1	9.65×10^{-3}	15.351
^{17}O	5/2	3.7×10^{-2}	6	−3.6	2.91×10^{-2}	13.557

[a]From Kemp (1986).
[b]Sensitivity relative to proton. To calculate the absolute sensitivity, multiply by the natural abundance.

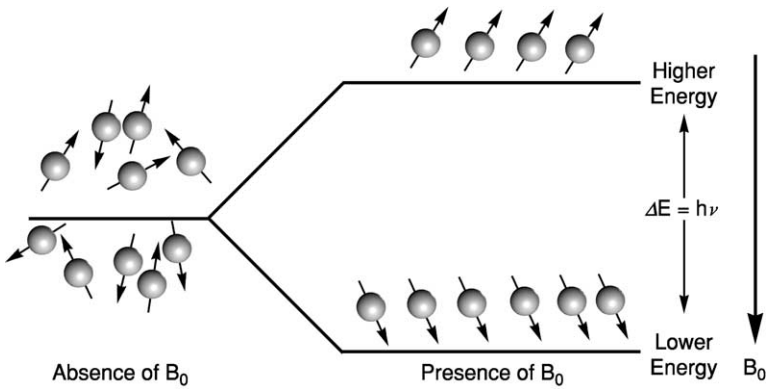

FIG. 20 Schematic illustration of magnetic nuclei, for the case of I = 1/2, in the absence and presence of B_0.

21 Tesla, which corresponds to ^1H resonance frequencies of 8.5 to 900 MHz, respectively) result in large differences in resonance frequency (see Table V for frequencies at $B_0 = 2.35$ T), making it possible to observe each NMR-active nucleus independently.

In a basic pulsed NMR experiment (for I = 1/2), when a sample is placed in the applied magnetic field (B_0), the nuclear spins distribute themselves between parallel and antiparallel positions, according to Boltzmann distribution [Eq. (11)] (Figure 21A). The number of spins in the parallel position is slightly greater than that in the antiparallel position. At equilibrium, the spins are precessing randomly (i.e., lack phase coherence). The populations

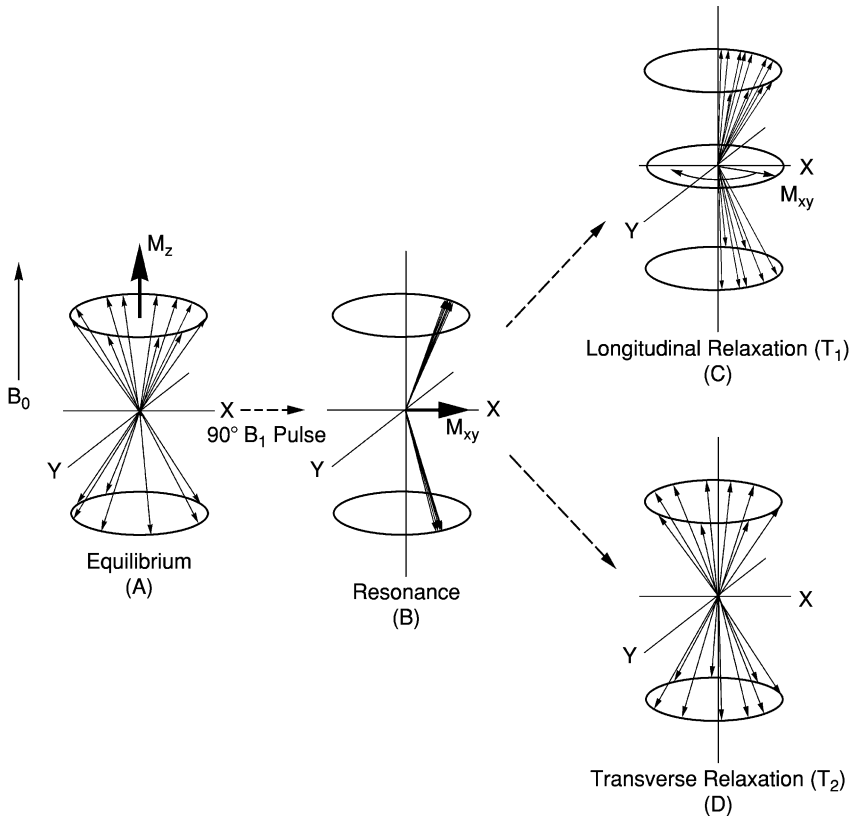

FIG. 21 Schematic illustration of the changes in spin states experienced by I = 1/2 nuclei during a basic NMR experiment. (A) In the presence of B_0, nuclear spins are distributed in parallel (lower energy) and antiparallel (higher energy) positions, according to the Boltzmann distribution [Eq. (11)]. The spins are precessing randomly (i.e., lack phase coherence). Net magnetization along the z axis (M_z) is at a maximum. (B) Immediately following application of a 90° B_1 pulse, the populations of parallel and antiparallel positions are equalized, and the spins precess in phase (i.e., exhibit phase coherence) at the Larmor frequency. The sample magnetization (M_{xy}) is at a maximum value. (C) The longitudinal relaxation process restores the equilibrium distribution of spins to the parallel and antiparallel positions. (D) The transverse relaxation process is a loss of phase coherence of the spins. Longitudinal and transverse relaxation processes occur simultaneously.

of parallel and antiparallel positions are equalized by the absorption of photons with energy equal to the difference in energy between the spin states (Figure 21B). This excitation energy is supplied to nuclei in a sample by an oscillating magnetic field (B_1) at right angles to B_0, through the coils of the

NMR probe, with a frequency equal to the Larmor frequency. In pulsed NMR, the excitation field is applied in a short pulse (or pulse sequence), usually of a few microseconds. Before the B_1 pulse is applied, the magnetic moments are out of phase with one another and the net magnetization lies along the z axis (M_z), and M_z is at a maximum value (Figure 21A); however, the net magnetization in the x–y plane (the signal detection plane) (M_{xy}) is zero. When the B_1 pulse is applied, the magnetic moments get in phase with one another (called phase coherence), and the sample magnetization precesses about B_1. The angle of precession (θ; called the flip or tip angle), which depends on the duration and strength of B_1, determines the magnitude of M_{xy}. For example, a flip angle of $\theta = 90°$ (or $2/\pi$) focuses the entire sample magnetization in the x–y plane, and M_{xy} is at a maximum value (Figure 21B).

Immediately after the 90° B_1 pulse is turned off, the sample magnetization returns to precessing about B_0. This process, referred to as relaxation, produces an electromotive force or voltage. Detection of the loss of energy (through the process of relaxation) occurs through the same coil used for excitation. As the magnetization relaxes, it contains both a longitudinal component (along the z axis; Figure 21C) and a transverse component (in the x–y plane; Figure 21D). The magnitude of the transverse relaxing signal, as a function of time [$M_y(t)$], is called the free induction decay (FID). The FID can be analyzed directly (as discussed later) or can be Fourier transformed from the time domain into the frequency domain, yielding an NMR spectrum. A great deal of chemical information (e.g., molecular structure and chemical analysis) can be extracted from an NMR spectrum, as each resonance peak provides fingerprint-like information, including position (called chemical shift, δ), area (or intensity), width, and multiplicity (called spin–spin or J coupling).

The decay of the longitudinal component is called longitudinal relaxation or spin–lattice relaxation and is characterized by a time constant T_1 (s) or a rate constant R_1 (s^{-1}), which equals $1/T_1$. The longitudinal relaxation process restores the equilibrium distribution of spins to the parallel (lower energy) and antiparallel (higher energy) positions (Figure 21C). Longitudinal relaxation occurs because of the existence of magnetic fields fluctuating at the correct frequency, which are able to induce transitions between the antiparallel and the parallel positions of the spins in the applied magnetic field. If these fluctuations are associated with a lattice, then exchange of energy can occur between the spin system (the nuclei being probed) and the lattice (the molecular assembly in which the spins are embedded). There are many physical processes that result in locally fluctuating magnetic fields. The most important such interaction in liquids is the dipole–dipole interaction. Additional relaxation mechanisms are mentioned in the next section.

Because the excitation/detection coil is in the x–y plane and the longitudinal component relaxes along the z axis, T_1 cannot be measured directly from an NMR spectrum, but must be obtained using a pulse sequence. The most commonly used pulse sequence to measure T_1 is an inversion recovery pulse sequence (Kemp, 1986). Other commonly used pulse sequences for measuring T_1 are given in Ernst *et al.* (1987).

The decay of the transverse component is called transverse relaxation (or spin–spin relaxation) and is characterized by a time constant T_2 (s) or a rate constant R_2 (s^{-1}), which equals $1/T_2$. The transverse relaxation process is a loss of phase coherence (dephasing) of the spins after an excitation pulse (B_1) due to differences in the magnetic field experienced by individual magnetic moments and to exchange of energy between identical nuclei (Figure 21D). These processes result in a loss of magnetization in the x–y plane. Magnetic field differences arise from two distinct sources: static magnetic field inhomogeneity (imperfections in B_0, minimized by shimming) and local magnetic fields arising from intramolecular and intermolecular interactions in a sample (true or genuine transverse relaxation). The total relaxation time constant, designated as T_2^*, is a combination of both sources:

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_{2(\Delta B_0)}} \tag{12}$$

where T_2 refers to the contribution from the true relaxation process and $T_{2(\Delta B_0)}$ to that from field inhomogeneity (ΔB_0). $T_{2(\Delta B_0)}$ equals $1/\pi\gamma\Delta B_0$, where $\gamma\Delta B_0$ is the spread in frequencies caused by field inhomogeneity (Eads, 1998). For single exponential relaxation (i.e., Lorentzian line shape), T_2^* can be obtained from the line width of an NMR spectrum resonance at half-height ($\Delta\nu_{1/2}$):

$$T_2^* = \frac{1}{\pi\Delta\nu_{1/2}} \tag{13}$$

Measurement of a true T_2 can be obtained using a spin-echo pulse sequence, such as the Carr–Purcell–Meiboom–Gill (CPMG) sequence, which minimizes the loss of phase coherence caused by inhomogeneities (Kemp, 1986).

A parameter related to T_2 is $T_{1\rho}$, the rotating-frame relaxation time. To obtain $T_{1\rho}$, the equilibrium spin magnetization is first subjected to a 90° pulse, which rotates the equilibrium spin magnetization along the y axis. A spin-locking frequency field (amplitude $\omega_1 = \gamma B_1$) is immediately applied for a time, τ, along the y axis. The spin-locking field is then turned off and the resultant FID is recorded. A plot of the signal amplitude as a function of

the spin-locking time, τ, exhibits an exponential decay with time constant, $T_{1\rho}$. A discussion of the potential usefulness of $T_{1\rho}$ to probe the molecular dynamics of water is given by Hills (1998).

In addition to T_1 and T_2, which reflect the rotational motion of water, NMR can also be used to measure the translational motion of water. If an additional, relatively small (compared to B_0), steady magnetic field gradient is incorporated into a pulsed NMR experimental setup, a translational diffusion coefficient (D, m^2/s) can be measured (called pulsed field gradient NMR).

Up to this point, water mobility values obtained are average values for an entire sample. However, if magnetic field gradients in the *x, y*, and *z* directions are incorporated into a pulsed NMR experimental setup, the spatial distribution aspects of water mobility (T_1, T_2, and D) can also be measured via the use of magnetic resonance imaging (MRI) techniques.

A vast number of NMR experiments can be devised using the basic NMR principles presented earlier. Eads (1999) organized all the possible NMR experiments into five classes (Table VI). The forms of data for each class, as well as references for additional study, are included in Table VI.

TABLE VI
CLASSES OF MAGNETIC RESONANCE MEASUREMENTS ADAPTED FROM EADS (1999)

Class	Forms of data	References
NMR relaxometry	Free induction decay (T_2*) or solid echo Spin echo decay (T_2) Magnetization recovery curve (T_1)	Eads (1998)
NMR diffusometry	Decay of spin echoes in the presence of a magnetic field gradient (echo attenuation curve)	Price (1996, 1997, 1998a)
High-resolution liquid and solid NMR spectroscopy	One- or two-dimensional NMR spectra	Claridge (1999); Harris (2001)
NMR imaging	Images (one-, two-, or three-dimensional array of voxel intensities) pixel-specific relaxation curves; maps, and movies (i.e., density, T_1, T_2, or D weighted)	Hills (1998); McCarthy (1994); Price (1998b)
Volume-localized NMR spectroscopy	NMR spectrum from voxel of interest	Eads (1999)

2. Connecting relaxation and mobility

NMR spin relaxation is not a spontaneous process, it requires stimulation by a suitable fluctuating field to induce an appropriate spin transition to reestablish equilibrium magnetization. There are four main mechanisms for obtaining relaxation: dipole–dipole (most significant relaxation mechanism for $I = 1/2$ nuclei), chemical shift anisotropy, spin rotation, and quadrupolar (most significant relaxation mechanism for $I > 1/2$ nuclei) (Claridge, 1999).

Both T_2 and T_1 relaxation times are coupled to molecular mobility, but the specifics of their relationship are different and vary depending on the nucleus being probed (Belton, 1995; Campbell and Dwek, 1984; Eads, 1998). In the simplest case of relaxation in a single proton pool (e.g., pure water), each water proton experiences a randomly fluctuating local magnetic field due to transient dipolar interactions with other water protons as water molecules rotate and translate (via Brownian motion). Fluctuating fields at an appropriate frequency (the Larmor frequency, ω_0) are able to induce transitions between antiparallel and parallel spin states, resulting in longitudinal relaxation. Hills (1998) and Claridge (1999) give details of the relationship between the rate of relaxation and the amplitude and frequency of fluctuating fields.

A schematic illustration of the dependence of T_1 on molecular rotational correlation time, τ_c (the average time taken for molecule to rotate through one radian), is shown in Figure 22. The dependence of T_1 on mobility shows a minimum, when $\tau_c = 1/\omega_0$ (or the product $\omega_0\tau_c = 1$). When $\tau_c \ll 1/\omega_0$, the system is in an extreme narrowing limit (also called a motionally narrowed regime), and when $\tau_c \gg 1/\omega_0$, the system is in a slow motion regime and T_1 is again large. Thus, it is possible to obtain T_1 values of equal magnitude for both liquid and solid domains, as well as for high and low temperatures.

Figure 23 illustrates the T_2 relaxation behavior of the three major mobility domains in foods—liquid, viscous liquid, and solid (crystalline and glassy). ^{1}H T_2 relaxation time values typically observed in these domains, as well as ^{1}H T_2 values specific for water in liquid and crystalline solid domains, are also given in Figure 22. The difference in T_2 relaxation behavior between liquids and solids is very dramatic and is the basis for using NMR for determining water content (Schmidt, 1991) and solid fat content (Gribnau, 1992). The dependence of T_2 relaxation on molecular correlation time is also illustrated in Figure 22. In the extreme narrowing limit, $T_2 = T_1$, whereas in the slow motion regime, T_1 becomes much longer than T_2. In general, based on Figure 22, shorter T_2 values mean less mobility.

NMR relaxation time measurements (T_1 and T_2) can provide valuable information for investigating the molecular dynamics of water in food systems. However, a number of factors can seriously complicate the analysis

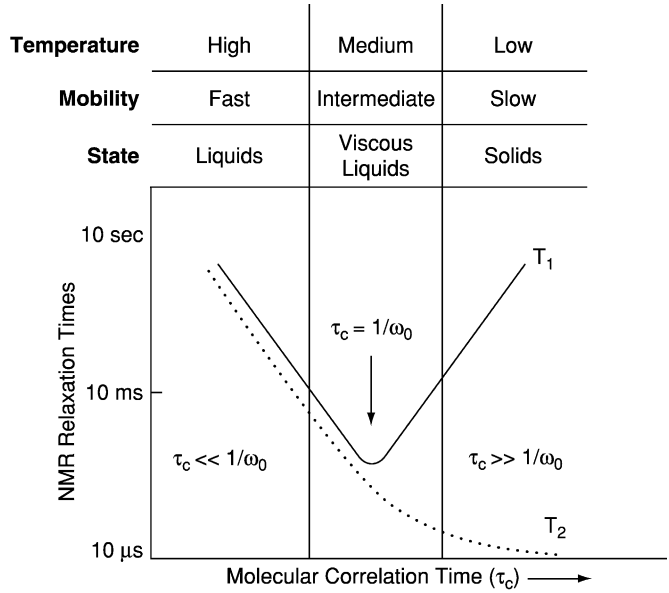

FIG. 22 A schematic illustration of the dependence of NMR relaxation times T_1 and T_2 on the molecular correlation time, τ_c, characterizing molecular mobility in a single-component system. Both slow and fast motions are effective for T_2 relaxation, but only fast motions near ω_0 are effective in T_1 relaxation.

and quantitative interpretation of the relaxation behavior of water, such as the presence of additional relaxation pathways, the water nucleus chosen, and the complex nature of most food systems. Additional pathways contributing to relaxation are discussed in detail by Belton (1990) and Eads (1999) and include (1) chemical exchange–physical exchange of protons between water and exchangeable solute protons, such as hydroxyl, amine, and carboxyl groups within homogeneous regions (also called proton exchange) (affects both T_1 and T_2); (2) diffusion exchange–physical movement between spatially separate regions (affects both T_1 and T_2); (3) cross-relaxation–transfer of z magnetization between spin states having different T_1 values (also called magnetization exchange or magnetization transfer) (affects T_1); and (4) paramagnetic relaxation–interaction of nuclear spins with unpaired electrons; occurs in the presence of paramagnetic species, such as iron, manganese, and dissolved oxygen (affects T_1 and T_2).

The water nucleus chosen also has an impact on relaxation data. Proton relaxation is affected by chemical exchange and cross-relaxation, ^{2}H by chemical exchange, and ^{17}O by proton-exchange broadening (scalar spin–spin coupling between ^{1}H and ^{17}O nuclei; affects T_2, but not T_1) (Glasel,

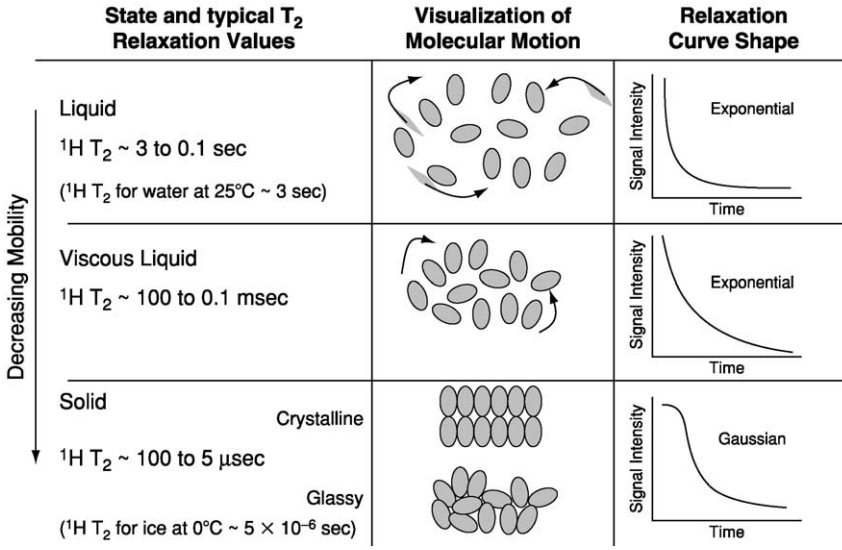

FIG. 23 A schematic illustration of the molecular motions and associated T_2 relaxation curve behavior for the three major domains in foods—liquid, viscous liquid, and solid (crystalline and glassy). Typical ^{1}H T_2 NMR relaxation time values observed in these domains, and values specific for water in liquid and crystalline domains, are listed.

1972; Halle and Karlstrom, 1983a,b). The effects of ^{17}O proton-exchange broadening can be eliminated by proton decoupling (Richardson, 1989). Deuterium and ^{17}O are quadrupolar nuclei ($I > 1/2$) and are not affected by magnetization transfer because quadrupolar relaxation is already very efficient, and these nuclei intrinsically possess weak dipolar interactions (Belton, 1990). The effects of spatial (or structural), compositional, and dynamical complexity of foods on relaxation time measurements are discussed in detail by Eads (1999). Because of the aforementioned complications, quantitative interpretation of T_2 and T_1 relaxation time measurements for water in foods often requires nucleus- and system-specific, sophisticated and detailed analysis and modeling (Belton, 1995). For the interested reader, Hills (1998) presents a comprehensive overview of water proton relaxation, ranging from that in dilute (solutions and gels) to more concentrated (rubbers and glasses) model food systems.

3. Distance and timescales involved in NMR

As discussed previously, foods display an enormous range of compositional, structural, and dynamical complexity. The structural complexity of foods can extend over distance scales ranging from subatomic to macroscopic.

Figure 24, presented originally by Belton (1995), illustrates the enormous range in distance scales that can be probed using various magnetic resonance spectroscopy and imaging techniques. Approximate distance ranges for molecular, microscopic, and macroscopic regions are provided for perspective on the left side of Figure 24. The criterion used for the demarcation between macroscopic and microscopic regions was based on the size of objects that are no longer visible with the naked or unaided eye, i.e., less than 40 μm (Hills, 1998).

Shortest-range interactions (over molecular distances of up to a few bonds away) examined by magnetic resonance are those that cause effects such as chemical shift, spin–spin coupling (also called scalar or "J"

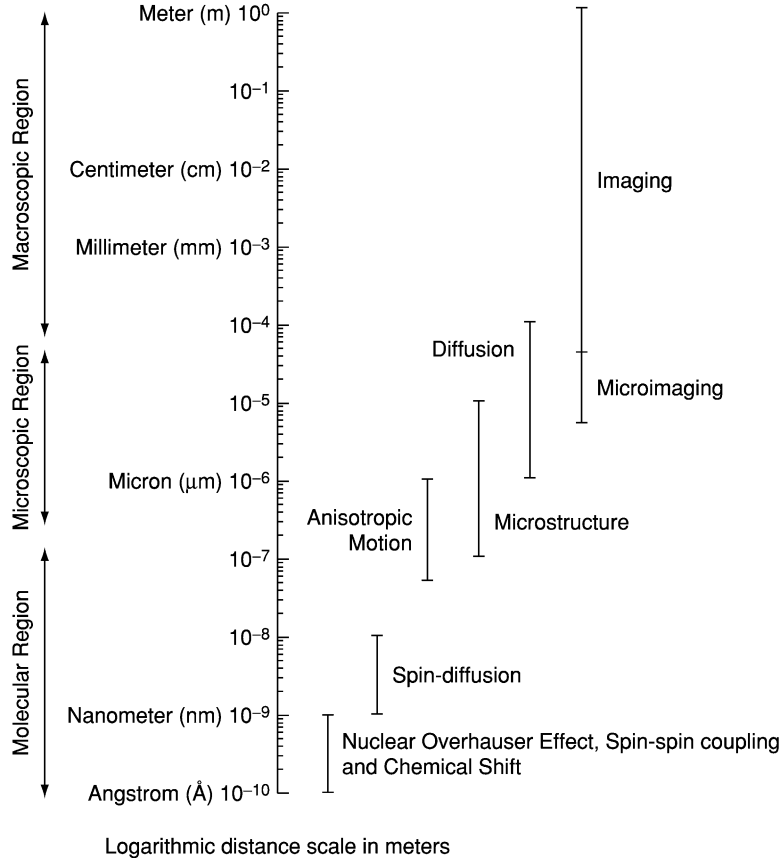

FIG. 24 The range of distance scales, from molecular to macroscopic, probed in NMR. See text for details.

coupling), and nuclear Overhauser. Chemical shift and spin–spin coupling effects occur through the electrons of chemical bonds, whereas the nuclear Overhauser effect (NOE) occurs through space. These effects form the foundation for why NMR is considered the premier structure identification tool. Somewhat larger distance scale information can be gleaned by considering the rate at which NOEs grow between spins (referred to as spin diffusion). Distance scales over which anisotropic order persists in oriented systems, such as muscle, can be calculated by combining information about the size of a residual anisotropic interaction with knowledge of translational motion values (Belton, 1995). Microstructural features of food materials, such as water and oil droplet sizes in food emulsions (Metais and Mariette, 2003; van Duynhoven *et al*., 2002), can be probed using relaxometery and diffusion techniques (Hills, 1998). Distance traveled by a molecule (e.g., water) diffusing through a food matrix (e.g., sugar glass) over time can be measured, and in turn can be used to explore the morphology of a system (e.g., restricted versus unrestricted diffusion). At the largest end of the distance scale are magnetic resonance microscopy and imaging techniques. NMR microscopy is defined by Hills (1998) as pertaining to a system in which one or more of the spatial voxel dimensions is less than 40 μm.

Because distance and time can be coupled by motion, we could also view the timescales available to be probed with NMR and would find the same staggering range (Belton, 1995). Time constants for molecular processes can be quantified by magnetic resonance techniques ranging from extremely fast (picoseconds, such as for the tumbling of water molecules) to extremely slow (tens of seconds, such as for selected chemical reactions or exchange).

4. Usefulness of NMR methods for foods

NMR is an incredibly versatile tool that can be used for a wide array of applications, including determination of molecular structure, monitoring of molecular dynamics, chemical analysis, and imaging. NMR has found broad application in the food science and food processing areas (Belton *et al*., 1993, 1995, 1999; Colquhoun and Goodfellow, 1994; Eads, 1999; Gil *et al*., 1996; Hills, 1998; O'Brien, 1992; Schmidt *et al*., 1996; Webb *et al*., 1995, 2001). The ability of NMR to quantify food properties and their spatiotemporal variation in a nondestructive, noninvasive manner is especially useful. In turn, these properties can then be related to the safety, stability, and quality of a food (Eads, 1999). Because food materials are transparent to the radio frequency electromagnetic radiation required in an NMR experiment, NMR can be used to probe virtually any type of food sample, from liquids, such as beverages, oils, and broth, to semisolids, such as cheese, mayonnaise, and bread, to solids, such as flour, powdered drink mixes, and potato chips.

Intact, "as is" food materials can be placed directly into NMR tubes for analysis. Thus, little to no sample preparation is needed beyond shaping the sample (when necessary) to fit into the bore of the magnet. In addition, it is possible to simulate various food processes (e.g., drying, freezing, microwaving, and frying) inside an NMR magnet and obtain real-time or near real-time measurements. NMR imaging has been especially useful in this regard (Duce and Hall, 1995; Hills, 1995, 1998, 1999; McCarthy, 1994; Schmidt *et al*., 1996; Sun and Schmidt, 1995). Sample size is limited only by the size of an NMR probe, which currently ranges from 0.1 to 2.5×10^5 cm^3, depending on the type of instrument employed (i.e., high-resolution spectrometer to an imaging spectrometer). Advances in NMR and MRI instrumentation, techniques, and applications are developing at an incredibly rapid rate, as discussed in Grant and Harris (2002). Many of these advances are just waiting to be applied by the insightful and ingenious food-focused researcher to further advance the study of water and solids in foods.

Because of the vast amount of information that has been published on the use of NMR to investigate food systems, it is not feasible to present a comprehensive survey of the usefulness of NMR for foods in this review. Rather, the approach taken here is to illustrate the usefulness of NMR specifically for probing water and solids mobility in foods by presenting selected papers from recent literature. Review papers and recent developments in each of the following areas are also included.

a. Molecular dynamics in concentrated sugar solutions and glasses. Hills *et al*. (2001) studied the molecular dynamics of water and sugars (sucrose and xylose) in concentrated sugar solutions and glasses above and below their glass transition temperatures. Extending previous studies on maltose (Hills and Pardoe, 1995) and saturated sucrose solutions (Hills *et al*., 1998), the approach taken was to use fast-field cycling measurements of the frequency dispersion in proton longitudinal relaxation. Reviews of applications of field-cycling NMR are given by Noack *et al*. (1997) and Belton and Wang (2001). In concentrated sucrose–water solutions well above T_g, proton frequency dispersion curves (R_1 plotted as a function of frequency) could be fitted to a single dispersion, conforming quite well to theoretical predictions. The main dispersion arises from sucrose (either the overall sucrose reorientation or from rotation of CH_2OH side chains or both), not from water. The sucrose correlation time for a 51% (w/w) sucrose solution at 298 K was calculated to be 20 ns (Hills *et al*., 2001). In concentrated sucrose–water systems well below T_g [90.1% (w/w) sucrose at 230.9 K; $T_g = 261.5$ K], a double dispersion was observed, again conforming quite well to theoretical predictions. This double dispersion strongly suggests that there are separate dispersive contributions from water and sucrose molecules. The water and

sucrose correlation times for the 90.1% (w/w) sucrose sample as a function of temperature are listed in Table VII. As can be observed, the water correlation time remains short, even in the glassy state (138 ns at 230.9 K). Hills *et al.* (2001) suggested that the systematic decrease in the correlation time for water as temperature decreases is perhaps due to an increasing decoupling of water and sucrose dynamics, as the system heads toward the glassy state. The water correlation times show no obvious break, as the temperature is lowered through the glass transition.

Sugar lattice dynamics were investigated using 100% xylose glasses in their protonated and deuterated forms. Dispersions for a 100% xylose deuterated glass (containing no water protons and no side chains) in the glassy state ($T_g = 282$ K) were able to be fitted with a single dispersion and a quadrupolar peak. This indicates that the observed dispersion arises from low-frequency vibrational modes in the three-dimensional xylose lattice. Fitting dispersion data with a stretched spectral density function yielded a single correlation time of 1.5 μs, thus showing no evidence for a distribution of correlation times corresponding to a range of amorphous environments that might have been expected to exist in the glassy matrix. The combination of NMR field-cycling and deuterium exchange was shown to be a powerful technique for investigating molecular dynamics both above and below T_g.

The composite picture that is developing [based mainly on NMR mobility and differential scanning calorimetery (DSC) T_g data] of these sugar–water glasses at temperatures below T_g is that the sugar is irrotationally frozen in a rigid three-dimensional amorphous matrix. The sugar molecules exhibit vibrational motion and experience a gradual relaxation (physical aging) toward equilibrium. The water and sugar dynamics are decoupled from one another in the glassy state. The water in the glassy system exhibits vibrational, rotational, and translational motions, albeit at rates much slower than in bulk water.

TABLE VII

TEMPERATURE DEPENDENCE OF WATER AND SUCROSE CORRELATION TIMES IN A 90.1% (W/W) SUCROSE–WATER SYSTEM ($T_g = 261.5$ K)

Temperature (K)	Water correlation time (ns)	Sucrose correlation time (ns)
298.0	265	732
268.7	202	1331
261.1	148	1299
230.9	138	1493

Other studies that have focused on mobility in sugar–water systems at or near the glass transition include Wachner and Jeffrey (1999), van den Dries *et al.* (1998, 2000a,b), and Sherwin *et al.* (2002). Wachner and Jeffrey (1999) used two-dimensional deuterium NMR to investigate reorientational dynamics in an 85% glucose–15% water system. They reported that reorientation is dominated by small-angle jumps (~3°) and a small fraction of large-angle jumps (~34°). van den Dries *et al.* (1998, 2000a,b) studied various carbohydrate glasses (maltose, glucose, and malto-oligomers) using ^{1}H NMR, DSC, electron spin resonance (ESR) spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. van den Dries *et al.* (2000b) reported that increasing water content from 10 to 30% (wt%) results in a decrease in spin probe (TEMPOL) mobility at T_g, whereas water mobility as measured by ^{1}H NMR increases at T_g. They explain this apparent paradox in terms of molecular packing. Sherwin *et al.* (2002) used solid-state techniques of cross-polarization/magic-angle spinning (CP/MAS) NMR to determine the mobility of glucose within a caseinate model system as a function of water activity (0.11, 0.33, 0.43, and 0.65), temperature (25, 35, 45 °C), and added humectants (glycerol and sorbitol). They reported that glycerol yielded the lowest T_g over the entire range of a_w values and imparted the greatest mobility to solid-state glucose, followed by sorbitol and finally the control formula containing no humecant.

b. Water distribution and dynamics in native starch granules. Tang *et al.* (2000) studied the microscopic distribution and dynamics state of water within native maize (A type), potato (B type), and pea (C type—a combination of A and B types) starch granules using NMR relaxometry and diffusometry. The distribution of water proton transverse relaxation times for a water-saturated, packed bed of native potato starch granules at two temperatures is shown in Figure 25. For both temperatures, the small intensity peak centered at approximately 3 s was assigned to residual supernatant bulk water (the majority of which was removed before measurements were made). The difficult assignments in the relaxation time distribution were the two peaks centered at approximately 8 and 50 ms at 290 K. The 50-ms relaxation time peak was assigned to bulk water in external interstitial spaces between the granules. This assignment implies that extragranular water exists as a thin layer between closely packed granules and that its relatively short relaxation time of 50 ms (compared to 3 s for free bulk water) was caused by fast proton exchange with starch hydroxyl protons. At 290 K, the 8-ms relaxation peak with a shoulder resolved into two separate peaks at 1 and 8 ms at 277 K. The 1 and 8-ms peaks were assigned to water inside granules.

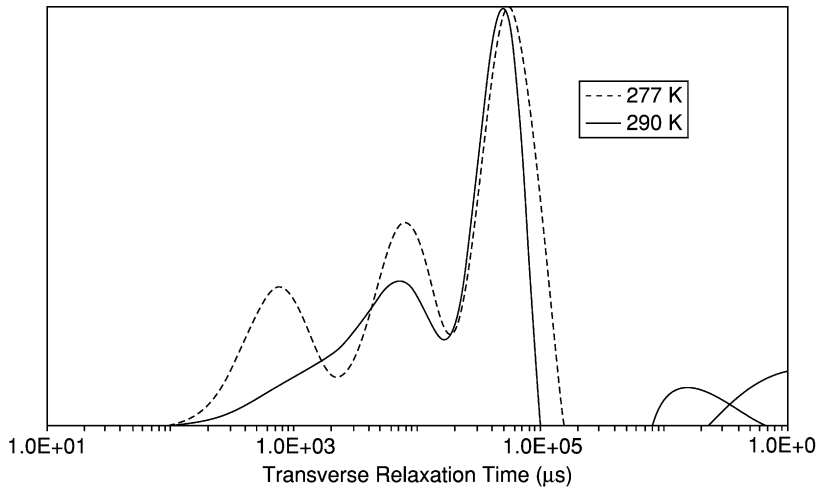

FIG. 25 The distribution of water proton transverse relaxation times for a water-saturated, packed bed of potato starch granules at two temperatures [reproduced with permission from Tang *et al*. (2000)].

Based on additional freezing and drying experiments, in addition to extragranular water (with a water proton transverse relaxation time of about 50 ms), Tang *et al*. (2000) identified three water populations inside native potato starch granules: (1) water in amorphous growth rings, (2) water in semicrystalline lamellae, and (3) water located in hexagonal channels within B type amylopectin crystals (called channel water). Water populations 1 and 2 above were found to be orientationally disordered and exchanging with each other on a millisecond time scale at 290 K. NMR diffusometry showed that water in packed granule beds undergoes translational diffusion in a two-dimensional space, either in thin layers between granules and/or in amorphous growth rings within granules. So-called channel water was characterized by a 1-kHz deuterium doublet splitting and was found to be in slow exchange with water in the other compartments on an NMR timescale. For the smaller maize granules, there was no evidence for the existence of channel water and all intragranule water populations were in fast exchange. For pea starch, NMR water proton and deuterium data showed composite A and B type starch behavior. For the interested reader, Tang and Hills (2001) also discuss the microscopic distribution of water among various subgranular compartments of native starches.

Other research using NMR techniques to study mobility in starch systems includes Li *et al*. (1998), who investigated the mobility of "unfreezable" and "freezable" water in waxy cornstarch using ^{1}H and ^{2}H NMR; Choi and Kerr

(2003a,b), who probed molecular mobility in regular and chemically modified wheat starch using ^{1}H NMR; Gonera and Cornillion (2002), who examined the effect of additives (guar gum, xanthan, glucose, and sucrose) on starch (corn, waxy maize, and potato) gelatinization using ^{1}H NMR relaxometry; and McCarthy *et al.* (2002), who monitored postcooking changes in moisture distribution over time in lasagna pasta.

c. Determination of self-diffusion coefficients in casein dispersions and gels. Mariette *et al.* (2002) used ^{1}H diffusometry to measure the self-diffusion coefficients of water and casein in casein solutions and gels. In the case of water self-diffusion measurements, they found that the water self-diffusion coefficient was insensitive to the structure of the casein whether in solution (Na-caseinate and micellar casein) or in a gelled state (acid gels and rennet gels). Figure 26 illustrates this observation, showing no difference between the water self-diffusion coefficients in a micellar casein dispersion (similar to Na-caseinate data, not shown) and in acid and rennet gels, throughout the protein concentration range investigated. The effect of casein concentration on the water self-diffusion coefficient was explained by obstruction from the casein molecule. In the case of protein self-diffusion measurements, researchers calculated an average casein self-diffusion coefficient of 3.4×10^{-12} m^2s^{-1} for a concentration of 0.08 g protein/g water. They noted that a large deviation from linearity was observed in an echo attenuation plot for a casein dispersion. However, they attributed this nonlinearity mainly to an effect of micelle size distribution and secondarily to the presence of a small amount of noncasein protein rather than to restricted diffusion behavior. For an overview of diffusion measurements by NMR and

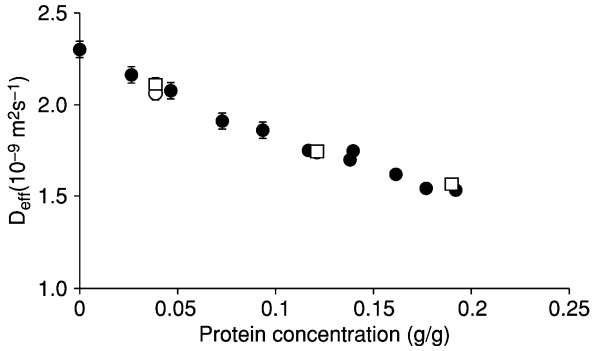

FIG. 26 Observed water self-diffusion coefficients as a function of the protein concentration (g protein/g water) for micellar casein dispersions (●), for acid gels (○), and for rennet gels (□) [reproduced with permission from Mariette *et al.* (2002)].

their applications, the interested reader is referred to excellent reviews by Price (1996, 1997, 1998a) and a special issue on NMR and diffusion in *Magnetic Resonance in Chemistry* (Morris, 2002a). The latter includes a very good discussion by Sorland and Aksnes (2002) on artifacts and pitfalls in NMR diffusion measurements.

Diffusion-ordered NMR spectroscopy (DOSY), a relatively recent adaptation of pulsed-field gradient spin–echo NMR, can be used to separate the NMR signals of different components of a mixture on the basis of their diffusion characteristics (Morris, 2002b). The first step in such an experiment is to obtain spectra attenuated by diffusion. Next, a diffusion coefficient and an estimated standard error are calculated for each resolved signal in the spectrum. A two-dimensional DOSY spectrum is then synthesized, in which the one-dimensional spectrum is extended into a second, diffusion domain (Pelta *et al.*, 2002). DOSY experiments employ a variety of pulse sequences, mainly variants of a pulsed-field gradient-stimulated echo (PFGSTE) sequence. A new one-shot sequence for high-resolution DOSY was introduced by Pelta *et al.* (2002), which allows data acquisition times of less than 1 min.

For examples of applications of DOSY, the reader is referred to Morris and Johnson (1993), Chen *et al.* (1995), Olson (1999), and Sobolev *et al.* (2003). Most relevant to the focus of this review is Olson (1999), who applied DOSY to investigate changes in water diffusion coefficients in gelatinized dent corn starch–water systems during retrogradation. Preliminary two-dimensional DOSY spectra revealed a distribution of water diffusion coefficients in retrograding starch gels, which increased as a function of both increasing starch concentration and time.

d. Measurement of solids mobility in low and high concentration solids systems. Low starch concentrations are used in a wide variety of food products, such as salad dressings, gravy mixes, and condiments. However, it is difficult with traditional solids techniques to probe changes in mobility (i.e., as affected by processing or as a function of storage time) of solid components. Cross-relaxation spectroscopy (CRS) allows for the observation of solids mobility at low solids concentrations, and the ability to monitor liquid properties independent of interference from solids. Lewen *et al.* (2003) employed cross-relaxation NMR to measure the mobility of water and solids in low starch concentration gels (5 to 25%). Parameters obtained from their CRS experiment were rate of magnetization transfer (R), solid transverse relaxation time constant (T_{2B}), liquid longitudinal relaxation time constant (T_{1A}), liquid transverse relaxation time constant (T_{2A}), and the number of solid protons that participate in cross-relaxation (M_0^B). As starch gels aged over a 29-day period (at 23 °C), it was found that T_{2B} did not change significantly, whereas M_0^B increased for each starch gel

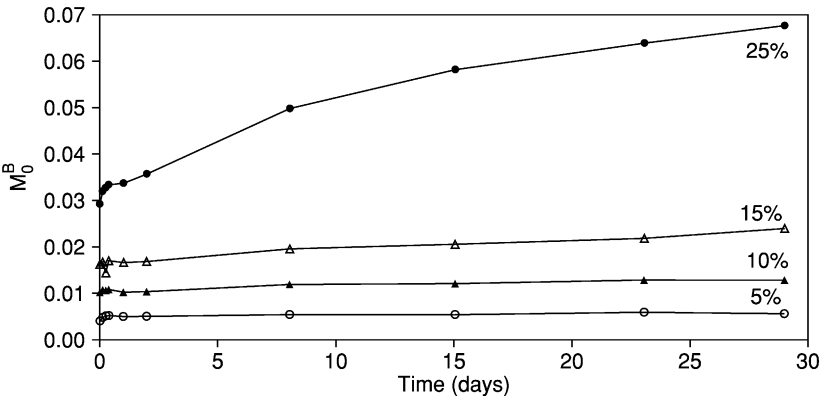

FIG. 27 Plot of $M_0{}^B$ for the 5 to 25% starch gel samples over a 29-day period after gelatinization [reproduced with permission from Lewen *et al.* (2003)].

concentration. Results for M_0^B are reproduced in Figure 27. These CRS results suggest that during retrogradation in low concentration starch systems, the highly mobile starch fraction converted to the less mobile solid state (increase in M_0^B), due to reassociation of starch molecules, but that the mobility of the solid component (constant T_{2B}) did not change over time.

Roudaut *et al.* (1999a) used low-frequency pulsed-proton NMR and dielectric dynamic mechanical spectroscopies to study molecular mobility in glassy bread (<9%) as a function of temperature. Based on NMR results, they reported that some (if not all) of the water molecules were much more mobile than the polymer matrix whose relaxation time could not be measured within the 20-μs dead time of the RF probe.

Magnetic resonance imaging techniques, such as stray field (STRAFI), single-point imaging (SPI), and single-point ramped imaging with T_1 enhancement (SPRITE), have been developed to obtain "solid-state" images for high concentration solids systems (Balcom *et al.*, 1996; Chudek and Hunter, 2002; Cornillon and Salim, 2000; Eads and Axelson, 1995). These techniques offer great potential for imaging the processing of low-moisture food systems, such as crackers, cookies, and snack foods. In addition, Eads and Axelson (1995) gave an example of using SPI to produce a mobility map for solid domains in a dilute particle gel of starch crystallites. Lee *et al.* (2002) used SPRITE (a refinement of SPI) to investigate the spatial distribution of nonfrozen water in beef, orange juice, and dough during freezing and frozen storage. Ziegler *et al.* (2003) used SPRITE to study moisture migration during the drying of starch-molded confectionery. Moisture profiles

within a porous bed of molding starch, where total proton density is low and T_2^* is quite short, were visualized using SPRITE. Similar images were not possible to obtain using more traditional spin–echo techniques.

e. Relationship between water and solids mobility and chemical and microbial stability. Kou *et al.* (1999) investigated the relationship between water and solids mobility and conidia mold germination. Water activity, a suite of NMR techniques, including ^{2}H NMR rotational mobility (R_1, R_2, and R_2^*), ^{1}H NMR translational mobility (water self-diffusion coefficient, D), and ^{13}C CP/MAS NMR ($T_{1\rho}$) solids mobility, and DSC were used to fully characterize water and solids mobility and T_g of the systems. Water content, a_w, and ^{2}H NMR R_1 and R_2 relaxation rates were found not to predict mold germination time. These workers concluded that the self-diffusion coefficient (translational mobility of water), DSC T_g (overall system mobility), and, to a more limited extent, ^{2}H NMR R_2^* relaxation rate and ^{13}C $T_{1\rho}$ (solids mobility) could provide alternative measures to augment a_w for predicting food stability and safety. Figure 28 shows water self-diffusion coefficient (D) as a function of weight fraction of solids for samples of sucrose, instant dent #1 starch, and a 1:1 sucrose/starch mixture. For starch and the sucrose/starch mixture, D decreased almost 10-fold near the corresponding weight fraction

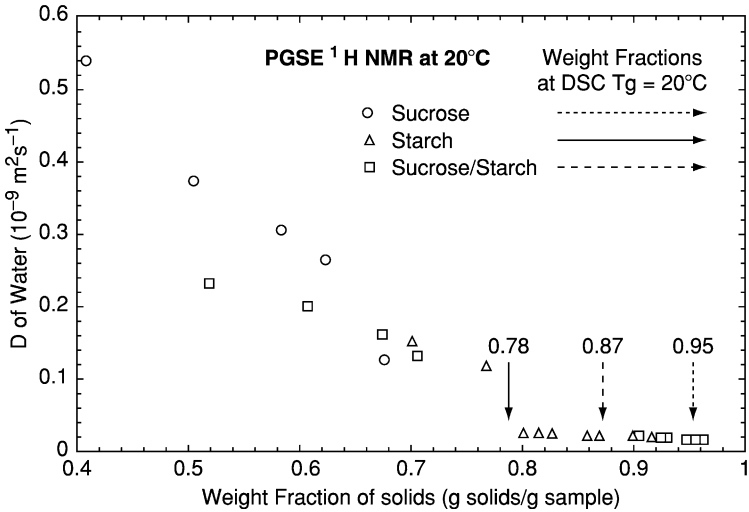

FIG. 28 Water self-diffusion coefficient plotted as a function of weight fraction of solids for samples of sucrose, instant #1 dent starch, and a 1:1 sucrose/starch mixture at 20 °C. The corresponding weight fractions at the DSC T_g equal to 20 °C are given for reference [reproduced with permission from Kou *et al.* (1999)].

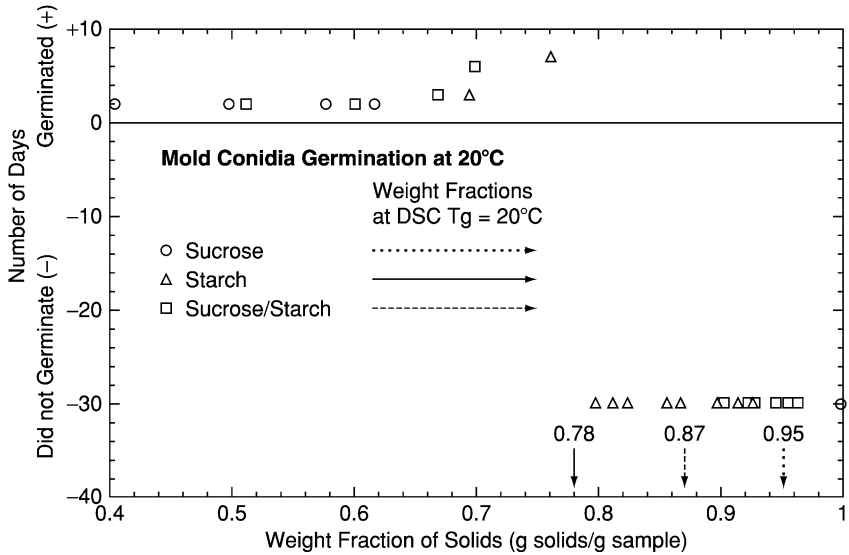

FIG. 29 *Aspergillus niger* conidia germination time as a function of weight fraction of solids at 20 °C for samples of sucrose, instant #1 dent starch, and a 1:1 sucrose/starch mixture. The corresponding weight fractions at the DSC T_g equal to 20 °C are given for reference. Conidia that did not germinate after 30 days were plotted on the graph as "did not germinate (−30 days)" [reproduced with permission from Kou *et al.* (1999)].

at which the DSC T_g was equal to 20 °C (the experimental temperature). Samples with D lower than this substantially reduced D no longer supported conidia mold germination, as shown in Figure 29. For sucrose, only samples with $a_w > 0.866$ were measured, as sucrose below this saturation a_w value (at 20 °C) remained in crystalline form.

Bell *et al.* (2002) investigated the relationship between water mobility as measured by oxygen-17 NMR (transverse relaxation rate obtained from linewidth at half-height) and chemical stability in glassy and rubbery polyvinylpyrrolidone (PVP) systems. Reported results suggest that water mobility in PVP model systems was not related to T_g. The study did not find a link between water mobility and reaction kinetics data (half-lives) for degradation of aspartame, loss of thiamin and glycine, and stability of invertase.

5. *Measurements utilizing NMR techniques for foods*

As described previously, there are a number of significant advantages to using NMR to examine food systems, such as the noninvasive and nondestructive nature of the technique, the limitless types of food samples that can

be probed, the ease of sample preparation, and the numerous pulse sequences and methods that can be employed to either embrace or overcome sample complexity. However, along with the bountiful advantages of NMR come three general disadvantages: (1) poor sensitivity, (2) high equipment costs, and (3) often times, the need for highly trained/experienced personnel for data collection and interpretation.

The relatively low sensitivity of NMR, compared to other spectroscopic techniques, such as infrared (IR) or ultraviolet (UV) spectroscopy, arises from the small differences between spin energy levels and thus small population differences exploited in an NMR technique. However, with the advent of higher external magnetic field strengths, the sensitivity of NMR has improved to nanomolar levels (Eads, 1999). In addition, NMR can be coupled with other techniques (referred to as hyphenated NMR), such as liquid chromatography-NMR (LC-NMR), so as to take advantage of the benefits of each technique, while overcoming their individual disadvantages (Duarte *et al*., 2003; Spraul *et al*., 2001).

The initial investment in NMR equipment can be rather expensive, with the magnitude of the cost depending on the equipment required and the type(s) of experiments to be performed. For example, a 400-MHz high-resolution spectrometer, for running a variety of advanced level experiments, costs approximately $400,000 for a well-equipped liquids system to $500,000 for an instrument with solids capabilities. However, a 20-MHz low-resolution tabletop NMR, for running relatively routine relaxometry analyses, costs $50,000, plus an additional $10,000 for a gradient accessory for enabling diffusion measurements. An additional important cost consideration, not reflected in the aforementioned prices, is the operational costs associated with using and maintaining the instruments, such as for personnel, liquid nitrogen and helium refills for high-resolution instruments, and use of consumables.

Measurements obtained utilizing NMR techniques can be made on virtually any food. However, depending on the nature of these measurements, the training needed by a person obtaining such measurements varies widely. For example, in the case of a routine online analysis, such as using NMR to measure sample moisture content, quality assurance personnel can be trained to obtain such measurements; however, calibration and upkeep of an instrument by more highly trained personnel may still be required. In contrast, in the case of experimental research, such as using NMR to probe water dynamics during processing, design of experiments and collection and interpretation of resultant relaxation or diffusion data require highly trained personnel with experience in carrying out sophisticated and detailed data analysis. In fact, if Hills (1999) is correct in saying that the most challenging task for the future is to develop realistic theoretical models capable of

incorporating all NMR and MRI data from all distance scales in an integrated fashion (and I believe he is!), then very highly trained and experienced NMR personnel are needed now more than ever before.

In addition to the three general advantages/disadvantages of NMR discussed earlier, there are also specific advantages/disadvantages associated with particular magnetic resonance techniques and experiments. For a thorough discussion of pros and cons associated with various NMR techniques for investigating intact food materials, see Eads (1999).

6. *Relationship between NMR relaxation rates and* a_w

A relationship between NMR T_1 and T_2 relaxation rates and a_w seems likely, as both parameters are a measure of the mobility of water in a system, although one reflects molecular mobility and the other macroscopic mobility, respectively. Richardson *et al.* (1987), who plotted ^2H and ^{17}O NMR R_2 data as a function of a_w for corn starch, showed linear behavior for both nuclei. For ^{17}O data, linear behavior extended from 0.97 to 0.80 a_w, below which ^{17}O NMR measurements could not be obtained, because linewidths for higher concentrations (>83% starch) were larger than the bandwidth of the spectrometer used. For ^2H data, there were two linear regions: region A, from 0.99 to 0.23 a_w, and region B, from 0.23 to 0.11 a_w. The break between the two regions of ^2H data corresponded closely to the value of $a_w = 0.20$ given by van den Berg (1981) for the approximate BET monolayer value for starch.

Hills (1998, 1999) proposed an empirically derived relationship between NMR relaxation rates and a_w. The model begins by describing observed "average" values for NMR (T_{av}^{-1}) and $a_w(a_{av})$ parameters as a weighted average of values over all water states:

$$T_{av}^{-1} = \sum_i p_i T_i^{-1} \tag{14}$$

$$a_{av} = \sum_i p_i a_i \tag{15}$$

where T_i^{-1} and a_i are the intrinsic relaxation rate and water activity of the ith state of water in a system and p_i is the fractional population of that state.

Eq. (14), which was originally postulated by Zimmerman and Brittin (1957), assumes fast exchange between all hydration states (i) and neglects the complexities of cross-relaxation and proton exchange. Equation (15) is consistent with the Ergodic theorem of statistical thermodynamics, which states that at equilibrium, a time-averaged property of an individual water molecule, as it diffuses between different states in a system, is equal to a

time-independent ensemble-averaged property [Eq. (15) being an ensemble-averaged expression], but ignores configurational entropy effects (Hills, 1998, 1999; Hills *et al.*, 1999). Next, Hills simplified both Eqs. (14) and (15) to a case of two states of water in fast exchange (e.g., bulk water exchanging with hydration water), yielding the following two equations, respectively:

$$T_{av}^{-1} = T_b^{-1} - \frac{m_o\left(T_b^{-1} - T_h^{-1}\right)}{W} \tag{16}$$

$$a_{av} = a_b - \frac{m_o(a_b - a_h)}{W} \tag{17}$$

where m_o is the weight of hydration water per unit weight of dry biopolymer, W is water content, defined as the weight of water per unit weight of dry solid, and water activity of bulk water (a_b) is set equal to 1. It should be noted that Eq. (16) is only valid when water relaxation is single exponential (requires rapid diffusive exchange between all water populations) and Eq. (17) is only valid for $W > m_o$, as W values less than m_o correspond to the removal of hydration water, a region of an isotherm where the BET isotherm equation is applicable (Hills *et al.*, 1996a).

Based on the correspondence between Eq. (16) and (17), Hills combined the two equations by rearranging Eq. (17) to solve for m_o/W and then substituting the results of this term into Eq. (16), yielding Eq. (18), which linearly correlates NMR relaxation rates to water activity:

$$T_{av}^{-1} = T_b^{-1} + C(1 - a_{av}) \tag{18}$$

where the constant C is $(T_h^{-1} - T_b^{-1})/(1 - a_h)$. This combined equation is valid within the limitations given for the individual equations (two states of water in exchange, water relaxation is single exponential, and $W > m_o$). Breaks in linearity (i.e., changes in slope) between otherwise linear regions indicate that one of the states of water has been removed or a new one has been introduced.

The linear relationship between ^{1}H NMR transverse relaxation rate and $(1 - a_{av})$ is shown in Figure 30 for pregelled potato starch (Hills *et al.*, 1999). The change in slope at about 0.90 a_w corresponds to the bulk water break (i.e., the removal of bulk water) in a corresponding adsorption isotherm. Equation (18) has been applied successfully to beds of Sephadex microspheres and silica particles using both ^{1}H NMR (Hills *et al.*, 1996b) and ^{17}O NMR, the latter of which is free from the complication of proton exchange when measured using proton decoupling (Hills and Manning, 1998).

Hills *et al.* (1999) clearly expressed the point that there is no implied fundamental physical relationship between a_w, an equilibrium thermodynamic quantity, and NMR relaxation, a nonequilibrium kinetic event, in

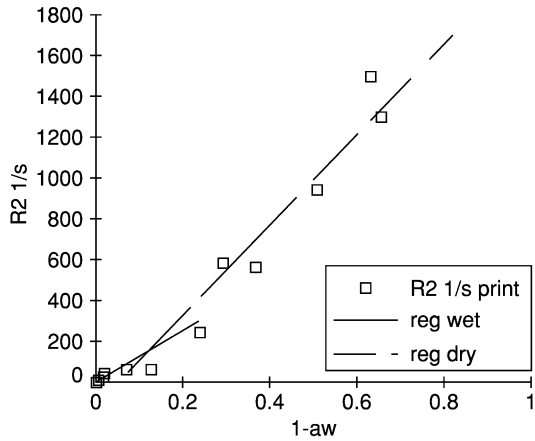

FIG. 30 Linear relationship between ^{1}H NMR transverse relaxation rate (recall $R_2 = 1/T_2$) and $(1 - a_w)$ for pregelled potato starch [reproduced with permission from Hills *et al.* (1999)].

this theory. Rather, all that is suggested is that the changing states of water in a biopolymer system affect both water activity and NMR relaxation similarly.

D. GLASS TRANSITION

Widespread application of the glass transition concept in foods is attributed to Slade and Levine and their introduction in the 1980s of the "food polymer science" approach for the assessment of food quality and safety—beyond that of the "water activity" concept of moisture management (e.g., Slade and Levine, 1985, 1988, 1991, 1995, 1998, 2002, 2003). One of the key elements of the food polymer science approach is the importance of "the glass transition temperature ... as a physicochemical parameter that can determine processibility, product properties, quality, stability, and safety of food systems" (Slade and Levine, 1991). Levine (2002) provided his own personal chronology of key milestones in the application of polymer science concepts to foods. Levine attributes his finding and reading of a paper, in 1979, by Felix Franks and co-workers (1977) on biological cryoprotection as the beginning of the story. Levine (2002) also cites a number of historical papers he read on glasses, glassy states, and glass transitions, including a seminal review by White and Cakebread (1966) and van den Berg's 1981 doctoral thesis, which helped shape the "food polymer science" approach.

Since its introduction, the food polymer science approach has been used to understand structure–function relationships in foods, the effect of

plasticization by water on a number of thermal and mechanical properties of foods, and the relative stability of foods in a nonequilibrium glassy state versus the instability in a rubbery or viscous liquid state (Slade and Levine, 2003). The glass transition concept has been especially useful in understanding and enhancing the processing, quality, and stability of concentrated foods, i.e., low-moisture and frozen foods.

Based on the pioneering efforts of Slade and Levine, there has been a constantly increasing number of studies, review papers, book chapters, books, symposia, conferences, and short courses devoted to investigating, teaching, and critically evaluating applications of the glass transition concept to foods. Because of the large number of excellent recent books and book chapters (Blanshard and Lillford, 1993; Levine, 2002; Rahman, 1995; Roos, 1995) and review articles (Bhandari and Howes, 2000; Champion *et al*., 2000; Hancock and Zografi, 1997; Le Meste *et al*., 2002; Roos, 2003; Roos and Karel, 1991; Roos *et al*., 1996; Slade and Levine, 1991, 2003) on the subject, the approach taken here is to briefly summarize the current status of the glass transition concept and its measurement methods and to highlight its usefulness and limitations in foods.

1. Physical states and state transitions

Matter can exist in three basic physical states: solid, liquid, and gas. Interconversions between these physical states are termed phase transitions and are caused by a change in temperature and/or pressure. Phase transitions can be classified into two main groups: first order and second order. This classification is based on observed discontinuities that occur in state functions at transition temperatures (Roos, 1995). First-order phase transitions are those for which the first derivatives of the chemical potential and of Gibbs free energy exhibit discontinuous changes at the transition temperature. During first-order transitions, the physical state of matter (at constant pressure) transitions isothermally from one state to another by an absorption (i.e., solid to liquid) or release (i.e., liquid to solid) of latent heat. Phase transitions that occur among the three basic physical states are first-order transitions and take place at very well-defined temperatures. Recall the six phase transitions (three pairs of two—melting and crystallization; evaporation and condensation; sublimation and ablimation) that occur in water, as shown in the phase diagram for pure water (in Figure 7).

Second-order phase transitions are those for which the second derivatives of the chemical potential and of Gibbs free energy exhibit discontinuous changes at the transition temperature. During second-order transitions (at constant pressure), there is no latent heat of the phase change, but there is a discontinuity in heat capacity (i.e., heat capacity is different in the two

phases). The glass transition is often labeled as a second-order phase transition, as it has some apparent features of a second-order phase transition at very slow rates of heating or cooling (i.e., exhibits step changes in heat capacity and thermal expansion coefficient with temperature) (Roos, 1995). However, it exhibits other features (e.g., it occurs over a temperature range and is time and measurement method dependent) that suggest that it should not be classified as a second-order transition, but rather as a kinetic and relaxational transition (Labuza *et al*., 2001). In addition, because the glass transition is a property of a nonequilibrium system, it cannot be classified as a pure phase transition, but is rather considered as a state transition (Roos, 2003; Slade and Levine, 1991).

Food materials (ingredients or whole systems) can be composed of matter in one, two, or all three physical states: solid (crystalline or amorphous or a combination of both), liquid, and gas. The crystalline state is an equilibrium solid state, whereas the amorphous glassy state is nonequilibrium solid state. The main transitions that occur between the physical states of materials of importance to foods are summarized by Roos and Karel (1991) and Roos (2002). The most important parameters affecting the physical state of foods, as well as their physicochemical properties and transition temperatures, are temperature, time, and water content (Slade and Levine, 1988; Roos, 1995). Pressure is not included in this list, as food materials usually exist under constant pressure conditions.

The physical state of relevance to the glass transition is the amorphous solid state. The amorphous solid state is an energetically metastable, nonequilibrium state that retains the disorder of a liquid state (Rahman, 1995; Roos, 1995). An amorphous material can be in either a supercooled liquid state (also called the rubbery state or rubber) or a solid state (also called the glassy state, glass, or solid solution). A common feature of amorphous solid materials is that they contain excess free energy and entropy, as compared to their crystalline counterparts at the same temperature and pressure conditions (Roos, 1995). The transformation between supercooled liquid and solid amorphous states is known as the glass transition and is illustrated schematically in Figure 31. The viscosity of amorphous materials in the glassy state is typically $\geq 10^{12}$ Pa second. Over the glass transition temperature range, Young's modulus (E) drops dramatically from about 10^9 to 10^6 Pa (Sperling, 1986). A number of methods can be used to produce materials in the amorphous solid state. These methods usually involve two events (Figure 31): (1) rapid evaporation of solvent molecules (decrease in water content) and/or (2) sufficiently rapid cooling of a material to avoid formation of an equilibrium crystalline state (decrease in temperature). Also, depending on the rate of solvent removal and/or cooling into an amorphous solid state, glasses with different properties can be formed (Roos, 2003). For

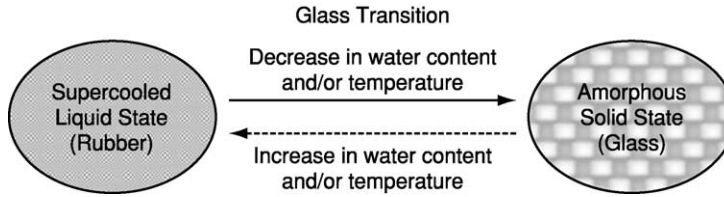

FIG. 31 Schematic diagram illustrating the transition between a supercooled liquid state (rubber) and an amorphous solid state (glass). The glass transition event is typically caused by a decrease in water content and/or temperature. The reversibility of the transition, as indicated by the dotted arrow, is material dependent (see text for further discussion of the reversibility of the transition).

example, a glass formed using a fast cooling rate possesses greater free volume and enthalpy and has a higher T_g value compared to a glass formed using a slow cooling rate (Hsu *et al.*, 2003; Roos, 2003; Schmidt and Lammert, 1996). As illustrated by the dotted arrow in Figure 31, a glass transition event may be reversible, depending on the material under study. The reversibility of the glass transition in food systems is discussed in more detail in the next section. Various food ingredients and food systems are produced in the amorphous state using a variety of processing methods that include one or both of the aforementioned events, such as spray-drying, freeze-drying, melting and subsequent quick-cooling, extrusion, baking, and encapsulation. Examples of products that contain amorphous or partially amorphous structures below their T_g are extruded snacks and breakfast cereals, low-moisture cookies and crackers, pasta, hard sugar-based candies, powdered drink mixes, and cotton candy.

Once in the amorphous solid state, undesirable changes in the properties of amorphous ingredients and foods (e.g., stickiness, caking, collapse, loss of crispness) can occur via a reversal in the two events discussed earlier: (1) an increase in moisture content (water plasticization) so that the T_g of a material is decreased to below room temperature and (2) an increase in temperature [thermal plasticization (Roos, 2003)] so that the temperature of the material rises above its T_g. In both cases and their combination, the once glassy material is now in a rubbery or liquid state and is undesirable and/or unfit for consumption.

State diagrams are very useful tools in the characterization of amorphous ingredients and food systems (Roos, 1995; Slade and Levine, 1991). Slade and Levine (1988, 1991), acknowledging the earlier work of Franks *et al.* (1977) and MacKenzie (1977), formulated a state diagram (called a ''dynamics map'' or ''mobility transformation map'') for food systems that includes four dimensions: temperature, concentration, pressure, and time. This state

diagram includes both equilibrium and nonequilibrium thermodynamics in a single figure. The equilibrium regions of the diagram are completely described in two dimensions: temperature and concentration (at constant pressure). However, the nonequilibrium regions require inclusion of the third dimension of time, expressed by Slade and Levine (1991) as t/τ, where τ is a relaxation time. Expressing the time in this dimensionless manner allows the time dependence of a dynamic process to be defined in terms of the relationship between an experimental timescale and the time frame of a relaxation process (Slade and Levine, 1991). The concept of mobility, as one of the underlying principles of the food polymer science approach, was stressed by Slade and Levine (1988), as they introduced their ''dynamics map'':

> 'Mobility' will be used as a transcendent principle to connote all of these interdependent concepts embodied in the dynamics map in Figure 1. Thus, mobility will be the key to all transformations, as well as the basis for defining appropriate reference states (page 1842).

A simplified state diagram (assuming constant pressure and omitting the time-dependence aspect) can be used to show the physical state of a material as a function of temperature and concentration (often expressed as percent weight fraction of solids). A general state diagram typical for a water-soluble food component (e.g., sucrose) is shown in Figure 32. This state diagram is composed of three main curves [the freezing curve (AB), the solubility curve (BC), and the glass transition curve (DEF)] and several anchor points, each of which is defined in the legend for Figure 32. For the interested reader, Slade and Levine (1991) and Roos (1995) not only furnish comprehensive explanations of the state diagram, but also give a variety of material-specific state diagrams (e.g., sucrose, glucose, lactose, fructose, starch, cereal proteins, and PVP-40).

Two locations on the state diagram are of particular interest to the glass transition concept. The first location is the high weight fraction of solids (i.e., low moisture content region) portion (DE) of the glass transition temperature curve (DEF), which is important for the processing and stability of low-moisture ingredients and foods. This low water content region is the main focus of this review. As illustrated in Figure 32, the glass transition temperature of an amorphous food decreases rapidly as moisture content increases (i.e., decreasing weight fraction of solids).

The second location of interest is the T_g associated with a maximally freeze-concentrated solute matrix, T_g' (point E), which is important to the processing and stability of frozen foods. The freezing of most foods results in the formation of an amorphous freeze-concentrated phase that is plasticized

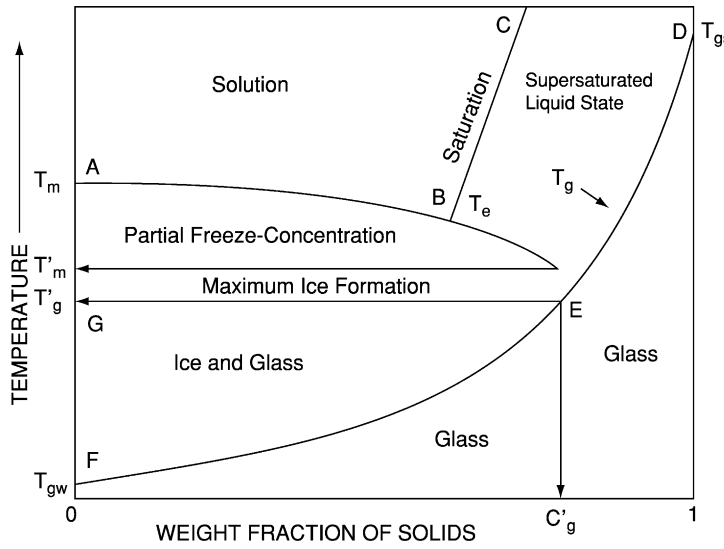

FIG. 32 General state diagram, typical of a water-soluble food component (e.g., sucrose), composed of three curves, the freezing curve (AB), the solubility curve (BC), and the glass transition curve (DEF), and several anchor points. T_m is the equilibrium melting temperature of pure ice, T'_m is the onset melting temperature of ice in contact with a maximally freeze-concentrated solution, T'_g is the glass transition temperature of a maximally freeze-concentrated solute matrix, C'_g is the solute concentration in a maximally freeze-concentrated solute matrix, T_e is a eutectic point, T_{gw} is the glass transition temperature of pure water [often given as $-135\,^{\circ}C$ (Angell, 1983)], and T_{gs} is the glass transition temperature of an anhydrous amorphous material [adapted from Roos (1995) and Rahman (1995)].

by unfrozen water within the aqueous phase. At sufficiently low temperatures ($< T'_g$), the freeze-concentrated phase solidifies into a glassy state (called vitrification), and ice formation ceases due to kinetic restrictions (Roos *et al.*, 1996; Slade and Levine, 1988). The importance of T'_g in frozen food systems is discussed in detail by Slade and Levine (1991), Roos (1995), Goff and Sahagian (1996), Roos *et al.* (1996), and Matveev and Ablett (2002).

State diagrams are an integral part of the food polymer science approach and are further explored and expanded upon in Section III.D.5. For the interested reader, Javenkoski (2001) developed instructional visualization media (three QuickTime animations) for aqueous phase transitions in food systems and investigated their use for improving the comprehension of phase transitions by students enrolled in an introductory food science and human nutrition course.

2. *Definition and assignment of glass transition*

From a conceptual point of view, the glass transition is a phenomenological passage from a glassy solid state, in which short-range vibrational processes are occurring, to a rubbery–liquid state, in which long-range translational and rotational (cooperative) processes are occurring, within a finite temperature range (Seyler, 1994c). The glass transition temperature (T_g) is a single temperature value that represents this finite temperature range. In addition to this widely accepted conceptual view of the glass transition, the ASTM has provided a standard definition and discussion of the glass transition and glass transition temperature. These are given here, as excerpted from Designation: E 1142, Terminology Relating to Thermophysical Properties (ASTM E 1142-97):

> **glass transition**—reversible change in an amorphous material or in amorphous regions of a partially crystalline material, from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one.
>
> **discussion**—The glass transition generally occurs over a relatively narrow temperature range and is similar to the solidification of a liquid to a glassy state. Not only do hardness and brittleness undergo rapid changes in this temperature region, but other properties, such as coefficient of thermal expansion and specific heat capacity, also change rapidly. This phenomenon sometimes is referred to as a second order transition, rubber transition, or rubbery transition. When more than one amorphous transition occurs in a material, the one associated with segmental motions of the backbone molecular chain, or accompanied by the largest change in properties is usually considered to be the glass transition.
>
> **glass transition temperature**—a temperature chosen to represent the temperature range over which the glass transition takes place.
>
> **discussion**—The glass transition temperature can be determined readily by observing the temperature region at which a significant change takes place in some specific electrical, mechanical, thermal, or other physical property. Moreover, the observed temperature can vary significantly depending on the property chosen for observation and on details of the experimental technique (for example, heating rate, frequency of test). Therefore, the observed T_g should be considered valid only for that particular technique and set of test conditions.

Three aspects of the ASTM definitions and discussions just given require further attention, especially when applied to food systems. The first is the reversible nature of the glass transition. In the proceedings of the 1993 ASTM Assignment of the Glass Transition symposium (Seyler, 1994a), Seyler (1994c) stated that the glass transition is not reversible, but rather more accurately described as ''bidirectional with hysteresis.'' In the case of some food ingredients and food systems, we may have to take this suggested

redefinition one step further. Because of the complex nature of foods and the possible irreversible effects of processing (e.g., heating and/or moisture uptake) on a material, the glass transition may occur at a very different temperature after processing (or measuring with an analytical method) compared to before processing. For example, gelatinization (via heat and moisture uptake) of starch and denaturation (e.g., by heat, acidic pH, or mechanical shear) of protein are two frequently encountered processes occurring in foods, which result in irreversible changes in these food polymers. If these irreversible changes occur while the glass transition is being measured, the glass transition will not be located in the same temperature range upon replicate measurement of the same sample; there will be a new glass transition, reflective of the new nature of the material. Thus, for foods, the definition needs to include the possibility that the glass transition can be only unidirectional in some cases (e.g., starch and protein) and bidirectional in others (e.g., sugar glasses).

The second issue with the ASTM definition is the statement in the glass transition discussion that "the glass transition generally occurs over a relatively narrow temperature range." Exactly what is meant by "relatively narrow" is not defined specifically. However, literature sources suggest that the temperature range may not be as narrow as that implied by the ASTM discussion. Wunderlich (1990) gave a general temperature range for the glass transition of 5 to 20 K (based on DSC), and Sperling (1986) gave a general range of 20 to 30 °C (based on a change in modulus). In an actual sample, Bair (1994) reported a DSC T_g range for polycarbonate of 17 °C (calculated as T_g end point minus T_g onset). These sources suggest that even for well-behaved synthetic polymers, the T_g range can be rather broad. Because of the complex, heterogeneous nature of many food systems, the temperature range over which the glass transition occurs in foods can also be quite large. Kou *et al.* (1999) reported an average T_g range (calculated as T_g end point minus T_g onset) of 10.25 °C for sucrose, 14.23 °C for starch, and 12.87 °C for a 1:1 sucrose/starch mixture. In general, the more complex a system, the broader and more difficult it will be to observe the glass transition. For the interested reader, Bair (1994) uses changes in an uncured, low molecular weight, light-sensitive acrylate adhesive to illustrate how broad and complex T_g can become with processing.

One additional point before we leave this second issue concerns the reporting of T_g. Regardless of how broad or narrow the glass transition is for a particular food system, it is important to recognize (and conceptualize) that the glass transition occurs over a temperature *range* and not at a single temperature value. As pointed out by Peleg (1997), the difference in terminology (glass transition temperature and temperature range) is more than just semantic and has several theoretical and practical implications. Because of

the confusion associated with using a single temperature value to represent an entire T_g range, this author strongly recommends that, when possible, researchers report not only the observed T_g value (and how it was assigned), but also the T_g range. For example, in the case of DSC, report the T_g midpoint value as T_g and, for the range, report both onset and end point T_g values. In addition to these three temperature values (T_g onset, T_g midpoint, and T_g end point) and the change in heat capacity (ΔCp), Wunderlich (1994) suggested reporting two other useful temperatures to characterize the DSC glass transition: T_1 and T_2, which are identified as the intersections of the tangent at T_g with the extrapolated glass and liquid heat capacities, respectively. Wunderlich (1994) also suggested that when using DSC, the glass transition should be measured on cooling at a specified cooling rate. Many researchers, however, measure the transition during heating rather than cooling.

The third issue with the ASTM definitions and discussions given earlier was raised in the earlier T_g discussion, where it was stated that "the observed glass transition temperature can vary significantly depending on the property chosen for observation and on details of the experimental technique." This issue was also discussed throughout the proceedings of the aforementioned 1993 ASTM symposium (Seyler, 1994a). Regarding assignment of the glass transition, Seyler (1994b) stated that "we do not measure THE glass transition temperature [of a sample] but rather make measurements to observe the glass transition and then assign a temperature, T_g, to mark its occurrence." As discussed in detail in the next section, the glass transition can be observed (and marked) by a number of analytical methods. The T_g obtained, however, is not a single value, but rather occurs over a temperature range (as discussed previously) and, moreover, is dependent on a myriad of intrinsic and extrinsic factors associated with a given sample and method. Therefore, in order to assign the glass transition reliably and reproducibly, a complete description of a system must also be given (Seyler, 1994c). This description must not only include the method and property whose changes are being used to identify the glass transition, but also a detailed accounting of the conditions of the sample, test, and atmosphere. This concept is illustrated in Figure 33, in which the large box encompasses the system that yields T_g. To accurately communicate the assigned T_g, we must not simply report a T_g value, but rather a T_g value plus SYSTEM details (Seyler, 1994c).

One final but very important point needs to be made regarding the glass transition. As highlighted by Ludescher *et al.* (2001), it must be kept in mind that the glass transition is a macroscopic manifestation of cooperative changes in molecular mobility (specifically, translational mobility) of individual molecules in a continuous amorphous phase—where the change in

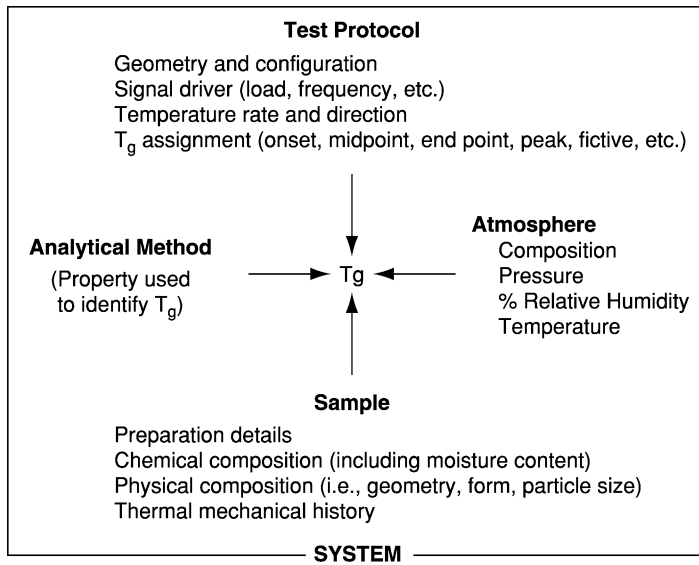

FIG. 33 An analytical method used to assign a T_g value to a sample. The large outer box encompasses the system that yielded the T_g value. Thus, in order to communicate the assigned T_g value accurately, a complete description of the system must also be given [adapted from Seyler (1994c)].

molecular mobility is the underlying cause (and as such, should be the focal point of investigation) and the glass transition is the effect. This focus on molecular mobility of a system, rather than on the glass transition effect, is also advocated by Fennema (1996) and is integrated into the views and discussion presented in this review.

3. *Measurement methods*

Several material properties exhibit a distinct change over the range of T_g. These properties can be classified into three major categories—thermodynamic quantities (i.e., enthalpy, heat capacity, volume, and thermal expansion coefficient), molecular dynamics quantities (i.e., rotational and translational mobility), and physicochemical properties (i.e., viscosity, viscoelastic proprieties, dielectric constant). Figure 34 schematically illustrates changes in selected material properties (free volume, thermal expansion coefficient, enthalpy, heat capacity, viscosity, and dielectric constant) as functions of temperature over the range of T_g. A number of analytical methods can be used to monitor these and other property changes and

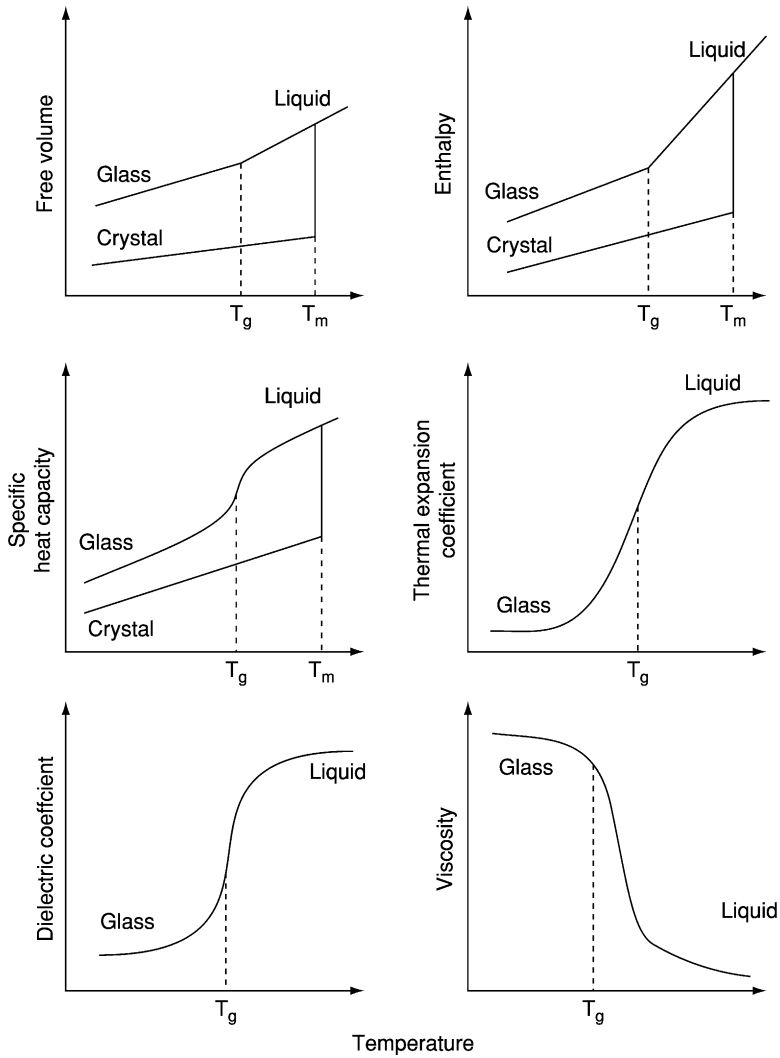

FIG. 34 Schematic illustrations of changes in selected material properties (free volume, thermal expansion coefficient, enthalpy, heat capacity, viscosity, and dielectric constant) as functions of temperature over the range of T_g.

thus identity the glass transition. The most common methods and their descriptions are given in Table VIII. Modulated DSC techniques have been introduced that may be helpful for observing the glass transition in systems with weak, broad, or overlapping transitions (De Meuter *et al.*,

TABLE VIII
;SELECTED ANALYTICAL METHODS USED TO OBSERVE T_g[a]

Analytical method	Description	ASTM designation and references
Differential scanning calorimetry (DSC)	Method involves continuously monitoring the difference in heat flow between a reference material (usually an empty pan) and a test material when they are heated or cooled at a controlled rate through the glass transition region of the test material and analyzing the resultant thermal curve to provide the glass transition temperature. The glass transition is manifested as a step change in specific heat capacity (ΔC_p), which occurs between the glassy (lower C_p) and the rubbery–liquid (higher C_p) states of the sample	ASTM E 1356–98 Wunderlich (1990)
Thermomechanical analysis (TMA)	Method uses thermomechanical analysis equipment to assign the change in dimension of a specimen observed when the material is subjected to a constant heating rate through its glass transition. This change in dimension associated with the change from vitreous solid to amorphous liquid is observed as movement of the sensing probe in direct contact with the specimen and is recorded as a function of temperature. The intersection of the extrapolation of the slope of the probe displacement curve before and after the transition is used to determine the glass transition temperature. In the TMA under tension method tensile mode is used	ASTM E 1545–00 ASTM E 1824–96 under tension Seyler (1994a); Wunderlich (1990)
Dynamic mechanical analysis (DMA)	A specimen of known geometry is placed in mechanical oscillation at either fixed or resonant frequency, and changes in viscoelastic response of the material are monitored as a function of temperature. The glass transition region is marked by a rapid decrease in the storage modulus and a rapid increase in the loss modulus. Glass transition of the test specimen is indicated by the extrapolated onset of the decrease in storage modulus, which marks the transition from a glassy to a rubbery solid	ASTM E 1640–99 Macinnes (1993); Seyler (1994a); Wunderlich (1990)

(*continued*)

TABLE VIII (*continued*)

Analytical method	Description	ASTM designation and references
Dielectric analysis (DEA)	Method involves placing a specimen between parallel plate capacitors and applying a sinusoidal voltage (frequencies ranging from 1 mHz to 1 MHz) to one of the plates to establish an electric field in the specimen. In response to this field, a specimen becomes electrically polarized and can conduct a small charge from one plate to the other. Through measurement of the resultant current, the dielectric constant and dielectric loss constant for a specimen can be measured. The sharp increases in both the dielectric constant and the dielectric loss constant during a temperature scan are correlated with the occurrence of T_g	Bidstrup and Day (1994); Roos (1995)
Nuclear magnetic resonance (NMR) spectroscopy	Method involves measuring the change in molecular mobility (rotational and translational mobility) experienced by nuclei associated with solid components (e.g., ^{1}H and ^{13}C). The temperature associated with an increase in solid component mobility is assigned as T_g	Ablett *et al.* (1993); Kou *et al.* (1999); Ruan and Chen (1998); Ruan *et al.* (1998, 1999)
Electron spin resonance (ESR) spectroscopy	Method involves measuring the change in rotational correlation time for a free radical probe (e.g., nitroxide spin probes) introduced into a sample being studied. The temperature associated with a decrease in the rotational correlation time of a spin probe is assigned as T_g	Hemminga *et al.* (1993); Roos (1996)

[a]Where possible, the ASTM test method description and designation have been included.

1999; Paeschke, 2002; Riga and Judovits, 2001). Additional methods are given in Rahman (1995), Roos (1995), and Slade and Levine (1995), and a discussion of some of the unsettled issues associated with various T_g methods is given in Levine (2002).

It is important to emphasize that the T_g of a given sample is not a unique value, but rather depends on the analytical method and protocol employed, as well as a complete description of the sample, its composition (e.g., moisture content), and its history (i.e., under what conditions was it made

and stored). Because each method "sees" a sample from its own perspective (i.e., property and level being probed), the T_g value observed by each method for a single sample may or may not be the same. For example, Ruan *et al.* (1998) reported T_g values for a DE-15 maltodextrin sample using DSC (reported as T_g) and ^{1}H NMR (T_{T1}—temperature assigned as marking the glass transition, using the longitudinal relaxation time, and T_{T2S}—temperature assigned as marking the glass transition, using the transverse relaxation time of the short-relaxing component). They found that T_{T2S} values were, on average, only 1.2 °C lower than DSC T_g values, whereas T_{T1} values were, on average, 11.2 °C lower than DSC T_g values. Additional examples comparing T_g values obtained using different methods for the same (or similar) samples are given in Schmidt (1999).

In addition to possible variations between methods, there may also be variations in T_g within a method, depending on the measurement protocol employed. For example, the DCS T_g midpoint for a quench-cooled (~100 K/min) maltose sample, heated at a scanning rate of 10 K/min, was 43.1 ± 0.21 °C, whereas for a maltose sample prepared using equal heating and cooling rates of 10 K/min the T_g was 41.2 ± 0.10 °C (Schmidt and Lammert, 1996). For the same samples, DSC T_g fictive temperatures were also calculated. T_g fictive for the quench-cooled sample was 41.0 ± 0.20 °C, whereas for the equal-rate sample, T_g fictive was 38.6 ± 0.06 °C.

Because of the possible differences in T_g obtained by different measurement methods, a question often arises as to what measurement method should be used? Since no one method yields an "absolute" or "true" T_g, any method performed correctly can yield a useful T_g value. What is important to remember is that the T_g obtained is dependent on the method used (i.e., reflects the experimental time scale of the method) and the system probed (recall Figure 33). Therefore, the measurement method should be selected according to the needs of an application.

By definition, the glass transition reflects changes experienced by the solid component(s) of a sample, as it transitions from an amorphous solid to a rubbery–liquid. Thus, the descriptions of the methods listed in Table VIII focus on changes experienced by solids in the glass transition region, and most often, what is measured is an average T_g for an entire system. What about the mobility experienced by the individual components that comprise a system, including water, relative to the glass transition for the entire system?

Recall that the glass transition for a given glass-forming solute–water blend (i.e., the glass transition for the entire system) is determined by the weight-average molecular weight ($\overline{M}w$) of the blend (Slade and Levine, 1991). In turn, as explained by Slade and Levine (2003), the relative mobility of an individual component in a multicomponent system is determined by

the molecular weight ($\overline{M}w$ or the number-average molecular weight [$\overline{M}n$], depending on which is appropriate to use) of that component, compared to $\overline{M}w$ of the system. For example, a molecule of higher molecular weight than that of the system (use $\overline{M}n$ in this case) would already be immobilized at the glass transition of the system, whereas a molecule of lower molecular weight (use $\overline{M}w$ in this case) than that of the system, such as water, would still be mobile at temperatures below the glass transition. A probe molecule of the same molecule weight (use $\overline{M}w$) as that of the system would be immobilized at T_g of the system. Thus, the molecular weight (and the configuration, in cases of equal or near-equal molecular weight) of a component determines its mobility relative to the glass transition of the system. A number of studies have shown that water retains a high degree of rotational and transitional mobility in glassy states relative to the glass transition of solid components (Ablett *et al*., 1993; Kou *et al*., 1999; Le Meste *et al*., 2002; Roudaut *et al*., 1999a; Tromp *et al*., 1997). This finding again emphasizes the importance of keeping in mind that results obtained depend on the viewpoint of the method and component being used to probe a system under study.

Differences in mobility of various components (e.g., starch, sucrose, water) within a food system (e.g., a cookie), as well as the inherent heterogeneity of many food systems (e.g., crust versus crumb of a cookie), suggest the need to measure more than an average T_g for a system. Ruan and Chen (1998) proposed the creation of a "T_g map" to capture the distribution of T_g values within a food system. Since conventional techniques used to measure T_g do not have the capacity at the present time to provide spatial information, Ruan and Chen (1998) suggested the use of MRI, as a function of temperature, to produce a "T_g map."

4. Distance and timescales involved in glass transition

The distance scale associated within the glass transition is related to the method used. For example, thermal and mechanical techniques provide macroscopic views of the glass transition, whereas spectroscopy techniques yield a molecular-level view. Thus, it is not surprising to find that molecular-level techniques, such as NMR, may result in lower T_g values compared to those obtained using a macroscopic technique, such as DSC. Both T_g values are correct, but not necessarily equal, given the different points of view the two methods are probing.

As discussed earlier, the amorphous state is a nonequilibrium state at temperatures below the equilibrium melting temperature of a material. Because of the nonequilibrium nature of the amorphous state, various properties of amorphous materials, such as the glass transition, are dependent on time and temperature (Slade and Levine, 1988, 1991; Roos, 1995, 2003). Therefore,

methods using different experimental timescales, such as frequency and cooling/heating rates, can result in different locations of the glass transition for the same material. In addition, various enthalpic relaxations may be associated with the observed glass transition, depending on the rates of glass formation and measurement [e.g., slow cooling followed by fast heating in a DSC experiment results in an endothermic peak in the heat capacity curve (Wunderlich, 1990)], as well as the process of physical aging that can occur in the glassy state (Roos, 2003). In the case of physical aging, an endothermic relaxation peak is observed during measurement of the glass transition by DSC. The size of the endothermic peak increases with aging time and has been shown to interfere with the accurate assignment of T_g (Richardson and Saville, 1975), especially when one uses standard instrumental software to obtain T_g. For example, Wungtanagorn and Schmidt (2001), studying the aging of glucose and fructose glasses, reported that T_g values obtained using the instrumental software increased as a function of aging time, whereas theoretically these T_g values should decrease with aging time. Factors responsible for this artificial increase in software-measured T_g values with aging time are discussed in detail in Wungtanagorn and Schmidt (2001).

5. *Usefulness of the glass transition concept for foods*

There is no doubt that the introduction and application of Slade and Levine's food polymer science approach to better understand processing and stability of food systems have been exceedingly stimulating and have led to a number of important scientific advances. On many fronts, the usefulness of the food polymer science approach has been widely demonstrated. However, use of the glass transition as the single ultimate index temperature of food stability, as it was first embraced, is said by some to be untenable (Chirife and Buera, 1996; Le Meste *et al*., 2002). Rather, the glass transition, as is the case with water activity, is more useful and applicable in some situations compared to others. This last statement is in no way meant to lessen the significance of the glass transition concept in foods, but rather reflects an increased focus on the importance of other independent factors, such as pH, temperature, and reactant and product concentrations (Roos, 2003).

The compilation of ideas about the usefulness of the glass transition concept in foods, presented in this section, was influenced by the following sources: Rahman (1995), Chirife and Buera (1996), Fennema (1996), Roos *et al*. (1996), Champion *et al*. (2000), Labuza *et al*. (2001), Le Meste *et al*. (2002), Bhandari and Howes (2000), Slade and Levine (2003), and Roos (2003). Because there are a number of reviews (including those just listed) that specifically address the usefulness of the glass transition in food processing and stability, only a brief summary is provided here.

a. Development of state diagrams, expanded state diagrams, and mobility and stability maps. As introduced earlier, state diagrams are very useful tools for describing relationships among the physical state of food materials, temperature, concentration, pressure, and time (Karel *et al.*, 1993; Roos, 1995; Slade and Levine, 1991). State diagrams can be expanded and plotted in a variety of creative ways to enhance their usefulness and to facilitate the understanding of complex series of events that can occur in the processing and storage of food systems. State diagrams have been augmented by adding paths associated with [see, e.g., Figure 17.13 in Levine and Slade (1993), Figures 4–6 and 8 in Strahm (1998), and Figure 2 in Zweifel *et al.* (2000)] or areas important to [see, e.g., Roos (1995)] various food processes and technologies, such as drying, baking, cooling, freezing, heating, hydration, and extrusion. Product types have been indicated on state diagrams of major components comprising those products [see, e.g., Figure 2.13 in Karel *et al.* (1993)]. Constant-relaxation time lines, as well as isoviscosity lines, have been plotted on state diagrams [see, e.g., Figure 3 in Parker and Ring (2001), Figures 5 and 6 in Roos (2002), and Figures 2.13 and 2.14 in Roos (1998)]. The relative locations of food quality-deteriorating events, such as crystallization, collapse, caking, and stickiness, have also been indicated on state diagrams [see, e.g., Figures 7.7 and 10.12 in Roos (1995)], illustrating stability in the glassy state and time-dependent changes in the rubbery state (Roos and Karel, 1991). Additional discussions of applications of state diagrams can be found in Roos and Karel (1991), Karel *et al.* (1993), Nelson and Labuza (1993), and Roos (1995).

More recently, Slade and Levine (2003) developed a combination glass transition-universal isotherm diagram (Figure 35) to illustrate the concept that multiple texture stabilization requires control of moisture content, sample RH, molecular T_g, and network T_g. The diagram contains portions of the glass curves for sorbitol (T_g sorbitol), for a nonnetworked biopolymer (T_g biopolymer), and for a permanent network (T_g permanent network) positioned relative to a "universal isotherm curve" as a means of showing, e.g., that molecular T_g controls water vapor migration, while network T_g controls bulk liquid water migration.

Using the time-dependent aspect of state diagrams, Roos (2003) illustrated the effects of temperature, water activity, or water content on relaxation times and relative rates of mechanical changes in amorphous systems (Figure 36). This diagram can be considered as a type of mobility map, where mobility increases (relaxation time decreases) as temperature and/or water content/activity increases. Le Meste *et al.* (2002) suggested the establishment of "mobility maps" for food materials showing characteristic relaxation times for different types of molecular motions as a function of temperature and water content.

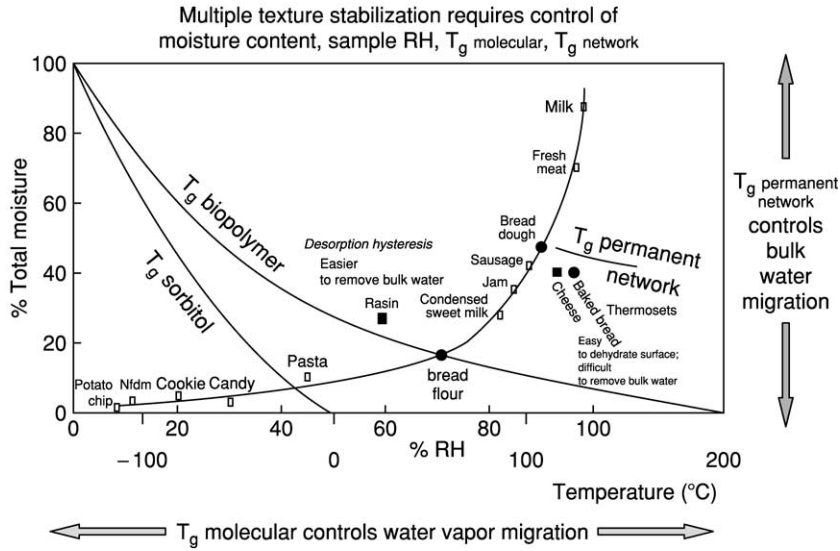

FIG. 35 Percentage relative humidities of common foods at room temperature and typical steady-state moisture contents plotted as a "universal sorption isotherm" with portions of three glass curves (relatively positioned) for sorbitol, for a nonnetworked biopolymer, and for a permanent network [reproduced with permission from Slade and Levine (2003)].

In addition to these state diagram-based maps, various stability (or quality) maps have been created to depict the stability of a system as influenced by the T_g or associated critical water activity value. For example, in Figure 12.4 of their paper, van den Berg *et al.* (1993) plotted a T_g curve as a function of %RH for safe storage of amorphous sucrose and labeled the temperature–%RH area below the curve as stable and the area above the curve as unstable. In another example, Roos *et al.* (1996) plotted relative rates of typical mechanical and deteriorative changes in foods as (1) a function of temperature and included T_g (see Figure 5A in Roos *et al.*, 1996) or (2) a function of water activity and included a critical water activity value (see Figure 5B in Roos *et al.*, 1996). The latter stability map is similar in concept to the original water activity stability map in Labuza *et al.* (1970) (illustrated previously in Figure 15), but instead of including a sorption isotherm, critical water activity is used as the point at which molecular mobility and rates of diffusion-controlled changes begin to increase. Figure 37 shows a stability map of the latter type, specifically for dairy powders containing amorphous lactose, developed by Roos (2003). Roos also developed schematic diagrams

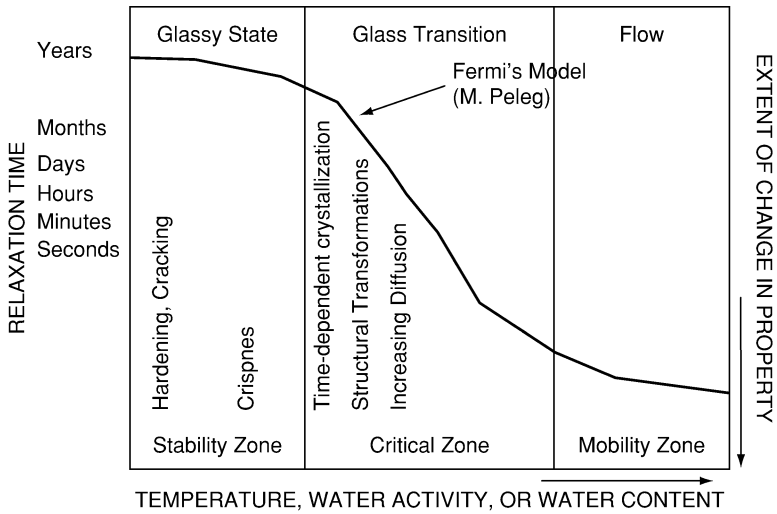

FIG. 36 Effects of temperature, water activity, or water content on relaxation times and relative rates of mechanical changes in amorphous materials [reproduced with permission from Roos (2003)]. M. Peleg reference is Peleg (1996).

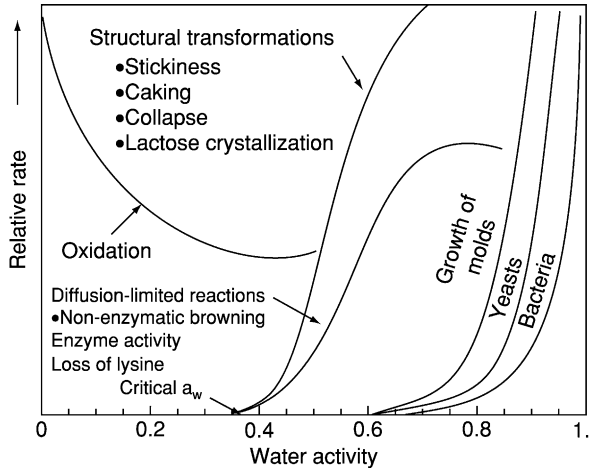

FIG. 37 Stability map for dairy powders containing amorphous lactose. The critical water activity (0.37 a_w) corresponds to the water activity of amorphous lactose with T_g of 24 °C (and a moisture content of 6.8 g water/100 g solids) [reproduced with permission from Roos (2003)].

illustrating the time dependence of crystallization as a function of water activity and moisture content in lactose (see Figure 23 in Roos, 1992) and in foods containing amorphous sugars and carbohydrates (see Figure 2.11 in Roos, 1998).

b. Selection of ingredients. Because, for a glass-forming solute–water blend, T_g is determined by the weight-average molecular weight ($\overline{M}w$) of that blend (Slade and Levine, 1988), T_g of a food matrix can be manipulated by the selection of ingredients incorporated into the blend. In general, low molecular weight components, such as simple sugars, have low T_g values, whereas high molecular weight components, such as starch and proteins, have high T_g values (Slade and Levine, 1988). For the interested reader, Nelson and Labuza (1993) give several examples relating state diagrams for processes and ingredients to the texture of various cereal foods.

c. Determination of product stability and shelf life. The location of T_g influences the stability of food systems. In very general terms, low-moisture food ingredients and systems are most stable when produced and held at temperatures below, rather than above, their T_g. Above T_g, food stability decreases as the temperature of a food increases above its T_g (defined in terms of $\Delta T = T - T_g$) (Slade and Levine, 1991). However, it has been found that use of T_g as a universal index temperature for food stability depends on the specific aspect of stability (e.g., chemical, biochemical, physical, and microbial growth and toxin production) under consideration (Roos, 1995). In other words, T_g is a better predicator of stability in some instances than in others.

The most well-established relationship between T_g and food stability involves the control and prediction of physical processes in amorphous food systems, such as stickiness, caking, collapse, loss of crispness, and crystallization of amorphous solids (Roos, 2003; Slade and Levine, 1991). The rapid changes in viscosity and modulus that occur above T_g govern many of the aforementioned changes in physical properties (Peleg, 1993). Despite the very successful use of T_g to predict the stability of physical properties in many amorphous food systems, exceptions are noted and discussed in detail by Le Meste *et al.* (2002). One example involves work on glassy breads (Le Meste *et al.*, 1996; Roudaut *et al.*, 1998, 1999a,b). Le Meste *et al.* (2002), summarizing results from those studies, reported that the water content at which a loss in sensory crispness occurred (~9% wb) was lower than the water content corresponding to T_g (~15% wb) at the experimental temperature (25 °C). Thus, this important textural change took place while the material was in a glassy state. The underlying microstructural events responsible for those results are not completely elucidated

yet. However, Roudaut *et al.* (1998) suggested that the loss of sensory crispness, sensory hardness, and other mechanical properties in the glassy solid matrix is related to a secondary physical transition, from brittle to ductile, which occurs at a temperature. T_β, below T_g. The possibility of this sub-T_g influence on texture was alluded to previously by Slade and Levine (1991) and is discussed in Slade and Levine (2003) and Roudaut *et al.* (2002).

As far as a relationship between T_g and chemical and biochemical (e.g., enzymatic) reactions rates, no direct relationship has been universally established. In general, reaction rates do increase as temperature increases; however, rates for a variety of reactions have been reported to be significant at temperatures below the T_g for various food matrices. Such reactions have included rates of Maillard browning (Bell *et al.*, 1998; Craig *et al.*, 2001; Schebor *et al.*, 1999), hydrolysis of sucrose by invertase (Chen *et al.*, 1999), peptide bond hydrolysis (Streefland *et al.*, 1998), aspartame degradation (Bell and Hageman, 1994), and hydrolytic deamidation of asparagines (Lai *et al.*, 1999a,b). Results from these and other studies strongly suggest that reaction rates seem to be affected by a number of additional and independent factors, such as pH, temperature, reactant and product concentration and solubility, oxidation–reduction potential, water content, water activity, phase separation, and local differences in water sorption and microstructure, and not merely by an average macroscopic T_g of a food matrix (Fennema, 1996; Lievonen and Roos, 2002a; Roos, 2003; Sherwin and Labuza, 2003). Lievonen and Roos (2002b) demonstrated the feasibility of determining reaction rates for food systems in sealed containers at several temperatures as a method for further investigating the relationship between glass transition and reaction kinetics.

Despite the current lack of clarity regarding the relationship between glass transition and chemical reaction kinetics, it is still quite feasible that chemical and biochemical reaction rates may be governed by mobility, i.e., the mobility that is most rate limiting to a particular reaction scheme (e.g., water mobility, reactant mobility, molecular-level matrix mobility, local or microregion mobility), but perhaps not simply by an average amorphous solid mobility as reflected by the T_g. Ludescher *et al.* (2001) recommend the use of luminescence spectroscopy to investigate how rates of specific chemical and physical processes important in amorphous solid foods are influenced by specific modes of molecular mobility, as well as by molecular structure.

The relationship between T_g and microbial stability is the least studied of all the stability areas. Based mainly on mold germination data, Slade and Levine (1991) postulated that glass transition parameters, specifically T_m/T_g ratio, T'_g and W'_g (related to C'_g defined previously in Figure 32), could be useful for predicting the microbial stability of concentrated and

intermediate-moisture foods. Kou *et al.* (1999), who studied stability in sucrose, starch, and sucrose/starch systems, reported conidia germination of *Aspergillus niger* in only those samples that had DSC midpoint T_g values below 20 °C (the experimental temperature) (see Figure 29), which included two instant dent starch samples (0.946 and 0.976 a_w), four sucrose samples (0.890 to 0.976 a_w), and four 1:1 sucrose/starch samples (0.890 to 0.976 a_w). They reported no conidia germination in samples that had T_g values above 20 °C because those samples were in a glassy state. However, according to a critical review by Chirife and Buera (1996), there seem to be a number of unanswered questions regarding the widespread tenability of the relationship between T_g and microbial stability of foods. As suggested by Le Meste *et al.* (2002), additional research involving different types of microorganisms and substrates, including measurement of microbial growth and metabolic activity, not just spore germination, is needed to further investigate this relationship.

d. Influences on product behavior during processing. T_g is an important food matrix property of value in many food processing operations, such as drying, extrusion cooking, puffing, and flaking (Bhandari and Howes, 2000; Le Meste *et al.*, 2002; Lillford, 2003; Roos, 1995). The selection of appropriate processing parameters to produce and maintain foods of optimum quality and stability (at reasonable costs) in these unit operations is strongly influenced by the glass transition behavior of a product during processing and storage. For example, to avoid quality problems, such as collapse during freeze-drying, two temperature limits are essential. First, a material should be frozen to below the onset temperature of ice melting (T'_m in Figure 32) or, more practically, to below T'_g to ensure sample solidity and avoid viscous flow of an amorphous, freeze-concentrated solute matrix. Second, the temperature of a material, throughout both primary (sublimation of ice under vacuum) and secondary (removal of unfrozen water from a product) drying processes, should be maintained below the T_g curve of the material to keep the material from existing in a rubber–liquid state, which would result in structural collapse and loss of porosity and very poor rehydration properties (Craig *et al.*, 1999; Khalloufi and Ratti, 2003; Roos, 1995; Slade and Levine, 1991; van den Berg *et al.* 1993). Detailed explanations regarding the influence of glass transition behavior on a variety of other processing operations can be found in Slade and Levine (1991), Levine and Slade (1993), Roos (1995), Strahm (1998), Bhandari and Howes (2000), Zweifel *et al.* (2000), Roos (2002), and Vautaz (2002).

The introduction of Slade and Levine's food polymer science approach has mobilized (no pun intended!) a large number of researchers to pursue the question of how the glass transition concept applies to the processing and

stability of specific food systems. Although much progress has been made, still more needs to be accomplished. As with any process of inquiry, there is a good deal of constructive debate that remains to be resolved [e.g., see Chirife and Buera (1994, 1995, 1996); Labuza *et al*. (2001); Le Meste *et al*. (2002); Peleg (1996 and 1997); Slade and Levine (1991)].

6. *Measurement of glass transition temperature in foods*

As discussed earlier, the usefulness of the food polymer science approach to the study of water dynamics in foods has been widely demonstrated by numerous researchers studying both model and real food systems. Along with the success of the approach, there still exist a number of areas of concern that need to be mentioned.

Despite years of investigation, there remains an active controversy as to exactly what T_g is and is not. There are a number of theories associated with the nature of T_g, such as free volume and statistical mechanical theories, but as of yet there is no universally agreed-upon explanation for the phenomenon (Craig *et al*., 1999; Hancock and Zografi, 1997). The good news is that focused and complementary experimental efforts, numerical simulations, and analytical theory are helping to fill in some of the missing pieces (Stillinger, 1995).

As pointed out previously, T_g is not a single or unique value, even for a well-defined sample; rather, it occurs over a temperature range and is dependent on the measurement method used and the system involved (recall Figure 33). In addition, it is quite possible that complex, multiphase food systems possess more than one T_g. The complexity inherent in many food systems sometimes makes it difficult to observe a T_g value at all (Labuza *et al*., 2001; Vittadini *et al*., 2002).

The food polymer science approach is being applied successfully in the food industry for understanding, improving, and developing food processes and products. However, to date, the glass transition generally remains more of a research and development tool than a routine quality assurance measure of food processability and stability.

7. *Relationship between glass transition temperature and* a_w

Because both T_g and water activity are functions of water content, the two parameters can be correlated to each other. This can be done in two main ways, as presented by Roos (1995). The first is to measure T_g of samples humidified to known water activity values (i.e., using saturated salt solutions) and then plot T_g values as a function of water activity (e.g., see Figure 6.2A in Roos, 1995). Over the entire a_w range, a sigmoid-shaped curve was

observed (Roos, 1995). Another approach for correlating existing isotherm and glass transition data was presented by Slade and Levine (1991). Sorption isotherm data at different temperatures are transformed to a series of iso-RVP contours (i.e., combinations of moisture content and temperature that yield the same values of observed RVP) that are then plotted on a state diagram (a water/glass dynamics map as they called it) for the same (or a similar) material. For example, Slade and Levine (1991) converted literature sorption data for apple pectin at four temperatures (25, 40, 60, and 80 °C) to a series of iso-RVP contours and plotted them as a function of weight percentage solids on a state diagram (T_g as a function of weight percent solids) for hemicellulose (see Figure 26 in Slade and Levine, 1991).

The second way is to add a sorption isotherm obtained at a temperature of interest (usually ambient temperature) to a state diagram. Such a modified state diagram, as suggested by Roos (1995, 2003), can be developed by modeling water plasticization data using the Gordon–Taylor equation and modeling sorption isotherm data using the Guggenheim–Anderson–De Boer (GAB) equation (both equations can be found in Roos, 1995). In this approach, the moisture content associated with the T_g equal to the temperature at which an isotherm was obtained is identified (referred to as critical mc) and is then used to locate a critical water activity value. This approach is illustrated, for instant dent starch, in Figure 38 using starch isotherm data (obtained at 20 °C) and starch DSC midpoint T_g data from Kou *et al.* (1999). The critical moisture content was 21.8% (wet basis), which corresponds to a critical water activity value of 0.92. It is important to note that the critical moisture content and water activity values obtained may vary slightly depending on the specific equations selected to model the water plasticization and sorption isotherm data. For example, using the same Gordon–Taylor determined critical moisture content value (22% wet basis) for the instant dent starch discussed in Figure 38, an a_w value of 0.936 was obtained using the Smith (1947) equation to fit the sorption isotherm data (Kou *et al.* 1999) compared to the 0.92 a_w value obtained using the GAB equation.

IV. EMERGING PICTURE OF FOOD SYSTEM MOBILITY: SUMMARY AND FUTURE DIRECTIONS

Throughout this review, the concept of mobility has been highlighted as a key parameter for understanding and predicting the processability and stability of food systems. Mobility is the common denominator of the three methods examined in this review—water activity, nuclear magnetic resonance, and glass transition. An emerging aspect of the picture for food

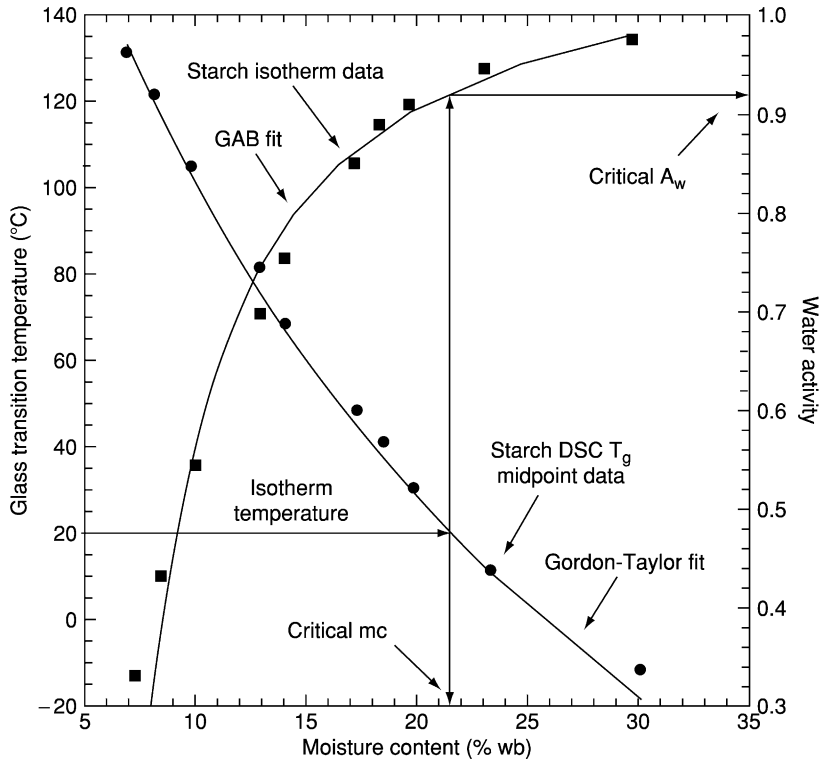

FIG. 38 Graph of a modified state diagram for instant dent starch, which includes both DSC T_g midpoint data plotted as a function of moisture content (% wb) and sorption isotherm data obtained at 20 °C. DSC T_g midpoint data were fit to the Gordon–Talyor equation, and sorption isotherm data were fit to the GAB equation. The moisture content associated with the T_g at 20 °C is called the critical mc and is equal to 21.8% (wb), and the corresponding critical water activity value is 0.92.

system mobility is that food systems do not possess one type of mobility, but many—depending on the species (i.e., water or a specific solid component), distance (molecular through macroscopic), and timescales (picoseconds through centuries) being probed. Thus, a single measure of mobility (or a single approach) is unlikely to provide us with the comprehensive and complete picture we seek so that we can solve the myriad of processing and stability problems that exist. In the past, researchers focused on water activity and water mobility as the "answers" to food stability. More recently, the focus has switched to solids mobility. However, what is being recognized is that a combined approach, which probes both water and solids mobility

(at various distance and time scales) and their individual and combined relationships to food stability, is most desirable.

However, even water and solids mobility are not completely sufficient, as there are still other factors that need to be taken into account and investigated, on a case-by-case basis, such as chemical properties, pH, oxidation–reduction potential, and temperature (Fennema, 1996). Development and application of complementary techniques are needed, such as those presented in this review, as well as others [e.g., optical luminescence (Ludescher *et al.*, 2001)], to continue to develop a full and complete picture of the time-dependent changes taking place in food systems during processing and storage. Much progress has been made in the study of the physicochemical properties of foods, recently termed the material food science field by Karel (1999), but as always there is still much more that needs investigating.

ACKNOWLEDGMENTS

I am grateful for the cohort of colleagues, students, and friends spread all over the globe who share my passion for investigating the complex nature of water and solids in edible things. Special appreciation is extended to Martin Chaplin, Professor of Applied Science and Head of the Food Research Centre, South Bank University, London, for the many e-mail discussions we had regarding the properties of water. A special thanks is also extended to Harry Levine, who spent a great deal of time and effort reviewing and editing a draft copy of this manuscript. I appreciate and could not do what I do without the love and support of my wonderful family, Art, Robbie, and Annie Schmidt, as well as my friends Mevanee and Phill Parmer. The artwork assistance of Carl Burton from the Visualization, Media, and Imaging Laboratory, Beckman Institute for Advanced Science and Technology, is also gratefully acknowledged.

GLOSSARY

Chemical shift Electrons of the atoms and molecules surrounding a nucleus interact with B_0 and induce an additional local field at the position of the nucleus being probed. The effect of this local magnetic field is to reduce the magnitude of the external magnetic field experienced by local nuclei. This results in a shift in the resonance frequency of nuclei. Chemical shifts are measured in parts per million (ppm).

Eutectic point (T_e) A single point on a temperature–concentration phase (or state) diagram for a binary solution (e.g., water and sugars or salts) where the solution can exist in equilibrium with both crystalline solute and crystalline solvent. Under equilibrium conditions, cooling at T_e results in simultaneous crystallization of solvent and solute in constant proportion and at constant temperature until maximum solidification has occurred (based on Fennema, 1996).

Hurdle technology Involves manipulating various growth-controlling parameters in a manner such that growth of microorganisms will not occur; each parameter serves as a "hurdle" to microbial growth (based on Fennema, 1996).

Hydrological cycle The cyclic transfer of water vapor from the Earth's surface via evapotranspiration into the atmosphere, from the atmosphere via precipitation back to earth, and through runoff into streams, rivers, and lakes, and ultimately into the oceans (U.S. Geological Survey, 2003).

Latent heat The quantity of heat that must be added or removed from a substance to change its phase without changing its temperature. The units of latent heat are commonly reported as cal/g.

Nuclear Overhauser effect Occurs as a result of cross-relaxation between dipolar-coupled spins resulting from spin–spin interactions through space.

Phase diagram Summarizes the pressure and temperature conditions at which each phase of a homogeneous material is most stable.

Sensible heat The quantity of heat that must be added or removed from a substance to change its temperature. The units of sensible heat are commonly reported as cal/g °C.

Spin–spin coupling (also called scalar or "J" coupling) Splitting of NMR resonance signals by neighboring magnetic nuclei. The coupling is a magnetic interaction that occurs through the electrons of chemical bonds connecting two spins.

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CONSUMER REACTIONS TO FOOD SAFETY CRISES

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ADVANCES IN FOOD AND NUTRITION RESEARCH VOL 48
ISSN: 1043-4526

I. INTRODUCTION

Improving nutrition is essentially a process of encouraging people to make healthful choices that improve their well-being (Wansink, 2005). What happens, however, when we believe contamination, terrorism, or a genetic incidence threatens a part of the food supply? Sometimes crises influence the recall, redesign, and communication efforts of individual companies (such as Tylenol, Perrier, Pilgrim's Pride). Others, such as the threat of "mad cow" disease (bovine spongiform encephalopathy, or BSE) in beef can compromise an entire industry.

One of the dangers of food safety crises is that they can be triggered by concurrent events that can distort reality (Bartholomew and Goode, 2000). The tragedy of 9-ll triggered hypersensitive concerns about anthrax poisoning, but such concerns could just have easily been triggered by an unrelated food poisoning. Yet the behavior of consumers in a crisis situation is not always consistent with the true level of risk they face. This chapter examines how seemingly inconsistent behaviors of consumers can be explained by differences in these risk perceptions and risk attitudes. Knowing the drivers of behavior provide insights on whether the solution to the crisis lies in more effective communication efforts or in more drastic measures with respect to the product supply (such as recalls or product eliminations).

The study of risk perception has been punctuated with controversy, conflict, and paradigm shifts. Despite more than three decades of research, scientists' understanding of risk assessment remains fragmented and incoherent. Until recently, eating food has been viewed as a low-risk activity and perceived risk was primarily related to matters of hygiene. Recently, however, the safety of food supplies has been called increasingly in to question. Consider a recent chronology of food scares (Scholderer, 2002):

1996: BSE/CJD link discovered
1997: Contagious swine fever in The Netherlands
1998: Arpad Pusztai and the GM potato hoax
1999: Contaminated Coca-Cola in Belgium
1999: GM maize kills Monarch butterflies
2000: BSE hits continental Europe
2001: Antibiotics and growth hormones in German pigs
2001: Foot-and-mouth disease all over Europe
2002: *Escherichia coli* in ConAgra Beef
2002: *Listeria* in Pilgrim's Pride chicken

Prior to these food safety scares, theories of risk have been constructed with reference to environmental and technological hazards, such as nuclear power, while neglecting food issues. In this last decade, however, attention

has moved toward the study of food risk. Within this, food risk research has focused almost exclusively upon attempting to explain the divergence of opinion that exists between experts and the lay public has neglected to address why this divergence exists (Knox, 2000).

Food safety crises illustrate dramatically the need to understand why and how consumers react in the way they do. Moreover, not all crises are created equal. While crises related to BSE and hoof-in-mouth disease have received a great deal of press (Abbott, 2001), it is illustrative to note other more isolated incidents that have occurred in the recent past (Smith *et al*., 1988). Some, such as those dealing with Tylenol or Perrier, are more brand based, whereas others are more commodity-based (see Table I). While each crisis is slightly different, they all involved a state of panic that could have been reduced, if not eliminated, if appropriate efforts had been taken through precrisis planning or though postcrisis response. One reason why many of these past food scares have been reasonably disastrous has been because little thought had been given to the potential of a crisis before it actually happened. Another reason is that people have been treated as responding in a homogeneous manner (Modan *et al*., 1983; Smelser, 1962). This is absolutely wrong to do.

An important theme to this review is that people respond to food crises differently. We can still, however, achieve a reasonable degree of predictability by segmenting them into somewhat homogeneous groups based—not on demographics—but on a person's risk perceptions and risk attitude. For every crisis there will be accountable, concerned, conservative, and alarmist segments of consumers. Knowing their relative size will enable us to better predict the effectiveness of different interventions.

Yet just as all people are not alike, neither are all food crises alike. They can vary in their familiarity, severity, proximity, consequence, and the extent to which they can be avoided. This review covers a wide range of crises from bacteria contamination, to product tampering, to fears related to irradiation and biotechnology. Different types of crises will be evaluated differently by different groups of consumers. What has been done in this review is to focus on "worst-case" scenarios involving initial responses to food safety issues. These will provide the most clear and illustrative profiles of consumer response. Less extreme scenarios will elicit less extreme responses.

After showing how consumer attitudes toward food safety are formed, this review distinguishes four different segments of consumers who would be most influenced and most influential during a food crisis. Decoupling the risk response behavior of consumers into the separate components of risk perception and risk attitude shows how these different segments of consumers will react differently in a crisis situation. Using these insights, suggestions are made for precrisis preparations and postcrisis responses.

TABLE I
WHAT IS THE POTENTIAL IMPACT OF A FOOD CRISIS?

Description	Consumer reaction	What was done	Aftermath
Tylenol and cyanide (1982, US). Seven people died in Chicago after ingesting Extra Strength Tylenol (Johnson & Johnson)	Nationwide panic.	Police drove through Chicago warning people with loudspeakers. FDA advised avoidance of Tylenol capsules. J&J immediately recalled 31 million bottles and alerted consumers not to consume capsules until source of tampering was determined. The production and advertising of Tylenol capsules were stopped, and tablets were exchanged for capsules.	Copycats afterwards, 36 product tampering episodes. Tylenol was reintroduced with new tripleseal tamper-resistant packaging six weeks later. J&J offers coupons, discounts, J&J affiliates make presentations to medical community; Tylenol comeback was a success.
Edwina Currie Fiasco (1988, GB). Junior Health Minister admitted most of UK's eggs were contaminated with *Salmonella*	Demand for eggs failed. Lingering downturn of egg consumption.	Four million hens were slaughtered and 400 million surplus eggs destroyed.	*Salmonella* poisoning is a permanent problem; 30,000 cases in England and Wales every year. Health minister resigned.
E. coli poisoning (1996, Scotland). 21 people died, 500 ill	It came from a local butcher shop (who had recently won the award for Best Scottish Beef Butcher of the Year).	The butcher was asked to stop selling cooked meat products the morning after the outbreak was discovered.	Scotland's most serious food poisoning event since 1964. Permanent problem everywhere; several cases every year, affecting thousands of people worldwide.

ConAgra Beef (June 2002, US). *E. coli* in beef products, 13 deaths	Twenty-five victims total. ConAgra agreed to pay the medical and lost-wage costs of 13 victims in Colorado ($1 million each)	ConAgra recalled 354,000 pounds of beef products. Media warned about *E. coli*	Victims accepted ConAgra's payment of medical expenses, also agreed not to file lawsuits against the company
Listeria in chicken (2002, US). Listeria in Pilgrim's Pride products, 23 deaths, 120 ill	Many people affected. Eight states renewed the push to reform the laws that govern meat inspection	Meat recalled by the company (27 million pounds). Was called by media the "U.S. largest meat recall," but discovered afterwards that it was exaggerated (two other events caused larger recalls)	2,500 cases of listeriosis occur annually in the United States
Taco Shells & Starlink (2000, US). Taco shells contained 1% corn not approved by FDA for human consumption	The environmental group Friends of the Earth, which commissioned independent lab testing of the corn product, first reported contaminated taco shells. Greenpeace writes: "Taco Bell or Taco Hell?"	Taco Bell and other food companies recalled 300 products (150 brands of corn chips, taco shells, corn dogs, corn bread, breakfast cereals and polenta), but decided to continue selling taco shells obtained from the same supplier.	Thousands of Taco Bell restaurants and others filed a lawsuit alleging that a group of national and international corn and biotechnology firms acted together to cause a collapse of the U.S. corn market.
Perrier water and benzene (1990, US). Levels of benzene found in Perrier, a bottled water drink known for its purity	Few people panicked, except then-senator Al Gore: "I am not going to be satisfied until thousands of rats have consumed millions of bottles of Perrier and survived."	Perrier recalled its entire U.S. inventory (72 million bottles) and stopped production worldwide.	It was an "all-natural" health scare. The company discovered benzene occurred naturally in the spring that served as the source for Perrier, it just needed a filter change (a pack of cigarettes had up to 2000 times the level of benzene found in the tainted Perrier.)

While precrisis preparations can eliminate the crisis altogether, postcrisis responses can help manage a crisis when it does occur.

II. A FRAMEWORK FOR UNDERSTANDING PUBLIC PANIC

The study of risk perception has been punctuated with controversy, conflict, and paradigm shifts. Despite more than three decades of research, scientists' understanding of risk assessment remains fragmented and incoherent. Until recently, eating food has been viewed as a low-risk activity with the only risks or fears being related to matters of either hygiene or scarcity. Consequently, theories of risk have been constructed with reference to environmental and technological hazards, such as nuclear power, while neglecting food issues. Following a decade of "food scares," however, attention has moved toward the study of food risk. Unfortunately, it has focused almost exclusively upon attempting to explain the divergent opinions between experts and the public, and little attention has been focused on food risk and panic itself (Knox, 2000).

A basic, but misguided view of how consumers respond to a food safety crisis is often characterized in Figure 1 as a linear process: There is a crisis, there are crisis-related communications (from an company, industry, or government), consumers hear these messages, and they respond.

In reality, consumer response is more sophisticated. Different segments respond differently, and precrisis considerations (such as previous knowledge and precrisis communication) need to be accounted for. Therefore, a more complete and useful framework of how consumers respond to food crises is presented in Figure 2.

At the center of the framework is the notion that there are different segments of consumers who will respond to a food crisis in different ways. Instead of trying to define them demographically by their education level, ethnicity, or income, they are instead defined psychographically by whether they have low or high perceptions of risk (e.g., "What is the risk of this beef having BSE?") and by whether they have low or high levels of preexisting attitudes toward risk (e.g., cautious versus not cautious). Based on a combination of the risk perceptions of these consumers and their preexisting attitudes toward risk, consumers are identified as belonging to one of four different segments: accountables, conservatives, concerned, and alarmists.

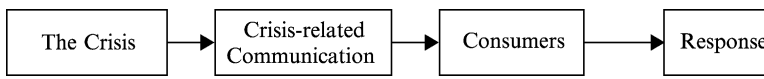

FIG. 1 Stimulus response model of crisis communications.

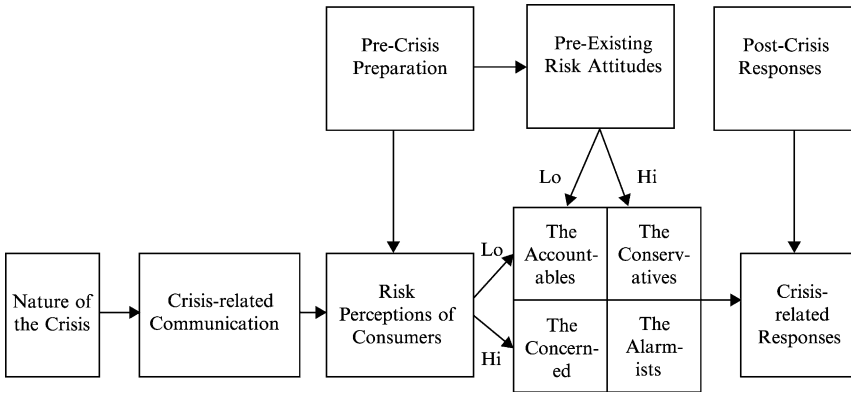

FIG. 2 Consumers responses to food safety crises.

The focus on this chapter is in understanding the four segments in the center of the framework. Following this, various efforts related to precrisis preparations and postcrisis responses are described. Before doing so, it is important to understand how consumers form their basic perceptions of risk.

III. UNDERSTANDING CRISIS-RELATED COMMUNICATION

It is important to realize that when it comes to food safety issues, it is not the dramatic, catastrophic events that are the greatest current concern. Studies by the Food Marketing Institute indicate that bacteria, product tampering, and pesticide residues top the list of the items most likely to constitute a health risk (see Figure 3). Interestingly, however, the two concerns that have increased since the late 1990s are those related to product tampering and biotechnology. Since the late 1990s, increases in food safety-related fears relate to direct human intervention. In some cases, this is intentional malevolent intervention (such as bioterrorism or sabotage), whereas other cases are nonmalevolent interventions that simply have tragic unforeseen consequences.

In recent times, awareness of food safety crises comes primarily from the media. The media can inform but also scare the public with headlines such as "Restaurants from Hell" or with the use of evocative, tabloid-selling terms like "frankenfoods." The effectiveness of the media in instilling a sense of urgency or panic in people can often be seen in the way they cover publicity-related efforts from special interest organizations, such as associations centered on the environment, animal activism, and ecoterrorism.

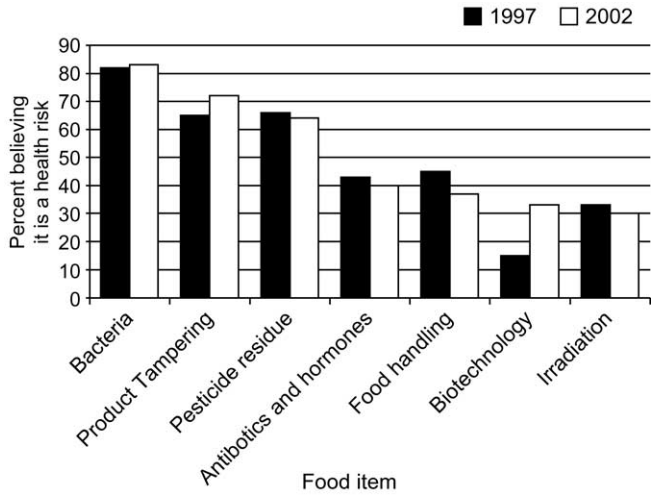

FIG. 3 Which food-related items constitute a health risk? From the Food Marketing Institute (2003).

In evaluating the effect of the media, consider the phrase "food scare." As Figure 4 indicates, it was not until the mid-1980s (with the Tylenol scandal) that the term "food scare" appeared in the media. Since then its use has become widespread, despite no greater incidence of food-related crises. This enhanced coverage of food safety is also illustrated with the dioxin scare. During that time, the Belgian government responded to this dioxin scare with a traditional telephone help line and a Web site. The help line received 3000 calls in 2 days, while the Web site received 150,000 "hits."

In communicating information about a food scare, there is recent evidence that the media might be more influential than one-on-one interactions. Empirical research conducted in April 1998 indicated that mass media had a negative impact on consumer risk perceptions, health concerns, and attitude and behavior toward meat. Compared to alarming reports of the press, personal communication (through butchers for meat products, for example) had only a small effect on consumer decision making (Verbeke *et al.*, 1999).

A. DOES THE MEDIA MAKE THE CRISIS?

Although the media can be more effective than some forms of personal communication, it is not clear whether it simply reports a crisis to be or whether it is instead instrumental in creating the crisis. Despite the allegation

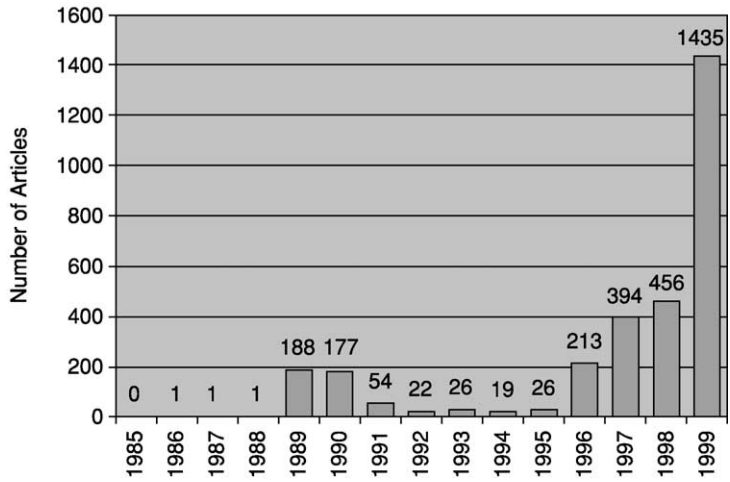

FIG. 4 English-language media articles mentioning the words "food scare." From Reuters Business Briefing Database (2003).

that the mass media tend to exaggerate risk and sometimes "blow it out of proportion," there is little empirical evidence of this. However, Frudenburg *et al.* (1996) analyzed how emotionalism influenced the actual coverage levels of 128 hazard events that were sampled systematically. Somewhat surprising to some, their analyses indicated that the reporting of events did not have a significant impact on emotionalism when compared with the driving influences of objective information, such as the number of causalities or the level of damage (in dollars, pounds, or Euros).

For many incidents (including those with nuclear or toxic hazards), the net effect of the full stories was often to lessen the emotions associated with the events. The one potential bias these researchers discovered was that media coverage tended to create an overall impression that the "responsible authorities" were acting more responsibly than might be assumed based only on factual summaries. It may be that the widespread impression of media as crisis maker may well have to do with the selective perceptions of those making the allegations than with the actual pattern of media reporting (Freduenburg *et al.*, 1996).

A cross-national study looked at how newspapers in Sweden and the United Kingdom characterize a variety of risks, focusing on 2 months around the 10th anniversary of the Chernobyl accident (Rowe *et al.*, 2000). Approximately four times as many reports about the risk

were found in Sweden as in the United Kingdom, possibly reflecting Swedish safety culture. In addition, reports about hazards tended to be alarmist rather than reassuring and rarely used statistics to express degrees of risk.

As noted earlier, food safety crises can be triggered by concurrent events that can distort reality. The tragedy of 9–11 triggered hypersensitivity about anthrax poisoning, and these concerns could just have easily been triggered by an unrelated food poisoning. Similarly, when the outbreak of health complaints happened in Belgium in June 1999, the public allegedly overreacted. This reaction was partly related to it occurring in the wake of a major food crisis (the PCB/dioxin contamination of animal feed) that had erupted shortly before.

B. SOURCE CREDIBILITY AND CRISIS COMMUNICATIONS

Factors such as hazard type and source credibility have been identified as important in the establishment of effective strategies for risk communication (Frewer *et al*., 1997). One means by which to measure credibility is the Meyer's credibility index (McComas and Trumbo, 2001). This has proven useful for measuring source credibility in the context of environmental health-risk controversies, and it would seem to be relevant for measuring food risks in a food crisis situation. A key element of this credibility index is trust.

Trust in risk information about food-related hazards is an important determinant of public reactions to risk information. One of the central questions addressed by the risk communication literature is why some individuals and organizations are trusted as sources of risk information whereas others are not. Industry and government often lack public trust, whereas other sources are highly trusted (such as consumer organizations, selected media, and physicians). Their analyses indicate that knowledge in itself does not make one a trusted source, but that trusted sources are characterized by multiple positive attributes.

A study of the perceived trustworthiness of different sources of information about food safety was reported in the Eurobarometer (1998). It indicated the trust in consumer associations was the highest, followed by national authorities. Overall, sources of information about food safety were least trusted from producers, companies, and market venders. Following is the percentage of respondents perceiving each of the information sources as completely trustworthy:

52% trustworthy—Consumer associations
27% trustworthy—National authorities

21% trustworthy—European institutions
19% trustworthy—Small grocers
18% trustworthy—Supermarkets
16% trustworthy—Market venders
12% trustworthy—Producers

Another study indicated that attitudes toward biotechnology changed depending on whether the source of information was attributed to consumer organizations, the government, or to government–consumer organization collaboration. Admission of a certain amount of risk uncertainty increased trust in the attributed source by consumers with prior negative attitudes (Frewer *et al.*, 1998).

Who could most effectively deliver a food safety message? The most trustworthy sources are consumer organizations (Van Ravenswaay *et al.*, 1992), environmental groups, and researchers, while industry is seen as the least trusted source (Borre, 1990a). In parallel findings, when Mistra *et al.* (1995) asked respondents to express their confidence about different food safety information sources, the most trusted group was university scientists, followed by independent laboratories, and consumer groups. Given this distrust toward companies, one way to help improve their credibility is to use consumer groups to corroborate, support, or deliver the appropriate message.

In further analyzing how the crisis influences consumers, Smith *et al.* (1999) discovered that confidence in all sources dropped after their announcement of a BSE/Creutz–Jakob disease (CJD) crisis in March of 1996 in Great Britain. Consumers were asked about seven different information sources, as well as the extent to which "I trust the following sources of information in terms of the advice they give about the safety of meat/BSE." Although confidence in all sources dropped, the confidence in family and friends dropped the least.

Loss of belief in science is the result of media reports of contradictory research by scientists on a wide range of (mainly health) issues and a belief that science was often used for questionable ends (cloning, developing drugs for profit, and others). Trust in medicine is diminishing following media coverage of mistakes and bad practice by doctors. These concerns influence perceptions of food and food safety: if scientists and medical researchers cannot all be trusted, this undermines the information and opinions they provide about food.

The case of BSE illustrates important issues related to trustworthiness. A study of Germany, the Netherlands, and the United States indicated a strong relationship between how these people trust information from their government and how concerned they are with eating beef (Pennings

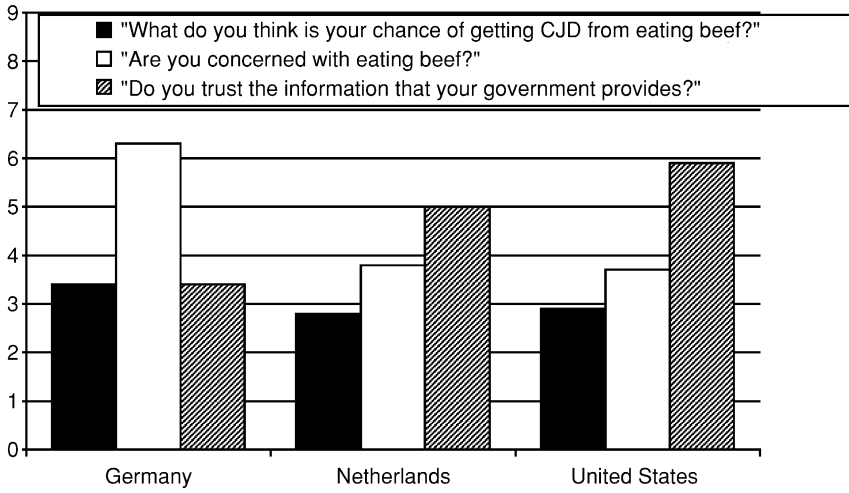

FIG. 5 As trust in government-related BSE information increased, fear decreased.

et al., 2002). Figure 5 illustrates that as trust in government-related BSE information increased, fear with eating beef decreased. This occurred even though the perceived likelihood of contracting CDJ disease was seen as relatively constant. That is, in countries where people trusted the information, such as the United States and The Netherlands, people were less concerned with eating beef than in Germany, where people did not trust information from the government. This had nothing, however, to do with the actual risk of contracting the disease because this risk was seen as constant in all three countries.

It has generally been believed that the expertise level and the trustworthiness of a source affects whether we are influenced by his or her messages. Evidence suggests that our attitudes toward a behavior like eating food (its benefits and its risks) are more related to our prior attitudes and to food neophobia than to what a trusted expert tells us.

In their study of biotechnology, Frewer *et al.* (2001) found that while overall prior attitude and food neophobia influenced both the perception of a source's expertise and trustworthiness, no source-related factor had any increased effect on the perceived benefit or perceived risk of consuming the product (see Figure 6). This finding is important because it directly contradicts the conventional belief that these benefits and risks are influenced by an information source. In some cases, they seem to be influenced more by prior views than by the messenger.

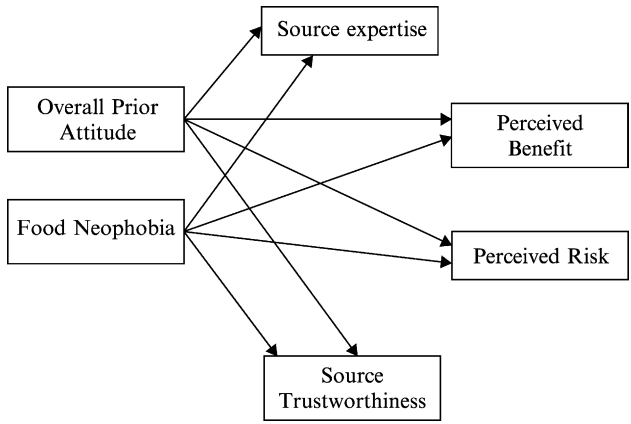

FIG. 6 How does source trustworthiness influence attitude change? From Frewer *et al.* (2001).

IV. PERCEPTIONS AND ATTITUDES: THE FOUNDATION OF CONSUMER RESPONSES

Behavior related to food crises is based on risk perceptions and on risk attitudes related to the crisis (Wildavsky and Dake, 1990). This section focuses on how these can be combined to influence behavior. When examining how people form attitudes, it is useful to examine biotechnology. It can best illustrate how attitudes are formed under conditions of uncertainty (Tait, 1988).

A. HOW PERCEPTIONS AND ATTITUDES ARE FORMED

Consumers' attitudes toward biotechnology are divided and do not appear to be moving toward consensus. When asked "What is your opinion toward biotechnology?" one mail survey of 1036 Americans indicated that 31% favored it, 18% opposed it, 26% had mixed feelings, and 26% did not care or had no opinion (Doyle, 2000). Even within each of these groups, their opinions are as diverse as the people expressing them (Fischoff *et al.*, 1978). The differential acceptance of genetically modified products among consumers can be attributed to the different ways in which they process information about biotechnology and related products. Some people carefully weigh potential benefits more heavily than risks. Others form these attitudes solely based on "sound bites" they hear on TV or at work.

Some consumers focus on the benefits of biotechnology, whereas others focus on the risks (Frewer *et al.*, 1997). Some study the issue carefully, while others view it emotionally (Anderson, 2000b). According to consumer psychology, there are two general ways or routes—central and peripheral—in which their attitudes are formed (Petty and Cacioppo, 1981). When people are motivated to understand an issue and have the ability and opportunity to do so, their attitudes will be formed through a *central route of attitude formation*. When they are not motivated to understand the issue, lack the technical or cognitive ability to understand it, or lack the opportunity to think about it, any message they hear will be processed peripherally.

In this framework, a person's values, beliefs, and information processing style all contribute to how he or she understands the benefits and risks of the biotechnology process and of specific biotechnology foods (Frewer *et al.*, 1998). These factors, in turn, combine to form a person's attitude toward biotechnology. Figure 7 illustrates the two different routes of forming attitudes toward biotechnology and emphasizes the distinction between accepting the *process* of biotechnology versus accepting the *products* of biotechnology.

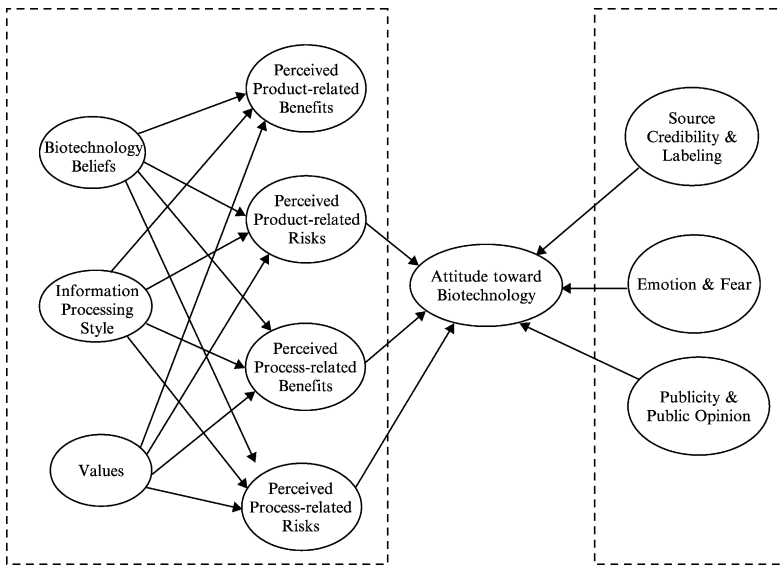

FIG. 7 Determinants of consumer attitude food risks: The case of biotechnology (Wansink and Kim, 2001).

1. *The central route to persuasion—trading-off benefits and risks*

When attitudes are formed centrally, a consumer's attitude toward biotechnology is determined by beliefs about various aspects of biotechnology weighted by the importance he or she gives to each belief (Fishbein and Ajzen, 1975). Attitude is the net sum of all positive and negative beliefs about the target weighted by their importance [attitude $= \sum$ (belief$_i$ * importance weight$_i$)]. Because beliefs are subjective, they are not always correct and can vary dramatically across consumers. Furthermore, the importance weights given to specific information or beliefs can vary across people even if they share some common beliefs. These differences can lead two people with very similar experiences and beliefs to have different attitudes toward biotechnology.

Studies have shown that many consumers generally view genetic engineering technology as a risky process (Sparks *et al.*, 1994; Wohl, 1998). Some people perceive environmental risks (threats to ecological balance and reduced biological diversity), safety risks (lack of control and difficulty in measuring safety), and ethical considerations (the discomfort with "playing God," concerns for health and welfare of animals, and religious concerns). However, if genetically modified products offer important benefits, these benefits can outweigh the perceived risks related to genetic engineering technology (Hamstra, 1995). For instance, just as there were environmental risks, there are also environmental benefits (reduced use of chemical pesticides and water and soil protection), healthcare benefits (development of medicines and "edible vaccines" along with better nutrition and food quality), and agricultural benefits (protection against diseases, increased productivity, and biodiversity and sustainability).

2. *The peripheral route to persuasion and the silent majority*

When consumers have little motivation to process biotechnology information, little ability to understand it, or little time to digest it, the peripheral route will form their opinions. The information may be too complex or too general to integrate into a belief system. For instance, Frewer *et al.* (1993) observed that while risks from microbiological hazards are often reported in quantitative terms (i.e., number of occurrences and percentage of increase or decrease), risks from food applications can instead be stated using unqualified terms such as "bad" and "thus should be avoided." If this is true, then either type of information will lend itself to being processed centrally.

This lack of access to understandable information combined with the lack of ability to process complex biotechnology information leads many

consumers to engage in more heuristically or peripheral processing when forming attitudes toward biotechnology (Bredahl *et al*., 1998). Their focus is not on the claims and arguments made in the message, but is instead on nonmessage factors or cues, such as public opinion, sound bites, emotions generated by advertising, labeling, or the credibility of spokespeople or endorsers.

This general notion that people can be aware of an issue without having specific knowledge of it is well supported. Sheehy *et al*. (1998) reported that the majority of consumers, even highly educated ones, had little or no *knowledge* of biotechnology. Their *awareness* of biotechnology, defined as "having heard of the term," was high, however. This "high awareness but low knowledge" characterization is common in the biotechnology area because genetic engineering is new and complex (Roberts, 1994). Therefore, consumers can be aware of a biotechnology application while making no associations between it and the genetic engineering process that created the novel characteristics.

B. HOW RISK PERCEPTIONS INFLUENCE BEHAVIOR

Food safety crises have the potential to dramatically illustrate the need marketers have to understand why and how consumers react to a crisis. Such crises can be seen as widespread, catastrophic, and of irrevocable consequence. The crisis of mad cow disease is a very representative example of such crises because of its economic consequences to an entire industry and an entire continent (Aldhous, 2000). To examine how different countries are influenced, Pennings *et al*. (2002) conducted two field studies with consumers in Germany, The Netherlands, and the United States that have responded differently to the crisis. They showed that the relative influence of risk perception and risk attitude on consumers' reactions depend on the accuracy of knowing the probability of being exposed to the risk. These results suggest that while clear, forthright, and consistent communication is effective in some countries, other countries require more extreme measures with respect to product supply (Dake, 1991). Decoupling risk attitudes from risk perceptions can be valuable in determining what really drives various segments of consumers in crisis situations. Knowing these drivers suggests what solutions will be most effective in controlling such crises.

Perceived risk is a key component of consumer behavior (Frewer *et al*., 1994). However, decision making and behavior are often analyzed and reported *only* in terms of perceived risk (Brockhaus, 1980; Srinivasan and Ratchford, 1991). Perceived risk, however, only partially explains actual behavior. It is only when combined with a person's attitude toward risk can we understand and predict behavior to food-related issues.

Risk perceptions refer to a consumer's estimate of how likely they will be exposed to the content of the risk ("I have a 1 in 100,000 chance of contracting a BSE-related disease if I eat beef"). *Risk attitude* reflects a consumer's general predisposition to risk in a consistent way. It is important to emphasize that risk attitude and risk perception are two different concepts. Whereas risk attitude deals with a consumer's interpretation of the content of the risk and how much he or she dislikes it, risk perception deals with a consumer's interpretation of the likelihood of being exposed to the content of the risk.

While both a consumer's risk attitudes and risk perceptions individually influence their behavior, it has been shown—in the context of BSE—that it is the *combination* of risk attitude and risk perception that has the biggest influence on behavior (Pennings *et al*., 2002). That is, regardless of one's risk attitude, there will be no change in one's behavior if a person perceives no risk in a situation. However, if a person does believe a behavior has some risk involved (such as eating beef during the BSE scare), it is their attitude toward risk (it is worth the risk to eat beef vs. it is not worth the risk) that eventually determined their behavior and not simply their assessment of the risk itself.

When risk-averse consumers perceive risk, they will exhibit risk management behavior (behavior that decreases risk exposure). However, when risk-seeking consumers perceive risk, they will exhibit risky behavior or seek out ways to increase their risk (because of the corresponding payoff). The interaction between risk attitude and risk perception represents how one intends to cope with risks in the channel combined with the risks their actions generate.

It has been claimed that people's perceptions of risk and benefit associated with particular products and applications will determine acceptance (Frewer *et al*., 1998; Slovic, 1987, 1993). This is not the case; the acceptance of a product is determined by a combination of both risk perceptions and risk attitudes.

By decoupling risk response behavior into the separate components of risk perception and risk attitude, a more robust conceptualization and prediction of consumer reactions are possible. The insights that result from decoupling risk perceptions and risk attitudes can yield important implications. Consider the two following outcomes from a program of research by Pennings *et al*. (2002):

> Outcome #1. Suppose that risk perception is the main driver of a consumer's reaction to a food safety scare. This would suggest that communicating research information effectively is a powerful tool in changing behavior. That is, providing and communicating the "true" probabilities of being exposed to the risk (when possible) will be a useful way to respond to consumers concerns.

Outcome #2. Suppose, however, that risk attitude is the true driver behind a consumer's reaction to a food safety scare. In such a case, even if probabilities of being exposed to the risk are small, an effective communication of these probabilities will have little influence on a consumer's behavior. Instead, marketers will have to focus on ways to eliminate the risk. This may involve a total recall or an elimination of the risk (slaughtering of all potentially infected cattle or recall of all potentially tainted food).

Compared to other risky activities, such as parachuting or motorcycling, risks related to food safety are unique. While some risks can be avoided, food safety-related risks can only be bypassed to a limited extent. Even when a person switches from one product to another, contaminated food still remains harder to avoid than parachuting, especially in the incipient phase where the risk is not yet known to the public and when consumers do not have full control over these risks.

As can be seen in Figure 8, risk perceptions can vary quite dramatically across segments and these perceptions are not always related to the reality of the risks. Germans perceive there is a higher likelihood of fatalities from eating BSE-tainted meat than Americans. While this can be a function of a great many things (such as media coverage and trust in government agencies), this can have a dramatic influence on behavior depending on whether a consumer is risk averse or not.

Although such tendencies are often viewed individually or by segments, it also appears that generalizations can even be made across some country segments. For instance, it appears that Germans are much more influenced by their attitudes toward risk than by their actual perceptions of risk. In a controlled scenario-based study involving consumers from Germany, The Netherlands, and the United States, these consumers were asked the extent to which they would consume beef under four different risk scenarios in

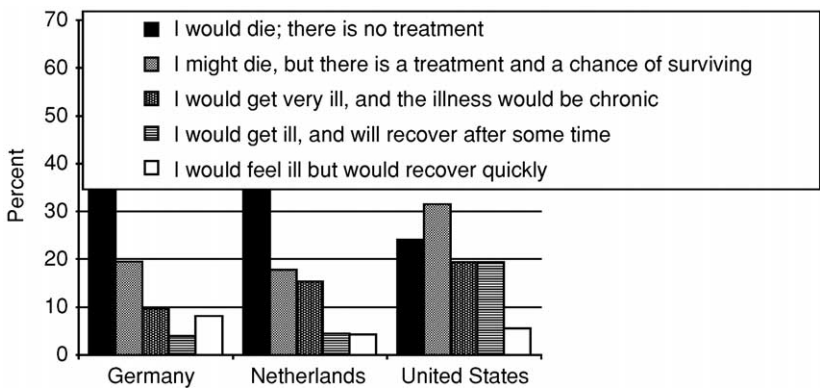

FIG. 8 Risk perceptions related to BSE vary dramatically across countries.

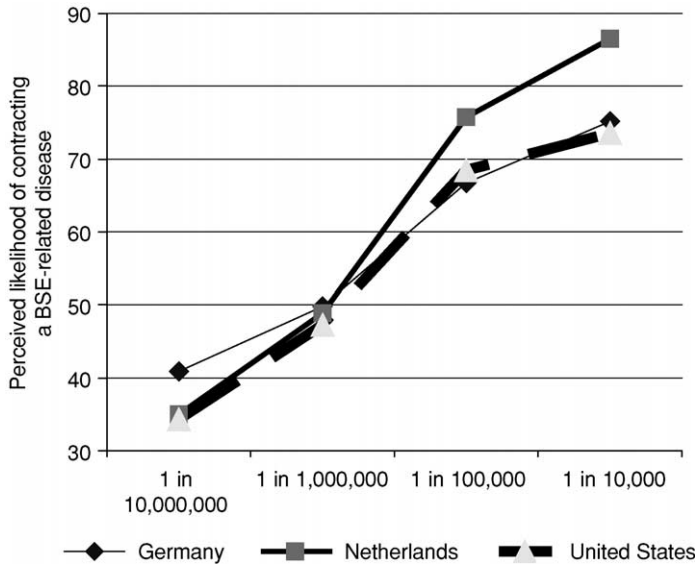

FIG. 9 Risk perceptions drive Dutch consumption of beef, but risk attitudes drive German consumption of beef.

which there was (a) 1 in 10,000,000, (b) 1 in 1,000,000, (c) 1 in 100,000, or (d) 1 in 10,000 chance of contracting a BSE-related disease. As can be seen in Figure 9, the behavior of the Dutch was most correlated with the likelihood of contracting the disease, whereas the behavior of the Germans was least correlated with the likelihood of contracting the disease (with the Americans in between). What this indicates is that another factor—risk attitudes—is a relatively greater driver of behavior among Germans than among the Dutch.

V. PROFILING CONSUMERS TO PREDICT RESPONSES

Whereas the previous section introduced the notion of the difference between risk perceptions and risk attitudes, this section shows how the different segments—or profiles—can be used to predict responses to food safety crises more accurately (Wansink and Cheong, 2002; Wansink and Westgren, 2004). This is because the risk level of any particular activity (such as getting sick from eating warm potato salad or contracting Creutzfeldt–Jacob disease from eating BSE beef) is perceived differently across different consumers. How consumers cope with perceived risk will depend on their risk attitude.

People's perceptions of risk and benefit associated with particular foods and applications will help determine their acceptance of the food.[1]

As noted earlier, *risk perception* reflects a consumer's interpretation of the likelihood they will be exposed to the illness or disease. *Risk attitudes* reflects a consumer's general predisposition to risk in a consistent way. Some people are risk averse whereas others are not. That is one reason why all people in the world do not skydive, ride motorcycles without helmets, or hang glide. It is important to emphasize that risk attitude and risk perception are two different concepts (Pennings and Wansink, 2005). Whereas risk attitude deals with a consumer's interpretation of the content of the risk and how much he or she dislikes the risk, risk perception deals with the consumer's interpretation of the likelihood of being exposed to the content of the risk.

A. FOUR PROFILES OF CONSUMERS

The following matrix (Figure 10) presents four different profiles of consumers based on their level of risk perception and risk aversion. Consumers' level of risk aversion (or consumers' attitude toward risk) can range from low to high. The higher the attitude toward risk, the more likely consumers are to refuse any risk under any condition. Simultaneously, risk perception ranges from low to high. The higher the perception of risk, the less likely consumers are to accept a risky situation. When combined to describe a consumer's profile, risk aversion and risk perception are separated into four categories.

1. The accountable segment

The low-risk aversion–low-risk perception profile corresponds to consumers who are risk seekers. They view themselves as accountable for their own behavior and what results from it. They ignore any available information

[1]The typical person is influenced by both an optimistic bias and an illusion of control (Frewer *et al*., 1994). When these are lost or compromised, panic can occur. While panic disorder can afflict an individual, panic also occurs as a collective phenomena. While it has been thought that emotional instability will lead some people to be more likely to panic, this is not always found. However, people who are emotionally unstable are more likely to attach importance to information provided during the crises than more emotionally stable individuals (Verbeke and Van Kenhove, 2002). Furthermore, some people are more likely to believe they are sick or affected than others. Feldman *et al.* (1999) examined the panic predisposition of people based on their classification by the "big five" personality factors. People were inoculated with a common cold virus, and those who were classified as "neurotic" were more likely to report unfounded illness and more symptoms than other groups. In contrast to this, "openness to experience" was associated with reporting unfounded symptoms in those with verifiable colds, whereas "conscientiousness" was associated with reporting unfounded illness in those who were not ill (Feldman *et al*., 1999).

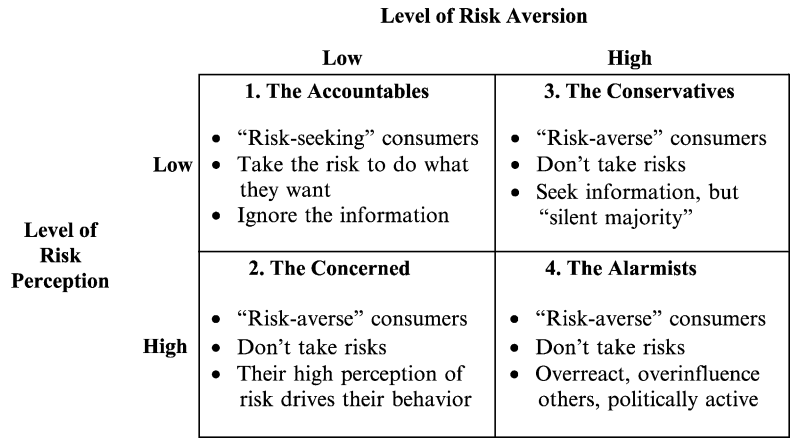

FIG. 10 Four profiles of consumers according to risk perception and risk aversion levels.

on risk and keep their habits, even though some risk may be involved in their behavior.

2. The concerned segment

This is the low-risk aversion–high-risk perception segment. The concerned segment has the risk of most behaviors in perspective. Because they are not risk averse to begin with, their behavior is dictated primarily by their perception of risk. As their perception of the riskiness of an action increases, they will eventually get to a point where they will not participate in the action at all.

3. The conservative segment

This consists of high-risk aversion–low-risk perception consumers. The conservative segment is composed of cautious, risk-averse consumers who do not take any unnecessary risks. They can also be seen as being the silent majority in many ways (Miller, 1985).

4. The alarmist segment

This high-risk aversion–high-risk perception profile corresponds to risk-averse consumers. This alarmist segment is composed of people who are prone to overreacting to many situations (Radovanovic, 1995). They are also the most assertive in their tendency to become politically involved or to actively attempt to influence others.

Although seeing the world as roughly consisting of four different profiles of consumers is helpful in predicting responses to a crisis, it is most useful

when combined with scenario planning. Scenario planning is one of the most effective methods used in preplanning military crises and it provides perhaps the best model for setting up both precautions and a response plan.

B. CRISIS-RELATED RESPONSES: WHAT COULD POSSIBLY HAPPEN?

When considering how consumers might respond to a food crisis, it is not sufficient to simply "brainstorm" and list a number of disconnected behaviors. While doing this is better than giving it no forethought, there are more appropriate methods of thinking about behavior and conducting the steps that would help minimize any unnecessary fallout from these behaviors if the food crisis occurs.

Independent of the scale of the crisis (local vs national vs global), a consumer's response can be characterized by different factors that all contribute to certain behavioral responses. A large part of predicting the response that consumers will have to a food crisis is to examine their risk profile. Consider the four consumer segments: (1) accountables, (2) concerned, (3) conservatives, and (4) alarmists. Each consumer profile segment will have a different response in case of a food crisis. Their response can be described by three characteristics: the level of aggressiveness (passive vs aggressive), the level of rationality (irrational vs rational), and the length of the response (short term vs long term). The behavioral responses for each of the four consumer profiles are described in Table II.

1. Passive vs aggressive responses

When faced with a food crisis, a consumer can respond along a continuum of passive and aggressive responses. A passive response involves simply modifying one's behavior to avoid the danger. In the case of BSE or foot-and-mouth disease, this would simply mean avoiding beef by substituting another product such as chicken or fish.

Consumers can also take a more aggressive response, which might be to demand restitution or to try and change the market structure by campaigning for new laws, guidelines, or regulatory systems. Both of these responses can critically wound an industry. In Australia, tainted metwurst caused several known deaths and resulted in an economic boycott of the entire metwurst industry. Now, many years after the fact, the industry is still decimated.

2. Irrational vs rational responses

Consumers can respond either rationally or irrationally to a food crisis given the nature of the scare. If the objective facts merit an extreme response (such as not eating the food), then such an extreme response is rational. If, however, the objective facts merit a less extreme response (such as fully

TABLE II
BEHAVIORAL RESPONSES TO CONSUMER'S RISK PROFILE

Consumer segment risk aversion/risk perception	Passive vs aggressive responses	Irrational vs rational responses	Short- vs long-term responses
The alarmists (high-risk aversion and high-risk perception)	Most likely to respond aggressively Involved politically on the food issue Overinfluence their peers to not take risks	Irrational, overreacting to food issue and risk level Extreme behavior not always justified	Most likely long term as food habits change drastically to avoid risks
The conservatives (high-risk aversion and low-risk perception)	Passive reaction, the "silent majority" Aware of potential risk but no overreaction	Most likely to behave irrationally and not to take any risks because risk adverse	Short or long term, depending on the level of risk aversion
The concerned (low-risk aversion and high-risk perception)	Rather passive Will avoid personal risk, but won't campaign for it	Most likely to behave irrationally and not to take any risks	Short or long term, depending on the level of risk perception
The accountables (low-risk aversion and low-risk perception)	Passive behavior Maintain his/her food habits	Rational Ignore information when risk perception is low	Most likely short term because both perception and aversion of risk are low

cooking the food or not eating it raw), then a less extreme response would be considered rational. Irrational responses comprise those where the reaction of a consumer is either more extreme than merited or is less extreme than merited. In the former case, they would be overreacting to the danger. In the latter case, they would be underreacting.

3. Short-term vs long-term responses

The length of a consumer's response to a problem can be either short term or long term. The response can persist for a reasonably short time, as the risk has been sufficiently eliminated through structural factors (food inspections or new standards). However, the response can last longer than necessary.

Consider trichinosis. The last case of trichinosis in the United States was reported shortly before World War II, yet the fear still persists in many

households today. Whereas the resulting impact on the pork industry has not influenced current sales of pork, the preparation of pork has been modified in what is perhaps an overly conservative manner. While it may not be necessary to still take all the precautions of cooking (or overcooking) pork, this illustrates how residue from a food scare can last long after the risk has been diminished.

Risk may be perceived differently across societal groups, and how consumers cope with perceived risk will depend on their risk attitude. Before a person is able to respond to risk, risk must first be perceived (Trimpop, 1994). Stone *et al*. (1994) modeled the identification of risks as a cognitive process of identification, storage, and retrieval. The level of risk that a food-related behavior provides depends on the consumer's risk perception (Sparks *et al*., 1995).

Perceptions and attitudes of risk are influenced not only by prior experiences, but also vary dramatically across experts. In a study by Bark and Jenkins-Smith (1993), the similarities and differences in risk perceptions (particularly regarding nuclear wastes) between 1011 scientists and engineers were examined. Significant differences were found. In contrast to physicists, chemists, and engineers, life scientists tended to perceive greater risks from nuclear energy and nuclear waste management, perceiving higher levels of overall environmental risk. They also found that independently of field research-related percentages of risk, these perceptions of risk varied with the type of institute in with the scientist is employed. Scientists in universities or state governments tend to see the risks of nuclear energy as greater than scientists who work as business consultants, for federal organizations, or for private research laboratories (Barke and Jenkins-Smith, 1993).

Table III presents selected crises of the 20th century, which ended up representing no health dangers (''fake crisis''). Nevertheless, consumer reactions often exhibited panic-like behaviors, threatening an entire industry (e.g., the U.S. apple industry in the case of the Alar apple scare). Depending on what was done by the institutions to limit the scare, the aftermath was either positive or negative for the industry or type of products involved.

VI. FALSE ASSUMPTIONS ABOUT CONSUMER BEHAVIOR TO FOOD CRISES

The area of biotechnology or genetically modified foods is an excellent context in which to examine how consumers form perceptions and attitudes toward a new technology (or even toward older technologies such as irradiation) related to food. Both proponents and opponents of biotechnology argue that their goal is to educate consumers so that they can make informed

TABLE III

EVEN CRISES THAT PRESENT NO HEALTH DANGERS CAN DEVASTATE INDUSTRIES

Description	Consumer reaction	What was done	Aftermath
Margarine (US, 1875) Described as unnatural and fraudulent substance	Consumers bought butter instead of margarine	U.S. butter lobby legislation enacted to prevent margarine being visually mistaken for butter (colored bright pink in some states and white in many others)	Took until the 1950s for margarine consumption to increase significantly inside the United States
Cranberry scare (1959, US) Use of aminotriazole, weed killer, thyroid cancer scare	Widespread panic; secretary of state for health told housewives not to buy cranberries	Ban on cranberries sales in several states right before Thanksgiving	No real threat for public health, (a human would have to consume 15,000 pounds of aminotriazole-treated berries every day for a number of years)
Beef and DES (1972, US) Diethystilbestrol-for use as a cattle growth stimulant. DES is an estrogen, and all estrogens are animal carcinogens (FDA approved in 1954) caused vaginal cancer	Sen. E. Kennedy described DES as a "known cancer-causing agent ... on thousands of American dinner tables." Consumers create groups such as the "Committee to Get the Drugs Out of the Meat" (DOOM) and criticize the FDA	The FDA ultimately banned DES use during pregnancy Hormone was still used in cattle. The FDA issued a final ban on DES in June 1979	Scientists: "estrogens occur naturally in milk, honey, eggs, at levels "thousands to millions of times higher than those found in the livers of DES-treated cattle." A woman would need to eat more than 62 tons of beef liver to match the 125-mg DES dose given to pregnant women

(*continued*)

TABLE III (*continued*)

Description	Consumer reaction	What was done	Aftermath
Artificial sweeteners and saccharin (1977, US) High doses of the artificial sweetener had caused bladder cancer in lab rats	Negative public reaction to the FDA ban. Consumers tried to stock up saccharin products against the coming ban; diabetics lobbied Congress to reverse the ban (no other nonsugar sweetener available at that time); consumers asked for a warning label on the product instead	FDA tried to ban saccharin	No studies have shown yet humans can develop cancer from exposure to sweeteners. ACSH: "the enormous doses necessary for such experiments ... may overwhelm the animal's natural defenses." Saccharin still available, but its use has decreased since 1983 (aspartame approval's year)
Coffee and pancreatic cancer (1981, US) Coffee drinkers have at least twice the chance of developing pancreatic cancer compared to noncoffee drinkers (Harvard School of Public Health)	News media jumped on the story, but didn't create the great public reaction expected	The Harvard study findings were immediately questioned by other researchers	The proportion of coffee consumption has to be more than 50%. Harvard scientists failed to confirm its original findings during a follow-up study
Alar apple scare (1989, US) Use of chemical (alar), by-product causes lung and kidney tumors in mice	Called "the most potent cancer-causing agent in our food supply" on a U.S. television program. Hysterical public reaction, general atmosphere of panic	National Research Council: "There is no evidence that pesticides or natural toxins in food contribute significantly to cancer risk in the U.S."	No real threat for public health: scientists from WHO and FAO concluded that Alar was nononcogenic in mice. Humans would have to ingest vast quantities of the product to get effects (thousands of quarts of apple juice every day). Apple growers lost $250 million, Apple processors lost $125 million

Dioxin in chicken (Belgium, 1999) Animal feed contaminated with dioxin, carcinogenic chemical by-product (herbicide)	All meat and dairy products thought at risk, people eat vegetable, fruit, mussel, and fries!	Temporary export bans on Belgian meat and poultry products by many nations	In fact, levels of chemical were extremely low
Electric blankets (1989, US) Report of possible relationship between childhood cancer mortality and power lines (high electromagnetic fields); then, *Consumer Reports* recommended that children and pregnant women avoid electric blankets	After remaining stable for many years (since mid-1940s), sales of electric blankets dropped by 11 percent	Eighteen congressmen asked that electric blankets be labeled as hazardous for children and pregnant women. As a result, all U.S. blanket manufacturers now include warnings with their products, advising that children not be permitted to use electric blankets.	1990 study: researchers reported finding a modest increased risk of childhood cancer in relation to the mother's use of an electric blanket during pregnancy. Subsequent studies of brain tumor occurrence and electric blanket use have not supported the 1990 study.
Coke scare (Belgium, 1999) Dozens of people end up at hospital after drinking Coke	Stop drinking Coke for a while in Belgium	Coca-Cola located the cause of problem in two factories and recalled 2.5 million potentially dangerous bottles. Belgian, Dutch, Luxembourg, and French governments banned all Coke drinks for a while	No long-term injuries. Coke's stock dropped by 2% after the scandal. Cost at least $150 million to restore consumer confidence. People still drink Coke

decisions (Bauer, 1960). While opponents focus on educating consumers about the risks of biotechnology, proponents focus on the benefits. However, if we consider education as an objective, neither group has been decidedly successful (Doyle, 2000). Wansink and Kim (2001) argued that part of the ineffectiveness of these efforts is due to the inaccurate assumptions both opponents and proponents of biotechnology have about consumers. This leaves their efforts often misdirected or weakly leveraged.

Proponents of biotechnology have based their marketing campaign around key assumptions about the consumer that are reflected in the way they communicate. Many of these assumptions are based on years of familiarity with "market share advertising" and a commodity promotion mindset. Such expectations self-limit their effectiveness by leading them to assume that (1) the biotechnology issue will "blow over," (2) once consumers have the facts, they will be biotechnology advocates, (3) science sells and fear fails, and (4) biotechnology is an industry issue.

Opponents or skeptics of biotechnology do not make these same mistaken assumptions. Instead, while their guerilla campaigns may have gotten attention, these strategies are embedded in grassroots experiences that lead them to make different counterproductive assumptions about consumers. Their efforts show that they assume (1) consumers want to be informed, (2) consumers need to be informed, (3) changing consumer attitudes will change their behavior, and (4) risks of the unknown are more important than benefits.

Using key principles of consumer psychology to reexamine these assumptions will better enable us to understand how consumers learn about foods that subsequently influence their reactions in a crisis situation.

A. EDUCATION FALLACIES OF OPPONENTS OF FOOD TECHNOLOGIES

Effectively educating consumers about the benefits and risks of food technologies (biotechnology, specific food processes, and food radiation) requires the proper assumptions about how consumers learn. To date, both opponents and proponents of food technologies are making assumptions about consumers that limit their effectiveness in communicating their message to the public. Without any hard evidence against the outcomes of a particular technology, opponents have tended to focus on the process itself. They have used demonstrations and publicity campaigns to target consumers and lobbying to target governmental agencies. The foundation of their approach has been to focus on ethical and social issues and the fear caused by uncertainty (Papanikolaw, 2000). These efforts, and others, suggest a set of assumptions that opponents of food technologies in general have about educating consumers. To be more effective, each of these assumptions must be revised.

1. Opponent fallacy #1. People want to be informed

Consumers vary greatly in how much they desire to "be informed" about issues. The most successful daily newspapers in the world penetrate less than 40% of the households in their market, and situation comedies generate more viewers than the average network news broadcast. While some consumers centrally process and actively formulate an informed opinion about food-related issues, others have a greater willingness to trust outside agencies to make food safety decisions for them. Sheehy *et al.* (1998) termed the first group "information seekers" and the latter group "institutionalists."

Most consumers appear to be institutionalists when it comes to food-related issues, believing that decisions about the safety of food technologies should be left to the experts (Optima Consultants, 1994). While these experts are often scientists or regulatory agencies, they can also include the moral expertise of religious groups or the perceived ethical expertise of a special interest group. In that way, whatever alternatives are presented to them will have been preapproved. Although one might assume that "institutionalists" tend to be people with less formal education, Hadfield *et al.* (1998) found that even those with advanced educational backgrounds find themselves ill-equipped or unwilling to spend time studying the issue. They welcome the opportunity to involve experts who can provide them with the conclusion to the issue and not the details it takes to arrive at that conclusion (Wansink, 2003a).

In contrast, there is a segment of consumers who do want to know about the details behind food technologies issues. When these "information-seeking" consumers want to learn of the risks and benefits of food technologies and genetic engineering, they turn first to the media and personal discussions and then to informational brochures (Borre, 1990a; Heijs and Midden, 1995). Sheehy *et al.* (1998) reported that another group of consumers acquires food-related information from magazines, government publications, consumer organizations, and research institutes. Knowing where these people go for information is important. Reading newspaper reports of demonstrations and protests is less important and less persuasive to information seekers than reading a more balanced view in a magazine or a brochure.

2. Opponent fallacy #2. People need to be informed

Unlike many other countries, the United States has benefited from a strong food regulatory system for many years. As a result, food safety vigilance is not an important issue and it is generally entrusted to regulatory organizations. One poll indicated that 83% of Americans trust the U.S. Food and Drug Administration (FDA) (Hadfield *et al.*, 1998). It is the most trusted government agency next to the Supreme Court.

For many busy people, second guessing the food-related decisions of a risk-averse government is not worth their time or effort. Food scares in the United States have been tied directly to violations of FDA standards or regulations, not to oversights or mistakes with these regulations themselves. Given this track record, many consumers believe there is no reason to distrust or second guess the regulatory system. Many consumers do not want to be informed, largely because they do not believe they need to be informed.

3. Opponent fallacy #3. Risks of the unknown are more important than benefits

Benefits are often more important than risks to consumers. Consumers become willing to accept products processed with specific technologies when they become convinced that these products offer significant benefits over other products. These benefits can include decreases in price as well as increases in product quality, such as taste and naturalness; purity, such as reduced use of chemicals; and wholesomeness, such as better nutrition (Kuznesof and Ritson, 1996). Hamstra (1995) reported that perceived benefits of biotechnology products had greater statistical influences on Dutch consumer attitudes and acceptance than perceived risks.

Even for opponents of certain food technologies, benefits often outweigh risks. Sometimes, however, *social* benefits become weighed more heavily than *personal* benefits. Sheehy *et al.* (1998) demonstrated that consumers considered genetically engineered potatoes that reduced the need for environmentally harmful pesticides as being significantly more beneficial than potatoes that had prolonged shelf life and improved taste.

History has shown us repeatedly that most principles, to most people, have a price. For example, a principle standing against the radiation that emanates from microwaves becomes a nonissue after one receives a microwave oven for a birthday present. An opponent of fur becomes a silent champion after inheriting a coat with fur trim. The "white meat only" advocate secretly enjoys beef when the price of fish becomes too expensive. A philosophical stance against biotechnology has a price even though it would not show up in consumer surveys. It is sometimes measured as a difference in cost; other times as a difference in convenience. In still others, it fades as the audience for the cause fades or becomes weary of the issue.

4. Opponent fallacy #4. Changing consumer attitudes will change their behavior

The assumption that negative attitudes toward specific food technologies will dissuade people from purchasing a product processed with these technologies seems reasonable. However, attitudes often do not predict behavior, and

food-related issues provide no exception. Heijs and Midden (1995) investigated the impact of attitudes on behavioral intentions across four examples of genetically engineered food. Intention to buy each of the foods was used as a measure of positive intentions, whereas intention to protest against the foods was a measure of negative intentions. When favorable about biotechnology, consumers indicated they would purchase the food. In contrast, attitudes did not explain a similar correspondence with the negative intention measure (Heijs *et al*., 1993). In essence, there was little relation between biotechnological attitudes and behavior. This can be attributable to the weak impact between attitudes and behavior once notable differences exist between the cost and convenience of products (Wansink and Ray, 1996).

Confusion often ensues because food technologies and processes can be complex and difficult to understand. When consumers are confused, they sometimes defer their choices until they develop proper evaluation criteria and acquire enough information. When benefits begin to outweigh risks, behavior can reverse dramatically and purchases will be made by all but the most extremely opposed segments of consumers. Likewise, as people see more and more products processed with these technologies under more realistic and normal (nonlaboratory) conditions, they will generally come to accept certain food technologies because of their familiarity (Frewer *et al*., 1996b).

Studies on biotechnology purchase decisions that used the theory of planned behavior (Fishbein and Ajzen, 1975) generally yielded results that support consumers' attitude toward biotechnology as an important determinant of purchase decisions. However, one important point to note is that the most important attitude in purchase decisions was the one toward the specific product in question, not the general attitude toward biotechnology.

The fact that consumers are not familiar with genetically engineered food products implies that they will find it difficult to imagine the types of products discussed and, even more so, to generalize in stating and explaining their purchase intentions. The predictive validity of studies on consumers' purchase decisions on genetically engineered food products can be strengthened greatly by focusing on specific products rather than investigating purchase decisions with regard to biotechnology food products in general.

B. EDUCATION FALLACIES OF PROPONENTS OF FOOD TECHNOLOGIES

Proponents have their own set of incorrect assumptions. Their basic strategy has been to focus on the advantages of the technology and on the long-term benefits that are not specific to consumers but are more focused on the "global good" aspects (Gardner, 2000). These actions, and others, suggest

a series of misperceptions or incorrect assumptions about consumers. These assumptions limit how efficient they can be in communicating to consumers (Roberts, 1994). To be more effective, each must be revised.

1. *Proponent fallacy #1. The food technologies controversy will be forgotten*

Opponents of certain food technologies generally discuss their opinions with other opponents, and proponents discuss theirs with other proponents. Therefore, proponents can underestimate the seriousness of the issue, believing that most people believe the way they do. Many firms think erroneously that a new food technology, such as biotechnology, will lose its controversy and "blow over."

This belief—or hope—was a critical mistake made by British firms (Frewer *et al.*, 1995). In 1994, public sentiment toward biotechnology was neutral if not moderately positive. The industry, therefore, took no real efforts to build public support or enthusiasm for biotechnology because attitudes toward it appeared to be improving each month (Vacek, 2000). However, although attitudes were improving, they were neither fully formed nor stable. As a result, when "mad cow disease" became an issue, the industry had not generated the appropriate level of education nor a solid enough basis of support to keep the issue in perspective and to keep biotechnology moving forward.

Some proponents in the United States believe that the improving sentiments of the nonvocal majority indicate that the biotechnology controversy will pass. The fallacy of their assumption is that they are only one "mad cow disease" episode away from losing all the technological ground that has been gained. Because of the highly sensitive nature of this issue, even a moderately unrelated event could cause an ill-informed majority to generate a fatal overreaction in public opinion. Even if the biotechnology controversy passes, proponents would be critically wrong not to continue to focus on counteracting public misperceptions and to focus on educating consumers about the benefits of food technologies.

2. *Proponent fallacy #2. Science sells and fear fails: people will be food technology advocates once they have the facts*

Consider the case when a person's attitudes have been formed through the peripheral route to persuasion. With relatively low awareness and knowledge of food technology along with no established measures of benefits and risks, his or her attitudes could be swayed easily by peripheral cues such as public opinion, publicity, sound bites, source credibility, labeling,

and emotion and fear. To this person, careful scientific reports and expertly articulated third-party testimonials will have little direct impact on their attitude toward food technology. Indeed, even a judicious FDA endorsement might have less impact than a memorable phrase or the negative portrayal of genetic engineering applications in a movie (e.g., *Species, Jurassic Park, Gattaca,* or *DNA*).

One indicator of how peripheral processing dominates attitude formation can be found in the significant role that religious and ethical influences can play dogmatically in influencing public concerns about food technology applications. For example, animal rights activists protest biotechnology on the ground that genetically modified animals might suffer vulnerability to specific diseases as the result of such modifications. Some religious groups oppose the use of biotechnology on the ground that experimenting with lives is "playing God." These religious and ethical concerns will become even more vocal as further advances in gene technology bring fear of human gene selection and cloning. Groups opposing the use of biotechnology on these grounds authoritatively dictate specific viewpoints to consumers without encouraging objective evaluation (Mitcham, 1990). Phrases or sound bites, such as "playing God," can lead one to process the issue peripherally and to label biotechnology as wrong without considering its benefits.

The fallacy that "science sells" is based on the notion that if consumers are given the facts, they will come to the proper conclusions. However, even with identical information and beliefs, people will arrive at different conclusions. A well-to-do vegetarian might believe cost savings are less important than caring for animals. A second person might focus more on how food technology increases the world food supply and slows land commercialization. A third person might focus on comparing organic gardens of yesterday to the unknown issues of tomorrow. Recalling Figure 10, attitude formation is complicated further by the fact that consumers not only have different information, but they have different values and different ways of combining this information.

3. Proponent fallacy #3. Food technology education is a trade association issue

Food technology education is not a trade association issue. The first step of food technology education is partly a branding issue. Before people will listen to a proponent's perspective, food technology must provide a clear, systematic, vivid, focused message that is potentially important to consumers. In the biotechnology marketing battle, the opponents of biotechnology clearly have the upper hand. The powerful "brand" visuals that are associated with names such as "FrankenFoods" and "Super Weeds" leave

little wonder why the public is able to latch on to "bumper-sticker logic" and be swayed toward skepticism or opposition. These vivid phrases promote peripheral processing instead of a thoughtful consideration of benefits and risks.

Trade associations, scientific organizations, and the government probably cannot effectively brand food technology in a way that leaves it clear in a consumer's mind (see Thayer, 1992). The majority of trade association efforts in this regard have not been as effective as hoped for or claimed (Wansink, 1994). The most notable examples (such as the "Got Milk" campaign) won awards, but reportedly contributed little to increase sales among nonusers. If firms are to compete with the "spin" that opponents of food technology create, they need to realize that branding food technology deserves some of their best marketing minds (Franz, 2000). It is too important to be outsourced or trusted to a risk-aversive, consensus-building trade association or government agency.

4. Proponent fallacy #4. Good for medicine means good for food

Consumers accept technology for medicinal purposes, but not necessarily for foods. These different attitudes toward medicine and food can be explained by the way the situation is framed—or perceived—by consumers. As Kahneman and Tversky (1986) have shown, people show a risk-taking tendency when the outcome is seen as the reduction of a loss ("I do not want to be sick"), but show a risk-aversive tendency when the outcome is identified as a gain ("I want to be healthy").

In general, technological applications in the medical domain fall in the loss reductions category. For example, the benefit of a new medicine developed with biotechnology can be generally believed as improving the lost health of an already ill patient. The benefits of a food product produced with biotechnology, however, are perceived as improved nutrition and quality for a product that already has satisfactory quality and nutrition from a consumer's point of view. Thus, it is seen as an increase of a gain or benefit.

If the differences in the acceptance of food technologies across application domains are due to differences in how the benefits and risks are perceived or framed, how can opinions be changed? Consumer acceptance of food-related technology may be improved by framing the benefits in terms of the reduction of potential dietary hazards instead of framing them in terms of enhanced nutrition or quality (Wansink and Ray, 1996). The reduction of these gains and losses is food specific. As these benefits and losses become more evident, they can be promoted on a food-specific level (e.g., broccoli) or on a category-specific level (e.g., green vegetables). Similarly, an environmental position would take the same approach. In this case, consumer

acceptance could be improved by framing the benefits in terms of the reduction of destructive pesticides and waste instead of framing these benefits in terms of enhanced ecological balance.

A large part of the confusion consumers have about biotechnology is based on the misguided assumptions proponents and opponents of biotechnology use when communicating to them. It is the prior successes that proponents and opponents have had in related fields that lead them to make many of the wrong assumptions about consumer behavior that limits their effectiveness, but food safety issues are different. Its tremendous potential and risks dictate that assumptions be changed because the stakes are too high for too many people. Contrary to what proponents think, the biotechnology controversy will not be forgotten, nor will all people become advocates when they see the science, nor is this simply a trade association education issue. Contrary to what opponents think, many people do not care to be informed about the details of biotechnology, and the risk of biotechnology will not keep them from enjoying the personal or even social benefits of it.

For both opponents and proponents, continuous education is critical even if it appears that many consumers are not interested in the issue. While a person can be uninterested in a topic, there are different times in their life or different windows of opportunity when they are open to learning about new ideas. Continuous education keeps informed consumers informed and offers disinterested consumers the opportunity. The more effort that is invested into consumer education, the less risk there is that consumers will overreact on the basis of emotion, fear, memorable phrases, or unfounded benefits.

The education strategies suggested here may read as though they are relevant only for large institutions, companies, or well-organized political action groups. However, the same basic concept—understanding the processing style of your target and how it influences attitudes—is relevant to individual researchers and scientists who want their research to have more impact. Whether it be in the way researchers write, in the way they organize public and professional talks, or how they are interviewed by the media, knowing these principles will prevent them from making the same well-meaning, but misguided, mistakes of companies and well-organized activists.

Through commercial applications, biotechnology may improve health, agriculture, farming practices, and the quality of foods. However, along with the array of potential benefits are potential risks and uncertainties surrounding the commercial applications of biotechnology. Public support for a controversial food technology is crucial for deriving any benefits associated with the technology (Blane *et al.*, 2002).

VII. USING PRECRISIS PREPARATION TO MANAGE RESPONSES

The components for managing the stigma associated with potential future food safety issues involve the following precrisis preparations: (1) promoting a hierarchical understanding of food production, (2) integrating distinct communication channels, (3) accommodating consumer needs and concerns with packaging and labeling, (4) positioning products as comparable alternatives, (5) addressing public concerns, and (6) creating a single information authority.

A. PROMOTE A HIERARCHICAL UNDERSTANDING OF FOOD PRODUCTION

There are wide differences in the knowledge consumers have about food technology (Hamstra, 1991, 1993). When combined with the fact that consumers also have different information-processing styles, this suggests that the most effective communication strategies to disseminate food technology information would take a stepwise approach (Wansink *et al*., 2002). That is, consumers first need to accept the processes of food technology, and only after that can they adopt specific products. Therefore, having information and confidence about food technology is necessary before they can accept products made using these technologies.

To accomplish this, a hierarchical model of communication strategy is proposed. As illustrated in Figure 11, it will first be necessary to disseminate general information such as what food technology is and what would be affected by it. Consumers must have some basic level of knowledge about food technology in order to process more specific and detailed information. Next, information about food technology used by specific industries can be communicated and better understood. Once the technology or process itself is understood and accepted by consumers, then information about the benefits and risks involved with specific products can be conveyed more effectively. This way, consumers will be able to develop a knowledge base on which they can make educated decisions regarding specific food products (Wansink and Chan, 2001). Figure 11 illustrates how the hierarchy of communication objectives can be structured in relation to the level of consumers' food technology knowledge.

B. INTEGRATE DISTINCT COMMUNICATION CHANNELS

Consumers acquire food safety-related information from various sources, such as government publications, consumer organizations, research institutes, and the media (van Ravenswaay and Hoehn, 1991; Young, 2000). Because

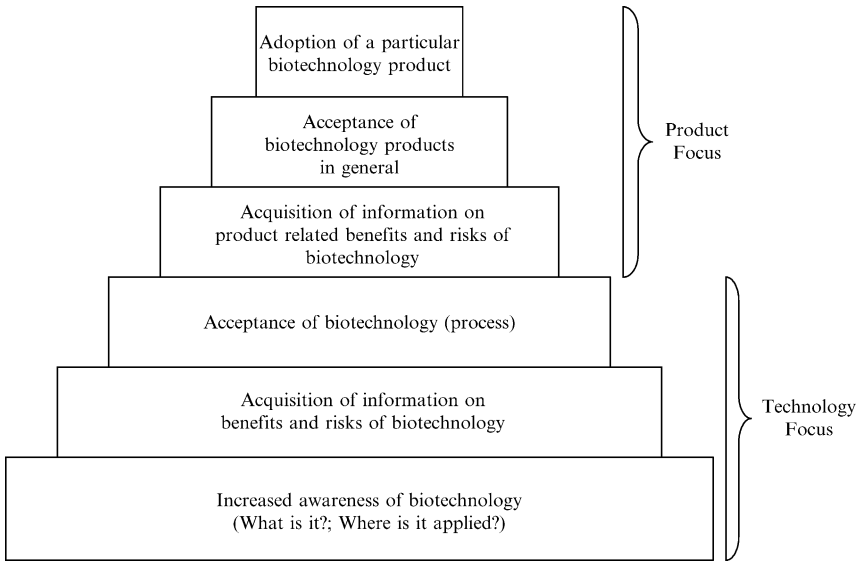

FIG. 11 Layered hierarchy of "take-aways."

consumers perceive that there are conflicts among these sources, the resulting confusion can lead to rejection or deferral of acceptance of food technology products. An integrative and coordinated communication effort by the multiple information sources is essential in increasing consumer acceptance. Government, universities, other research institutions, the industry, and the media all have a distinct but primary role to play in the management of a crisis.

Consider new technologies such as beef hormones and biotechnology (see Table IV). Although the media has long been a prime information source for consumers, it is less of a source of biotechnology information. The effect of the mass media in disseminating biotechnology information has been inhibiting (i.e., distributing news about biohazards) rather than facilitating. A variety of strategies to use mass media as the key information source should be considered creatively. This would include advertising campaigns promoting biotechnology and public relations in forms of articles or programs that disseminate biotechnology information via various media formats.

C. ACCOMMODATE REASONABLE CONCERNS WITH LABELING

There are at least three functions of labeling products, such as those produced with unfamiliar technologies: (1) protect consumer choice, (2) provide information on product ingredients for health reasons (e.g., allergies), and

TABLE IV
ONGOING CRISIS: POTENTIAL HEALTH DANGERS UNKNOWN OR NOT YET PROVEN

Description	Consumer reaction	What was done	Aftermath
GM food (ongoing) Scientists fear that GE plants and fish can contaminate wild populations, increasing weed problems and unbalanced ecosystems, and create new allergens or toxins. Supporters say yields and quality are increased	Refusal to buy GM seeds from several countries Societal groups and consumers ask for labeling	Attempt to label GM products in EU	Ongoing
Hormone-fed beef (1989, EU) In U.S. beef production, growth implants and bovine growth hormone (somatotropin) administration increase lean accretion and decrease fat deposition	Europeans do not want hormones in beef, Americans don't mind	EU ban U.S. hormonefed beef, stating that economic, environment, and consumer concerns must be considered in addition to the scientific evidence	May 2000: EU propose a definitive ban on estradiol in farm animals, U.S. refuses to comply with WTO if passed

(3) encourage companies to provide safer products by having disclosure requirements. While the main function of labels is the provision of information, the last function suggests that labeling may function as a cue for product safety. Some consumers may use such labeling to avoid products processed with specific technologies. In contrast, consumers may perceive explicit labeling as a sign of the manufacturers' confidence in product safety, as they are willing to display such information even though disclosure is not required by law (Wansink, 2003b).

Care must be taken, however, in how such products are labeled. Results of the 1991 Euro-barometer survey, for instance, reported an interesting finding related to labeling biotechnology products. Results indicated that the way biotechnology products are labeled influenced both perceptions of and attitudes toward such products. The survey was conducted using a split

ballot in which half of the respondents were questioned using the word "biotechnology" and the other half were questioned using the term "genetic engineering." Twice as many respondents in the "genetic engineering" condition thought that the technology would make their lives worse than respondents did in the "biotechnology" condition. Clearly, consumers have predisposed attitudes toward particular terminology such as "genetic engineering." Regardless of the reasons behind these attitudes, it is important to accommodate the uneasiness invoked through the terminology. To do so, manufacturers should seek to avoid the use of potentially negative terms either through omission or the use of alternate terminology.

Consumers generally view product labeling as an important source of information when developing attitudes toward food technology products. Therefore, any labeling and product packaging should reflect the positive aspects of the industry and methodology involved in production. If reasonable, consumer advocacy organizations and research institutions could be utilized as endorsers for the products or technology as they are viewed as most trustworthy.

In the meantime, it is important to provide consumers a sense of control over their choices. Even though consumers are ill-equipped with knowledge, they still desire control in choosing what they eat. The use of labeling to provide food technology information in product preparation should be considered. Labeling of food technology products serves not only as an informational function but also as a safety signal. Food technology communication strategies should provide consumers with criteria for evaluating food technology products. Consumers will become more comfortable and confident in accepting the technology as their confusion about how to choose their food diminishes. In deciding whether or not to label, the issue of how to label also becomes an important consideration.

D. POSITION PRODUCTS AS COMPARABLE ALTERNATIVES

When contemplating product positioning in their product at the individual store level, marketers should seek to align products with their nontechnological counterparts (Wansink, 2002). This avoids the assignment of a stigma on the products as being "fake" or "synthetic" (Wansink, 2003c). Even so, this is not as important as when targeting food technology-savvy markets wherein differentiation techniques can even work as an advantage.

Additionally, efforts should be made to "tie in" the products with brands and images that are highly regarded and which can further reinforce the natural aspects of the food (Wansink, 1994). Through the use of brand equity leveraging, innovative promotion, and product pairing, these products can achieve an air of familiarity, quality, and conventionality (Wansink, 2005).

E. ADDRESS PUBLIC CONCERNS CORRECTLY

Controversy over safety and ethical issues involved in the use of certain misunderstood technologies is a persistent problem that often continues to haunt all those involved even after the product or technology has been largely accepted. Food technology is advancing into the future and some of the current safety issues may become nonissues. However, current public concerns are grounded on what has happened with past misuses, especially regarding biotechnology. Concerns may be partially due to the fact that living organisms are adaptive and their change is neither predictable nor controllable (Table V).

Therefore, in the long run, the food technology industry and researchers, as well as the government, should try to safeguard potential hazards. First, objective measures of potential risks of hazards involved in food technology and related products must be developed. Without such measures, it will be impossible to convince consumers of the safety of new technologies (Frewer and Shepherd, 1994). Second, some legal and self-regulatory protection devices must be put in place by the government and industry. Third, and most importantly, a code of ethics that guards against the potential misuse of food and biotechnology must be established and adopted by those

TABLE V
REVISING CURRENT ASSUMPTIONS ABOUT CONSUMERS AND NEW FOOD TECHNOLOGIES

	Current assumptions	Better assumptions
Proponents of food technologies	Controversies will be forgotten	Continuous education is critical
	Once people have the facts, they will be advocates	For the majority of consumers, facts may mean less than memorable phrases
	Science sells and fear fails	The emotion of feared technologies often wins over logic
	Technology-related education is a trade association issue	Specific technologies are an issue of branding and education
Opponents of food technologies	People want to be informed	Many consumers do not care to be informed
	People need to be informed	Only active decision makers believe they need to be informed
	Changing consumer attitudes will change their behavior	Product benefits can cause a person to act differently than their philosophical position would indicate
	Risks are more important than benefits	Benefits are more important to most people than risks

who participate in that field. Smart marketers can coordinate with key industry groups to build a wider base of understanding, influence, and safety. Consider the following cooperative efforts.

1. Self-regulation by food and biotechnology industry

Generally, consumers perceive food technology information provided by the industry to be the least credible, and they are most distrustful of an industry-regulated safety system. The biotechnology industry is the major provider of biotechnology products that consumers make choices about. Therefore, it is critical for the industry to earn consumers' trust. A self-regulatory effort by the industry may help gain consumers' confidence. The industry should strive to develop objective measures for the risks and benefits of products and establish self-regulated safety measures of the processes used.

2. Role of government as the safeguard

Despite some doubt regarding the efficiency of the government, many focus groups and surveys indicate that consumers believe the government should play an important role in providing regulation and safety protection with respect to food technology. These provisions and assurances of safety by the government will contribute to the elimination of some of the concerns consumers hold about food-related issues in general, particularly about biotechnology issues. The government should take the responsibility of setting the direction and pace of development in order to prevent questionable or premature application of certain food technologies.

3. University and research institutions

Universities and other research institutions account for the majority of genetic engineering and food technology research and development. Therefore, they are well positioned to play a safety-assurance role as well as provide up-to-date information on technological advances and applications. While industry sponsorship raises some concerns, the public views academic institutions as a credible and trustworthy source of information. This being said, a more active effort to establish and maintain integrity and impartiality of research by these institutions is important.

F. CREATE A SINGLE INFORMATION AUTHORITY

The U.S. war on terrorism both domestically and abroad has underscored the importance of having a single federal agency whose position it is to oversee the safety of the nation against terrorism. Analogously, in the

context of food safety, it is appearing increasingly important to create a single federal agency position in the United States that oversees the safety of the nation's food supply. According to a 2000 Food Marketing Institute position paper, "The public is never in more need of assurance than when a food safety crisis arises . . . Because it is rare that single agency has committed jurisdiction over the entire scope of a major food safety problem, it becomes impossible to find a spokesperson who can rapidly clarify the facts and reassure the public." What instead usually happens is that consumers are faced with a lengthy delay while our overlapping bureaucracies search for experts and attempt to create a coordinated response. The longer this takes, the more consumer confidence erodes and fear increases (Lee, 2002).

In addition to coordinating information, this source could also spearhead related efforts, such as those proposed in the National Safety First Initiative. In these such initiatives, the basic premises involve issues related to safety criteria, verification standards, follow-up standards, and safety leadership standards (Golodner, 2002; Kapuscinski, 2002).

VIII. MANAGING REACTIONS TO FOOD CRISES THROUGH CRISIS-RELATED RESPONSES

The way marketers respond to food crises should take into account whether a country's food consumption is influenced more by risk perceptions or by risk attitudes. The relative influence of risk perception and risk attitude on consumption depends, among others, on the accuracy of knowing the probability that negative health side effects could occur from eating food products.

A. COMMUNICATION EFFORTS: HOW SHOULD INSTITUTIONS RESPOND TO FOOD CRISES?

If the probability of contracting a disease is not accurately known, research indicates that different policies are appropriate for different types of countries. Consider the BSE crisis. In countries such as the United States, tough measures are required to prevent a BSE crisis, as risk attitudes drive consumption and little can be done to change consumers' risk attitudes. This means testing and eliminating suspected food products. In countries such as Germany, both risk perceptions and risk attitudes drive consumer behavior. This not only suggests the need for tough measures, but also extensive and responsible dissemination of accurate information by the government, industry, and media. In contrast to the United States and Germany, Dutch consumer behavior is driven mainly by risk perceptions. In this case, honest and consistent communication by both the government and

the food industry is more effective than a mass recall and destruction of food products.

If the probability of contracting a disease is known accurately (or becomes more accurate), risk perception can become a more important driver of food consumption than risk attitude. In low-risk situations, messages from the government, the food industry, and the media will have a notable impact on helping consumers respond to the food crisis. In contrast, with high-risk situations, tough measures—recall or elimination—are also necessary. In the case of strongly risk-aversive consumers, however, any level of risk is treated as a high-risk situation. As a result, tough measures and information are important in even low and mildly risky situations. On the production side, an ounce of prevention is worth a pound of cure, but on the policy side, an ounce of information is worth even more.

In food crisis situations, the potential for stigmatization is tremendous (Frewer *et al.*, 1996a). Well-publicized outbreaks of food-borne pathogens and the emotionalism related to agricultural biotechnology are two recent examples of how science, policy, and public perception interact. Current risk management research indicates that it is essential for authorities (either industrial or governmental) to communicate effectively and provide evidence that they are reducing, mitigating, or minimizing a particular risk (Powell, 2000).

B. DEVELOPING RISK MANAGEMENT MEASURES

Risk management measures can be separated into genuine risk management measures and ingenuine, "auxiliary," risk management measures. While only the former should be considered seriously, the latter is reviewed briefly lest a responsible marketer or public policy official finds himself or herself leaning in ill-advised directions.

As alluded to in the BSE illustration given earlier, genuine risk management measures can focus on systematic hazard removal based on the HACCP system or on some other alternative or more appropriate system. In some cases, this can involve the isolation of the cause of the problem. In other cases, it can involve the conservative elimination of all suspected contaminants. Concurrent with this is the importance of reporting these efforts in a proactive means and keeping consumers informed about decisions, processes, and progress.

Ingenuine efforts are classified as "auxiliary" risk management efforts and typically involve doing nothing about the cause or concern of the problem, but simply trying to displace negative attention. These often take the form of denial, blaming a scapegoat, redefining a hazard, or claiming ostensible stakeholder consensus. While no one in a noncrisis situation would advocate

such underhanded efforts, such events become astonishingly common in crisis situations. It is then important to realize that there may be more of an unintentional reliance on these in the heat of the moment than what one would want. Being forewarned is being forearmed.

Consider the following case study. Garibaldi Smallgoods was the metwurst category leader in south Australia until 1991. In 1991, a bride and some guests fell ill with food poisoning after eating Garibaldi salami at a local wedding reception. Following this, the company director assured the health commission that they would set up a quality control program, upgrade their processes, provide precise end-product specifications, and provide proper coding and labeling of all batches. In January of 1995, however, 1 child died and 24 other people were hospitalized due to Garibaldi metwurst, which was contaminated with *E. coli* O111. While Garibaldi indicated they would remove all product from the market, they were slow to do so and resisted turning over their information regarding meat sources and quality assurance procedures. On January 31, they agreed to turn over the information, if a request was made in writing. The following day, a 4-year-old child died from the illness. As a result of the Garibaldi case, metwurst category sales in Australia fell to less than 10% of the level achieved before the incident and have never fully recovered since then. Consumer trust in the product was destroyed and retailers were reluctant to stock it (www.Food-Crisis.com 2003).

C. DEALING WITH POTENTIAL COMPLICATIONS

Even in the face of a well-planned emergency response plan, complications can arise. One common area where this happens is with systematic hazard removal. When existing evidence is poor, HACCP will require extensive risk assessment and may not be as easy to implement as one would hope. Nevertheless, it is important to realize that the resources allocated to risk assessment have important signal value to the public. Depending on the level of resources dedicated to a cause, an absence of investment can either cause a further increase in the perceived risk or lead to a feeling of frustration that nothing is being done. A perceived balance needs to be maintained.

In some cases, a hazard may turn out to be more severe or more widespread than previously stated. When this occurs, information sources whose previous statements are proven wrong may lose their credibility.

There are also potential complications that can occur because of proactive consumer information. In these cases, information that is intended to educate the public may also have unintended signal value, suggesting the existence of previously undisclosed or underestimated hazards. Indeed, information that is intended to restore consumer trust may actually raise

consumers' suspicions, pointing to a hidden agenda of the information source. In such a situation, consumers are more likely to stick with the previous risk judgment and trust the information sources to the degree in which the provided information matches their personal risk judgments.

IX. CONCLUSIONS

The accelerating growth of new food technologies and their applications are indeed causing interference with consumer understanding. Incomplete understanding of food technology is leading to divided opinions. By providing a theoretical framework for understanding what factors affect consumers' acceptance of food technology, there are clear implications for labeling, promoting, publicizing, advertising, and pricing technological food products. A two-phase strategy for managing public opinion—focusing on precrisis interventions and postcrisis responses—is the key planning tool, which provides structure for the more tactical efforts.

It is critical to understand that not all consumers are created equal. They include the (1) accountable segment (who ignore any available information on risk and keep their habits, even though some risk may be involved in their behavior), (2) the concerned segment (who are not risk averse to begin with so their behavior is dictated primarily by their perception of risk; as their perception of the riskiness of an action increases, they will eventually get to a point where they will not participate in the action at all), (3) the conservative segment (who are cautious, risk-averse consumers who do not take any unnecessary risks), and (4) The alarmist segment (who are prone to overreacting to many situations). Addressing specific efforts toward each of these segments helps guarantee that generic efforts will not be wasted.

Managing the potential problems associated with any food safety issue involves the following five precrisis preparations: (1) promote a hierarchical understanding of food production, (2) integrate distinct communication channels, (3) accommodate consumer needs and concerns with packaging and labeling, (4) position products as comparable alternatives, and (5) address public concerns correctly. The responses following the crisis relate to open communication, risk management measures, and dealing with the potential complications that may arise.

Certainly not all crises are alike. As noted earlier, they can vary in their familiarity, severity, proximity, consequence, and the extent to which they can be avoided. Different types of crises will be evaluated differently by different groups of consumers. One group may respond to biological fears with the same panic as others view bacteria contamination. Viewing individual consumers as segments is the key to predicting the impact of any food

crisis on consumers. The crisis can change, but for every crisis there will be an accountable, concerned, conservative, and alarmist segment of consumers. Knowing their relative size will enable us to better predict the effectiveness of different interventions.

As noted at the beginning of this chapter, studies related to perceived risk have only recently turned toward issues of food safety. Consequently, many of the studies presented in this chapter were exploratory in nature and many of the observations that are made are based on one or two studies on a topic and not on a broad set of converging findings. This area is ripe for studies that systematically test some of the general predictions here across a wide range of food safety issues both natural and technological.

ACKNOWLEDGMENTS

Special thanks to the National Soybean Research Center at the University of Illinois at Urbana-Champaign and to the Illinois–Missouri Biotechnology Alliance.

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AN ENZYMATIC PROCESS FOR CORN WET MILLING

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I. Introduction: Corn Wet Milling Industry
II. Structure and Composition of the Corn Kernel
III. Conventional Corn Wet Milling Process
IV. Use of Enzymes in the Conventional Corn Wet Milling Process
V. Development of the Enzymatic Corn Wet Milling Process
VI. Benefits of the Enzymatic Corn Wet Milling Process
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VIII. Future of the Enzymatic Corn Wet Milling Process
Acknowledgments
References

I. INTRODUCTION: CORN WET MILLING INDUSTRY

In 2002, approximately 2.2 billion bushels of corn were processed in the United States for the production of food, fuel, and industrial products. Of that 2.2 billion bushels, 19.22 million tonnes (757 million bushels) were used for high fructose corn syrup (HFCS), glucose and dextrose, 6.34 million tonnes (250 million bushels) for pearl starch, 26.69 million tonnes (1051 million bushels) for fuel and beverage alcohol, and 4.75 million tonnes (187 million bushels) for cereals and other products (Corn Refiners Association, 2003). More than 50% of the corn processed in the United States is done so using the corn wet milling process.

Wet milling is a process in which wet (40–45% moisture content) corn kernels are fractionated in such a way that the individual components of corn kernels are separated, using an aqueous medium, in relatively pure

ADVANCES IN FOOD AND NUTRITION RESEARCH VOL 48
ISSN: 1043-4526

form. From 25.4 kg (1 bushel) of corn, 14.3 kg (31.5 lbs) of starch can be produced, 6.1 kg (13.5 lbs) of corn gluten feed (animal feed), 1.2 kg (2.6 lbs) of corn gluten meal (animal feed), and 0.7 kg (1.5 lbs) of corn oil can be produced (National Corn Growers Association, 2002). Starch can be further converted into other high-valued products. From the 14.3 kg (31.5 lbs) of starch, another 15 kg (33 lbs) of sweetener or 9.5 liters (2.5 gal) of ethanol can be produced (National Corn Growers Association, 2002).

The corn wet milling process was developed in the early 19th century at which time alkali was used. The use of alkali was abandoned when the SO_2 process was invented in 1875. The alkali wet milling process was considered inferior to the SO_2 wet milling process because the steeping of whole corn kernels in the presence of alkali for 40–50 hr resulted in the pericarp being dissolved completely, in excessive starch solubilization, and in undesirable bacterial fermentation. Since then, many processing changes have been made and new technologies have been developed. New unit operations and equipment design have improved the conventional corn wet milling process greatly and made it more efficient. In the United States, there are currently 28 corn wet milling plants; more than half have been built in the last few decades (Johnson and May, 2003). During the last few years, growth in the corn wet milling industry has been 4 to 6% per year.

In the corn wet milling process, the use of SO_2 is very important. It breaks down the protein matrix that surrounds the starch particles and increases starch yield during milling. The use of SO_2, however, has some health and environmental problems associated with it. Previously, research has been done to develop alternative processing methods that do not require the use of SO_2 (Meuser and German, 1984; Meuser *et al*., 1985, 1989), but due to lower starch recovery or inferior separations, have not resulted in a commercialized wet milling process. Another alternative process developed for fractionating corn kernels that does not require the use of SO_2 is the sequential extraction process (SEP) (Chang *et al*., 1995; Hojilla-Evangelista *et al*., 1992). However, the SEP process is best suited for the production of ethanol and coproducts. An enzymatic corn wet milling process has been developed that shows the potential to reduce or completely eliminate the use of SO_2 and produce starch yields comparable to the conventional corn wet milling process. The objective of this article is to review the enzymatic corn wet milling process and to compare it to the conventional corn wet milling process.

The corn wet milling process involves taking apart a corn kernel into its individual components. To take apart a corn kernel for maximum and high-quality starch recovery, it is important to understand the structure and composition of the corn kernel.

II. STRUCTURE AND COMPOSITION OF THE CORN KERNEL

A corn kernel has four main parts: (1) tip cap, (2) pericarp, (3) germ, and (4) endosperm. Earl *et al.* (1946) gave the percentage component parts and the composition of these parts of dent corn kernels, as shown in Table I.

Endosperm constitutes the main part of the corn kernel and consists of 85 to 90% starch, 8 to 10% protein, and a small amount of oil and other compounds. Corn endosperm can be divided into two distinct parts: floury and horny endosperm. In floury endosperm, starch particles are round and are dispersed loosely in the protein matrix. In the horny endosperm, the protein matrix is stronger and starch particles are held more firmly. Starch granules are encased in the continuous protein matrix. The tighter setting in horny endosperm gives starch particles a polygonal shape. On average, the amount of horny endosperm in the corn kernel is twice that of the floury endosperm. However, this ratio is a function of the corn kernel protein content (Wolf *et al.*, 1952).

Germ (embryo) constitutes 11 to 12% of the corn kernel. It can be divided into three parts, of which one turns into leaves (plumule) and another turns into roots (radicle) when the kernel is planted. The third part (scutellum) provides high-energy oil to the plant for growth (Blanchard, 1992). The remaining parts of the corn kernel are the pericarp and tip cap. The pericarp is the dense outer layer of corn kernels consisting of layers of dead cells. One of these layers is a spongy tissue known as cross and tube cells, which facilitate the absorption of water into the kernel. Underneath the cross and tube cells is a layer of semipermeable cells known as the seed coat. The tip cap is the remaining fibrous material that connects the corn kernel to the cob. It is only through the tip cap and then through the cross and tube cells

TABLE I
PERCENTAGE COMPONENT PARTS AND COMPOSITION OF THESE PARTS OF DENT CORN KERNELS[a]

Corn kernel component	Dry weight of whole kernel (%)	Dry basis (%)				
		Starch	Protein	Oil	Ash	Sugar
Tip cap	0.8	5.3	9.7	3.8	1.7	1.5
Pericarp	5.3	7.3	3.5	0.98	0.67	0.34
Germ	11.5	8.3	18.5	34.4	10.3	11.0
Endosperm	82.3	86.6	8.6	0.86	0.31	0.61

[a]From Earl *et al.* (1946).

that water or other liquids can penetrate the kernels (Wolf *et al*., 1952). The cutinized outer layer of the pericarp prevents the absorption of water into the corn kernel.

III. CONVENTIONAL CORN WET MILLING PROCESS

Corn is delivered to the processing plant by rail car, truck, or barge. Currently, no rapid and precise methods are available to determine the wet millability (wet milling quality of the incoming corn). Corn for wet milling is usually purchased based on the United States Department of Agriculture (USDA) grain standards, which do not indicate directly the wet milling characteristics. Normally, #2 grade corn is purchased because of its price and availability and not because of quality. Different factors affecting the quality of grain for wet milling (Freeman, 1973) can be classified into three main categories: (1) hybrid or genetics (Anderson, 1962, 1965; Anderson and Griffin, 1962; Anderson and Pfeifer, 1959; Anderson *et al*., 1960; Watson and Yahl, 1967; Weller, 1987; Zehr and Eckhoff, 1995; Zehr *et al*., 1995, 1996), (2) environmental or growing conditions (Singh *et al*., 1996), and (3) postharvest handling (Brown *et al*., 1979; Lasseran, 1973; Le Bras, 1982; MacMasters *et al*., 1954, 1959; Singh *et al*., 1998b; Vojnovich *et al*., 1975; Watson and Hirata, 1962; Weller, 1987; Weller *et al*., 1989) and storage (Lasseran, 1973; Roushdi *et al*., 1979; Singh *et al*., 1998a).

The first and foremost operation in the corn wet milling process is cleaning to remove foreign material (sand, weeds, pieces of cob, and other cereal grains) and broken corn kernels, which restrict the flow of steepwater through corn kernels and result in understeeped corn and reduced separation performance (Blanchard, 1992; Johnson and May, 2003; Watson and Eckhoff, 2004). Broken kernels increase the amount of solids in steepwater (Wang, 1994) and can also release some starch into steepwater, which becomes gelatinized upon evaporation and makes steepwater viscous (Watson and Eckhoff, 2004), causing fouling of heat transfer surfaces (Madson and Manceaux, 1995). Reciprocating screens and aspiration are used to remove the broken corn and foreign material (BCFM). Cleaned corn is conveyed to steep tanks where it is steeped countercurrently (new corn with oldest steepwater) in 0.1 to 0.2% SO_2 at 48 to 52 °C for 24 to 36 hr. Steeping is accomplished in a battery of interconnected 6 to 18 stainless steel tanks, each of 254 to 635 tonnes/day (10–25,000 bu/day) capacity (depending on the plant size). Each steep tank is equipped with a pump to recirculate the steepwater or to move the steepwater to the next tank. Each tank, or a combination of 2 to 3 tanks, has a heat exchanger to maintain the temperature. Steeping is done to soften the corn kernels so that

subsequent milling and separation of corn components can be accomplished easily.

The conventional countercurrent steeping process can be divided into three distinct 8- to 12-hr duration stages (Watson and Eckhoff, 2004): (1) lactic acid-dominated stage, (2) sulfur dioxide diffusion stage, and (3) sulfur dioxide-dominated stage. In the first stage the soluble sugars leached from the corn kernel are fermented into lactic acid by *lactobacillus sp*. Several studies have been done to determine the role of lactic acid in the steeping process. Although the mechanism is not completely understood, a significant effect of lactic acid on increasing starch yields has been found (Eckhoff and Tso, 1991; Roushdi *et al*., 1981a,b; Singh *et al*., 1997, 1999a; Watson *et al*., 1951). Moreover, the effect of lactic acid on increasing the starch yield has been found to be hybrid dependent (Singh *et al*., 1997). It has also been observed that other weak or strong acids do not have the same effect of increasing starch yields as observed with lactic acid (Du *et al*., 1996; Kerr, 1950). There is something unique about lactic acid and there is probably some synergistic effect of lactic acid and SO_2 during steeping (unpublished data). Research has shown that lactic acid fermentation is not required to see its beneficial effects in increasing starch yields (Watson and Eckhoff, 2004) and the addition of externally produced lactic acid has the same effect as that produced by *in situ* fermentation.

The second stage of steeping is the sulfur dioxide diffusion stage in which sulfur dioxide diffuses with the water into the corn kernel through the base end of the tip cap and moves through the cross and tube cells of the pericarp to the kernel crown and then slowly into the horny endosperm. The second stage is diffusion limited because of the specific path required for water going into the kernel.

The third stage is the sulfur dioxide-dominated stage. During this stage the maximum amount of SO_2 is absorbed in the corn endosperm and cleaves the disulfide bonds in the protein matrix that encapsulates the starch granules and loosens up the protein matrix (Watson and Eckhoff, 2004). A balance between these stages has to be maintained in order to achieve optimum steeping. At the end of steeping, corn kernels have approximately 43–45% moisture content, leached out 6–6.5% of soluble solids (mainly from the germ), absorbed about 0.2–0.4 g of sulfur dioxide per kilogram, and become sufficiently soft so as to rupture when squeezed between the fingers (Watson and Eckhoff, 2004).

After steeping, corn is passed through attrition mills, which tear open the kernels and release the now rubbery germ. The objective is to release the maximum amount of germ with minimal germ damage and is usually done in two steps: a first grind and a second grind. The mills are equipped with one fixed and one rotating Devil's tooth plate, which mesh closely and are

designed specifically for corn (Blanchard, 1992; Johnson and May, 2003). Mill plates can be adjusted to different gap settings. The plate gap setting and revolutions per minute of the mill control the impact and shearing force on the kernels and, therefore, affects the quality of the germ recovered. Most of the germ and approximately 50% of the starch are released in the first grind. All of the ground slurry is collected in a tank (first grind tank) from where it is fed to the germ separation unit. Starch released at the first grind increases the density of the slurry in the first grind tank to a specific gravity of about 1.058–1.066 (8–9 Baumé). At this Baumé the germ, which contains about 45–55% oil, is lighter than the other corn components and, therefore, floats on top of the slurry and can be separated by density difference. Germ separation is done by passing the ground corn slurry under pressure through hydrocyclones, which are conical tubes ranging from 7.6 to 22.9 cm (3 to 9 in) in diameter and 0.91 to 1.37 m (3 to 4.5 ft) in length. The slurry is fed tangentially through the inlet port, causing a rapid swirling motion. The heavier particles (endosperm starch and fiber particles) are forced against the walls and come out through the underflow, whereas the lighter particles (germ) stay in the middle and are recovered through the vortex finder as the overflow (Blanchard, 1992).

Germ recovery is also done in two steps: primary germ separation and secondary germ separation. Each step has two sets of hydrocyclones, A and B, in which the volumetric ratio of overflow to supply (O/S) is different. A cyclones have an O/S ratio of 20%, and B cyclones have an O/S ratio of 30–50%. The underflow of A cyclones is fed to B cyclones. In primary germ separation, 80 to 85% of the germ is recovered and most of the remaining germ is recovered in the secondary germ separation. Any whole or broken germ not recovered in the secondary germ separation is lost in the slurry and is recovered later as a part of the fiber fraction. Oil released from broken germ ends up in the gluten (protein) fraction. The germ separation system is set up in recycle loops. Germ recovered with B cyclones is fed to A cyclones. Also, germ recovered from the secondary germ separation system is fed to the primary germ separation system. The only place from which germ is removed from a wet mill is overflow of the A cyclones of the primary separation system (Blanchard, 1992). The recovered germ is washed countercurrently over a set of screens to remove loose starch and protein and is dewatered in a germ press to 50 to 55% moisture content. Dewatered germ is subsequently dried to 2 to 4% moisture content and is processed further to recover corn oil, a valuable coproduct. If the corn oil is recovered at the plant site, germ meal is added later to the fiber fraction to produce corn gluten feed (CGF).

Corn slurry from underflow of the B cyclones of the secondary separation system is passed over screens (the third grind screens) to remove free starch

and protein from the endosperm and fiber fractions. This step reduces the load on the third degermination mill by removing approximately 50% of the solids. The third grind mill usually consists of two independently driven, grooved mill plates rotating in opposite directions. The plates together give a cutting action that reduces the amount of starch bound to fiber by 20 to 30% (Johnson and May, 2003). These mills are also known as refiner mills. Another type of third grind mill is the impact mill, or Entoleter mill. An impact mill has one rotating disc plate fitted with pins. The corn slurry fed to the mill is forced against the rotor and the stator pins to release starch and minimize disintegration of the fiber fraction. Refiner and impact mills give almost the same performance (Watson and Eckhoff, 2004).

The slurry, which contains starch, protein, and fiber, is passed through a series of five to six pressure-fed, or DSM, screens to separate fiber from starch and gluten. Usually a 120° concave wedge bar type of screen is used for fiber washing. The slurry is forced tangentially at fixed velocity across the screen surface. The concave surface and the velocity of the slurry across the surface provide the centrifugal force, which holds the slurry against the screen surface (Dorr-Oliver, 1990). The spacing between the wedge bars allows the starch and protein particles to pass through and the fiber particles to flow across the screen, with continuous dewatering and without clogging the screen. Usually the first fiber wash screen has a 50-μm spacing between the wedges. It is also known as the fiber block because it prevents fine fiber from passing through the screen and, therefore, prevents fine fiber from entering the centrifuges and the starch hydrocyclones. The subsequent four to five screens have a 75-μm spacing. With countercurrent washing, fiber coming off the last set of screens contains about 15 to 20% starch, of which about half is bound and half is free (Watson and Eckhoff, 2004). After washing, fiber is dewatered by centrifugal screens and screw presses to about 60% moisture content. Fiber is then dried partially, mixed with heavy steepwater, and dried further to about 10% moisture and mixed with germ meal (defatted germ) to make corn gluten feed. The final corn gluten feed contains 18 to 22% protein and 1.0% fat (Blanchard, 1992).

The starch and gluten (protein) slurry, known as mill starch or mill stream, is combined from the fiber wash and the underflow of the third grind screens. Normally, mill starch contains about 5–6% protein (db). Mill starch is passed through a set of degritting cyclones to remove any sand or other foreign material to prevent damage or blocking of centrifuge nozzles. After degritting, the mill starch, at a specific gravity of 1.043 to 1.058 (6 to 8° Bé), is concentrated to a specific gravity of 1.074 to 1.090 (10 to 12° Bé) by passing through centrifuges [mill stream thickeners (MST)] before the final starch separation (Blanchard, 1992). Concentrated mill starch is passed through another set of centrifuges [primary separators (PS)] to separate

the starch and the gluten fractions based on their density differences (1.5 g/cm^3 for starch particles vs 1.1 g/cm^3 for gluten particles). Primary centrifuges consist of a rotating bowl in which a stack of conical discs are separated by a distance of 0.4 to 1.0 mm, depending on the density of particles to be separated. On the periphery of the rotating bowl, there are 6 to 12 nozzles. The mill starch enters the rotating bowl from the top or the bottom. Due to centrifugal force, the heavier starch particles are forced toward the periphery of the rotating bowl and exit through the nozzles as underflow. The starch slurry coming out from the primary separator has a protein content of 2 to 4% and a specific gravity of 1.160 to 1.198 (35 to 42% dry solids). Lighter gluten particles move up between the discs and exit out as overflow. Gluten slurry from primary centrifuges comes out at a concentration of 15 to 30 g/liter (2 to 4 oz/gal) and contains about 68 to 75% protein (db). Routine maintenance is required to optimize performance.

The gluten slurry is concentrated from 15 to 30 g/liter (2 to 4 oz/gal) to 150 to 165 g/liter (20 to 22 oz/gal) by using another nozzle-bowl gluten thickener (GT) (Blanchard, 1992). Further dewatering of gluten is done with rotary vacuum filters, which consist of a rotary drum with a filter belt. The rotary drum dips partially into a trough of concentrated gluten; a vacuum is applied to build a cake on the belt surface. As the drum moves out of the trough, the vacuum sucks water out of the cake. The cake (approximately 60% moisture) is discharged from the belt onto a screw conveyer, and the belt is washed with high-pressure nozzles to remove the fine gluten particles and open the pores. Gluten dryers (flash or steam tube) further dry the cake to 10 to 12% moisture content to make corn gluten meal.

The starch slurry coming from the PS contains 2 to 4% protein. Further purification of starch is achieved by multistage countercurrent starch washing in 9 to 15 stages of small liquid cyclones to decrease the protein content to less than 0.35% db. These cyclones are similar to hydrocyclones used in germ separation, except the diameter and length of these cyclones are small. The diameter of these cyclones is about 10 mm and the length is about 152 mm. Because the capacity of individual cyclones is small, several hundred cyclones are mounted in parallel in a ''clamshell.'' The starch slurry is pressure fed at 690 to 896 kPa (100 to 130 psi) to the central compartment of the ''clamshell'' and then into the cyclones. Fresh water enters at the very last stage of starch washing and comes out as overflow and is added to the second to last stage of starch washing. Finally, water leaves the starch washing system as overflow from the first washing stage. The only place in a corn wet milling plant where fresh water is added is in the starch washing stage. Underflow of the last starch washing stage is the starch slurry at 60% moisture content, which is dried further to recover pearl starch or is processed to produce corn syrups.

Water leaving the starch washing stage picks up 25% of the total starch fraction, which is recovered by centrifuges, known as clarifiers. Before being fed to the centrifuges, this diluted starch slurry is cooled. Clarifier centrifuges concentrate the starch slurry to a specific gravity of 1.074 to 1.090 (10 to 12° Bé). This starch slurry is mixed back with the mill starch and fed to the PS. The clarifier centrifuge overflow is used primarily as wash water for the PS and the surplus is used for germ or fiber washing. Overflow of the MST is used mainly as steepwater after the addition of sulfur dioxide. GT overflow is used mainly for germ washing fiber washing, and rotary vacuum filter belt washing. Most of the U.S. wet milling plants use a four-centrifuge system (MST, PS, GT, and clarifier centrifuges); there are a few plants that operate with a three centrifuge system (no MST) Chiang and Lee (1995) presented a new design of centrifuge and a new process in which the efficient separation of starch and gluten can be achieved by only two-centrifuge systems. This process offers considerable savings in capital and operating costs.

IV. USE OF ENZYMES IN THE CONVENTIONAL CORN WET MILLING PROCESS

Enzymes have been used previously in the conventional corn wet milling steeping process to reduce the steeping time and the residual protein in the final starch fraction. Roushdi *et al.* (1981b) evaluated the use of different proteases (pepsin, papain, bromelain, and trypsin) in addition to SO_2 during the wet milling steeping process. No significant difference was observed in the residual protein in the final starch fraction from intact kernels. However, with broken kernels, a small but significant difference in the residual protein content of starch was observed with enzyme addition. Use of enzymes on grits (endosperm particles produced during dry milling) have also been investigated as either pretreatment for air classification (Spanheimer *et al.*, 1972) or to overcome the adverse effects of high-temperature drying on starch–gluten separation during subsequent milling (Eckhoff and Tso, 1991). Single enzymes or a combination of enzymes (cellulases, hemicellulase, xylanases, pectinases, and proteases) have also been tested during steeping to increase the starch yield and to reduce the steep time (Caransa *et al.*, 1988; Hassanean and Abdel-Wahed, 1986; Moheno-Perez *et al.*, 1999; Steinke and Johnson, 1991; Steinke *et al.*, 1991). These studies show small but significant improvements in the starch yield when high doses of enzyme were added during the steeping step. Most of these studies focused on using enzymes to provide increased starch yield in addition to the increase provided by sulfur dioxide. These studies were not aimed at removing or reducing the amount of SO_2 in the conventional corn wet milling process.

V. DEVELOPMENT OF THE ENZYMATIC CORN WET MILLING PROCESS

Most of the previous studies that showed improvements in starch yield with the addition of enzymes in the conventional corn wet milling process did not address adequately the specific enzymes responsible for those improvements. Initial work with the enzymatic corn wet milling process was done to reproduce the published results and to determine the specific enzymes responsible for improving starch yields. Several different enzymes and combinations of enzymes reported previously (Johnston and Singh, 2001) for their use in corn wet milling were tested using a precise 100-g laboratory conventional corn wet milling procedure (Eckhoff *et al.*, 1996). Results indicated no significant difference in starch yields when compared to the conventional procedure (0.2% SO_2 and 0.55% lactic acid) (Figure 1).

Due to the structure of the corn kernel (cutinized outer layer of the pericarp surrounding the corn kernel), the diffusion of water and chemicals inside the kernel is through a very specific pathway. Initial results with the use of enzymes during steeping (Figure 1) indicated that enzymes were not able to penetrate the kernels and break down the protein matrix surrounding starch particles. For enzymes to penetrate the corn kernel, it was necessary

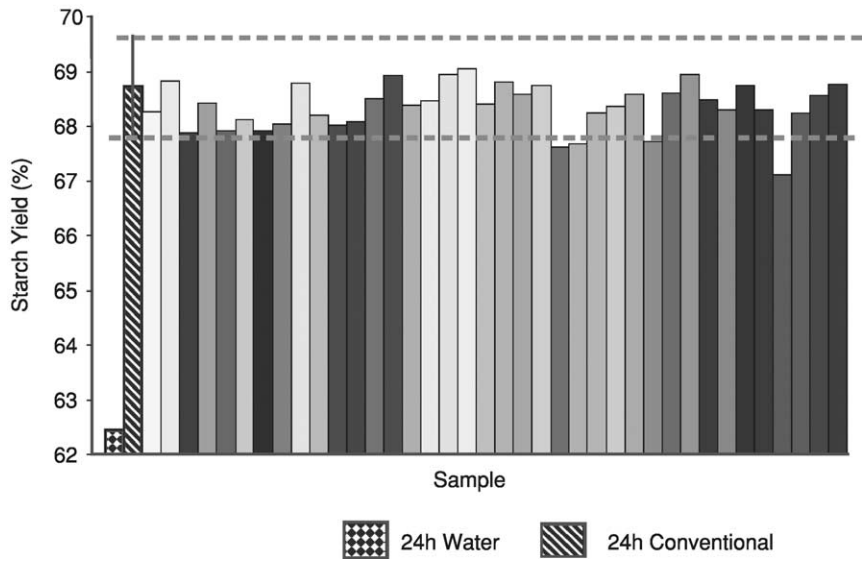

FIG. 1 Effect of different enzymes or combination of enzymes (cellulases, xylanases, cellobiases, β-glucanases, and proteases) on starch yield in the conventional corn wet milling process.

to do a size reduction to remove the diffusional barriers. However, any size reduction of kernels without adequate hydration could lead to germ damage. Germ is the most valuable component of the corn kernel. Germ damage in a corn wet milling plant has two disadvantages: (1) the value of germ is lost and (2) the oil released from the germ creates problems during the separation of other corn components.

Dailey (2000) studied the hydration of germ and endosperm in four different soaking solutions maintained at 52 °C (water; 0.55% SO_2; 0.5% lactic acid solution; and a mixture of 0.22% SO_2 and 0.5% lactic acid solution) and found that the type of soaking solution had no effect on the hydration rate. He reported that germ hydrates to more than 40% moisture content in approximately 3 hr irrespective of the soaking solution. When hydrated to approximately 40% moisture content, germ becomes rubbery and does not break when ground coarsely using degermination mills. Based on Dailey's work and initial results from the use of enzymes in the corn steeping process, a new enzymatic steeping procedure was developed in which kernels were initially soaked in water for hydration before size reduction (Johnston and Singh, 2001, 2003). After soaking, the kernels were cracked to disrupt the diffusional pathways and to allow the enzyme to penetrate the corn kernel. The ground corn slurry was incubated with the same enzymes and combinations of enzymes reported previously with intact kernels in the conventional corn wet milling steeping process. Also, with the new procedure, no SO_2 was added to the steep solution. The effects of enzyme addition were not apparent in the presence of SO_2 because SO_2 was giving beneficial effects. Results showed significant effects of enzyme additions on starch yields (Figure 2). With the enzymatic milling procedure, certain classes of enzymes gave starch yields comparable to those of the conventional wet-milled samples. A closer look at these enzymes showed that it was mainly the proteases giving the beneficial effects and, specifically, bromelain. Comparison of the enzymatic corn wet milling process with the conventional corn wet milling process showed that significantly higher amounts of starch (approximately 1.0%) and total gluten solids (approximately 3.5%) could be obtained with the enzymatic corn wet milling process (Table II). Further optimization of the bromelain concentration and incubation time showed that increases in enzyme concentration and incubation time improved starch yields significantly (Johnston and Singh, 2001).

Based on these results, several different commercial and experimental protease samples were obtained from enzyme companies and were tested for starch yield using the enzymatic corn wet milling process (Figure 3). Two commercial protease enzymes (enzymes A and C) gave starch yields comparable to the conventionally wet milled sample. Pasting properties, residual protein in starch, and surface characteristics of starch samples obtained from

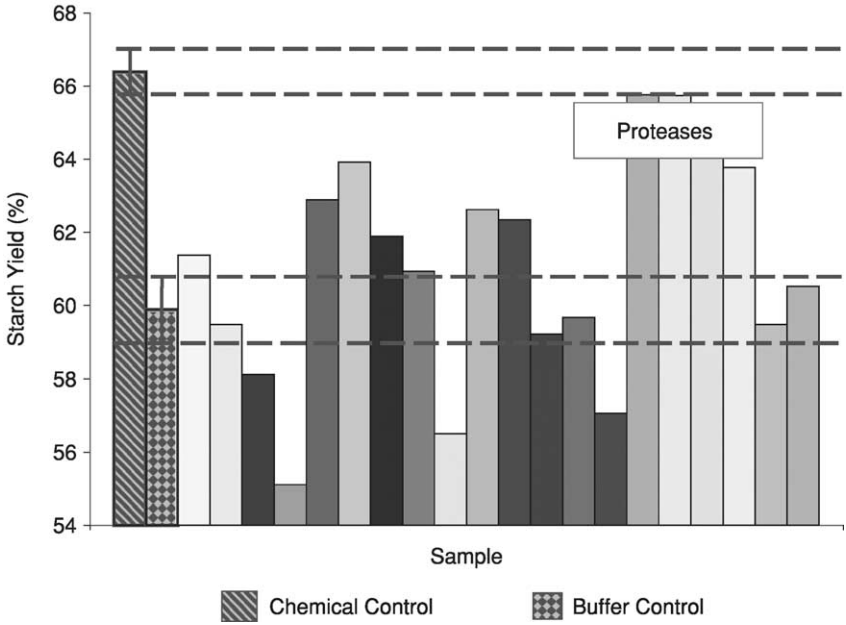

FIG. 2 Effect of different enzymes or combination of enzymes (cellulases, xylanases, cellobiases, β-glucanases, and proteases) on starch yield using the enzymatic corn wet milling procedure.

TABLE II
COMPARISON OF FRACTION YIELDS FROM THE ENZYMATIC AND CONVENTIONAL CORN WET MILLING PROCESS IN A 1-KG LABORATORY PROCEDURE

	Yields (%)		
Fractions	Enzymatic milling	Conventional milling	Difference in yields (%)
Soluble solids	0.12 B[a]	4.30 A	−4.18
Germ	6.15 B	6.73 A	−0.58
Fiber	9.83 B	10.20 A	−0.37
Starch	70.22 A	69.00 B	1.22
Total gluten	12.80 A	9.28 B	3.52
Total	99.13	99.51	

[a]Yields followed by the same letter within a row are not significantly different at a 95% confidence level.

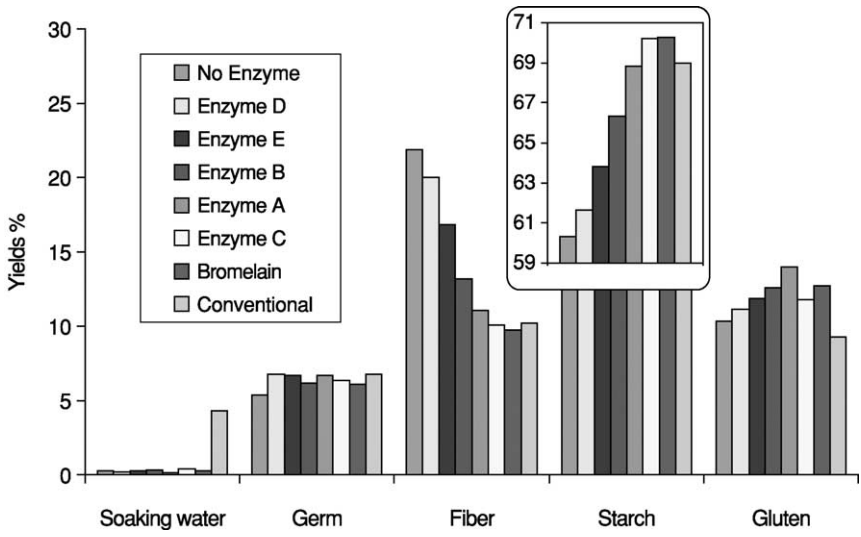

FIG. 3 Starch yields obtained with the use of different commercial protease enzymes and their comparison with the starch yield from a conventionally wet milled corn sample.

proteases were found to be comparable to the conventionally wet milled starch samples (Singh and Johnston, 2002).

VI. BENEFITS OF THE ENZYMATIC CORN WET MILLING PROCESS

The main benefit of the enzymatic corn wet milling process is that it is not a diffusion-limited process and does not require the use of SO_2. Therefore, no steeping is required and the total time required before conventional milling can be shortened to less than 6 hr. Conventional corn wet milling steeping is the most expensive, energy-intensive, and time-consuming unit operation in the corn wet milling process. The elimination of steeping and the reduction in time before milling could have a significant economic impact on the process economics of corn wet milling. Starch and protein yields from the enzymatic wet milling process are approximately 1.5 and 3.5% higher, respectively, when compared to starch and gluten yields from conventionally wet-milled samples. Increased starch yields with the enzymatic wet milling process come from reduction in the loss of starch in the fiber fraction and a cleaner separation of starch and protein fractions. Another potential benefit of the enzymatic wet milling process is the reduction in the amount of water

used in the corn wet milling process. These benefits could potentially reduce the capital cost of a new corn wet milling plant and reduce the operating cost of existing corn wet milling plants. Enzymatic corn wet milling technology potentially could allow existing plants to increase their milling capacity without increasing the steeping capacity of the plant.

VII. ISSUES WITH THE ENZYMATIC CORN WET MILLING PROCESS

The biggest challenge remaining for the enzymatic corn wet milling process is the cost of the enzymes. One of the commercial protease enzymes that works extremely well in the enzymatic corn wet milling process currently sells for approximately $15/lb. Preliminary economic analysis done with the enzymatic corn wet milling process shows that a 30-fold reduction in cost of the enzyme is required for the process to be economically comparable to the conventional corn wet milling process (Singh and Johnston, 2002). In this preliminary analysis, only the increase in prime product yield and removal of SO_2 was factored in. If all the potential benefits of enzymatic milling are factored in the analysis, such as elimination of steeping, steepwater evaporation, reduction in the amount of water used, and reduction in utilities, then only a 2- to 3-fold reduction is required in the cost of the enzyme. It is possible that several other commercial protease enzymes may be available that will provide similar results and are less expensive. Currently, the screening of commercial protease enzymes is ongoing.

Another issue that remains to be resolved with the enzymatic corn wet milling process is possible microbial problems in the soaking and milling unit operations. One of the roles of SO_2 in the conventional corn wet milling process is the control of microbial contamination. It is possible that if the SO_2 is eliminated entirely, as in the enzymatic milling process, some fungi or other microorganisms might grow and cause odor problems or the total microbial count in final starch might increase. It has been shown that a small amount of SO_2 (200–600 ppm) (enough to keep microbes under control), when used in conjunction with the protease enzymes, does not have any detrimental effect on the starch yield and starch quality (Johnston and Singh, 2001). Currently, research is underway at the Eastern Regional Research Center, Agricultural Research Service, United States Department of Agriculture and the University of Illinois to develop strategies for microbial control in the enzymatic corn wet milling process.

The protein obtained from the use of bromelain in the enzymatic corn wet milling process is different from that of the conventional corn wet milling process. Bromelain has a very wide spectrum of protease activities. Bromelain not only degrades the glutelin matrix that surrounds starch

particles, but also breaks down other classes of proteins in the corn kernels. Comparison of Sodium dodecyl sulfate–polyacrylaxide gel electrophoresis (SDS–PAGE) data for protein samples showed lower molecular weight peptides with bromelain when compared to the conventionally wet milled sample (Figure 4). Excessive breakdown of the protein fraction possibly could create recovery problems on the gluten belt filters (equipment used currently by the wet milling industry to recover protein). However, this problem is reduced greatly with the use of the commercial protease (mentioned previously) in the enzymatic corn wet milling process. Protein quality and profile, obtained with the commercial protease (using SDS–PAGE), is comparable to the protein quality of conventionally wet milled samples.

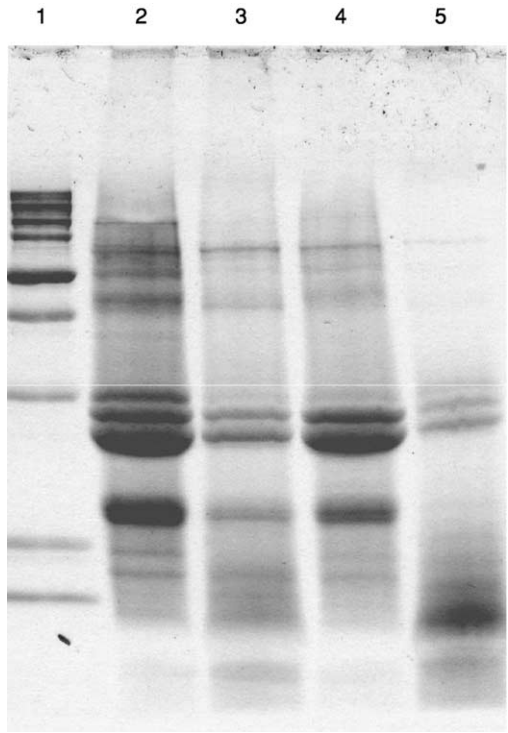

FIG. 4 SDS gel electrophoresis of insoluble gluten samples from laboratory corn wet milling. Lane 1: Molecular mass standards (250, 150, 100, 75, 50, 37, 25, 15, and 10 kDa). Lane 2: Enzymatic milling with commercial protease with added SO_2 and lactic acid. Lane 3: Enzymatic milling with commercial protease and no added SO_2. Lane 4: Conventional laboratory milling. Lane 5: Enzymatic milling using Bromelain and no added SO_2.

VIII. FUTURE OF THE ENZYMATIC CORN WET MILLING PROCESS

The enzymatic corn wet milling process has passed the proof of the concept stage. Scale-up studies (pilot plant and plant trials) are currently being planned with corn wet milling and enzyme companies. It is anticipated that this process will be adopted by corn refiners in the next 10 years. At the time of writing of this article, a commercial license for the enzymatic corn wet milling process is being negotiated.

Although the enzymatic corn wet milling process was developed for corn wet milling, it currently is being investigated for use in the dry grind ethanol process with additional modifications (Singh *et al*., 2003). In the dry grind process, the kernel is ground using a hammer mill. The dry granular material is mixed with water to form a slurry, which is cooked at approximately 160 °C using pressurized steam to break down the crystalline structure of starch granules. α-Amylase is added to break down starch polymers into short chain molecules, called dextrins, to form mash. The mash is held at an elevated temperature (~70 °C) for a short period of time, cooled to approximately 32 °C, and transferred into the fermentation vessel. Glucoamylase and yeast are added for simultaneous saccharification and fermentation. In the mash, glucoamylase breaks down the dextrins into sugars, such as glucose, while yeast ferments these sugars into ethanol. At the end of fermentation, the resulting beer is transferred to a holding tank called a beer well. From the beer well, the beer is transferred to a stripper/rectifier column to remove ethanol. Overflow from the stripper/rectifier column is an ethanol and water mixture, and underflow from the column is whole stillage (all nonfermentable components of corn, yeast, and water). The ethanol and water mixture is processed further through a distillation column and molecular sieves to remove remaining water from the ethanol. Whole stillage is centrifuged to produce thin stillage (water and soluble solids) and wet grains (suspended solids). Using an evaporator, thin stillage is concentrated into syrup and is mixed with the wet grains, which is dried to produce a coproduct with 12% moisture content. This coproduct is marketed as distiller dried grains with solubles (DDGS). The value of DDGS is lower relative to the coproduct value of germ, protein, and fiber from corn wet milling. Also, the traditional markets for DDGS utilization currently are near saturation in the United States. There is a need to reduce the volume of DDGS and diversify the markets for its utilization.

New process modifications have been developed for the conventional dry grind corn process such as quick germ (Singh and Eckhoff, 1996, 1997) and quick fiber processes (Singh *et al*., 1999b; Wahjudi *et al*., 2000). These

process modifications allow cost-effective removal of germ and pericarp fiber as coproducts at the beginning of the dry grind corn process. The quick germ process involves soaking kernels in water for a short period (12 hr) followed by a coarse grind and germ recovery by density separation using germ hydrocyclones. Maintaining the right density of the slurry is critical for effective germ separation. The quick fiber process requires increasing the density of the slurry further to allow pericarp fiber to float and using germ hydrocyclones to recover pericarp fiber (Singh and Eckhoff, 2001). Savings in capital costs can be realized by combining the quick germ and quick fiber processes. Benefits of the quick germ and quick fiber processes are (1) recovery of germ for corn germ oil and fiber for corn fiber oil; (2) removal of nonfermentable components (germ and fiber) from the fermenter, therefore, potentially increasing fermentation capacity of the process; and (3) removal of germ and fiber (Singh and Eckhoff, 1997; Singh *et al*., 1999; Taylor *et al*., 2001), which increases the protein content of the residual DDGS after fermentation.

Combining the quick germ and quick fiber processes for dry grind corn processing with the enzymatic corn wet milling process, followed by a process to recover cellular fiber, would allow dry grind ethanol producers to recover individual components of the corn kernel at a much lower capital cost when compared to a wet mill. Moreover, the unresolved issues observed with the enzymatic corn wet milling process are resolved when the enzymatic process is applied to dry grind. In the dry grind process, microbes are controlled by thermal sterilization and not SO_2 and, therefore, the microbial problem is not an issue. Dry grind ethanol plants are currently set up to recover soluble as well as insoluble proteins and, therefore, any breakdown of the corn proteins by the proteases is no longer a problem.

The commercial protease enzyme that worked well in the enzymatic corn wet milling process is currently used by the dry grind ethanol industry to increase the free amino nitrogen (food for yeast microorganisms) during the fermentation process. In the enzymatic dry grind ethanol process, the point of addition of this enzyme would change; otherwise, the dosage and its effect (on fermentation) should remain the same.

Enzymatic milling, when applied to dry grind, adds more value to the dry grind ethanol process, reduces the volume, and increases the protein content of DDGS. Singh *et al*. (2003) reported results from enzymatic milling applied to dry grind and showed that the protein content of DDGS increased to about 58% and that the volume of DDGS was reduced by more than 60%. It is very likely that enzymatic milling will be adopted by the dry grind ethanol industry prior to it being adopted by the wet milling industry.

ACKNOWLEDGMENTS

This material is based on work supported partially by the Cooperative State Research, Education, and Extension Services, U.S. Department of Agriculture, under Agreement No. 00-52104-9703 and by a grant from Corn Refiners Association, Inc., Washington, DC.

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PRESENT AND FUTURE IN PROCESS CONTROL AND OPTIMIZATION OF OSMOTIC DEHYDRATION

FROM UNIT OPERATION TO INNOVATIVE COMBINED PROCESS: AN OVERVIEW

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ADVANCES IN FOOD AND NUTRITION RESEARCH VOL 48
ISSN: 1043-4526

I. INTRODUCTION

Consumer demand has increased for processed products that keep more of their original characteristics. Translated into industrial terms, this requires the development of operations that minimize the adverse effects of processing. Conventional and new food processing techniques should enhance the nutritional, hygienic, and sensory quality of food products; improve the processing characteristics of raw materials and semifinished products; increase the variety of products; and take into account the economic and environmental aspects of food processing. Traditional techniques such as chilling, freezing, convective drying, pasteurization, and sterilization are the major processes employed for food preservation. However, there is a vast literature that refers to the deterioration in sensory quality, to vitamins, microelements, and aroma losses, and to oxidation and so on due to a severe treatment or one not suitable for the nutritional characteristics of a certain product. Every type of treatment should have as its goal the preservation of the sensory characteristics that are an important aspect of the processed food and of the nutritional elements associated with it. It is common knowledge that, today, not all the technological preserving processes are adequate enough to reach this objective.

Because the aforementioned points are becoming key aspects in food processing, there has been an increasing interest in osmotic dehydration mainly, but not only, for fruit and vegetable processing. In fact, since the early 1990s, significant developments have taken place to perfect this process as a cost-effective drying unit operation, either free standing or combined with other preservation processes. The question that arises is how can an osmotic step, such a simple and old practice, reproposed by Ponting *et al.* (1966), help in such a complex matter as the quality improvement of processed food? The reason for this renewed interest is the high versatility of the process, due mainly to the twofold transformation of the food item, that could be achieved.

The process involves placing the solid food (whole or in pieces) into solutions of high sugar or salt concentration. Le Maguer (1988), Raoult-Wack (1994), Fito and Chiralt (1997), Behsnilian and Spiess (1998), Spiess and Behsnilian (1998), Lazarides *et al.* (1999), and Torreggiani and Bertolo (2002) have reviewed the basic principles, modeling and control, and specific applications of osmotic dehydration on fruit and vegetables. Additionally, the most recent research advances in this field can be obtained from the European-founded network on "osmotic treatments" (FAIR, 1998).

It is well known that when solid food is immersed in a hypertonic solution, a driving force for the diffusion of water from the food into the solution is set up because the food cellular surface structure acts as a

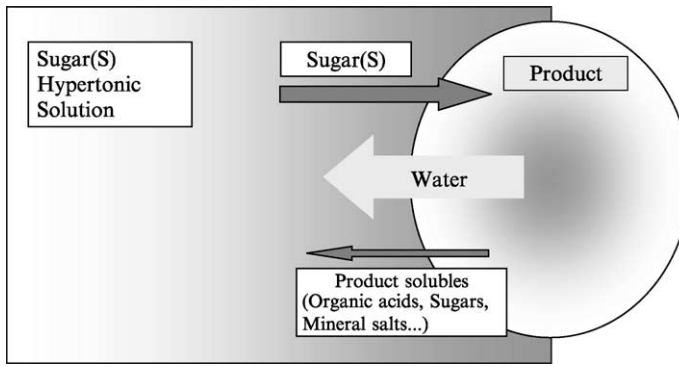

FIG. 1 Mass transport phenomena during the osmotic process.

semipermeable membrane (Figure 1). The diffusion of water is accompanied by the simultaneous counterdiffusion of solute from the osmotic solution into the food. As long as the tissue membranes are intact, osmosis will be the mechanism controlling any transfer phenomena initiated by concentration differences, with the plasma membrane as the major resistance to mass transfer (Le Maguer and Yao, 1995). Because the membrane responsible for osmotic transport is not perfectly selective, other solutes (sugar, organic acids, minerals, salts, etc.) present in the food are also leached into the osmotic solution. Although quantitatively negligible, solute leakage may be essential as far as sensory and nutritional qualities are concerned. Some of the osmotic syrup may not migrate into the cell actively, but simply penetrate into the intercellular spaces. This impregnation effect may be important, and the term "dewatering—impregnation—soaking in concentrated solutions" (DIS) instead of "osmotic dehydration" has been proposed by Raoult-Wack and Guilbert (1990).

The main unique feature of osmotic dehydration, compared to other dehydration processes, is the penetration of solutes into the food material. Through a calculated incorporation of specific solutes into the food system, it is possible, to a certain extent, to change nutritional, functional, and sensory properties, making it more "suitable" to processing by

- Adjusting the physical–chemical composition of food by reducing water content or adding water activity-lowering agents.
- Incorporating ingredients or additives with antioxidant, or other preservative properties, into the food.
- Adding solutes of nutritional or sensory interest.
- Providing a larger range of food consistency.

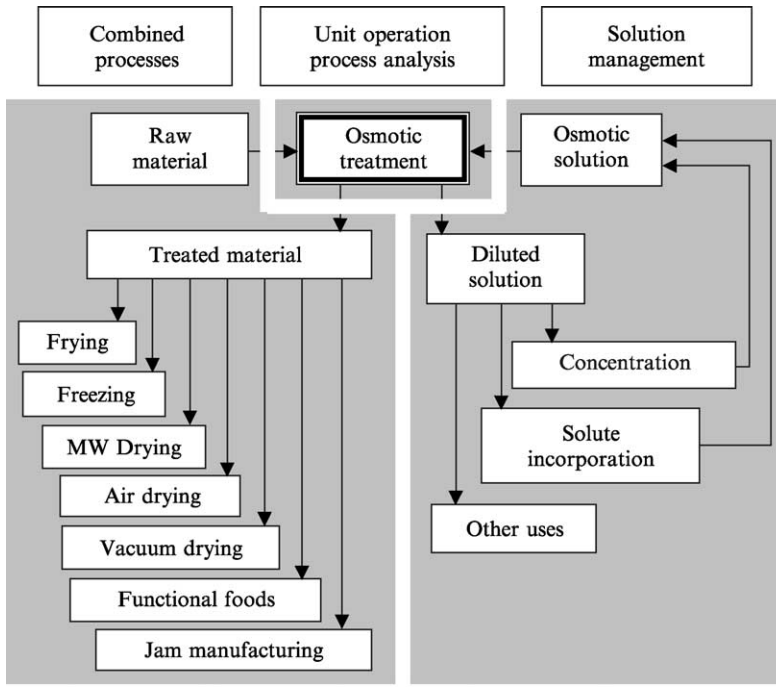

FIG. 2 Key research areas.

This direct formulation (Torreggiani, 1993; Torreggiani *et al.*, 1999c), together with a partial dehydration, is the distinctive aspect of the process and the way to develop a new product. There is also an economic interest in osmotic treatments, which focuses on reduced energy consumption for water removal without phase change, as compared to convective drying, and the possible reduction of the refrigeration load by partial concentration prior to freezing of fruit and vegetables.

There is already much practical experience available on the osmotic treatment itself. To fulfill consumer, industrial, and environmental expectations, however, some problems remain to be solved. Osmotic treatments have been applied frequently as a low-cost processing method neglecting process optimization, but the current interest in this technique and the development of industrial applications on a large scale demand controlled processes. For successful process control and optimization, efforts have to be made in the following key areas (Figure 2).

- Development of predictive models through better understanding of the mechanisms of mass transport responsible for the water removal and

solute uptake, and the relationships among osmotic process variables and modifications achieved in the material.
- Prediction of the behavior of osmotically modified materials during further processing and storage.
- Response to environmental and economic questions for the management of osmotic solutions.

Scientific knowledge in these key areas was improved through the work of a concerted action, organized within the framework of the fourth EU-Framework program. In this action, 15 research centers and universities of 11 European counties, Israel, Poland, and Canada participated, and the project was funded by the Directorate General XII of the Commission of European Communities under Research Grant FAIR-CT96-1118.

The state of the art and the progress in the aforementioned key areas, specifically referring to fruit and vegetables, are discussed and evaluated in this review in the light of industrial, environmental, and consumer needs. There is just a hint on osmotic treatments of fish and meat products.

II. UNIT OPERATION/PROCESS ANALYSIS

A. PROCESS VARIABLES

As the name of the process indicates, osmosis is the mechanism responsible for high water losses with reduced solute uptake, at least as long as the tissue membranes are intact. The rate of water removal depends on many factors, such as the concentration and temperature of osmotic solution, contact time, the level of agitation in the solution, the size and shape of the food, the solution-to-food ratio, and the vacuum level, if applied. A number of publications have described the influence of the main processing variables on mass transfer and on product quality (Lazarides *et al.*, 1997; Panagiotou *et al.*, 1998; Rastogi and Raghavarao, 1997; Rastogi *et al.*, 1997, 2000a). However, all this previous knowledge has to be reviewed under a new light of complexity. First of all, the parameters for the cellular properties of the material (e.g., diffusivity, tortuosity, and porosity) have to be taken into account, in addition to the properties of the solution (e.g., viscosity, diffusivity, and density) and processing conditions (e.g., temperature and shape of the material). In fact, depending on the tissue and the operating conditions, such as temperature and pressure, diffusion, convection, and flux interactions may occur at the same time and contribute to the complexity of the process. Furthermore, modification in composition and structural changes (shrinkage, porosity reduction, cell collapse), taking place in the food material during osmotic treatment, modify the heat and mass transfer

behavior in the tissue and must be considered. New concepts of the cellular level approach start from previously proven findings.

- Independently from the kind of raw material, the dewatering effect is always greater than the penetration of sugars into the plant tissue as long as the membrane is intact.
- Rates of water loss and solid gain reach their highest values at the beginning and drop drastically within the first hour to almost level off within 3 h of dehydration.
- Temperature has the largest effect on moisture and solute diffusivity, as confirmed by Kayamak-Ertekin and Sultanğlu (2000) on apple ring slices. Tissue damage due to too high a temperature causes a dramatic decrease in dehydration efficiency through increased solute and decreased moisture diffusivities.
- Increased concentrations give increased moisture and decreased solute diffusivities. Dehydration efficiency (water loss/solid gain) increases with concentration but decreases or remains constant with temperature.
- Process conditions have a dramatic impact on process "efficiency." Water loss/sugar gain ratios for different process conditions may differ by up to 120% or more.
- The larger the solute molecular size, the higher the water loss and the lower the sugar uptake under fixed process conditions. Using the right size of osmotic solute, satisfactory moisture diffusivities, with nearly zero net solute uptake, can be obtained.
- High molecular weight solutes are the most effective in forming a dense solute barrier layer at the surface of the product, thus enhancing the dewatering effect during soaking in the concentrated solution (Raoult-Wack *et al.*, 1991). Formation of the barrier layer promoted by high molecular weight solutes and/or high solute content could also be useful in reducing loss of natural fruit solutes.
- By increasing the surface area in contact with the solution, water removal and solid gain are enhanced, as confirmed by Van Nieuwenhuijzen *et al.* (2001) on apple cylindrical slices.
- Agitation of the solution enhances the water loss/solid gain ratio, especially during the first hour of treatment; the intensity of motion does not have a marked effect on the rate of mass exchange. In any case, the movement should be gentle to avoid mechanical damage to the food.
- Mixing of sucrose and salt in different proportions may be used for both plant and animal tissue treatments to reduce impregnation and to obtain higher water loss/solid gain ratios than those obtainable using solutes in binary solution. The antagonistic effect between the two solutes on product dehydration and salt gain was confirmed on apple sticks by Sacchetti

et al. (2001) and on paprika disks by Ade-Omowaye *et al.* (2002a). A higher dependency of water and solid diffusion coefficients on the sodium chloride concentration could be explained by the osmotic pressure variation linked to the molecular weight of the osmotic agent. The presence of a high level of sugar in the osmotio-dehydrated product can reduce the saltiness threshold; the presence of salt also has an enhancing effect on sucrose sweetness. Gekas *et al.* (1998) analyzed mass transfer properties of solutions relevant for osmotic processing of foods, whereas Sereno *et al.* (2001) reviewed models to correlate and predict water activity in aqueous solutions of single and multiple solutes, including electrolytes.

B. NATURE OF PLANT MATERIAL

The nature of the plant material subjected to osmotic dehydration is the key point for both modeling and optimizing the osmosis in itself and as a pretreatment to further processing. The same osmotic medium, applied to different raw materials, under identical process conditions causes substantially different rates of dehydration and solute uptake. Data on these findings were reviewed previously (Lazarides *et al.*, 1999; Torreggiani, 1995) and have been confirmed by recent research.

During osmotic dehydration of apple, pumpkin, and carrot in sugar solution at 30 °C, the rate of water loss was 5–10 times higher than the rate of solid gain and depended on advancement of the dewatering process (Kowalska and Lenart, 2001). Under the same dewatering conditions, pumpkin and carrot reached smaller water contents than apple (Figure 3).

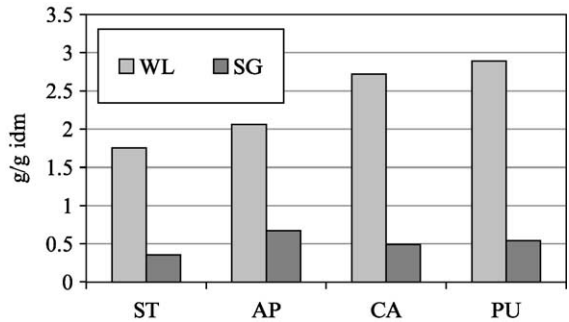

FIG. 3 Water loss (WL) and solid gain (SG) expressed on initial dry matter (idm) of strawberry (ST) slices (Brambilla *et al.*, 2000) and apple (AP), carrot (CA), and pumpkin (PU) cubes (Kowalska and Lenart, 2001) after 60 min osmotic dehydration in a 60% (w/w) sucrose solution at 30 °C at atmospheric pressure.

Structural differences may explain the quantitatively different behavior; apple has a much more open structure, which facilitates the penetration of osmoactive substances. These data confirm previous results obtained for apple and potato (Lazarides *et al*., 1997) intracellular volume is bigger in potato than in apple, and a dramatically higher (by an order of magnitude) intercellular porosity (25% for apple and 2–5% or even less for potato) allows for the substantial transport of solutes into the intercellular spaces. Comparing different fruits (apple, strawberry, and mango) subjected to osmotic dehydration in sucrose, solute gain in apple is faster when the osmotic solution concentration increases and is faster in strawberry and mango when it decreases (Lazarides *et al*., 1997; Talens *et al*., 2000, 2001). Furthermore, highly concentrated sugar solutions seem to limit the leaching of strawberry internal solids (Talens *et al*., 2000).

Further evidence was provided by Mavroudis *et al*. (1998) on the importance of initial structural differences within apple parenchymatic flesh on mass transfer rates during osmotic processing. The shrinkage phenomena, encountered in the fruit tissue of apple undergoing osmotic processing, was also studied by the same authors. In both the apple varieties analyzed (Kim and Granny Smith), two structures were detected. The inner parenchymatic tissue has a higher bulk density than the outer; this fact is linked to differences in interconnectivity of intercellular spaces and cell morphology. The significance of the initial structure on the kinetics of osmotic processing has been demonstrated, at least between 5 and 40 °C processing temperature. In fact, solution penetration into the pores takes place more in the inner than in the outer parenchyma, thus lowering water loss and contributing to the higher solid gain rates in the inner specimens. Furthermore, a strong linear relationship between volume changes and water removal was found in osmotic dehydration, similar to findings in air drying. In osmotic processing, the bulk density depends on the initial structure, variety, and drying conditions in contrast with reported findings on air drying. The different bulk density behavior between osmotic and air drying could be attributed to solute uptake. Results obtained by Moreira and Sereno (2001) on apple cylinders treated with osmotic solutions suggest that volumetric shrinkage is essentially due to water removal/solid gain and offer a simple way to predict such changes during industrial processing.

The importance of the initial cellular structure is demonstrated when optimum processing conditions have to be located. For diced green peppers, while temperature, agitation, and tissue to solution ratio were not important factors, time, salt, and sorbitol concentrations were highly significant (Ozaslan *et al*., 1998). Temperature was also significant for water loss but only during early stages of the process. The importance of sorbitol is linked to its capability to hinder the entrance of excessive salt into the product.

Changing vegetable tissue changes the factors mainly influencing solid–liquid exchanges; for cauliflower the factors were temperature and salt concentration and for apple the factors were temperature and sugar concentration (Lazarides *et al*., 1995; Vijayanand *et al*., 1995). When pieces of mango were subjected to osmotic dehydration in sucrose solution, the influence of temperature on solid–liquid exchanges was maximum while shape factor was minimum; furthermore, the temperature and syrup concentration showed opposite trends in terms of their influence on distribution coefficients (Sablani and Rahman Shafiur, 2003). The effect of vacuum pulse on fruit and vegetable composition changes depends strongly on the tissue characteristics (Gras *et al*., 2001; Salvatori *et al*., 1998b). In kiwi tissue, for example, the effect of vacuum pulse was relatively slight (Talens *et al*., 2003) compared with other fruits, such as apple (Barat *et al*., 2001), probably due to the scarce porosity of the tissue (Salvatori *et al*., 1998b). Nevertheless, solute gain was greater than that observed in similar process conditions for strawberry halves (Talens *et al*., 2000).

C. RAW MATERIAL TREATMENTS PRIOR OR DURING OSMOSIS

As underlined previously, the rate of transfer during osmotic dehydration takes place through the semipermeable membranes present in biological materials, usually in the range of 5 to 8 nm thickness. Because the membrane offers dominant resistance to the osmotic treatment, among the numerous factors influencing the rate of diffusion during the process, treatments of the material prior to or during osmosis could play a very important role. It is worth remarking that all the variables studied can only be manipulated over a limited range, outside of which they affect quality adversely, even though the rate of transfer may be enhanced. Blanching, freeze-thawing, sulfating, acidification, and high process temperatures, all affecting the integrity of natural tissues, improve water and solute diffusivities within the product, resulting in faster equilibrium in favor of higher solute uptake (Lazarides *et al*., 1999). A number of techniques have been tried to improve the mass transfer rate with a minimal alteration in quality. Due to consumer demand for minimally processed food products with high sensory and nutritional qualities, most of the techniques under study are nonthermal processes and include the application of ultrahigh hydrostatic pressure or high-intensity electrical field pulse (PFE) to the material prior to osmotic treatment (Figure 4) and ultrasound or partial vacuum during treatment (Figure 5).

Looking more deeply into these ongoing studies, for example, the application of ultrahigh hydrostatic pressure, leads to significant changes in the tissue architecture. This resulted in increased mass transfer during the osmotic dehydration of pineapple and potato slices due to the combined effect

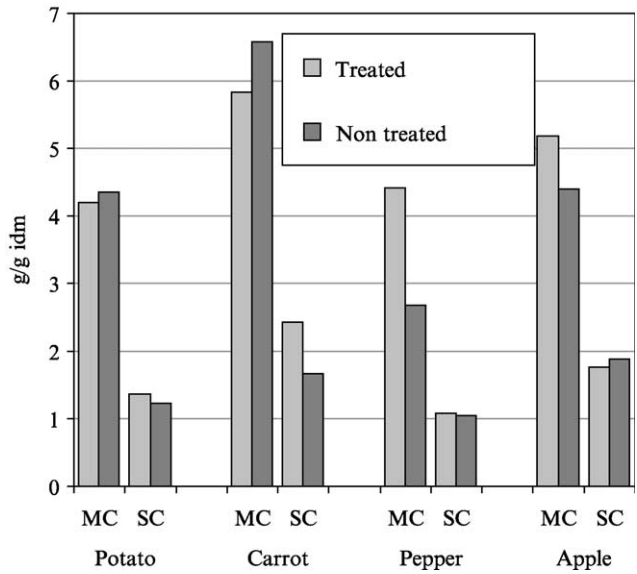

FIG. 4 Effects of varying raw material treatments prior to osmotic dehydration on moisture (MC) and solid (SC) content expressed on initial dry matter (idm). Potato slices, high hydrostatic pressure (Rastogi *et al*., 2001); carrot slices, PFE (Rastogi *et al*., 1999); bell pepper disks, PFE (Ade-Omowaye *et al*., 2002b); and apple slices, edible coatings (Lenart and Dabrowska, 1998).

of cell permeabilization due to osmotic stress (as the dehydration proceeds) and high pressure induced permeabilization (Rastogi and Niranjian, 1998; Rastogi *et al*., 2000b, 2001) (Figure 4). The increase in cell permeation index (Zp) values (or tissue softening or loss of texture) following high pressure treatment is due to the destruction of cell membranes and partial liberation of cell substances. Upon high pressure treatment, the polymethylesterase (PME) enzyme, which is bound to the cell wall, is liberated, not completely inactivated, and brought into close contact with its substrate, the methylated pectin. This causes deesterification not only during high pressure treatment, but also after the release of high pressure (standing time), which results in time-dependent softening of vegetable tissue (Basak and Ramaswamy, 1998).

Among the emerging nonthermal processes of interest as a pretreatment, pulsed electric field (PFE) could induce cell membrane permeabilization within a very short time (microsecond to millisecond range), leaving the product matrix largely unchanged, while positively affecting mass transfer rates in the subsequent processing of foods (Knorr *et al*., 2002). Accelerated mass transfer rates during osmotic dehydration of PFE pretreated carrots, apples, and red bell peppers were reported by Rastogi *et al*. (1999), Taiwo

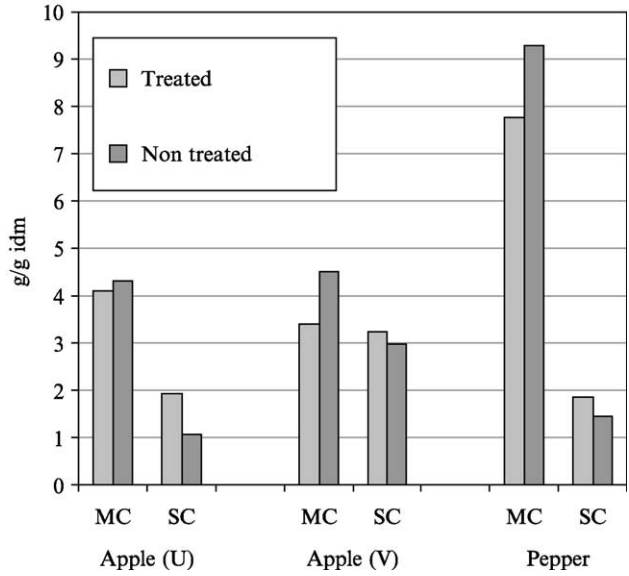

FIG. 5 Effects of varying raw material treatments during osmotic dehydration on moisture (MC) and solid (SC) content expressed on initial dry matter (idm). Apple cubes, ultrasound (U) (Simal *et al.*, 1998); apple slices, vacuum (V) (Salvatori *et al.*, 1998b); and bell pepper disks, high temperature (Ade-Omowaye *et al.*, 2002b).

et al. (2001), and Ade-Omowaye *et al.* (2002b), respectively (Figures 4 and 5). Effective diffusion coefficients of water and solute, determined using the Fickian diffusion model, increased exponentially with electric field strength up to 1.0 kV/cm. During PFE processing of cellular foods, attention needs to be given to the degree of disintegration of the initial tissue structure because of its impact on food quality and functionality. Studies have demonstrated that formation of a conductive membrane after PFE treatment is not an instantaneous process, suggesting that the development of pores within the cell membrane, after PFE treatment, is a dynamic process, i.e., time dependent (Angersbach *et al.*, 2002). A statement of the time interval after PFE pretreatment and the beginning of the subsequent process, such as osmotic dehydration, is important for meaningfully interpreting the contribution of PFE to mass transfer enhancement (Ade-Omowaye *et al.*, 2003). Combined PFE and osmotic dehydration may have potential as a processing step in the production of intermediate moisture foods, where minimal solute uptake is desired.

Another promising technique is ultrasound application during osmotic dehydration. Used on porous fruit such as apple cubes, it affects mass

transport, increasing both water losses and solute gain (Simal *et al.*, 1998) (Figure 5). It would be necessary to maintain the solution temperature at 70 °C, when using agitation, to achieve a similar solute gain to that obtained at 40 °C with sonication. Ultrasonic osmotic dehydration technology uses lower solution temperatures to obtain higher water loss and solute gain rates while preserving the natural flavor, color, and heat-sensitive nutritive components.

Application of vacuum during osmotic dehydration deserves a broader discussion as, through the adequate control of the process parameters, it may be used as a tool not only to improve mass transfer, but also to develop engineered products (Fito *et al.*, 2000, 2001a,b). This latter aspect is dealt with later on in Section III.E. The vacuum impregnation (VI) operation consists of immersing the porous product in the solution, applying vaccum pressure (p_1) for a short period (t_1) in order to promote the outflow of the internal gas, and then restoring the atmospheric pressure (p_2) for period t_2 in which the hydrodynamic inflow of the external solution in the pores is promoted. The amount of the external solution that has penetrated in the tissue, due to the action of the hydrodynamic mechanism (HDM), has been modeled as a function of the product effective porosity (ϵ_e), the applied compression ratio ($r \approx p_2/p_1$), and the sample volume deformations provoked by pressure changes (Fito, 1994; Fito *et al.*, 1996; Rastogi and Raghavarao, 1996). It has been demonstrated that the VI of porous fruits is greatly effective in promoting mass transfer kinetics in the tissue (Salvatori *et al.*, 1998b) (Figure 5). The greater the product porosity, the more effectively the action of hydrodynamic mechanisms promotes the desired composition changes in short time operations, without any temperature requirements (Chiralt *et al.*, 1999). Although VI promotes solute gains by diffusion through the apple intercellular spaces, when the solution viscosity increases, a delay in this phenomenon was observed (Martìnez-Monzò *et al.*, 1998a). In addition to promoting diffusional mechanisms in the pores, VI brings with it a different structural development of the tissue through the osmotic process, thus affecting the tissue response to mass transport (Barat *et al.*, 1998a, 2001). Microstructure observation of osmodehydrated tissue, at different times of the osmotic equilibration process, shows that two main periods can be distinguished in terms of structural changes. In the first period (24–48 hr depending on osmotic conditions) the prevailing water loss leads to the shrinkage of plasmalemma together with the cell walls (in OD, osmotic dehydration at atmospheric pressure) or the separation of both cell elements (in PVOD, pulsed vacuum osmotic dehydration) in line with the cell cavity filling up with the external solution. In both cases the mechanical energy accumulated in the deformed cell wall matrix was released throughout the second period, producing the volume recovery of cell

walls in both kinds of treatments. Mechanical relaxation promotes suction of the external osmotic solution. However, irreversible deformations in a practical timescale can be appreciated specially for a high osmotic syrup concentration without previous vacuum impregnation.

As well as the aforementioned pretreatments, another technique exists that has been developed to increase the low selectivity of cell membranes: the application of more selective barriers such as edible coatings. Edible coatings are applied to many food products for a variety of aesthetic and protective purposes (Krochta *et al*., 1997). Coating the food to be dehydrated with an artificial barrier on the surface may efficiently hinder the penetration of solute inside the food, not affecting the rate of water removal (Guilbert *et al*., 1995; Ishikawa and Nara, 1993). Water loss during osmotic dehydration of coated apple slices was found to be dependent on the type and thickness of polysaccharides coating, and solid gain was either reduced or remained similar for coated and uncoated apples (Lenart and Dabrowska, 1997) (Figure 4). A low methylated pectin solution of 2% concentration and a 10-min drying time were optimal for coating apple slices before osmotic dehydration considering the highest water loss and the lowest dry matter gain (Lenart and Dabrowska, 1998). The use of edible chitosan films has been proposed as a barrier for solid gain in papaya slabs subjected to osmotic dehydration (Jamet and Larios, 2001). Results indicated that chitosan covers reduced solid gain and increased water loss significantly, which led to products more like the fresh counterparts. The efficiency of the process can be increased up to 10 times through an increase of process temperature and a decrease of the number of chitosan covers. When fruits or vegetables have to retain their skin throughout processing, specific pretreatments have to be devised. A good example is when the osmotic treatment is applied to tomatoes. Physical skin-puncturing treatments, to be followed by osmotic dehydration of whole tomatoes, was proposed to produce high-quality intermediate moisture (IM) tomatoes (Shi *et al*., 1997). This type of IM tomatoes can be diced and used as an ingredient by the food service in preparing tomato-based convenient food items such as pizza and pita bread. Physical skin treatments led to higher water removal than chemical ones and did not create waste material. To obtain the best results, the number of pin holes must be more than 80 holes/cm^2.

D. MODELING

The lack of adequate predictive models is an obstacle to industrial applications. The poor understanding of the fundamentals of mass transfer in biological cellular structures—a problem common even to other areas of food processing dealing with transport phenomena—is the main hindrance

of advance in this field. Existing engineering or mathematical models, reviewed by Le Maguer and Yao (1995), are not discussed here in detail, whereas structural or mechanistic ones are analyzed. The aforementioned authors classified the models according to two main approaches, i.e., macroscopic and microscopic. The first approach assumes that the tissue is homogeneous, and modeling is based on concepts of diffusion and irreversible thermodynamics. These models try to describe mass transport in mathematical terms, ignoring the mechanisms taking place at the cellular level, and are generally useful in the individual case. However, both driving force and cellular structure are today recognized as two of the major factors in the understanding and control of mass transfer phenomena occurring in food processing in general and in osmotic processing in particular (Gekas, 2001; Gekas *et al*., 2002; Le Maguer *et al*., 2002; Spiess *et al*., 2002). Details of the food structure at a cellular level determine the pathways of both water and nutrient transport, so affecting rates of mass transfer from or to the cells, and influencing the final quality of stored or processed foods.

The microscopic approach looks at heterogeneous properties of the tissue and has been developed for plant material on the basis of plant physiology studies on the effect of osmosis on water balance and transport in growing plants.

Plant tissues are complex systems consisting of a solid matrix, intercellular space, extracellular space, and occluded gas. There are three generally accepted pathways of mass transfer in plant material: apoplasmatic transport (outside the cell membrane), symplasmatic transport (through small channels between two neighboring cells in the intracellular space), and transmembrane transport (between the cell and the free space comprising the intercellular space and cell wall) (Le Maguer and Yao, 1995) (Figure 6).

During the process, the solute diffuses into the intercellular space and, depending on the characteristics of the solute, it may pass through the membrane and enter the intracellular space. Differences in chemical potentials of water and solutes in the system result in fluxes of several components of the material and solution; water drain and solute uptake are the two main simultaneous flows. Together with the changes in chemical composition of the food material, structural changes such as shrinkage, porosity reduction, and cell collapse take place and influence mass transfer behavior in the tissue.

Le Maguer and Yao (1995) presented a physical model of a plant storage tissue based on its cellular structure. The mathematical equivalent of this model was solved using a finite element-based computer method and incorporated shrinkage and different boundary conditions. The concept of volume average was used to express the concentration and absolute pressure in the intracellular volume, which is discontinuous in the tissue, as a

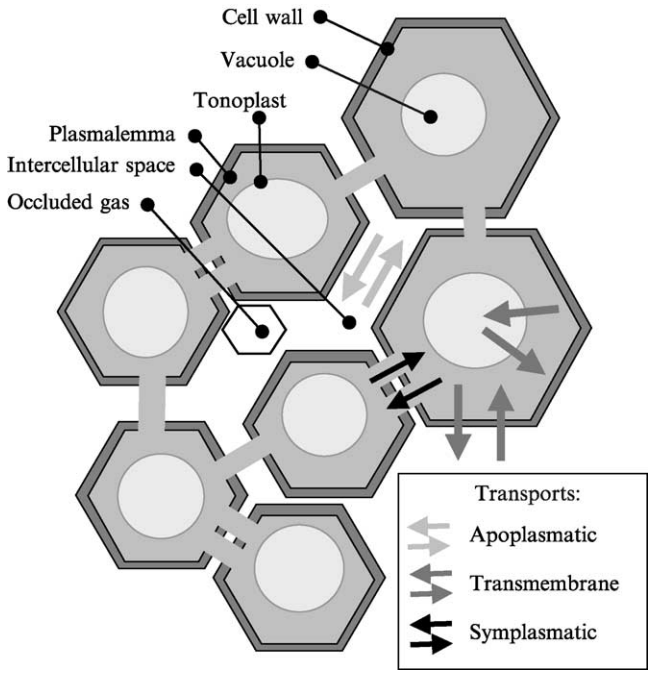

FIG. 6 Transport mechanisms inside plant tissues.

continuous function in the model. Simulations based on this model showed that the solute gradient is controlled mainly by the sharpening effect of the bulk flow on the concentration, with bulk flow removing about 90% of the water from the tissue and washing back about 60% of the solute that has diffused in.

However, many other tissue parameters, such as membrane permeability, porosity, and cell size, are required for the development of models regarding all the mechanisms acting on the various components (intercellular and extracellular spaces, vacuole, etc.). For most tissues subjected to osmotic treatment, lack of data required for this modeling approach represents a hindrance to progress.

The function, the mechanism of transport of the biological membrane, and its fate during various processing conditions are most important for the food process engineer. Within this frame, the impact of three disaccharides—sucrose, maltose, and trehalose—on cellular shrinkage and cell viability, which is undergone by onion epidermis and strawberry cortex tissue during osmotic treatment, was investigated using a fluorescence method through a

confocal scanning laser microscope (CSLM) (Ferrando and Spiess, 2001). Differences in cellular response to osmotic stress were observed between these two plant tissues of distinct origin and morphology. The different sugars, used as osmotic agents, influenced the cellular shrinkage behavior of onion epidermis significantly, yet in strawberry cortex tissue, cellular shrinkage was not affected by the nature of the osmotic agent. The sugar concentration, however, had a significant effect on membrane integrity. Maltose and trehalose had a protective effect on the plasma membrane of the onion epidermis cell, maintaining its properties as a barrier, as indicated by these sugars significantly lower effective water diffusivity in comparison with sucrose. Trehalose played a main role during rehydration of the onion epidermis, leading to the highest swelling rate. However, parenchymatic cells of strawberry tissue were not susceptible to any protective effect, whatever the kind of disaccharides employed.

The proportion of intact, damaged, and ruptured (nonintact) cells (Zp) due to osmotic stress during the osmotic treatment of potato were monitored using electrophysical measurements based on electrical impedance analysis (Rastogi *et al.*, 2000a). Osmotic stress on potato cell culture made cell membranes shrink, thereby damaging the cells. The proportion of intact cells reduced rapidly at the beginning but the rate slowed down toward the end of the process. The equilibrium cell disintegration index (Zp_{eq}) value increased exponentially with the concentration of osmotic pressure. In the case of potato slices and tissue, there is a critical osmotic pressure above which the rate of water removal increases. As the dehydration front moves toward the center of the material, disintegration of cell membranes occurs, which results in diffusion through these types of material: diffusion of water from the intact core of material to the transition layer (dehydration front), diffusion of water at the transition layer, and diffusion of water through a layer where the cells have been damaged by the osmotic stress to the surrounding medium.

Analyzing vegetables at the cellular level, another important variable that must be considered, so as to understand solid–liquid exchanges during osmotic dehydration is cell viability. The way water is removed from the tissue affects strongly its respiratory activity (Lewicki *et al.*, 2001). Respiration of apple tissue decreases with increasing dry matter content. Freeze-drying affects less respiration pathways than convective drying, whereas osmotic dewatering affects respiration in a different way. The diffusion of sugars into tissue increases the pool of substrates for respiratory pathways, but, at the same time, by increasing the concentration of solutes, causes structural changes in membranes and cell organization, as well as reduced availability of water for biological reactions. At the beginning of osmotic dewatering, the first process prevails over the second.

Inside the plant tissue, under osmosis, different parenchimatic structures can be found together with a concentration profile, both of which should be taken into account in process modeling. Concentration profiles in apple tissue, during osmotic dehydration, were studied and compared with simultaneous structural changes (Albors *et al*., 1998; Salvatori *et al*., 1997, 1998a, 1999). Establishment of a fully developed concentration profile required a longer time than that usually employed in industrial processes. The occurrence of an "advancing disturbance front" (ADF) was proposed and can describe the kinetics of concentration changes in samples during osmotic dehydration. This model describes mass transfer in terms of a characteristic dimensionless parameter of the material (K), a zone of broken cells near the interface (z_0), a constant advancing rate of the ADF (V_f), and a quickly perturbed distance near the interface (d_f) describing the faster transport mechanisms occurring near the interface.

In order to model simultaneous mass transfer and structural changes, Barat *et al*. (1999, 2001) analyzed the sample volume changes of apple slices throughout the osmotic process both at atmospheric pressure and by applying a vacuum pulse at the beginning of the process. Sample volume changes in porous fruits can be explained in terms of the fruit liquid phase (LP) volume decrease, in line with fluxes of water and soluble solids, and of changes in the volume of sample gas phase (GP), associated with the cell matrix shrinkage, which can contribute greatly to the change in total volume. Even when a great part of the initial gas is removed by applying a vacuum pulse, the GP plays an important role in sample volume development, as pressure changes provoke gas and cell matrix compression, mainly from a critical value of the viscosity of the external solution. Magnetic resonance imaging (MRI) has been put forward as a useful tool in modeling mass transfer and structural changes, as it can uniquely reveal important parameters related to the environment of water molecules in the food. The specific aim of a study on strawberry tissue during drying by osmotic dehydration, air drying, and their combination was to measure one-dimensional maps of the magnetic resonance (MR) parameters T_2 and M_0 (Evans *et al*., 2002). The T_2 parameter (water proton spin–spin relaxation time) gives an indication of the molecular mobility of the water and generally increases with increased mobility; proton density (M_0) is determined from the magnitude of the MR signal and is a quantitative measure of water density. The one-dimensional MR method, described in this study, also enables the evaluation of tissue shrinkage with good temporal and spatial resolution. Results indicated that during a relatively short osmotic pretreatment (1–2 hr), water diffusivity was fast enough to replenish water lost at the surface, thereby maintaining molecular mobility throughout the slice. A classic Fickian modeling approach may be applicable for the osmotic

dehydration of strawberry slices over short periods of time. Further studies are required to investigate the effects of longer osmotic dehydration protocols on T_2 values in strawberry tissues.

III. COMBINED PROCESSES

As mentioned previously, osmotic treatments have regained interest as a prestep to further processing and are applied as a tool to obtain intermediate and end products of improved quality by conventional and new processes (Torreggiani and Bertolo, 1999). Osmotically treated materials may be processed into finished products by applying varying stabilizing operations, such as mild heat treatment, drying, freezing, and other techniques. The optimal balance between water removal and solute uptake is determined in each case by the properties of the raw material, subsequent processing steps, and the expected improvement of the product. Knowledge of the changes occurring during the osmotic step should enable a better design of combined preservation procedures to maintain quality characteristics, such as color and texture, and nutritional properties. What must not be forgotten for a successful industrial implementation of combined processes is the need for specifically designed items of equipment, particularly where a high level of dehydration is necessary. A paper by two of the most active research groups in this area, the CIRAD, both in Montpellier and in Réunion, and the ENSIA in Montpellier, defined the functions required by users of osmotic dehydration equipment and presented 17 principles used to make foods come into contact with a concentrated solution (Marouzé *et al.*, 2001). This wide range of technical solutions, based on a variety of different principles, is currently available for the industrial implementation of osmotic processes. These solutions can be chosen according to the type and shape of the food to be treated, the required method of treatment, and the nature of the concentrated solution.

A. MINIMALLY PROCESSED FRUITS AND VEGETABLES

Osmotic dehydration, both at atmospheric pressure or preceded by the application of subatmospheric pressure for a short time, has been proposed in the production of minimally processed fruits and vegetables, which are convenient, ready-to-eat, high-moisture but ambient stable foods. The consumer prefers minimally processed foods, as these foods have appealing fresh-like characteristics and thus superior sensory quality. However, at the same time, these foods must be microbiologically safe and stable. These somewhat conflicting goals are achievable by the application of

advanced hurdle technology (Leistner, 2002). Application of the aforementioned technology in Latin America has created a new line of minimally processed, fresh-like fruits that, for several months, are microbiologically safe and stable at ambient temperature (Alzamora *et al.*, 1995; Lòpez-Malo *et al.*, 1994; Tapia *et al.*, 1996). The hurdles that proved suitable for this group of food products are a mild heat treatment (blanching), a slight reduction of water activity (a_w) and pH, and a moderate addition of preservatives (sorbate and sulfite) through an osmotic step. The blanching of fruits is important for microbial stability because even though vegetative microorganisms might survive this mild heat treatment, their number is reduced and thus only fewer and lower hurdles are essential. The number of surviving bacteria, yeasts, and molds decreases rapidly during ambient storage of the products, probably due to metabolic exhaustion, as they are not able to multiply in stable hurdle technology fruits. However, the added sulfite and sorbate deplete during storage of these fruits too, which is beneficial for the consumer but diminishes microbial stability. Therefore, a recontamination of the fruits during storage should be avoided (Leistner, 1995). Within this frame of risks, hazards, and consumer trends, predictive microbiology emerges as a powerful tool to quickly explore the microbiological impact of varying conditions within food formulation, processing, and/or distribution and retail conditions (Alzamora and Lòpez-Malo, 2002; Tapia and Welti-Chanes, 2002).

Moreno *et al.* (2000) analyzed the combined effect of two kinds of blanching (steam and microwave) and osmotic treatments (OD, atmospheric pressure, and PVOD, pulsed vacuum) treatments on some physical–chemical and quality parameters of minimally processed strawberries. Microstructural features, associated with treatments, as well as the microbial stability of the processed fruits, were also studied. Poliphenoloxidase (PPO), present in strawberry tissues, causes a loss of red color because of the deterioration of anthocyanin pigments (Markakis, 1974) and browning, linked to cellular disruption and access of oxygen (Cano *et al.*, 1997). Therefore, blanching treatments are recommended before minimally processing strawberries in order to preserve color during shelf life. The use of microwaves (MW) to reduce PPO activity in strawberry (Moreno *et al.*, 1998) and banana slices (Cano *et al.*, 1990) led to satisfactory results. Changes in the tissue, induced by steam or MW treatments, such as cell decompartmentation, led to a faster mass transfer rate, even by hydrodynamic mechanisms, in agreement with the results of Alzamora *et al.* (1997) on apple. Steam blanching promoted the highest texture reduction, especially in combined steam–OD and steam–PVOD treatments. OD and PVOD treatments alone only represent a 2–4% of force decay; the softness associated with loss of fruit turgor seems to be partially compensated with hardening due to the dehydration effect.

Steam-treated strawberries showed a degree of cell decompartmentation near the fruit skin, greater than MW-treated samples, at the same distance to the fruit surface. These observations agree with the major sucrose gain observed in steam–OD and steam–PVOD treatments. The steam–PVOD treatment was the most effective in a_w depression due to the highest sucrose gain during osmotic treatment. This also implied one of the highest losses of firmness and color changes, but these parameters maintained reasonable values. At the same time it induced the greatest microbial stability, probably by the reduction of the initial microbial count by thermal effect.

Not only is the mild heat treatment fundamental for microbial stability of minimally processed fruits, but the osmotic syrup concentration as well. In fact, concerning minimally processed kiwifruit slices, the concentration of the osmotic solution played a key role in the adhesion kinetic of *Metschnikowia pulcherrima* on the fruit surface (Gianotti *et al*., 2001). A high sucrose concentration prevented the formation of biofilms on the fruit surface, mainly due to a reduction of the mobility of the microorganisms, linked to the increase of solution viscosity. Furthermore, a high concentration of the osmotic medium slowed down the microbial growth during the storage of osmotically dehydrated kiwifruit slices.

Optimization of vacuum pulse osmotic treatment for minimally processed pineapple cylinders led to processed fruits, which exhibited a close likeness to fresh ones, without microbiological problems (Navarro and Corzo, 2001).

B. DRYING

Osmotic treatments have been studied mainly as a pretreatment to different drying operations, such as convection drying, freeze-drying, vacuum drying, and microwave drying. The combination osmosis–convective air drying is suggested frequently to produce fruit and vegetables with water activity values of 0.6–0.7, to reduce or even avoid sulfating, to stabilize plant pigments and flavor during processing and storage, and to reduce shrinkage (Torreggiani, 1995). The structural and functional properties of the osmotically treated product will depend on the changes in composition due to the impregnation and the impact of the process on the cell wall and middle lamella, as well as the degree of damage to the plasma membrane due to processing.

1. Drying techniques

a. Air. Early studies on the effect of osmotic dehydration and blanching, prior to conventional drying, on the rate of moisture transport have shown that the influence of these operations differs widely as the tissue

properties change from one commodity to another (Alzamora and Chirife, 1980; Saravacos and Charm, 1962; Vaccarezza and Chirife, 1975). Mazza (1983) observed that as the concentration of sucrose, used for dipping carrot cubes, was increased from 5 to 60%, the rate of moisture transport during air drying decreased due to the depression of water vapor pressure in the product by the dissolved sugar. This decrease was also due to the impairment of heat transfer and lowering of the diffusivity of water vapor within the product linked to the crystallization of sucrose during the air-drying process. Pineapple that had been osmodehydrated was found to have lower drying rates than fresh pineapple due to a higher initial solid content and/or to the action of solute on the water sorption behavior (Rahman and Lamb, 1991). Effective diffusivity of moisture transport during air drying decreased with the increase of solid gain due to the osmotic pretreatment. Islam and Flink (1982) concluded that the uptake of sugar and/or salt increased internal resistance to moisture movement in potato slices, and Karathanos *et al.* (1995) found that the effective moisture diffusivity of water (D_{eff}) decreased significantly for apples pretreated in concentrated sugar solutions mainly due to the lower porosity. These results were confirmed by Sankat *et al.* (1996) on air drying of pretreated banana slabs. Strawberry and apple air-drying behavior, after blanching and/or sugar impregnation, was examined by Alvarez *et al.* (1995) and by Nieto *et al.* (1998), respectively. The strong decrease in the moisture transport rate during the first falling rate period of drying was attributed to glucose uptake as well as volume shrinkage. Furthermore, sugar distribution in the cellular tissue appears to have a role in drying behavior. In fact D_{eff} values for blanched impregnated apples are lower than those corresponding to nonblanched impregnated ones at the same water activity (0.95 or 0.93) (Nieto *et al.*, 1998). There could be an absorption of the sugar by cellulose, pectic substances, and other polysaccharides of the cell wall. Perhaps the blanching treatment exposed and/or produced some reactive groups available for hydrogen bonding, increasing glucose adsorption in cell walls and consequently increasing the cell wall resistance to water flux. However, for strawberry, blanching pretreatment increased the D_{eff} and glucose dipping after blanching caused no additional effect (Alvarez *et al.*, 1995). This fact was attributed partially to modifications of the strawberry cell structure: disruption of membrane and degradation of the middle lamella and hemicellulosic polysaccharides, present in the cell wall, by heating and a very severe ultrastructural damage of the cell walls, resulting from the sugar impregnation step. Blanching might enhance D_{eff} due to elimination of the cell membranes resistance to water diffusion and a decrease in the resistance of the cell walls to water flux. Glucose dipping caused no additional consequences due to two counterbalancing effects: solute uptake, which increased water transport resistance, and the

significant reduction of cell wall resistance due to degradation. Thus, the effect of pretreatments on the drying rate depend very much on the kind of raw fruit, as confirmed by the results of Nieto *et al.* (2001) and Castañón *et al.* (2001a) on the kinetics of moisture transfer during air drying of blanched and/or osmotically dehydrated mango (Figure 7). Osmotic dehydration influenced the drying rate adversely; this effect increased as the glucose concentration of the impregnation solution increased and fruit water activity decreased (Nieto *et al.*, 2001). The air behavior of pretreated mango was ascribed, as for apple (Nieto *et al.*, 1998), to glucose uptake during the impregnation step, volume shrinking, low modification of the cell wall resistance to water flux, by pretreatments, and/or gelatinization of starch and denaturation of protein–carbohydrate mucilage. However, the drying time needed to reach a final moisture content of 0.5 g water/g dry matter was 50 to 75% lower in osmotically treated mango than the time needed for fresh mango (Castañòn *et al.*, 2001a). Sugar uptake and loss of water due to an osmotic pretreatment increase the internal resistance to moisture movement also in papaya slices, and the time needed to reach an equal water activity value was 50% lower as the initial a_w decreased from 0.99 to 0.97 (Castañòn *et al.*, 2001b). Even pineapple rings dehydrated osmotically needed a lower process time than fresh ones to reach the same final moisture content (Vélez-Ruiz *et al.*, 2001). The drying time was shortened by decreasing water activity of the fruits and by increasing air velocity and temperature.

Differences in behavior were observed by Tan *et al.* (2001) between pineapple and potato osmodehydrated for 3 hr in sucrose and in NaCl, respectively, at increasing concentrations (10, 20, and 30% NaCl and 30,

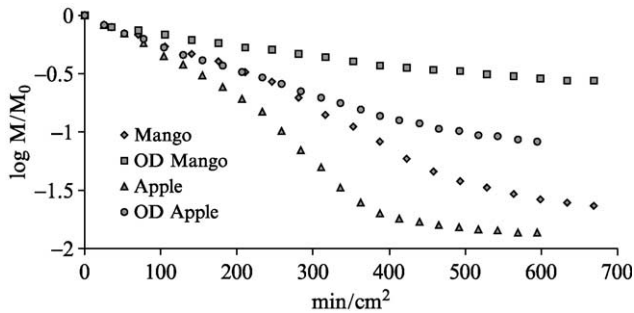

FIG. 7 Effect of 90-min osmotic dehydration (OD) in 40% (w/w) glucose solution at 25 °C at atmospheric pressure on drying rates (M/M_0: moisture content/initial moisture content) at 60 °C of infinite plate-shaped mango (Nieto *et al.*, 2001) and apple (Nieto *et al.*, 1998).

50, and 70% sucrose). The rate of drying of the osmodehydrated potato is consistently lower than that of the nonpretreated sample; this difference, at the beginning of the drying process, could be up to fourfold. However, for pineapple, the drying rates were rather similar in all cases, probably because of its natural high sugar content.

Campolongo (2002) found that 1-hr osmotic dipping in sucrose or sorbitol, instead of decreasing, enhanced moisture transfer during apricot cubes air drying, confirming once more the utmost importance of the raw material properties (Figure 8). The osmotic step, both in sucrose and in sorbitol, increased the initial drying rate of apricot cubes in the first (up to 2 kg water/kg dry solids) falling rate phase, probably due to the 60-min soaking loosening the surface cellular structure, which was already observed in strawberry tissue (Brambilla *et al.*, 2000). Apricot cubes osmodehydrated in 60% (w/w) sucrose solution showed a drying rate reduction below 2 kg water/kg dry solids when compared to nonpretreated ones. This could be a result of the reduction of tissue porosity due to sugar infiltration (Karathanos *et al.*, 1995) and/or the formation of a peripheral layer of sugar (Collignan *et al.*, 1992a). Sorbitol intake though did not cause any drying rate reduction. Cubes pretreated in 14% (w/w) sucrose solution, isotonic with the fresh fruit, showed the highest drying rate throughout the drying process. This behavior could be related to surface cellular structure loosening caused by 60-min soaking and not counterbalanced by sugar infiltration. As for air drying of vegetables, tomatoes of two varieties were dried by convection at

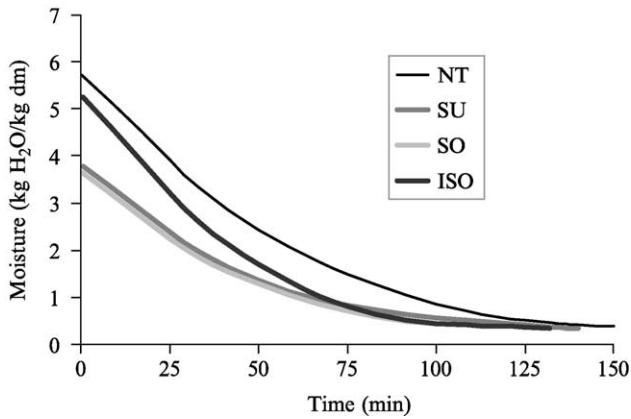

FIG. 8 Effect of 60-min osmotic dehydration at 25 °C at atmospheric pressure in 60% (w/w) sucrose (SU) or sorbitol (SO) solution or 14% (w/w) sucrose (ISO) solution added with 1% ascorbic acid and 0.5% citric acid on drying rates at 70 °C of apricot cubes (NT, not pretreated) (Campolongo, 2002).

60 °C (Lewicki *et al*., 2002). The skin was removed and tomato quarters were pretreated either by soaking in a $CaCl_2$ solution or by soaking in this solution followed by osmotic dewatering or by osmosis in a hypertonic solution containing sucrose and calcium chloride. Pretreatments of tomatoes with calcium chloride increased the rates of convective drying and osmotic dewatering as well. The convective drying time of pretreated tomatoes was 20% shorter than that of raw material. Pretreatment with $CaCl_2$ increased by 20% the amount of water removed during osmotic dehydration and facilitated the infiltration of sucrose. Treatment with $CaCl_2$, followed by osmotic dewatering, was more effective than osmotic treatment in sucrose solution containing calcium chloride, but rehydration properties of pretreated and dried tomatoes were poor. It was suggested that interactions of calcium with polymers stiffened the structure, which, on one hand, improved drying processes, but, on the other, restricted polymers hydration and swelling during rehydration.

As the transport rate in air-drying processes is affected greatly by tissue structure and composition, vacuum infusion pretreatments can lead to a different drying behavior of fruit and vegetables, as well as to different final properties of the product (Fito *et al*., 2001a). VI pretreatment with an isotonic solution slowed down the drying rate of apple slices (Martìn *et al*., 1998, 1999). The increased density of the product and the limitation of diffusion in the sample pores are the main factors that made the drying process rather slow. However, when combined air drying–microwave drying is applied, the drying rate of apple slices VI pretreated overtakes that of nonpretreated samples, probably due to the induced changes in dielectric properties (Martìn *et al*., 1998, 1999).

Artificial neural network (ANN) models were used for predicting quality changes during the osmoconvective drying of blueberries for process optimization (Chen *et al*., 2001). Osmotic dehydration, in fact, affects several associated quality factors, such as color, texture, and rehydration ratio, as well as the end drying time, which is dealt with in Section III.B.2. Ideally, an optimized condition should be aimed at resulting in the lowest drying time, highest rehydration ratio, lowest color difference, and minimal hardness. From the results reported by the aforementioned authors, significant differences exist between the optimal processing conditions for different optimization objectives, and ANN models could be used effectively for predictive modeling and optimization of osmotic processing conditions for the osmoconvective drying of blueberries. The same university department developed models, based on a central composite rotatable design (CCRD), to predict the product moisture content in the two-stage drying process of apple slices as a function of osmotic treatment conditions (Ramaswamy and van Nieuwenhuijzen, 2002).

b. Infrared and microwave. In addition to convective drying, osmotic dehydration can be combined with other drying techniques in order to improve drying efficiency and dried product quality further. Decreasing the drying time, without degradation of food quality, is the main concern for all dried agricultural food producers. One possible method of shortening the drying time of the combined osmoconvective process is the introduction of infrared sources, which are inexpensive, very reliable, have a long service life, and a rapid time response with low maintenance costs (Ratti and Mujumdar, 1995). A combination of intermittent infrared and continuous convective heating was proposed to dry osmotically pretreated potato and pineapple cubes and led to a significant reduction of drying time, without affecting the color of dried products (Tan *et al*., 2001).

Microwave energy can be applied successfully in several unit processes in the food industry because of the volumetric heating of the material. The combined use of microwave and convective drying not only could enhance the drying rate greatly, but also improve the final vegetable product quality (Torringa *et al*., 1996). Dried vegetables and fruits are an important sector in the ingredient market; in fact, in Europe the dehydrated vegetable market is estimated at around $8–9 \times 10^8$ kg with a value of 5–6 billion Euro (Torringa *et al*., 2001). Dehydrated vegetable products are suited to a broad range of food formulations (Tuley, 1996), but, unfortunately, they are often difficult to rehydrate because of case hardening and shrinkage during the drying process, resulting in not fulfilling the consumer expectancy for processed products that keep more of their original characteristics.

Combined microwave–hot air drying could improve the structure and bulk volume of dried mushrooms greatly (Nijhuis *et al*., 1998). However, the geometry and dielectric properties of mushrooms are such that overheating of the center hampers the application of this technology. Osmotic dehydration has proved to be an effective method used to improve mushroom suitability to microwave drying (Torringa *et al*., 1998, 2001). The increased salt concentration, due to osmotic pretreatment, has a strong effect on the loss factor so that the vegetable is heated more homogeneously, due to reduced center heating, has a slightly shorter drying time, shows improved rehydration properties, slightly reduced shrinkage, and higher open-pore porosity (Figure 9).

Microwave-assisted (0.1 or 0.2 Wg^{-1}) convection drying was also applied to osmotically dehydrated blueberries, leading to dried berries that were comparable to freeze-dried ones in much shorter time (Venkatachalapathy and Raghavan, 1998). Frozen blueberries were also dried in a microwave and spouted bed combined dryer (MWSB) after a pretreatment using ethyl oleate and a NaOH dipping solution followed by sucrose osmotic treatment (Feng *et al*., 1999). Osmotic dehydration prevented the blueberries from

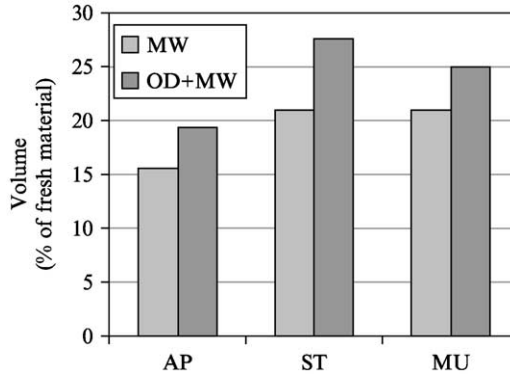

FIG. 9 Effect of osmotic dehydration [180 min, 60% (w/w) sucrose solution at 25 °C for apple and strawberry; 30 min, 10% NaCl at 20 °C for mushroom] on volume (percentage of fresh material) of apple (AP) and strawberry (ST) microwave–vacuum dehydrated up to $a_w < 0.5$ (Erle and Shubert, 2001) and mushroom (MU) microwave–hot air dehydrated up to a moisture content of 0.05 g/g dry matter (Torringa *et al.*, 2001).

bursting, when microwaved, but resulted in a high bulk density and low rehydration ratio.

The combination of osmotic pretreatment in sucrose and microwave–vacuum dehydration of strawberry halves and apple slices was studied by Erle and Shubert (2001). The use of a microwave overcomes the usual problem of poor heat transfer in vacuum drying. In microwave–vacuum drying, the heat is not transferred to but is generated into the tissue. This allows for energy transfer rates much higher than in conventional drying operations, especially in the falling rate period (Roussy and Pearce, 1995). The application of an osmotic treatment prior to microwave–vacuum drying combines the advantages of both unit operations in an unique way: because no phase transition takes place in osmotic dehydration, energy consumption is especially low, even if the diluted solution needs to be reconcentrated by evaporation. Microwaves require electricity, an expensive form of energy, but they are employed in the final stages of drying, where they can be used more efficiently than hot air (Gunasekaran, 1999). Selecting the conditions during osmotic treatment offers the possibility of improving both the efficiency of microwave dehydration and the quality properties of the final product. Compared with solely microwave–vacuum-dried fruits, osmotic pretreatment improves volume retention from 20 to 50% for strawberries and from 20 to 60% for apples, based on the fresh fruit volume (Figure 9). Scanning electron microscope (SEM) pictures revealed that the cellular structure is also preserved better when osmotic pretreatment is used. Gel

formation among pectins, sucrose, and, when used, calcium ions is believed to be the main cause of structure buildup.

c. Osmotic treatment after drying. Impregnation after partial dehydration instead of the more common osmoconvective drying, where the osmotic treatment precedes air drying, was proposed by Dalla Rosa *et al.* (2001) on strawberry halves and blueberries to obtain semimoist products to be used as ingredients in complex foods, such as dairy and bakery products. Combined convective air drying followed by osmotic dehydration resulted in a larger water loss compared with a single osmotic treatment for a given process time, confirming data of Robbers *et al.* (1997) on kiwifruit. Furthermore, the desired lowering of water activity needed to obtain the compatibility between the food basis and the ingredient is reached at a higher water content than in the stand-alone air-drying process.

2. Quality characteristics improvement

Although effective moisture diffusivity decreased normally in osmotically treated fruits, there are some quality characteristics that are always better in osmodehydrated-dried than in fresh-dried ones.

a. Color. An osmotic step could improve the stability of color and vitamin C during air drying and frozen storage of osmodehydrofrozen apricot cubes by the modification of sugar composition (Camacho *et al.*, 1998; Forni *et al.*, 1997). The higher the sugar enrichment, the higher the protective effect on vitamin C during air drying, with maltose being the most effective carbohydrate. Also, browning, expressed as the browning index, calculated from the color coordinates L^*, a^*, and b^* ($[(L_f^* \bullet b_f^*)//(70 \bullet a_f^*)] - [(L^* \bullet b^*)/(70 \bullet a^*)]$; index f refers to fresh fruit values), was significantly lower in cubes pretreated in concentrated solutions of both sucrose and maltose (Figure 10).

Apricot cubes pretreated in the sucrose solution isotonic with fresh fruit have, before drying, the same vitamin C content as cubes pretreated in concentrated solutions, but a lower sugar concentration. The same browning effect was observed in nonpretreated apricot cubes, confirming the protective effect of sugar concentration. The lower ascorbic acid degradation observed in apricot cubes treated in sucrose and maltose could also be related to the fact that these fruits have Tg' values higher than those of untreated ones, hence lower T-Tg' values. As a consequence, they could have lower structural collapse during drying (Levi and Karel, 1995; Roos and Karel, 1993; Slade and Levine, 1991), which may also affect diffusion-controlled deteriorative changes such as nonenzymatic browning (Karmas *et al.*, 1992),

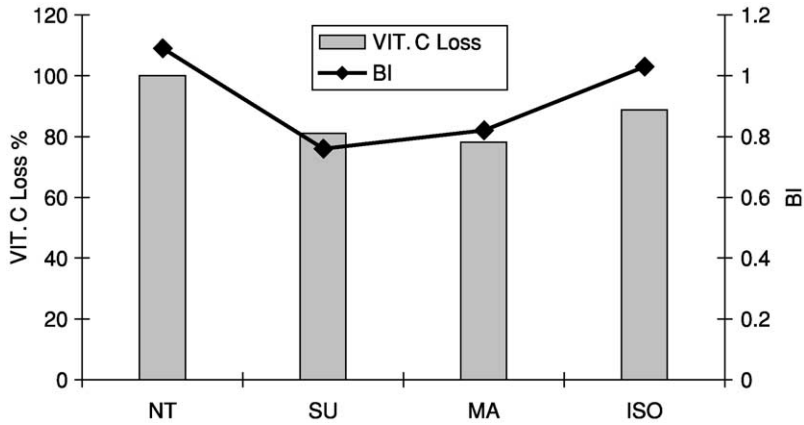

FIG. 10 Vitamin C loss (percentage of apricot content before drying) and browning index (BI) of apricot cubes air dried (NT) or air dried following 60-min osmotic dehydration at 25 °C at atmospheric pressure in 60% (w/w) sucrose (SU) or maltose (MA) or 13% (w/w) sucrose (ISO) solution added with 1% ascorbic acid and 0.5% NaCl (Camacho *et al.*, 1998). All samples were dried at 60 °C up to $a_w = 0.80$.

phenolase activity, and thus the ascorbic acid degradation rate. Further research has underlined the influence of different sugars on the level of structural collapse during air drying of both apricot and clingstone peach cubes (Riva *et al.*, 2001, 2002) and is discussed in Section III.B.2.b.

Color parameters of osmotically treated apple and banana cylinders and potato and pineapple slices showed a remarkable stability over the whole duration of subsequent air drying, whereas untreated samples experienced an extensive browning, proved by a significant higher color difference ($\Delta E = \Delta\ L^{*2} + \Delta\ a^{*2} + \Delta b^{*2}$) values when compared with fresh ones (Krokida *et al.*, 2000a; Tan *et al.*, 2001) (Figure 11). The suggested explanation is that sugars act superficially by increasing the osmotic pressure of the surface layers of fruits and vegetables, reducing enzymatic-browning reactions.

As for vegetable dehydration, by incorporating sorbitol into red pepper cubes, a lower color degradation could be obtained when they are subjected to air drying to produce reduced moisture red pepper ingredients (Torreggiani *et al.*, 1995a). As already observed in frozen strawberries during storage (Torreggiani *et al.*, 1995b), even in vegetables and during air drying at 65 °C, sorbitol showed a significant protection of the red color and thus of the anthocyanin pigments. Red pepper cubes, osmodehydrated in a new type of syrup (HLS, hydrolyzed lactose syrup from cheese whey ultrafiltration permeate), added with sorbitol, showed the lowest color differences when

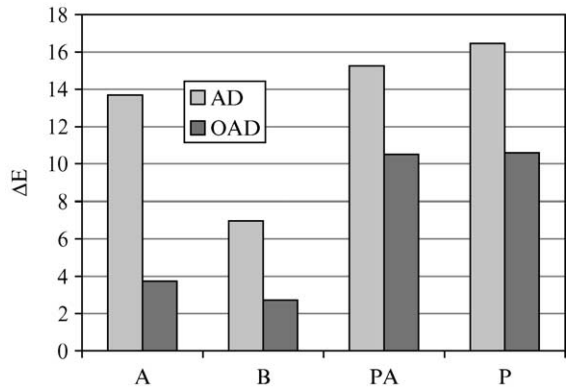

FIG. 11 Color changes (ΔE) of apple (A) and banana (B) cylinders (Krokida *et al.*, 2000a) and pineapple (PA) and potato slices (P) (Tan *et al.*, 2001) air dried (AD) or air dried following 300-min osmotic dehydration (OAD) at atmospheric pressure in 50% (w/w) sucrose solution at 30 °C for apple and banana, 30% (w/w) sucrose solution at 25 °C for pineapple, or 10% (w/w) NaCl solution at 25 °C for potato.

compared with fresh ones. Results also suggested that for red pepper at low water activities, the combination of osmo- with air-dehydration could even be detrimental to color characteristics if a "nonprotective" sugar other than sorbitol is utilized as the osmotic medium.

As for tomatoes, conservation of lycopene during the processing of tomato products is of commercial significance. The degradation of lycopene affects not only the attractive color of tomato products but also their nutritive value and flavor. Four dehydration methods (air drying, vacuum drying, vacuum drying following osmotic pretreatment, and osmotic treatment) produced slight differences in the total lycopene content but resulted in quite a different distribution of the isomer composition (Shi *et al.*, 1999). Osmotic treatments reduced lycopene losses through a higher retention of total lycopene and induced only slight changes in the distribution of all-*trans* and *cis* isomers and in color attributes (Figure 12). The osmotic-vacuum treatment had less effect on lycopene loss and isomerization than vacuum drying and conventional air drying. In air drying, isomerization and oxidation (autoxidation) affected simultaneously the decrease of total lycopene content, distribution of *trans* and *cis* isomers, and biological strength. A possible explanation of this result is that sugar enters the tomato matrix and strengthens the binding force of lycopene. Furthermore, osmotic solution (sugar) remaining on the surface layer of the tomato prevents oxygen from penetrating and oxidizing lycopene.

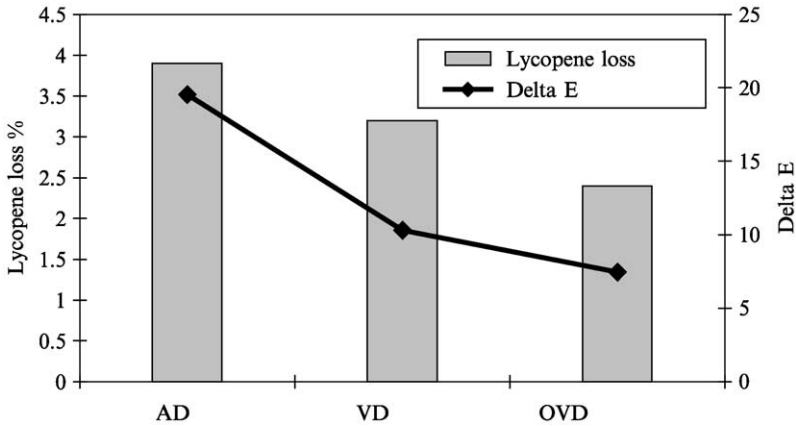

FIG. 12 Lycopene loss (percentage of raw tomato content) and color changes (ΔE) of whole tomatoes air dried at 95 °C (AD), vacuum dried at 55 °C (VD), or vacuum dried at 55 °C following 240-min osmotic dehydration (OVD) in 65% (w/w) sucrose solution at 25 °C (Shi *et al.*, 1999). All samples were dried up to 3–4% moisture content.

b. Shrinkage. The incorporation of sugars has been demonstrated to improve not only color, but also the structure stability of dried fruits in general. Pretreated and air dried apples were more tender and retained their shape better than untreated air-dried ones (Collignan *et al.*, 1992; Lewicki and Lukaszuk, 2000). Color and structure characteristics of both clingstone peach and apricot cubes were preserved better during air drying when fruits were pretreated in different sugar solutions (Campolongo, 2002; Riva *et al.*, 2001, 2002) (Figure 13). In this work, color attributes and geometric features were evaluated by image analysis after acquisition of a significant number of images per sample (Papadakis *et al.*, 2000). Mathematical transformations were applied to the image parameters to also estimate volume reduction, related to absolute moisture content. During subsequent air drying, sugars added during the osmotic step helped decrease structural collapse, with the improvement being reflected by 25–30% and 10–15% increases in the final volume of pretreated clingstone peach and apricot cubes, respectively, confirming the results reported by Lozano *et al.* (1983), del Valle *et al.* (1998), and Reppa *et al.* (1998) on apple cylinders. Both clingstone peach and apricot pretreated in sorbitol showed the lowest structure collapse, retaining a better surface smoothness. Protective effects of the osmotic step in sorbitol on geometric features appear to be linked to the lower heat damage (testified by the lower shift of the color attributes) during the air-drying step and could be related to the higher replacement of air in intercellular spaces by the sorbitol solution that penetrates via capillarity (del Valle *et al.*, 1998).

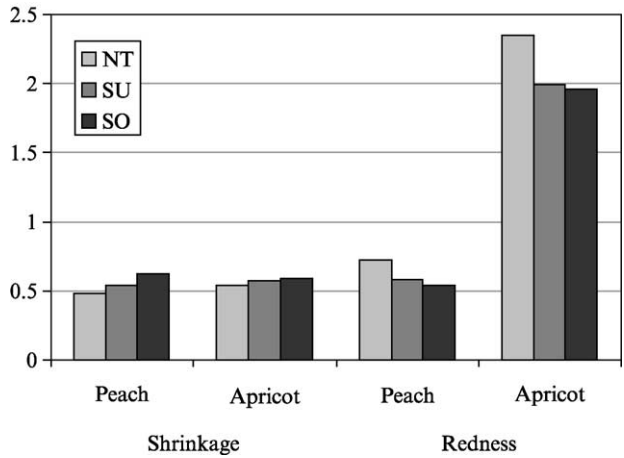

FIG. 13 Shrinkage coefficient (volume/initial volume) and redness (a*/10) of peach and apricot cubes air dried at 70 °C up to 35% weight reduction without (NT) or following 60-min osmotic dehydration at 25 °C at atmospheric pressure in 60% (w/w) sucrose (SU) or sorbitol (SO) solutions, added with 1% ascorbic acid and 0.5% citric acid (Campolongo, 2002; Riva *et al*., 2001, 2002).

A simple relationship was not found between shrinkage and "glass"–"rubber" transitions of both peach and apricot tissue (Campolongo, 2002; Riva *et al*., 2001, 2002). Even when sorbitol use increased ΔT ($= T - Tg'$) values, both the color and the structure showed the highest stability. The fact that sorbitol performed better than sucrose indicates that the chemical nature of the infused solute is more important than its glass transition temperature in preventing structural collapse, in accordance with the results reported by del Valle *et al*. (1998).

As for the mechanism explaining the protective effect of sugar, the protection of almost completely dried (below 2% of water content) plant material against cell death has been linked to the presence of disaccharides, which play a significant role in preserving the membrane functionality in the dry state. Among the disaccharides, trehalose was found to be the most efficient in the preservation of the cell membrane (Crowe *et al*., 1993). The presence of trehalose during drying prevents, therefore, lipid-phase transitions between the dry and the next rehydration state. This hypothesis was partially confirmed by results reported by Ferrando and Spiess (2001), which have already been referred to in Section II.D. Maltose and trehalose had a protective effect on the plasma membrane of onion epidermis cells subjected to osmotic stress, maintaining its properties as a barrier, as indicated by their significant lower effective water diffusivity in comparison with sucrose. Trehalose played a main role during the rehydration of the onion epidermis,

leading to the highest swelling rate. However, parenchymatic cells of strawberry tissue were not susceptible to any protection effect regarding the kind of disaccharides employed, thus underlining the utmost importance of the species (Ferrando and Spiess, 2001).

c. Aroma compound retention. Aroma is one of the major determinants of fruit quality, and the retention or loss during osmotic dehydration and air dehydration of strawberry has been analyzed (Di Cesare *et al.*, 1999). The concentration of strawberry slices obtained through osmotic treatment in concentrated sucrose solutions improved the volatile retention during air drying at 60 °C of the fruits. During the osmotic step, furanones, pyranones, and, to a lesser extent, esters remain in the fruit tissue, while alcohols and carbonyl compounds move from the fruit to the syrup, probably due to the different solubility of these compounds in water. Furthermore, the concentration of strawberry slices, through osmotic dehydration, improves the volatile retention during air drying in such a way that previously osmodehydrated strawberry slices could be dried up to higher drying levels when compared to non pretreated fruit.

d. Rehydration. While the osmotic step significantly improves color, structure stability, and aroma, it could be detrimental when the product has to be rehydrated.

Knowledge of sorption characteristics of fruit and vegetable, after osmotic dehydration, has important practical effects, especially in dry product rehydration and rehydrated product stability, and is essential in designing combined dehydration processes. Despite the massive volume of literature on osmotic pretreatments, publications on sorption characteristics of osmotically dehydrated products are rather limited (Krokida *et al.*, 2000a,b; Lenart, 1991; Tan *et al.*, 2001). Osmotic treatment resulted in lowering of the sorption isotherms for both apple and banana (Krokida *et al.*, 2000a) and for potato slices, whereas the shift for pineapple slices occurred only at a higher level of moisture content (Tan *et al.*, 2001). In terms of rehydration behavior, the observed isotherm shift indicated higher rehydration characteristics for air-dried samples compared to osmotically pretreated ones. This sorption shift may be due to sugar content changes causing differences in binding site availability and bond energies for different structures (Van den Berg and Bruin, 1981). At low moisture levels, water is bound strongly to active sites and does not enhance solution or plastering processes. At higher levels, a combination of actions occurs, resulting in a sharp increase in adsorptive capacity. Such actions include solution, new site creation, plastering, and water–water adsorption. Minor sugars and other soluble constituents probably dissolve before the main sugars.

C. FREEZING

Freezing damages the tissues of fruit and vegetables both physically and chemically. During this process, a part of the aqueous fraction freezes out and forms ice crystals that damage the integrity of the cellular compartments. The cellular membranes lose their osmotic status and their semipermeability (Tregunno and Goff, 1996). The metabolic system of the plant tissue is interrupted, dislocation of the enzymatic system occurs, and the cell loses its turgor. In addition to a dramatic change in texture of the tissue, biochemical deterioration reactions are highly probable. Dehydration prefreeze treatments can aid in reducing or even preventing this problem (Huxsoll, 1982). The process of freezing primarily dehydrated foods is known as dehydrofreezing.

If water is removed partially from the food prior to the freezing process, the cytoplasmatic components within the cells are concentrated and the freezing point is depressed, with a consequent increase of supercooling and microcrystallization. There is a lower ratio of ice crystals to unfrozen phase, with a consequent reduction of structural and sensory modifications. Convective air dehydration is usually used for partial dehydration, but some fruits are affected negatively by any air-drying technique, with kiwifruit being a good example (Forni *et al*., 1990). For these fruit, air drying must be replaced or combined with osmotic dehydration, which is effective at room temperature and which operates away from oxygen.

1. Texture

Even though osmotic treatments have been proven to be a useful tool in fruit and vegetable cryoprotection, the changes in mechanical properties, caused by the process itself, have to be taken into account.

Different factors contribute to the mechanical properties of plant tissue: cell turgor, which is one of the most important ones, cell bonding force through middle lamella, cell wall resistance to compression or tensile forces, density of cell packaging, which defines the free spaces with gas or liquid, and some factors, also common to other products, such as sample size and shape, temperature, and strain rate (Vincent, 1994). Depending on the sample properties (mainly turgor and resistance of middle lamella), two failure modes have been described (Pitt, 1992): cell debonding and cell rupture.

The main changes induced by an osmotic treatment affecting the mechanical behavior of plant tissues are loss of cellular turgor, alteration of middle lamella (Alzamora *et al*., 1997), alteration of cell wall resistance, establishment of water and solute concentration profiles (Salvatori *et al*.,

1997, 1998a, 1999), changes in air and liquid volume fractions in the sample (Fito *et al*., 2002), and changes in sample size and shape.

Chiralt *et al*. (2001b) evaluated the effect of process variables in osmodehydrated kiwi, mango, and strawberry brought to the same soluble solid concentration by applying different processing conditions. All the fruit analyzed were softer than fresh ones, and relaxation measurements showed that infusion (atmospheric or vacuum) decreased the elastic component of reological behavior sharply, confirming the results obtained by Muntada *et al*. (1998) on kiwifruit and by Sormani *et al*. (1999) and Brambilla *et al*. (2000) on strawberry slices.

To define the influence of osmotic dehydration on fruit tissues, the changes, produced at the structural level, were studied, through texture and microscopic analysis, on strawberry slices subjected to osmotic dehydration at atmospheric pressure for different lengths of time (Brambilla *et al*., 2000). A good agreement was obtained between structural and texture changes. Light photomicrographs of osmodehydrated strawberry tissues revealed that there is a deterioration in the cell links and that the cell walls already lose their shape after 4 hr of osmotic treatment, with a consequent texture decrease (Figure 14). Furthermore, comparing dehydration methods, air-dried strawberry slices appeared tougher than osmotically dried samples at the same water content (O2/D4, O4/D5) (Brambilla *et al*., 2000; Chiralt *et al*., 2001b) (Figure 14). Similar results were obtained by other authors on kiwifruit (Robbers *et al*., 1997). This could be due to the different sample concentration profiles developed in each treatment, as the driving force is very different in each case, or to a greater degree of alteration of middle lamellae through the osmotic process. Not only the analysis of how differently soluble pectin fractions are modified, but also the analysis into the enzymatic activity during processing could help better understand the phenomenon. These results also suggest, for strawberry, osmotic pretreatments shorter than 2 hr. Also, for kiwifruit, a long immersion time in the osmotic solution did not seem to favor textural properties of the final product (Chiralt *et al*., 2001b; Muntada *et al*., 1998). Microscopic observations showed that atmospheric solute infusion of kiwifruit halves for 6 days to attain a_w equilibrium caused a contraction of cellular membranes, degradation of cell walls, and intercellular contact decrease, while a much shorter vacuum pulse infusion led to cell wall optical density similar to fresh cells (Muntada *et al*., 1998). Calcium lactate infiltration increased failure forces due to enhanced cell cohesion and increased cell wall integrity.

A decrease in firmness, linked to osmodehydration in both glucose and sucrose, was also observed in apple cylinders (Reppa *et al*., 1998). This could be due to loss of turgor pressure, which makes the cells of plant tissues less rigid, i.e., fracturability disappears while deformability increases (Aguilera

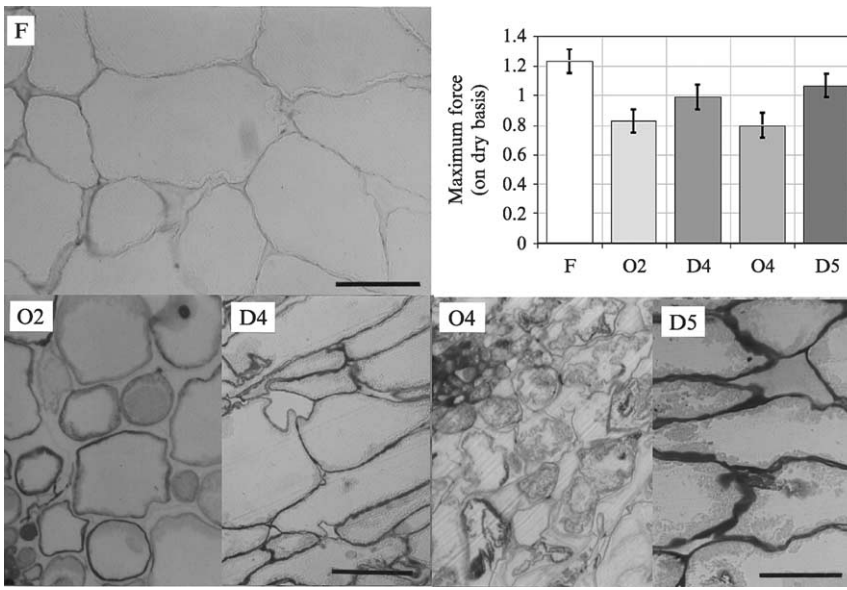

FIG. 14 Photomicrographs and texture values expressed as maximum force (kg) on dry basis of strawberry slices before (F) and after osmotic dehydration for 60 (O2) and 240 (O4) min in 60% (w/w) sucrose solution, at 25 °C at atmospheric pressure, and after air dehydration at 60 °C up to 40% (D4) and 50% (D5) weight reduction. Bars: 100 μm (Brambilla *et al.*, 2000).

and Stanley, 1990). Softening may be also caused by the formation of soluble pectins, which is promoted by low turgor, by calcium leaching from the cell wall, and by degradation of the middle lamellae (Poovaiah, 1986). Osmotically dehydrated apples had a semichewy consistency. As textural properties of fruits are closely linked to cellular structure and pectic composition (Ilker and Szczesniak, 1990), three cultivar of strawberry and a cultivar of kiwifruit at three ripening stages were studied for the influence of osmotic treatment on the modification of texture and of water-soluble, oxalate-soluble and residual insoluble pectin fractions (Forni *et al.*, 1998; Torreggiani *et al.*, 1998a,b). For strawberry, the cultivar influenced solid–liquid exchanges during osmotic dehydration applied for 1 hr in a 70% (w/w) fructose syrup, showing the great importance of the tissue structure and the size and architecture of the intercellular spaces. Osmotic dehydration caused a slight decrease of texture values of strawberry, correlated with a decrease in the oxalate-soluble and residual pectin (protopectin) fractions, considered as determining fruit firmness. As for texture, and thus ripening stage of kiwifruit, the lower the texture level, the lower the solid gain, while water loss

was higher in firm (unripe) fruit. No relationships were found between texture changes and pectic composition of kiwifruit during osmotic treatment applied for 2 hr in a 70% (w/w) sucrose syrup, confirming the utmost importance of species. Knowledge of the changes in mechanical properties, linked to osmotic dehydration conditions and to fruit and vegetable characteristics, will be of essential importance in the optimization of the combined process of dehydrofreezing.

Vast literature indicates the usefulness of partial water removal prior to freezing, referring to numerous species of fruits (Torreggiani, 1995), which has also been confirmed for muskmelon and guava. Muskmelon spheres, predehydrated by osmotic dehydration, were significantly more acceptable than those preair dehydrated, confirming the suitability of osmotic dipping as a pretreatment in the production of innovative high-quality frozen products (Maestrelli *et al*., 2001). Blanching and osmotic treatments improved texture and color retention and also reduced drip losses of freeze-thawed guava halves (Aguilar-Bernal *et al*., 2001).

The combined technique of dehydrofreezing has proven to be useful even in improving the quality of a delicate tissue such as that of strawberry. The structural collapse, after thawing–rehydration of strawberry slices, was reduced by adopting partial removal of water through air dehydration, osmotic dehydration, or their combination (Maestrelli *et al*., 1997). A reduction in moisture content of at least 60% is needed to improve the texture characteristics of thawed–rehydrated fruit, irrespective of the dehydration method used. These data were confirmed by Martìnez-Navarrete *et al*. (2001) on strawberry halves; changes, promoted by freezing on mechanical and color attributes of the fruit, were smaller in samples osmodehydrated previously, thus having a lower water content.

Microscopic analysis on predehydrated and freeze-thawed strawberry slices confirmed these findings, showing that the reduction of freezing damage is due to the decrease in moisture content (Sormani *et al*., 1999). Predehydrated strawberry slices retain the tissue organization after thawing, whereas untreated ones show a definite continuity loss and thinning of the cell wall. Osmotic dehydration, applied for 4 hr, even if it causes structural damage by itself, has been proven to improve tissue organization of the thawed fruit; the protective effect, due to the reduction of water content, overcomes the tissue damage induced by the process. Although the processing time is longer, application of an osmotic step alone or in combination with air dehydration could, through the incorporation of sugars, improve color, flavor, and vitamin retention during frozen storage, as described further in Section III.C.2.C.

The analysis of how differently soluble pectin fractions of strawberry slices are modified by air dehydration, combined osmotic–air dehydration,

applied before freezing, and freezing itself indicated that protopectin (residual insoluble pectin fraction) content decreases significantly during air dehydration, with the osmotic step reducing the loss (Brimar, 2002) (Figure 15). Freezing causes a significant reduction of protopectin content, with the biggest effect occurring in strawberries not predehydrated before freezing. The different losses of protopectins in differently predehydrated fruits could explain the differences in texture observed in freeze-thawed fruits (Figure 15). Osmotic treatments using selective solutes can also allow cryoprotection of the cell during freeze-thawing (Burke *et al.*, 1976; Tregunno and Goff, 1996; Wolfe and Bryant, 1992).

Another interesting treatment is vacuum infusion with cryoprotectants (sugars from concentrated grape must) and cryostabilizers (HM pectin), which was applied to reduce ice crystal damage in frozen apple cylinders and to improve the fruit resistance to freezing damage through a notable reduction of freezable water (Martìnez-Monzò *et al.*, 1998a,b).

The addition of cryoprotectants and cryostabilizers in the formulation changed the glass transition temperature (*T*g') of the maximally cryoconcentrated food liquid phase and the freezable water content of strawberry impregnated, under vacuum or at atmospheric pressure, with sucrose and sorbitol acqueous solutions, added or not with ascorbic acid (Vidales *et al.*, 2001). The analysis of the product microstructure by light and transmission electron microscopy showed that tissues subjected to vacuum had higher cellular tissue integrity and that the ascorbic acid addition preserved the cellular tissue better in all the samples.

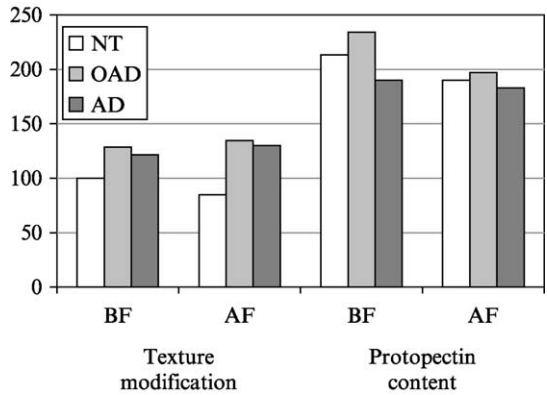

FIG. 15 Texture modification (percentage of raw fruit texture) and protopectin content (mg/100 g wet weight) before (BF) and after (AF) freezing of strawberry slices not pretreated (NT) or air dried at 80 °C up to 60% weight reduction without (AD) or following 60-min osmotic dehydration (OAD) in 60% (w/w) sucrose solution at 25 °C at atmospheric pressure (Brimar, 2002).

Partial dehydration before freezing could even enhance the resistance of texture of frozen strawberry slices and apricot cubes to a thermal treatment (Torreggiani *et al.*, 1999b,d). For fruit to be incorporated as a food ingredient, e.g., in yogurt, a heat treatment has to be applied, but this causes texture damage, as does freezing. To reach a texture improvement after the proposed heat treatment, a moisture reduction, before freezing, of at least 50% is needed for both strawberry and apricot, irrespective of the dehydration method used. This percentage of moisture reduction is what is required to reduce the freezing damage of the fruits at thawing (Maestrelli *et al.*, 1997), making it evident that the freezing step is the most crucial point in the production process of thermally stabilized strawberry and apricot ingredients. If the freezing damage is limited, then the fruit texture can be improved even after heat treatment.

2. Pigments and vitamins

Together with a texture improvement, the penetration of solutes, combined with a dehydration effect, could modify the fruit composition and improve pigment, color, and vitamin retention during frozen storage.

According to the kinetic interpretation based on the glass transition concept, physical and chemical stability is related to the viscosity and molecular mobility of the unfrozen phase, which, in turn, depends on the glass transition temperature (Champion *et al.*, 1997; Karel *et al.*, 1993; Slade and Levine, 1991). When the temperature is at or below Tg', diffusion-limited changes occur at very slow rates, i.e., stability, if based on diffusion-limited events, is excellent. However, it must be kept in mind that many chemical changes are not diffusion limited. The rates of presumed diffusion-controlled reactions are considered proportional to the difference between the Tg', also called mobility temperature (Reid, 1999), and the temperature of study. Manipulation of mobility temperatures, through composition, could therefore influence reaction rates. So, if through osmotic dehydration the fruit formulation can be modified and thereby an increase in the glass transition temperature could be obtained, then there could also be an increase in storage stability.

While the kinetic interpretation, based on the glass transition temperature, holds for chlorophyll and vitamin C stabilization in kiwifruit, for the anthocyanin pigments in strawberry, a simple relationship does not exist between the pigment loss and the amplitude of the difference between the storage temperature and the glass transition temperature of the maximally freeze-concentrated phase. Incorporation of an osmotic step of different sugars into kiwifruit slices modified their low temperature phase transitions and increased chlorophyll and vitamin C stability significantly during frozen storage at $-10\,^{\circ}$C (Torreggiani and Bertolo, 2001; Torreggiani *et al.*, 1994).

Kiwifruit pretreated in maltose, and thus having the highest *T*g' values, showed the highest chlorophyll and vitamin C retention.

The osmodehydrated strawberry halves showed pigment retention significantly higher than that observed in fruit frozen without a concentration pretreatment, but no differences were observed among fruit osmodehydrated in the different sugars, thus having different glass transition temperatures (Torreggiani *et al*., 1995b). The sorbitol-treated strawberry slices, which had the lowest glass transition temperature, showed the same anthocyanin retention as sucrose- and maltose-treated fruits, confirming the results obtained on strawberry juices added with different sugars (Torreggiani *et al*., 1999a). Other factors, such as the pH of the unfrozen phase and the specific chemical nature of sorbitol, could have influenced the anthocyanin degradation. Osmotic treatments carried out before strawberry freezing increased the ascorbic acid degradation rate during storage at −4 °C, while ascorbic acid retention was observed at −24 °C (Rubiolo and Amer, 2001).

3. Aroma compounds

Aroma is one of the major determinants of fruit quality, and the retention or loss during osmosis and air dehydration, applied before freezing, was investigated on muskmelon spheres in order to obtain high-quality innovative frozen products (Maestrelli *et al*., 2001). Results ascertained the crucial importance of the cultivar, which had a great influence on the quality characteristics of the end products. Among the pretreatments, air dehydration caused a significant increase of alcohols, while these "negative" aroma compounds, responsible for the fermented note, were stable in osmo-treated fruit (Lo Scalzo *et al*., 2001) (Figure 16). Furthermore, osmosis prevented the increase of alcohols during the freezing process. This finding could explain the higher sensory acceptability of the fruit pre-osmo when compared with those pre-air dehydrated.

The effect of osmotic process conditions on the volatile fraction of strawberries was analyzed by Talens *et al*. (2002), as well as the effect of freezing and frozen storage. Treatments with 65% (w/w) sucrose solutions showed the same behavior as observed by Di Cesare *et al*. (1999) and Escriche *et al*. (2000, 2001a): there was an increase in some ethyl esters and furaneol but a decrease in isobutyl ester and hexanal, with the changes being slightly lower in pulsed vacuum osmotic treatments (PVOD). Different changes in the volatile profile can be expected, depending on osmotic process conditions and duration. Freezing and frozen storage implied losses in all components, although in predehydrated strawberries the concentration of some esters (and furaneol) remained greater than in fresh ones due to the formation promoted during the osmotic step.

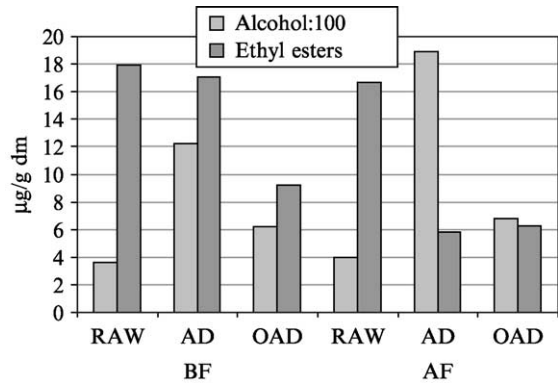

FIG. 16 Alcohol and ethyl esters content before (BF) and after (AF) freezing of melon spheres cv. Rony not pretreated (RAW) or air dried at 80 °C up to 50% weight reduction without (AD) or following 60-min osmotic dehydration (OAD) in 60% (w/w) sucrose solution at 25 °C at atmospheric pressure (Lo Scalzo *et al.*, 2001).

Osmotic dehydration also caused changes in the volatile profile of kiwifruit, depending on the treatment conditions applied (Talens *et al.*, 2003). The concentration of the ester fraction increased, whereas aldehydes and alcohols decreased. The behavior of the volatile profile was similar to that described for kiwifruit ripening (Young and Paterson, 1985). This suggests that osmotic stress might imply an acceleration of the maturation process at the cellular level, in line with an enhanced enzyme action (Escriche *et al.*, 2000, 2001a; Zabetakis and Holden, 1997), which results in volatile compound concentration. Migration of some compounds into the osmotic solution could also contribute to the observed decrease in hydrosoluble components. Vacuum pulse application and process time promoted ester formation. Nevertheless, the decrease in aldehydes and alcohols was greater in treatments carried out at atmospheric pressure. After 1 month of frozen storage of kiwifruit slices, a severe reduction of all compounds (esters, aldehydes and alcohols) occurred, which resulted in very small differences in the volatile profile of fruit directly frozen and previously dehydrated in different conditions. The sensory impact of these differences needs to be analyzed.

D. FORMULATION

Soluble solids uptake due to osmotic dehydration, in addition to improving color, aroma, and vitamin stability during both air drying and frozen storage, could also play a very important role in the preparation of new types of ingredients at reduced water activity (Torreggiani *et al.*, 1988). Due to the

soluble solid intake, the overall effect of osmotic dehydration is a decrease in water activity, with only a limited increase in consistency. Consistency is actually associated with the plasticizing and swelling effect of water on the pectic and cellulosic matrix of the fruit tissues. Hence, it depends primarily on the insoluble matter and water content rather than on the soluble solids and water activity. In this way, low water activities may be achieved while maintaining an acceptable consistency.

A general representation of the extent to which physical changes can be induced, and functional properties can be controlled in practical processing, can be obtained by developing, according to Maltini *et al.* (1993), a "functional compatibility map." These maps illustrate that functional properties, gained by using single or combined steps, are related to the water activity, which is the main parameter making the ingredients compatible with the food. In the maps, a relationship is reported among the phase composition (i.e., the relative amount of insoluble solids, soluble solids, and water), the texture index, and the water activity of the fruits after processing. The two sets of data, referring to partial dehydration of raw fruit and partial dehydration of osmotically treated fruit, are presented in the same diagram and give a pair of curves for phase composition and for texture.

The difference between the upper and the lower curves for phase composition and texture, at equal water activity, is the result of the solid gain after osmotic treatment. The higher the solid uptake, the higher the difference in texture. Compared to simple air dehydration, the combination of osmotic dehydration and air dehydration can produce a softer product at low water activity, which is more pleasant to eat by hand, or to incorporate into pastry, ice cream, cheese, yogurt (Giangiacomo *et al.*, 1994), and so on.

The choice of the osmotic syrup plays a very important role and the specific effect of the solution has to be taken into account. The choice depends mainly on taste, cost, and a_w-lowering capacity together with the possible kinetic hindering of the diffusion-controlled reaction during frozen storage. Fruit juice concentrates have similar osmotic properties to high fructose syrups (Maltini *et al.*, 1990), and resulting products are of total fruit origin. If a concentrated fruit juice is used as osmotic solution, an even softer product could be obtained because of the higher content of monosaccharides in the fruit juice compared to the amount contained in syrup from starch hydrolysis and because of the higher relative water content at a determined water activity (Torreggiani *et al.*, 1988). If a fructose syrup contains sorbitol, softer osmodehydrated apricot, clingstone peach cubes, and sweet cherry halves can be obtained when compared with the same fruit osmodehydrated in fructose alone (Erba *et al.*, 1994; Torreggiani *et al.*, 1997). The presence of sorbitol in HLS also leads to a lower texture in osmodehydrated red pepper cubes (Torreggiani *et al.*, 1995a). Moreover,

as reported previously, sorbitol has a specific protective effect on color during the air-drying step.

E. FUNCTIONAL FOODS

A functional food is defined as "any food or food ingredient that may provide a health benefit beyond the traditional nutrients it contains" (Mazza, 1998). Vacuum infusion allows the introduction of controlled quantities of a solution into the porous structure of fruit and vegetables (matrix) and can be used in the development of products fortified with physiologically active compounds (PAC) (Betoret *et al*., 2001; Fito *et al*., 2001b). Porosity of the solid matrix is the most crucial factor, which is involved in VI effectiveness; in plant tissues, porosity may be very high (20–30%) such as in apple, eggplant, or orange peel, meaning VI can be highly effective (Gras *et al*., 2001; Salvatori *et al*., 1998a) (Table I). From structural properties of food matrices and physicochemical characteristics of PAC solutions, the PAC concentration required in the impregnation solution to achieve an established percentage of PAC recommended daily intake (RDI) in a serving of the final product can be calculated through a mathematical model. The model has been validated with experimental data obtained with calcium-enriched eggplant, zucchini, and carrot using calcium lactate (Betoret *et al*., 2001). If ferric citrate is used, structural and physicochemical limitations make the process nonfeasible.

The effectiveness of VI can be evaluated through cryo-SEM observations comparing fresh and impregnated tissues (Fito *et al*., 2001b). Different tissues behave differently. The particular cellular arrangement in citrus peel albedo gives sponge-like properties to the peel with a great impregnating and swelling capacity. The eggplant parenchyma shows a similar structure to albedo in as far as the cell-bonding zones are enlarged or tubular, although cell sizes are greater.

The vacuum impregnation technique also represents a good choice for developing high-quality peel products alone or as ingredients, taking advantages of their interesting structure and composition. There has been a large increase in the amount of processed citrus fruits on the market in industrialized nations, which, however, has generated large amounts of by-products derived from peel. Citrus peel components provide many health benefits, among which the following should be pointed out: the effect of pectin on glycemic control, serum cholesterol concentration, cancer prevention, and control of mineral balance (Larrauri *et al*., 1995) and the effect of limonene on cancer prevention and the vitamin activity of carotenoids (Girard and Mazza, 1998). The development of new processing methods that preserve or increase the nutritional quality of peels is necessary in order to develop new

TABLE I
PHYSICAL–CHEMICAL PROPERTIES AND VACUUM IMPREGNATION RESPONSE OF FRUITS AND VEGETABLES

Product	Geometry	ρ_a [a]	$\gamma 1$ [b]	γ [b]	ϵ_e [c]
Apple, *Granny Smith* (Salvatori *et al.*, 1998b)	Cylinder ($d=20$ mm, $h=20$ mm)	802 ± 10	1.7 ± 0.3	-0.6 ± 1.2	21 ± 0.9
Apple, *Golden* (Salvatori, 1998b)	Cylinder ($d=20$ mm, $h=20$ mm)	787 ± 14	2.58 ± 0.2	-6 ± 0.5	17.4 ± 0.8
Mango, *Tommy Atkins* (Salvatori *et al.*, 1998b)	Slices ($t=10$ mm)	1022 ± 5	5.4 ± 0.5	8.9 ± 0.4	5.9 ± 0.4
Strawberry, *Chandler* (Salvatori *et al.*, 1998b)	Pieces ($d=50$ mm)	984 ± 9	2.9 ± 0.4	-4 ± 0.6	6.4 ± 0.3
Kiwi, *Hayward* (Salvatori *et al.*, 1998b)	Cubes ($l=50$ mm)	1051 ± 6	6.8 ± 0.6	0.8 ± 0.5	0.7 ± 0.5
Pineapple, *Española Roja* (Salvatori *et al.*, 1998b)	Cross slices ($t=10$ mm)	1030 ± 2	1.8 ± 0.4	2.3 ± 0.4	3.7 ± 1.3
Orange peel, *Valencia Late* (Cháfer *et al.*, 2001b)	Rectangles (2×7) ($t=5$ mm)	770 ± 2	2 ± 0.02	14 ± 0.03	21 ± 0.04
Mandarin peel, *Satsuma* (Cháfer *et al.*, 2001b)	Rectangles (2×7) ($t=4.5$ mm)	849 ± 3	-3 ± 0.02	12 ± 0.13	25 ± 0.11
Eggplant, *Soraya* (Gras *et al.*, 2001)	Cubes ($l=25$ mm)	417 ± 5	-1.8 ± 0.7	-37 ± 5	64.1 ± 2
Carrot, *Nantesa* (Gras *et al.*, 2001)	Slices ($t=10$ mm)	1036 ± 8	1 ± 1.1	3 ± 0.6	13.7 ± 2
Zucchini, *Blanco Griser* (Gras *et al.*, 2001)	Cross slices ($t=10$ mm)	841 ± 17	3 ± 8	4 ± 1.6	4.4 ± 0.9

[a] Apparent density (kg/m^3 of sample).
[b] Relative volume deformations of initial sample at the end of the vacuum step and at the end of the atmosferic step, respectively.
[c] Effective porosity.

peel products. In this sense, VI could represent a very interesting tool to be used to introduce sugars (Chàfer *et al*., 2001a), preservatives, nutraceuticals, and so on into their highly porous structure (Spiegel-Roy and Goldschimdt, 1996). The peel porosity (gas volume fraction) is located in the albedo zone, the white and spongy part of the peel, which consists of enlarged parenchymatous cells with great intercellular spaces (Spiegel-Roy and Goldschimdt, 1996), while the flavedo zone shows a very compact cellular structure, which is covered with a layer of natural wax, and contains oil glands (Storey and Treeby, 1994). The impregnation and swelling capability of orange peel, subjected to osmotic dehydration, was shown through the great uptake of osmotic solution in the product, especially when vacuum pulse was applied at the beginning of the osmotic process, thereby promoting the peel vacuum impregnation (Chàfer *et al*., 2001b,c). The great intercellular spaces in the albedo part were completely flooded by osmotic solution, as could be observed by cryo-SEM (Chàfer *et al*., 2001c). The VI impregnation response of orange, mandarin, grapefruit, and lemon peels was characterized by using different kinds of isotonic solutions, and the response was correlated with the peel microstructure (Chàfer *et al*., 2003). The particular cell arrangement of albedo explains the ability of the samples to swell in line with both the out flow of internal gas (during the vacuum step) and the impregnation of the pores with external liquid. Because cells are nonturgid and wide open in their packaging, they do not offer great resistance to structure swelling. Additionally, the great amount of water-soluble and compatible polysaccharides in the extracellular volume contributes to the retention of a great amount of water (from the external solution). Even in the case of compounds with very low water solubility, the required amount may be introduced because of the great amount of solution that can be impregnated into the samples.

F. JAM MANUFACTURING

Osmotic pretreatments of frozen strawberries have been proposed in the production of high-quality strawberry jams (Viberg *et al*., 1998). Density changes in the fruits when they are immersed in different osmotic solutions and volume changes of osmotically processed strawberries were studied. The reduction in density differences between the syrup and the berries reduced floating of berries, which may otherwise cause problems both during thermal treatment and after packaging. Thermal processing of the osmotically processed berries did not cause a notable change in their volume. Furthermore, when an osmotic medium is selected for the processing of strawberries or other fruit, which contain an active invertase, it should be noted that the composition can change in the course of processing (Viberg and Sjöholm, 1998).

Osmotic concentration kinetics were also studied for the purpose of manufacturing carrot preserves (Singh *et al.*, 1999). The preserve quality was assessed as a function of sugar solution concentration and sample-to-syrup ratio, and the kinetics of preserve manufacture were described using an empirical equation.

G. FRYING

In recent years, the consumer's interest for low-fat snack products has increased substantially. The effect of prefry drying on frying kinetics and quality of French fries has been examined by Gupta *et al.* (2000) and Krokida *et al.* (2001a). They both indicated that prefry drying decreased the fat content of French fries and affected their color and structure properties significantly. Osmotic dehydration can be an effective pretreatment to produce low-fat French fries (Krokida *et al.*, 2001b). The mass transfer phenomena (both water loss and oil uptake) that take place during the frying of French fries get less intense. Color darkening takes place during osmotic dehydration, as observed in other vegetables, and browning reactions during frying are promoted, resulting in more dark and red-colored fried products. Salt-treated samples have the most acceptable color. The osmotic pretreatment increases total porosity for both maltodextrine and salt solutions, with the exception of the sugar solution, which decreases the total porosity due to the higher solid gain. The specific volume of osmotically pretreated samples decreases for sugar while it increases for maltodextrine solutions in comparison with that of untreated samples during frying.

H. FOOD SALTING PROCESSES

Despite a wide range of possible applications (Figure 17), only a few studies have been carried out since 1992 to assess the osmotic treatment of fish and meat products in concentrated solutions. An exhaustive review of these processes has been presented by the leading research group in this field, belonging to CIRAD (Collignan *et al.*, 2001). The first part of the review focuses on the study of mass transfer that occurs when an animal protein structure is placed in contact with a concentrated solution, and this study is aimed at clarifying the mechanisms involved and evaluating the potential of this technique as an alternative to conventional processes. The second part assesses the process on the basis of product quality development during processing and storage. The third part investigates possible pilot applications of the process, while the fourth part presents successful technological applications. Several pilot development applications have been transferred

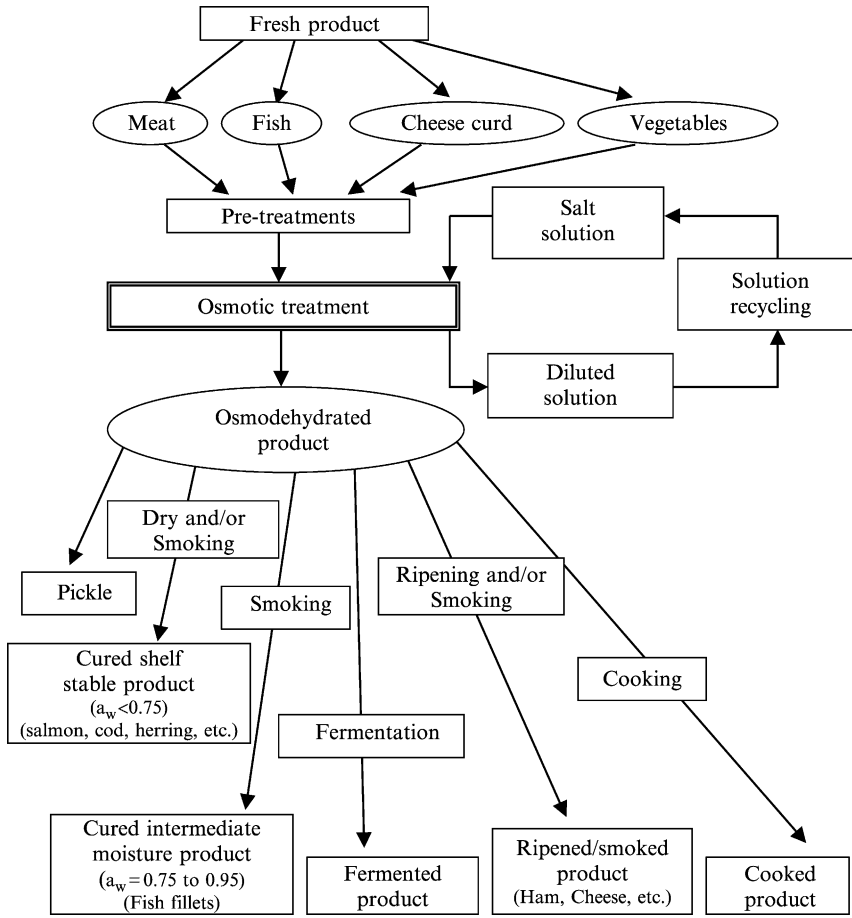

FIG. 17 Application range of salting osmotic treatment in specific fresh products.

to an industrial setting. Two patents were obtained for and extended to five EU countries for the processing of animal products. One involves a new salting, drying, and smoking process system that combines an immersion salting and drying process with electrostatic smoking (Collignan *et al.*, 1992b). The other patent was taken out for a dehydration and impregnation by drenching (DID) process system for marinating fish fillets (Marouzé *et al.*, 1996). Furthermore, a prototype for salting, drying, and cold smoking of fish has been developed for small-scale applications and validated under Réunion (French tropical island) production conditions (Collignan *et al.*, 2001). Processing in aqueous solutions also enables decontamination of a

product surface; an interesting avenue was explored in a study on stabilizing seafood products by quick treatment in an acid solution (Poligné and Collignan, 2000).

The use of brine vacuum impregnation (BVI), instead of dry salting or brine immersion (BI) at atmospheric pressure, was reviewed by Chiralt *et al.* (2001a). The influence of different process variables (length of vacuum pressure period, temperature, sample structure, and dimension) is analyzed in terms of kinetic data and process yields for meat (ham and tasajo), fish (salmon and cod), and cheese (Machego type cheese). VI can be highly effective in plant tissues, as porosity, the most crucial factor involved in the process effectiveness, may be very high (20–30%) such as in apple, eggplant, or orange peel (Gras *et al.*, 2001; Salvatori *et al.*, 1998b). Nevertheless, curd, meat, and fish are much less porous, and an important part of the matrix is occupied by the free liquid phase that may be released from the matrix by pressure changes. One consequence of the important role of food microstructure in BVI operations is a greater variability in the final salt content of the product than that obtained in conventional brining. This is due to the coupling of different phenomena throughout the salting process, all of which are affected by food structure: pore impregnation or partial collapse and diffusion in the fluid liquid phase, whose volume fraction is affected by the impregnation level. When characteristic times of deformation and impregnation of the solid matrix are very similar, each one can occur to different degrees with a notable repercussion on the salt transport behavior. Likewise, in products where porosity can be affected greatly by process conditions, such as pressed curd, a careful control of these variables is necessary to assure a constant value of porosity that implies homogeneous behaviour in BVI (Gonzàlez-Martìnez *et al.*, 1999). In general, the salt content, required in the product liquid phase to assure further product stability, is reached in BVI at higher moisture levels, which may imply a juicier product. In cured products such as cheese or Spanish ham, the different concentration profiles in the first ripening period may suppose small changes in the ripening patterns, texture (Pavia *et al.*, 1999), and volatile profiles (Escriche *et al.*, 2001b). Nevertheless, in practical terms, differences between production batches may be greater than those induced by salting methods. In conclusion, BVI techniques, if applied to porous foods, lead to a notable reduction of salting time, increasing the process yields in line with the greater values of the ratio salt gain to water loss. Likewise, samples lose natural gas or liquid phases entrapped in their structure and reach a flatter salt concentration profile than that obtained in conventional salting methods (Barat *et al.*, 1998b). Nevertheless, careful control should be taken with process variables, especially with those affecting the sample impregnation level, in order to ensure a homogeneous salting level.

IV. SOLUTION MANAGEMENT

The response to environmental and economic questions for the management of osmotic solutions has been recognized as one of the "technical hurdles" to the industrial outbreak of the process itself (Dalla Rosa, 1999). A very comprehensive review has been made by the participants of the "solution management subgroup" within the frame of the concerted action FAIR CT96-1118 and has been summarized by Dalla Rosa and Giroux (2001). This review takes into account items related to the solution changes during the process, the possibility to restore or reuse the solution itself, and the relationship between the food subjected to dehydration and the solution properties (Figure 18).

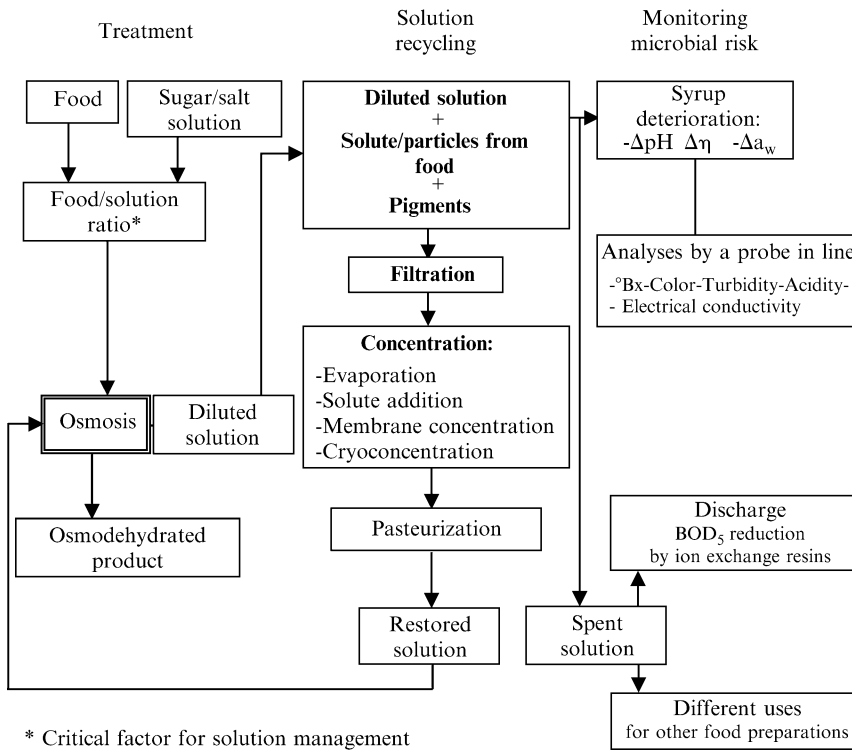

FIG. 18 Idealized flowchart of solution management and control system during direct osmotic treatments of plant or animal materials.

A. SOLUTION MASS AND DILUTION

As for the solution mass and dilution, a ratio food/solution 1:5 or lower, and thus a great amount of solution, has always been proposed in order to assure a constant rate of solid/liquid exchanges. The dilution rate can be modeled, and the dewatering capacity of the diluting solution can also be described and previewed easily in terms of reduction of chemical potential or difference of osmotic pressure between hypertonic solution and food. The dilution rate also depends dramatically on the type of food processed and reduces the osmotic capacity of the solution. Techniques have been developed to avoid large amounts of solution quantity, placing the food in equipment where the solution is sprayed onto the food; with this technology the food/solution ratio can be increased up to 1:2 (Marouze *et al*., 1996). This reduction of volume is also necessary to limit environmental impact, vis-à-vis a more demanding legislation.

B. SOLUTION RECYCLING

The most promising way to reduce environmental impact would be to reuse the concentrated solution for as long as possible. However, loss of solutes and particles from food into the solution were reported by many authors, leading to chemical, chemical–physical, and sensory changes of the osmotic solution itself. Specific research on the influence of the repeated use of a sugar solution has been carried out on treatments of papaya, pineapple, and peach (Argaiz *et al*., 1996), of apple (Valdez-Fragoso *et al*., 1998), of sour cherries (Szymczak *et al*., 1998), and of apple and stoned cherries (Giroux *et al*., 2001). It was shown that it was possible to reuse the solution between 5 and 20 times, depending on the treated fruit, without any impact on the main mass transfers in the products and with good microbial quality of the solution. The use of activated carbon or polyvinylpolypyrrolidone (PVPP) for decoloration of used syrup has been proposed by Szymczak *et al*. (1998) and has led, especially for the activated carbon, to nonsignificant differences on dehydrated fruit color between fresh and recycled syrups.

C. SOLUTION CONCENTRATION RESTORING

When reusing the osmotic solution, the first main problem is to restore the solute concentration. The technological answers that could be suggested include both phase and nonphase changing processes:

- evaporation (atmospheric at high temperature; under vacuum at moderate temperature)

- solute addition (no phase change)
- membrane concentration (no phase change)
- cryoconcentration

Evaporative restoring is probably the most popular technique to be implemented industrially for a medium/large production plant, as the cost of evaporators is relatively low. However, it is necessary to study the engineering and energetic aspects of the applied method of water removal, mainly the knowledge of the energy consumption in the osmotic process and the comparison between a per-unit energy consumption in this technique with that of other methods of water removal. The only research on this aspect related to fruit processing is still that of Lenart and Lewicki (1988) and Collignan *et al.* (1992a). Results indicated that per-unit energy consumption during convection drying of fruit and vegetables was two to three times higher than that of osmotic dehydration and syrup reconcentration through an evaporator. More recent data can be found for meat and fish osmotic treatment, mainly for processes already patented (Collignan *et al.*, 2001; Giroux *et al.*, 2001).

Restoring the solution concentration by adding dry solute or mixing with concentrated solution can save energy costs as it avoids heat of evaporation and the need for expensive plants. The method can be suggested successfully for small-scale production, at a low-technological level process, where the initial solution mass is small. Indeed, the main hurdle of this technique is the increase of the solution mass, even if a constant loss in volume of syrup (9–14%) is due to adherence to the food pieces (Bolin *et al.*, 1983).

Salt solution recycling is often a necessity in other food processing industries, such as in the cheese and table olive industry, where the reuse of salting brine is very common and the brines are worked for several cycles without any fresh brine addition. For this reason, great attention has focused on innovative technological solutions applied in these sectors, which could also be utilized for syrup recycling during osmotic treatments, e.g., the use of membrane concentration, which can reach different goals other than solution restoring. This technique could be useful because it combines filtration and reconcentration without any energy cost other than the energy required for pumping. Actually, membrane processing has to take into account the fouling phenomena at the membrane interface and the difficulty of working with relatively high viscosity fluids such as the osmotic solution (40–60 Pa * s in case of 60% of solids). The use of membranes has been applied successfully for remediation and/or recycling of dairy effluents (Horton, 1997) and for brine recycling in the table olive industry (Barranco *et al.*, 2001; Garrido-Fernàndez *et al.*, 2001). An innovative model system based on the use of membranes for osmotic solution management has been proposed by

Proimaki and Gekas (2000), where mass transfer among three concentric parts of an osmotic reactor is carried out.

D. MICROBIAL CONTAMINATION

When reusing the osmotic solution, the problem of microbial contamination also has to be faced. Different sources of contamination can affect the microbial stability of the used solutions, although the water activity values, ranging around $a_w = 0.90–0.95$, should be able to limit the growth of nonosmotolerant bacteria and yeast (Valdez-Fragoso *et al.*, 1998). During processing of fruit and vegetables with a pH $\leq$ 4.5, yeast, molds, and lactic bacteria are the most frequent microorganisms released from the product into the solution, but in this situation, pathogenic bacteria are not able to grow. During processing of animal products or low acid vegetables, such as potatoes, bacteria, even potentially pathogenic, are able to grow when the dilution of the initial solution leads to an increase of water activity. Individualization of critical control point and implementation of HACCP methodology for process control become a must when osmotic treatments are carried out in order to produce minimally processed shelf-stable foods (Leistner, 1995).

If the process is carried out in a nonsterile environment and the concentration restoring takes place by evaporation at low temperature or by nonevaporative processes, the sanitation of the solution comes out as a priority to maintain the microbial load at low level. Plate heat exchangers can be used despite the high viscosity of the solution (Dalla Rosa *et al.*, 1995), taking into account the protection demonstrated by concentrated sugar solutions on the heat inactivation of microorganisms (Torreggiani and Toledo, 1986). A big problem occurring as a consequence of heat treatment is nonenzymatic browning such as caramelization and Maillard reactions, as some amino acids or proteins have been extracted from the food. The susceptibility to thermal degradation depends mainly on the presence of reducing sugars and on the pH solution; the use of corn syrup instead of mono- or disaccharides can be useful.

E. POSSIBLE USES OF THE SPENT SOLUTION

When the end point of the solution recycling is reached and the suggested methods of purification are not applicable any more, the spent solution can be directed to different uses, even though there is a lack of specific literature. Solutions coming out from fruit treatment could be used as

- Syrup for fruit canning
- Jams

- Mixing with fruit juices
- Diluting with water and addition of carbon dioxide to obtain fruity soft drinks
- Production of natural flavoring
- Bee or animal feeding, after increasing the protein content

No further uses of spent brines have been suggested.

F. DISCHARGE OF THE SPENT SOLUTION

Spent solutions that cannot be used have to be discharged as wastewater. The main problem is related to the high biochemical oxygen demand in 5 days (BOD_5) of the concentrated solution, which in addition to containing carbohydates is now also rich in organic materials, such as protein, pectin, and acids. Ion-exchange resins have been proposed to reduce the nitrate content in spinach blanching water (Kristani *et al.*, 1999) and can be suggested, together with membrane processes (Horton, 1997), also for syrup sanitation. An alternative is a biological treatment, which has proven to be successful for the treatment of black olive wastewater (Borja *et al.*, 1993; Brenes *et al.*, 2000).

V. SUMMARY

The complexity and vastness of the scientific field that has been reviewed in this chapter bring forth, as a natural consequence, the parallel need for further in-depth studies into some key research areas. Knowledge of the process, as a unit operation, has jumped forward due to the fruitful work of the EU-FAIR Concerted Action CT96-1118 "improvement of overall food quality by application of osmotic treatments in conventional and new processes" and could already support the application of the technique at the industrial level as a prestep in innovative combined processes. The decisive challenge for a completely successful process control and optimization has to be focused on the following problematic aspects.

- Analysis of mass transfer in ternary media, until now, has mainly involved experimental studies of model and real food. Phenomenological models could be applied to obtain a more detailed description of the mechanisms involved. However, this would require an understanding of factors such as mass transport properties and transfer dynamics of different active compounds in concentrated solutions, which have yet to be characterized.
- In pulsed vacuum immersion, a phenomenological model would be difficult to develop as solution filtration and solute diffusion mechanisms have to be considered. The main problem to be solved concerning this aspect

is the measurement of some specific properties of processed products such as effective permeability, porosity, and specific surface.

- Up until now, product quality has mainly been evaluated through analyses of end products after processing and thus the results often remain factual. Kinetic analysis of mechanisms during processing is required to gain a broader understanding of quality development while focusing on close interactions between mass transfer and reaction mechanisms.
- Widespread research has to be focused on the potential of animal product surface decontamination, which is an additional feature of processing in concentrated aqueous solutions.
- As for the management of concentrated solutions, systems have been validated for relatively simple conditions of salting and drying products in a water–salt–sugar solution to obtain low product dehydration levels. When formulating products in more complex solutions (addition of liquid-flavoring agents, combinations of several different acids, etc.), the problem arises of measuring and sustaining optimal solute concentrations (development of specific sensors) and recycling the solution for further use (reconcentration, filtration, decontamination). The analysis of systems requiring a series of separate processing operations should be recommended.
- Predictive microbiology using growth models should be implemented in order to follow the microbial behavior in fruit osmotically dehydrated/impregnated and to compute their shelf life as a function of process variables, such as concentration of osmotic medium, initial contamination of the solution, and fruit storage temperature.
- Last but not least is the question of equipment. The study and development of equipment that can simultaneously perform osmotic dehydration and solution management are essential requirements for industry in the years ahead.

ACKNOWLEDGMENTS

The authors acknowledge the great contribution of Dr. Caterina Prinzivalli, without which this review would not have been fulfilled.

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INSECT MANAGEMENT IN FOOD PROCESSING FACILITIES

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ADVANCES IN FOOD AND NUTRITION RESEARCH VOL 48
ISSN: 1043-4526

I. INTRODUCTION

After harvest, as grain is stored, converted into processed commodities in food processing facilities, stored in warehouses, transported, displayed on retail shelves, and ultimately held in consumer pantries it is continually under pressure of becoming infested and degraded by insects. There are unsubstantiated estimates in the literature that claim 5–10% of stored grain in developed countries and 35% of stored grain in developing countries are lost to insect damage (Boxall, 1991). In many parts of the developing world, stored grain loss due to insect consumption and contamination can range up to 75% and directly threaten human health (Gorham, 1991). In the developed world, direct loss of grain material due to insect feeding is typically of less concern than contamination of food products. Tolerance for insect infestation of processed food for human and animal consumption is very low, and the direct and indirect cost to the food industry of insect infestation of grain-based products is substantial.

There are limited data on the economic cost of stored-product insects to the food industry, partly due to either difficulty in measuring the economic impact or reluctance to release the information. The diversity of commodities and facilities and the movement and blending of the commodity as it moves through postharvest systems make it difficult to estimate the impact of stored product insects. In bulk storage, insect damage is only a direct cost if the grain is rejected due to high levels of insect damaged kernels or assigned a lower grade, but the market penalties are set by the individual grain buyer and managers can manipulate damage levels by blending grain (Hagstrum *et al.*, 1999). Therefore, discounts for insects are highly variable and do not provide much incentive for controlling insects. Domestic flour millers have a zero tolerance for live insects (Kenkel *et al.*, 1993), and the presence of insects can result in the rejection of grain, which produces additional expenses associated with insecticide treatment, usually fumigation, and extra transportation costs. These additional costs of rejected loads can be as much as 10–20% of the value of the grain (Hagstrum *et al.*, 1999). Estimates of the cost of grain loss due to insect, mold, and mycotoxin damage to the 15 billion bushels of grain stored in the United States each year have ranged from $500 million (Harein and Meronuck, 1995) to in excess of $1 billion (Cuperus, 1995). The only costs that can be calculated accurately for insect damage in stored grain are costs for insecticides, which include contact insecticides and fumigants, and these costs can be quite high. Costs for empty bin treatments range from 0.033 to 25.9 cents/ton and the costs to fumigate bins range from 58.09 to 86.95 cents/ton, depending on the type of structure (Hagstrum *et al.*, 1999).

For processed cereal products it is the contamination of the food that is the major issue rather than loss of food material due to consumption by insects. Stored-product insects can add fragments to food that can indicate that the food is adulterated, cause a health hazard, and provoke allergic reactions (Olsen, 1998; Olsen *et al*., 2001), produce excretions that change the taste of food, and potentially carry disease-causing microorganisms (Foil and Gorham, 2000). Infestation of packaged commodities also imposes costs associated with loss of customer good will, degradation of commercial brand identity, failure to meet regulations or pass plant inspections, and handling of product returns and consumer complaints. There are also expenses associated with preventing and treating insect problems in facilities such as fumigation and sanitation. All segments of the food industry are susceptible to insect infestation (baking and confectionary, grain processing, cereals and prepared dry mixes, pasta, canning, meat and poultry, dairy, and frozen foods), but clearly segments that handle whole and processed grain will spend more on stored-product insect management.

Although considerable progress has been made in the protection of stored food using integrated pest management (IPM), many sectors of the food industry still depend primarily on chemical methods, and as chemical control options diminish, the potential for a significant increase in losses could correspondingly increase. Despite the low tolerance for insects in food by consumers and the food industry, pest infestations are still a problem. Surveys of insects in food plants, warehouses, and retail environments frequently document insect populations (Arbogast *et al*., 2000; Campbell *et al*., 2002; Doud and Phillips, 2000; Evans and Porter, 1965; Good, 1937; Zimmerman, 1990). Prevention and treatment of insect infestation of food are ongoing processes for the food industry that require careful monitoring and the application of multiple tactics to be truly effective. Pest management is complicated because a wide range of insect pests infest food, facilities along the food processing and distribution channels are highly variable, pest management within a facility requires continuous monitoring and adjustment of tactics to meet changing conditions, and often different groups of people are responsible for pest management at different points along the food distribution channel.

The goal of a modern integrated pest management program is preventing problems and targeting interventions in both space and time. This approach relies on an understanding of pest biology, behavior, and ecology within the context of food processing and storage facilities. Unfortunately, all too often pest management decisions are made without adequate information about pest populations, which can result in treating when and where treatment is not needed or not treating when and where treatment is needed. The food

industry has relied on calendar-based pesticide applications, often applied to the whole structure, but is currently facing profound changes in how pest management is conducted due to the pending loss of many chemical tools (e.g., methyl bromide fumigation) on which they previously relied.

There is a long and productive history of scientific research on stored-product insect biology, behavior, ecology, monitoring, and pest management, but the emphasis of the majority of this work has been on insects in bulk grain. This emphasis has been changing and advances are being made in our understanding of how to manage pest populations in environments such as mills, food plants, warehouses, and retail stores. This article presents an overview of the status of integrated pest management of stored-product insect pests in the processed food industry.

II. FOOD PROTECTION REGULATIONS

Modern food preparation typically occurs in large processing facilities and involves the production of food for thousands of people. Because of the risk of contamination, food processors in the United States are obligated to provide a contaminant-free product for consumers. To enforce these obligations there are laws and regulations that provide guidance on proper practices in food processing. Consumer acceptance and satisfaction are also important factors driving the production of contaminant-free products because consumer tolerance for the presence of insects or insect damage is very low. If an insect is found in a packaged food, the consumer is not only hesitant to purchase the product in the future, but will also tell other consumers about their bad experience and thus compound the negative impact. Allergic reactions to food contamination are also an important issue and its importance is increasing. As a result, food producers are sensitive about issues involving food quality and safety. However, because of the way processed and packaged food is distributed, it is possible for products to become infested anywhere along the distribution channel, not just at the point of manufacture.

Food laws and regulations have played a major role in the purity and quality of our foods and in driving pest management decisions by the food industry. In the United States, the national U.S. Pure Food and Drug Act was passed by the Congress in 1906 in response to two historical circumstances: change from local distribution of food products to national and export distribution and the development of new methodologies to detect adulteration in foods (Von Elbe, 1982). This act prohibited the adulteration or misbranding of food and drugs to protect public health and to secure fair commercial trade. It prohibited interstate commerce of products that were

adulterated or misbranded, but gave no authority for action against facilities where products were processed or manufactured and no authority to inspect warehouses.

A revision of the Pure Food and Drug Act, the "Federal Food Drug and Cosmetic Act," passed in 1938, added several provisions that impacted the food industry. Among those provisions were authorized factory inspections and the authority for court injunction to the previous seizure and prosecution actions (Janssen, 1992). Adulterated food was now defined as: "Sec. 402, A food shall be deemed to be adulterated if it consists in whole or in part of any filthy, putrid, or decomposed substance, or if it is otherwise unfit for food, or if it has been prepared, packed or held under unsanitary conditions whereby it may have become contaminated with filth, or whereby it may have been rendered injurious to health." The importance of the *whereby* clause is the concept that a food product need not be contaminated physically to be considered adulterated, but has been exposed to conditions that may have resulted in contamination of the food. This situation is vastly different from that which existed at the time the 1906 Food and Drug Act was passed.

Even though the Food, Drug, and Cosmetic Act of 1938 provided for factory inspections by the Food and Drug Administration (FDA), there was no published guideline for what would constitute conditions "whereby" a food may have become contaminated. In 1969, the FDA promulgated a regulation, "Human Foods: Current Good Manufacturing Practices (Sanitation) in Manufacturing, Processing, Packing, or Handling." This regulation and its revision have outlined conditions and criteria that were considered acceptable practice for producing foods under sanitary conditions. New approaches designed to prevent hazards to food safety from food pathogens, such as hazard analysis critical control points (HACCP), which is currently mandated by FDA for only some food products (e.g., seafood, fruit juices) but which has also been incorporated into FDA's food code and may be expanded to cover other food materials in the future (Hui *et al.*, 2003), may impact insect pest management.

There are three major categories of filth and extraneous material that constitute contamination: potentially hazardous, indicators of insanitation, and aesthetic defects (Zimmerman *et al.*, 2003). Potentially hazardous material includes physical hazards such as hard or sharp objects, chemical hazards such as mites that can cause allergic reactions (Olsen, 1998), or insects that may carry food-borne diseases. Even if insects do not present a health hazard, the presence of insects as foreign matter in food is considered an indication of unsanitary conditions (Zimmerman *et al.*, 2003). The presence of unsanitary conditions can be indicated by the presence of live or dead insects and by intact insects, fragments of insects, or insect products such as

feces or cast cuticles. Aesthetic defects are those that do not fall in the first two categories, but would still be objectionable to consumers. An insect example would be agricultural or incidental species harvested with the commodity and incorporated into the final product.

III. STORED-PRODUCT INSECT PESTS

A diverse community of organisms (microflora, arthropods, rodents, birds) are associated with human structures and stored food, and identifying and understanding the biology of the pests present are critical first steps to pest management. There are four major categories of pests that may contaminate processed food products (Zimmerman *et al.*, 2003). Obligatory pests are associated with human environments, are attracted to human stored food, and live and breed in the food product (e.g., stored-product pest arthropods). Opportunistic pests are attracted to human food, are associated with human modified habitats, and often inhabit human structures, but usually do not live in the products they contaminate (e.g., flies, cockroaches, ants, rats, and mice). Adventive pests are associated with human environments but are not particularly attracted to human food and not strongly associated with human structures (e.g., birds, bats, and some insect species). Natural enemies are parasitoids and predators of the other three groups and can occur in human structures, be attracted to food odors and hosts in or near human food, and end up being contaminates of food.

Arthropods are invertebrate animals that have a segmented body, jointed appendages, and an external skeleton (i.e., cuticle). This phylum contains insects, arachnids, and crustaceans, but the important pests of the food industry are in the class Insecta and Arachnida (e.g., mites). Arthropods comprise a large portion of the biodiversity in food storage and processing facilities. For example, 600 species of beetles in 34 families (Hinton, 1945) and 70 species of moths in primarily four families (Cox and Bell, 1991) have been reported to be associated with stored products. Fortunately, not all of these species are widely distributed nor are they all highly damaging. Many of these species are generalists and feed on a wide range of stored commodities, not just grain-based foods. The specific community of arthropods associated with food processing, storage, and retail facilities is influenced by a wide range of factors: geographic location, season, building construction and condition, food products available, management practices, etc. This section focuses on the obligatory pests, the diverse group of arthropods that feed directly on grain and cereal products.

Stored-product arthropods can be grouped in different ways based on taxonomy, feeding preference, and life history traits. To provide an

introduction, the arthropods are grouped into 11 groups based in part on the USDA Agriculture Handbook Number 500 and some of the major species in each group are discussed briefly. Some of these groups feed on whole seeds, typically with one portion of the life cycle occurring within the seed, and some feed on damaged (e.g., broken kernels, grain dust) and processed seeds. Insects in the second group tend to be secondary pests in bulk stored grain, but become much more important as pests in processed food facilities. For more detailed information on stored product pest biology and taxonomy, see Gorham (1987, 1991).

A. GRAIN WEEVILS

Grain weevils are in the family Curculionidae and contain three highly damaging pest species: *Sitophilus oryzae* (L.) (rice weevil), *S. granarius* (L.) (granary weevil), and *S. zeamais* Motschulsky (maize weevil) (Longstaff, 1981). Adults are 0.3–0.6 cm in length and have an elongated snout containing the mouthparts that are typical of all weevils. Grain weevils have a worldwide distribution, but none thrive in tropical and subtropical regions. They attack primarily whole grain and seeds and typically do not reproduce on fine products such as flour, but can infest formed cereal products such as pasta. Females deposit eggs singly in holes excavated into seeds and then cover the eggs with a mucilaginous egg plug. Adults live a long time and females can lay a large number of eggs over their lifetime (Richards, 1947). Larvae develop and pupate within the seed and after eclosion adults chew out of the seed. Because larvae, pupae, and adults can occur inside whole kernels, these species can be more difficult to detect and thus contribute to fragment counts in processed grain products.

B. GRAIN BORERS

Grain borers of the family Bostrichidae are another highly damaging group of whole grain pests. Two species of major importance are *Rhyzopertha dominica* (F.) (lesser grain borer) and *Prostephanus truncatus* (Horn) (larger grain borer). *R. dominica* is a cylindrical beetle about 0.3 cm long with its head tucked under the prothorax so that it is not visible from above. This species is cosmopolitan and is associated primarily with whole grain. Both adults and larvae feed and tunnel through grain and females can lay hundreds of eggs over their life. Eggs are laid on the outside of whole kernels and larvae burrow into the seeds. Feeding leads to fragmented kernels, powdery residues, and a characteristic pungent odor. *P. truncatus* originated in meso-America and has since spread widely, although it is not currently thought to be found in North America, and is now one of the most destructive pests of

stored corn and cassava in Africa (Hodges *et al.*, 1983; Pantenius, 1988). Adults tunnel through grain and lay batches of eggs in side chambers excavated off the main tunnel and then larvae tunnel through the grain in which the eggs were laid.

C. GRAIN MOTHS

Some moth species also attack intact seeds; the Angoumois grain moth [*Sitotroga cerealella* (Olivier)] is one of the most common species. Adults are small (0.125-cm wingspan), buff-colored moths with a fringe of long hairs on both pairs of wings. Adults do not feed and are short lived. Larvae feed and develop within the seed and before pupation chew an exit hole in the seed. Moths commonly attack grain before harvest, laying their eggs on or near grain such as wheat, corn, oats, or rice in the field. This pest can also infest grain after it is stored, especially in open storage such as corn cribs. Modern harvesting and storage methods have reduced the impact of this insect.

D. GRAIN AND FLOUR BEETLES

A diverse group of beetles share the characteristic that they attack primarily damaged kernels or processed grain products. The major pest species of the food industry in this group are two species of *Oryzaephilus*, the saw-toothed and merchant grain beetles, and two species of *Tribolium*, the red and confused flour beetles. The group also includes the flat grain beetle *Cryptolestes pusillus* (Schönherr) and the rusty grain beetle *Cryptolestes ferrugineus* (Stephens), which can be common in bulk grain storage.

Oryzaephilus surinamensis (L.) (sawtoothed grain beetle) and *O. mercator* (merchant grain beetle) (Silvanidae) are two morphologically very similar species. They are small beetles (0.3 cm in length) that have saw-like projections along each side of their thorax. Both are cosmopolitan pests of a wide range of foods, including stored grain, processed grain products, oil seeds, dried fruit, seeds, insect eggs, dead insects, and fungi (Howe, 1956; Loschiavo and Smith, 1970). The sawtoothed grain beetle is one of the major pests of packaged foods. Females start to lay eggs within a week after eclosion and can lay over 250 eggs during their life. Eggs are laid singly, primarily in crevices, and there are three larval instars. Before pupation, a larva will build a pupal cell and fasten itself to a solid object.

Although nine species of *Tribolium* are potential pests (Sokoloff, 1974), *Tribolium castaneum* (Herbst) (red flour beetle) and *T. confusum* (Jacquelin du Val) (confused flour beetle) (Tenebrionidae) are the most widespread and economically important species. Adult beetles are reddish-brown in color

and measure 0.3–0.5 cm in length. These beetles do not typically feed on whole grains, although they can feed on broken and damaged kernels. They are most damaging to flour and other milled products. Eggs are laid directly in food material. Adults of both species have developed wings, but only *T. castaneum* has been reported to fly. Adult *Tribolium* can live for more than 3 years and females can lay eggs for over a year under laboratory conditions (Good, 1936).

E. MEALWORMS

The yellow mealworm *Tenebrio molitor* L. and the dark mealworm *Tenebrio obscurus* F. (Tenebrionidae) are the largest of the stored product beetles (1.25 cm in length) (Cotton and St. George, 1929). They are most often associated with decaying grain or cereal products under dark and moist conditions, but will feed on a wide variety of foods. Females can lay hundreds of eggs and live for several months. Larval stages can survive for long periods of time under unfavorable environmental conditions and can wander far from food sources to pupate. Adults are strong fliers and are attracted to lights.

F. DERMESTID BEETLES

A large number of dermestid (Dermestidae) beetles are associated with human structures, but only two species, *Trogoderma granarium* Everts (khapra beetle) and *T. variabile* Ballion (warehouse beetle), are considered to be major food pests. In addition to damage caused by feeding, they can contaminate food with body parts, hairs, or cast larval cuticles that cause gastrointestinal irritation and allergic reactions for asthmatics and sensitized individuals (Olsen *et al.*, 2001).

Trogoderma granarium is one of the most destructive pests of grain in the parts of the world where it occurs and it is the only quarantine stored-product pest in the United States. It feeds on a wide range of stored products, but unlike other dermestids, it prefers whole grain and cereal products to animal-based products (Lindgren *et al.*, 1955). Adult khapra beetles are short lived, do not require food or water, and most eggs are laid during the first few days of the oviposition period. Larvae may enter a form of diapause where they continue to feed and molt intermittently, but do not pupate, and this diapause can be maintained for over 6 years when food is present (Nair and Desai, 1973). Diapause is influenced primarily by high density, but a density-independent diapause can also occur (Nair and Desai, 1973).

Trogoderma variabile are small (0.3–0.6 cm in length), oval-shaped beetles that are dark in color with varying levels of yellowish banding on the elytra.

This beetle is found on a wide range of foods, but develops best on animal feeds, whole grains, pollen, and various processed food commodities such as egg noodles and wheat germ (Partida and Strong, 1975). Adults are short lived and oviposition peaks after a few days and then declines rapidly. Eggs are laid singly either loosely or in crevices. This species has a larval diapause similar to *T. granarium*.

G. SPIDER BEETLES

Adult spider beetles (Ptinidae) are small (0.08–0.5 cm in length) with long legs and a head that is often not visible from above so they superficially resemble spiders. They feed on a wide variety of foods, including cereal grains, seeds, flour, dried fruits and vegetables, animal nests, and dead animals. They are generally scavengers, but occasionally can become pests, especially in northern regions, on processed grain products such as flour, bran, and feed meal. Typically they become a problem when commodities are stored a long time and near a source of moisture. Eggs are often laid outside of grain sacks and in flour debris in cracks and crevices. Larvae can bore into wood or cardboard boxes to overwinter in a pupal cell. Adults typically live 1 to 6 months and females can lay up to 100 eggs.

H. MISCELLANEOUS BEETLES

Lasioderma serricorne (F.) (cigarette beetle) is one of the most important species in this group. It is found around the world in tropical and subtropical regions and is associated with heated buildings in temperate zones (Howe, 1957). Adults are small (0.2–0.4 cm in length), tan-colored beetles with a hump-shaped appearance. Adults are short lived, on average 18 to 21 days, and can feed (Lefkovitch and Currie, 1967). Despite its name, immatures develop on a wide range of commodities, including spices, nuts, beans, dried fruits and vegetables, grain and grain products, and tobacco. Females lay eggs in crevices, and newly hatched larvae can enter small holes associated with food packages. When mature, larvae create cells of food and waste in which they pupate. A number of other beetles of varying degrees of economic importance are in this group, including the hairy fungus beetle *Typhaea stercorea* (L.) and the drugstore beetle *Stegobium paniceum* (L.).

I. FLOUR MOTHS

A number of moth species are found associated with food storage structures. *Plodia interpunctella* (Hübner) (Indianmeal moth) is one of the most damaging stored-product moths for the food processing industry, retail stores,

and homeowners. Adults have a copper-colored band of scales on the distal portion of the forewings and have a 0.13-cm wingspan. Larvae feed primarily on broken and damaged kernels, but sometimes chew into whole wheat kernels. Females lay 60–200 eggs on or near food during their brief life span. Eggs hatch in less than 2 weeks, and during the process of feeding, larvae produce silk that can web food particles together. Larvae feed on a wide range of foods such as dried fruits, flour, nuts, chocolate, pet food, spices, and pasta. Last instars enter a wandering phase prior to pupation and can often be observed crawling in exposed areas. They can also enter diapause to overwinter. Some other related moth species that attack a wide range of commodities and can be important pests in certain regions are *Pyralis farinalis* L. (meal moth), *Anagasta kuehniella* (Zeller) (Mediterranean flour moth), and *Cadra cautella* (almond moth).

J. PSOCIDS

A number of species in the insect order Psocoptera are often associated with human structures and stored food. They are often called book lice or bark lice because of their superficial resemblance to lice. They are small (1–6 mm long) soft-bodied insects with long thread like antennae and the species that occur primarily indoors usually lack wings. They are typically found in areas with high relative humidity that favor the growth of mold, which is a primary food source (e.g., damp spillage and wooden pallets that have become wet and moldy). Psocids typically occur at low densities and are not considered major pests in many parts of the world. However, in tropical countries and in subtropical zones with high temperature and humidity, psocids can build to large numbers and have an economic impact. They are also a problem in stored grain in Australia, where large populations can occur primarily as a secondary pest outbreak due to suppression of natural enemies as a result of fumigations (see citations in Rees and Walker, 1990).

K. MITES

Mites are arachnids in the order Acari and should not be classified or referred to as insects. Mites are typically very small (about 0.5 mm) and have oval bodies with little or no differentiation of their two body regions. Over 50 species of mites have been found associated with stored products: some feed directly on stored products, but others are predators, feed on fungi, or are parasites of other stored-product pests such as birds or rodents (Boczek, 1991). Mites can be important pests of stored food worldwide, but their economic importance varies considerably with location, commodity, and management practices. Some mite species can cause allergic reactions in

people. Mites are most likely to be a problem in temperate and humid climates, but some products such as cheese, pet food, and oilseeds are infested under warmer and drier conditions. Mites infest a wide range of stored food products, including grain, flour, cereals, dried fruits and vegetables, herbs, powdered milk, pet foods, cheese, tobacco, oilseeds, and livestock feed. During outbreaks, mites can build up to extremely high densities and become damaging.

IV. FOOD FACILITY LANDSCAPES AND THEIR INFLUENCE ON INSECT BEHAVIOR AND ECOLOGY

The foundation of an effective pest management program is an understanding of pest ecology and behavior at relevant spatial and temporal scales. In other words, we need to look at the environments in and around food facilities from the perspective of the insect and understand how they perceive and interact with this environment to monitor and target pest management more effectively. Most landscapes created or modified by humans tend to be highly fragmented (Wiens, 1976). Fragmented landscapes are a mosaic of resource patches that are separated from each other by barriers to movement or by patches of less hospitable habitat. The structure and dynamics of the landscape mosaic influence ecological processes such as population dynamics and spatial distribution (Turner, 1989; Wiens, 1997; Wiens *et al.*, 1993). Stored-product pests of the food industry are pests in large part due to their effectiveness at exploiting the temporally and spatially fragmented landscapes within food facilities and within which food facilities are located. The pattern of distribution of the food patches in a food facility ultimately influences the spatial distribution and abundance of the insects. Many studies have found that stored-product insects are not distributed evenly either spatially or temporally within buildings (Arbogast *et al.*, 1998, 2000; Campbell *et al.*, 2002). Therefore, targeting pest management in both time and space can increase the probability of suppressing the pest population and reduce the cost of management and risk of negative nontarget effects (Brenner *et al.*, 1998).

Any resource important for stored-product insects may be patchy and influence insect distribution directly or in combination with other factors (e.g., food, favorable environmental conditions, structural features such as harborages or refugia). This section focuses on the patchiness of food resources used for either feeding or egg laying because it is one of the major determinates of insect distribution in food facilities. The spatial scale at which landscapes need to be defined is based on the organism being studied and the questions asked (Pearson *et al.*, 1996; Wiens, 1989,

1997). Food resources for stored product insects are patchy at a range of spatial scales: individual pieces of food, packages of food material surrounded by packaging barriers, packages arranged on pallets, a warehouse, or a processing plant in a landscape that includes other food storage and processing facilities. In bulk storage, for example, a patch might be considered a single seed kernel if we are interested in how insects make oviposition decisions (Campbell, 2002; Cope and Fox, 2003) or a whole bin if we are interested in processes of immigration and emigration (Hagstrum, 2001). In a warehouse, a patch may be an individual piece of spilled product, a crack filled with food material, a whole package of commodity, or even the warehouse itself. All of these patch types can be separated from each other by barriers to movement (e.g., packaging and walls) and inhospitable habitat (e.g., cement floors and walls). The landscape structure at all of these spatial scales probably influences stored product insect populations, although our understanding of these processes is still very limited.

For postharvest pest management, we typically start with material that is considered to be free of live insect infestation (e.g., freshly harvested grain, milled flour, or extruded food) and this material is stored in ways that spatially separate the food into patches. As a result, most infestations of grain-based products, whether it is grain in a bin or a food package, result from failure to adequately remove insects from where product is being added and from stored product insects finding and exploiting the new patch of resource. In a simple classification scheme, we can think about the insects associated with food facilities occurring in one of three locations: outside of the facility, in the structure of the building, and in the target commodity we are trying to protect. Pest management focuses on reducing the infestation of the target commodity patches and responding to these infestations when and if they occur.

Resource patches can be extremely variable in size and quality and, from a pest management perspective, in degree of importance. Some of these resource patches represent the product(s) that we are trying to protect from infestation, some patches may be in or around the building and within the scope of a pest management program, and other patches may be in areas outside of a pest manager's control. Resource patches are also temporally variable due to anthropogenic (e.g., bins are emptied and refilled, packages are moved, exploitation by insects reduces patch quality, sanitation removes or moves patches of spillage) and nonanthropogenic reasons. Some food patches in a structure will tend to persist longer than others (e.g., food material in a wall void that is not accessible versus spillage in an aisle) and have a higher probability of becoming infested and contributing to the increase and persistence of pest populations. Patch quality (e.g., size and nutritional value) has an influence on the probability of being encountered

and a strong influence on the level of progeny production from the patch. These long-duration patches can produce large populations of pests that can contribute to pest problems over much larger spatial scales. For example, Campbell *et al.* (2002) identified a major source of warehouse beetles on one floor of a food processing plant and used mark–recapture methods to demonstrate that the beetles dispersed from this source across multiple floors and therefore contributed to pest problems in relatively distant portions of the facility. Thus it is not only necessary to identify and eliminate the food patches that are important for the buildup/persistence of pest populations, but also to prevent/eliminate the exploitation of target food patches.

The influence of environmental heterogeneity on movement behavior can have important consequences for the ecology of organisms (Hanski, 1998; Turchin *et al.*, 1991). Movement patterns of individuals in heterogeneous environments and residency time in different patches together determine spatial distribution (With and Crist, 1995) and the degree to which patches are interconnected (Wiens *et al.*, 1997). In food facilities, the distribution and movement of insects among different resource patches can be due to their own dispersal behavior or through human intervention (e.g., mixing of infested grain with uninfested grain, bringing infested packages into a warehouse, and moving the location of spillage through housekeeping activities).

The extent of insect movement among patches of food will influence the probability that stored products will become infested, the persistence of populations within storage facilities, and many aspects of pest management (e.g., the interpretation of trap catches or the effectiveness of insecticides and insect-resistant packaging). Stored product insects are often observed outside of food patches, can be highly active, and can disperse by walking or flying. Stored-product pests are trapped readily outside grain storage and processing structures (Doud and Phillips, 2000; Dowdy and McGaughey, 1994; Fields *et al.*, 1993; Throne and Cline, 1989, 1991) and are sometimes captured far away from anthropogenic structures (e.g., Cogburn and Vick, 1981; Sinclair and Haddrell, 1985; Strong, 1970; Vick *et al.*, 1987). This suggests that they have the capability for long-distance flight, although these captures may also indicate feral populations in proximity of the traps (Howe, 1965a; Khare and Agrawal, 1964; Stein, 1990; Wright *et al.*, 1990). The flight initiation behavior of several species has been well studied (e.g., Fadamiro and Wyatt, 1995; Perez-Mendoza *et al.*, 1999), but measurements of the actual distance that stored-product pests can fly are more limited. Chestnut (1972) demonstrated that the maize weevil *Sitophilus zeamais* flew up to 400 m, whereas Hagstrum and Davis (1980) found that *E. cautella* flew 300 m during a 10-min flight. *Prostephanus truncatus* flight duration in response to pheromone in a laboratory wind tunnel indicates that most flights are of short duration, but for young adults, long-duration flights

(>30 min) were possible and could lead to dispersal distances in still air of up to 1620 m in an hour (Fadamiro, 1997). Field observations of *P. truncatus* flight report shorter distances (see references in Fadamiro, 1997). Little is known about how far species that do not fly (e.g., sawtoothed grain beetle, confused flour beetle) are capable of dispersing.

Self-mark recapture has been used to measure stored-product insect movement in a commercial facility (Campbell *et al.*, 2002). With the self-mark recapture approach, pheromone-based self-marking stations are used where insects are attracted to a pheromone lure and during their visit they pick up fluorescent powder on their bodies. These individuals can then be captured in pheromone traps at other locations. This technique was used originally in stored product environments as a method to estimate pest population density (Wileyto *et al.*, 1994). A high degree of male *Trogoderma variabile* mobility was reported by Campbell *et al.* (2002) using the mark–recapture technique. Individual beetles were able to move across multiple floors and from 7 to 216 m through a warehouse. This suggests that there is considerable potential for these species to colonize and exploit patchy resources throughout a facility. Outside of structures, male *T. variabile* and *P. interpunctella* were also highly mobile. *T. variabile* were recaptured on average 75 m (range 21–508; $n = 203$) and *P. interpunctella* were recaptured on average 136 m (range 21–276; $n = 6$) from where they were marked outside a food processing facility (J.F. Campbell and M.A. Mullen, unpublished data). All of these measures of dispersal distance are likely to be underestimates of actual dispersal ability. Both of these species have also been marked outside of processing facilities and recaptured inside (J.F. Campbell, unpublished data), highlighting the potential for outside populations to cause infestations within structures and for outside populations to impact pheromone-monitoring programs within facilities. The downside of using pheromone monitoring for investigating dispersal is that for species with female-produced sex pheromones, only the dispersal of males is measured. In most cases we know very little about female dispersal by stored-product insects, but it is likely that they have different dispersal strategies from males. Hagstrum (2001) found considerable rates of immigration into farm grain storage bins.

Direct behavioral evidence of how stored-product insects move among patches is limited, but what is available shows that stored-product pests readily leave patches of food, can find and exploit multiple patches, and that these processes are influenced by a variety of endogenous and exogenous factors. The time *Cryptolestes ferrugineus* spent in refugia has been shown to be influenced by strain, sex, and age (Cox and Parish, 1991; Cox *et al.*, 1989, 1990). A variety of factors have been shown to influence the decision by red flour beetles to leave food patches, including insect density

(Hagstrum and Gilbert, 1976; Naylor, 1961; Ziegler, 1977b; Zyromska-Rudzka, 1966), age (Hagstrum and Gilbert, 1976; Ziegler, 1976), and patch quality (Ogden, 1970; Ziegler, 1977a). Campbell and Hagstrum (2002) found that red flour beetles were often observed outside of food patches and that females visited and laid eggs in multiple patches. Campbell and Runnion (2004) found that female red flour beetles adjusted the distribution of eggs among food patches in response to the amount of food in the patches. Food volatile odors and, for some species, aggregation pheromones are probably important in stored-product insects finding and exploiting patches (Phillips *et al.*, 2000b). Endogenous factors such as the sex of the pest will also influence its tendency to disperse and its behavior while dispersing (Campbell and Hagstrum, 2002; Cox *et al.*, 1990; Naylor, 1961).

V. INTEGRATED PEST MANAGEMENT

Integrated pest management is a central theme in most insect pest management programs today, particularly for those involving production agriculture such as row crops and fruit orchards. A central theme in this historical development of the IPM paradigm involved scouting and sampling to determine when an economic threshold (ET) was exceeded, thereby avoiding unnecessary applications of a control, which in most cases would be an insecticide. There is a continuum of IPM systems, ranging from those still largely dependent on chemical treatments, but relying on economic thresholds (Stern, 1973; Stern *et al.*, 1959) to determine the need for treatment, to those that rely on multiple prevention strategies and rarely if ever need chemical interventions. One of the central tenets of IPM is the reduction in the use of chemical insecticides and using more ecologically based control methods when possible. IPM is ideally a multiple-tactic approach that has redundant tactics to assure that pest populations are kept suppressed. IPM was originally developed by field crop entomologists (Kogan, 1998) and is generally a more information and management intensive operation than conventional chemical-based pest control. In principle IPM can be applied to pest management in food processing facilities, but as discussed later, it is not always directly analogous to pest management of field crops.

There are many definitions of IPM, but most definitions have two important elements: monitoring-based decision making and multiple control strategies (Hagstrum *et al.*, 1999). In stored-product systems there are often multiple control strategies available, but it has been difficult to have monitoring-based decision making. Monitoring of stored-product insects falls into three broad categories: direct counting of the number of insects in samples, detection of insect-related damage, and capturing of insects using

traps. As raw grains are harvested and loaded into bulk storage facilities, some of the concepts and practices of IPM are similar to management strategies for field crops (e.g., use of multiple tactics and pest prevention using techniques such as aeration). However, it is often difficult to adequately monitor and sample large grain bulks, particularly in commercial elevator facilities, due to the large volume of grain and the relatively low densities of insects that need to be detected. Precise threshold and injury levels have not been developed, and actual standards and rejection criteria are inconsistent and difficult to apply. As a result, treatments based on an economic threshold are not performed and control strategies are often applied preventively, even when using tactics such as fumigation that do not have any residual effect. An expert system has been developed to help manage farm-stored grain in the United States, which includes interpretations of sampling data and predictive models for insect population growth using different management strategies (Flinn and Hagstrum, 1990). A similar system is currently being developed for managing insects in grain elevators, which is based in part on an extensive field project whereby sampling data are used to recommend management strategies and intervention. The multiple-component strategy for managing stored grain is considered by many to be consistent with the IPM concept of controlling insect pests and is discussed in detail elsewhere (Cuperus *et al*., 1990; Hagstrum *et al*., 1999; Longstaff, 1994; Phillips *et al*., 2000a; White, 1992).

As grain products move from bulk storage to processing and milling facilities, then through distribution and marketing channels to consumers, IPM concepts become even more difficult to apply. Once products reach consumers, attitudes toward acceptable insect damage change dramatically. Often there is an idea of ''zero tolerance'' for insects, and controls become more preventative. There are no precise damage thresholds or injury levels and it may be impossible to adequately sample and monitor insects in some areas. Mills and processing plants routinely use insecticides to ensure that finished products are not infested when they leave the facility. Nonchemical methods such as sanitation, stock rotation, and environmental controls become part of the management strategy. Residual insecticides are used as surface treatments to floors and walls, particularly in urban settings where insects such as cockroaches are often found in the same environment as stored-product insects.

The IPM approach as developed for food processing facilities can involve but is certainly not limited to engineering design, sanitation and exclusion, insect monitoring and spatial analysis, fumigation, alternative environmental manipulations in the form of heat or cold treatments, and residual insecticides. In the food industry, multiple tactics are used to manage pests, although often these tactics are not necessarily integrated optimally

and there is still a heavy reliance on chemical insecticides. In retail situations there is even less monitoring and integration of control tactics. A survey of grocery stores in Oklahoma showed that management practices are still pesticide intensive, with little use of IPM alternatives (Platt *et al.*, 1998).

As discussed earlier, food storage environments are patchy landscapes and there is a dynamic relationship among insects emigrating from infested patches, moving among patches, and immigrating into uninfested patches. This relationship impacts all components of IPM programs for the food industry and presents a useful framework for viewing pest monitoring and management tactics (Figure 1). Insect monitoring can involve sampling of the commodity itself using visual inspection or traps to determine if the patch is infested or indirect sampling of the insects dispersing among resource patches using tools such as pheromone traps. Sampling the product directly is often destructive and can be difficult or prohibitively expensive, whereas indirect sampling is often easier to perform but the information obtained is more difficult to interpret and to use for making pest management decisions. This is because we are sampling primarily dispersing individuals, and often the methods used to trap these individuals bias capture toward a particular sex and/or physiological state. In most situations, we do not know the relationship between indirect sampling methods (i.e., sampling dispersing individuals) and direct sampling (i.e., sampling individuals in infested material). Nansen *et al.* (2004) showed that in a maize storage

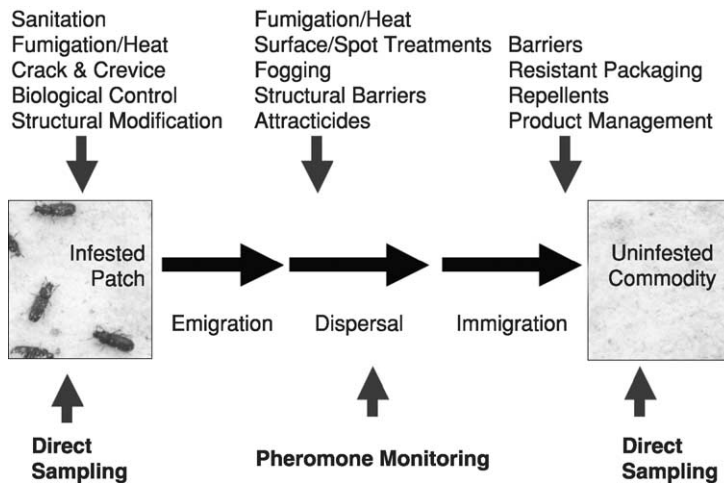

FIG. 1 Diagram illustrating the relationship between stored-product insect distribution and movement among resource patches, and the subsequent targeting of monitoring and pest suppression tools.

warehouse there was not a good spatial relationship between *P. interpunctella* adults captured on passive (no attractant) sticky traps above the surface of the grain and larval captures in the bulk corn.

Pest management practices fall into one of three categories: reducing/eliminating insects in food patches that are currently infested (e.g., fumigation, heat, sanitation, structural modification), putting up barriers to insect movement outside patches (e.g., screening on windows, fogging with pesticide), and reducing/preventing the pest from entering new patches (e.g., insect-resistant packages, repellents). The following sections review the status of many of the components of pest management programs for food processing facilities and warehouses. Our discussion focuses on management for stored-product insects and excludes cockroaches and other traditional urban pests.

VI. STORED-PRODUCT INSECT MONITORING TACTICS

The foundation of a successful integrated pest management program is an effective monitoring system that supplies information on not only the number and type of pests present, but also detects changes in pest populations over time and locates foci of infestation and routes of entry (Burkholder, 1990). With this information, pest management decisions can be based on monitoring data rather than calendar-based applications that may be optimally targeted both temporally and spatially. Monitoring strategies and tactics differ between bulk stored raw commodities and processed commodity facilities. Bulk stored commodity monitoring relies primarily on direct sampling for insects in the product, but for processed commodity facilities, a combination of direct sampling of spillage and indirect sampling is used most widely. The major difficulty with bulk grain sampling is that we need to estimate the number of insects present in a very large volume, but because of the small volume of samples relative to the total volume of stored grain, low density and nonuniform distribution of insects, and the difficulty in taking samples from throughout the grain mass, accurately extrapolating from sample data is not highly accurate. For processed commodities, the major difficulty is relating the number of insects observed and captured in traps placed outside of resource patches with the level and location of infestations.

In bulk raw commodities, the primary sampling methods are based on taking direct samples of grain and counting the number of insects present or the number of seeds showing signs of damage. Various sampling tools (e.g., grain trier, pelican sampler) are available for collecting grain samples depending on the volume of grain to sample and whether the grain is in a bin or being moved (Hagstrum, 1994; Subramanyam and Hagstrum, 1995).

Vacuum probe sampling is a relatively new method that can be used to sample through the whole grain profile, thus overcoming some of the limitations of other sampling methods. In an area-wide IPM project the vacuum probe was the most effective method used to sample large grain elevators (P. Flinn, personal communication). After the grain sample is collected, insects present in the sample must be determined. Sieving using either a hand sieve or an inclined sieve is effective at removing most insects that are external to the grain (White, 1983). The number of insects of each species present or the percentage of samples infested can be used to estimate total insect abundance. Many of the important bulk grain pests are internal feeders and are difficult to detect because only the adult stages that have emerged from the seeds can be sieved out of samples. There is a range of techniques to detect internal feeding insects (e.g., staining, flotation, X-ray examination, sound detection, nuclear magnet resonance, ELISA), but most are relatively labor- and time-intensive to perform (Pedersen, 1992). Near-infrared reflectance spectroscopy (NIR) technology has been used to detect internally feeding insects (Dowell *et al.*, 1998).

An approach used commonly by industry is to assess the number of insect-damaged kernels (IDK) present in samples. Grain Inspection, Packers and Stockyards Administration (GIPSA), formerly the Federal Grain Inspection Service (FGIS), has set a threshold of 32 IDK per 100 g of sample as being considered adulterated and unfit for human consumption, but most flour mills have lower reject levels. The problem with this approach, in addition to the issues associated with extrapolating population levels from small sample sizes, is that the correlation between IDK and number of internally feeding insects is not well established and, in some situations, may not be well correlated (Perez-Mendoza *et al.*, unpublished data). Some of the issues involved in developing sampling programs are reviewed by Subramanyam and Hagstrum (1995).

Traps that capture insects as they move through the grain can be more efficient at detecting the presence of insects than direct sampling, but species differences in mobility can lead to differences in trap capture and, as with direct sampling, only a relatively small portion of the grain mass is being sampled. Probe traps, which are a type of pitfall trap, can be used to sample and detect insect populations in bulk grain (Hagstrum *et al.*, 1998), but they provide an estimate of relative abundance, not absolute numbers. A new advance in this technology that is being commercialized is a probe trap that automatically counts the insects that are captured (Epsky and Shuman, 2001; Toews *et al.*, 2003). This technology is based on the falling insect breaking a light beam as it passes through the trap and this information being sent to a computer where it is compiled. In some cases, traps placed in the headspace above the raw commodity can provide a good prediction of

future pest problems. For example, capture of rusty grain beetle [*Cryptolestes ferruginens* (Stephens)] in sticky traps in the headspace of farm bins during the first 3 weeks of storage provided a good indication that the bin would become infested (Hagstrum *et al*., 1994).

Monitoring of insects in food processing and warehouse structures involves either direct visual sampling or the use of traps. Visual inspection done on a regular basis is one of the primary means by which insect infestation is monitored in food facilities (Mills and Pedersen, 1990). This is a time-consuming process that requires training to be done effectively. Its strength is that not only does it detect signs of insect infestation, but it can also identify potential problem areas such as accumulations of spillage before they become infested. It is direct sampling where potential food patches are identified and their status as infested or uninfested can be determined. However, in many cases, food patches are not detectable or access requires destructive sampling (e.g., opening packages), making it difficult to directly evaluate the level of packaged commodity infestation.

The use of traps to monitor insects is also common in food storage and processing environments and a range of trap types are available (e.g., pheromone traps, food attractant traps, sticky boards, light traps). Traps have the advantage that they sample continuously and with appropriate stimuli they can attract insects from a wide area. Thus, trapping can provide information more quickly and easily and, in many cases, earlier than visual inspections. Because most of these traps capture insects that are dispersing between resource patches, it can be difficult to make the connection between numbers captured in traps and actual levels of product infestation. The best use of this information may be to use the relative numbers captured and their spatial distribution to make targeted pest management decisions (i.e., indicative interpretation) rather than trying to estimate total abundance (Arbogast and Mankin, 1999). Areas of high trap capture should be followed up with additional investigation (e.g., direct sampling of packages and spillage, identifying routes of entry) to determine the probable cause(s). Monitoring trends in trap capture data over time is also a useful approach to evaluating the effectiveness of IPM programs.

Most trapping devices use some sort of attractant to increase capture rates (e.g., pheromones, food odors, light). Light traps are used commonly in food facilities for fly management, but some species of stored product insects are attracted to light sources and monitoring the species and number of insects captured in light traps can provide information on the pest flight activity (Hagstrum *et al*., 1977; Keever and Cline, 1983; Pursley, 1987). The type of light trap and its location can influence the effectiveness at trapping stored product pests (Rees, 1985). Food baits have been used effectively in warehouses containing bagged commodities to monitor pest populations

(Hodges *et al.*, 1985), but processing these packs can be labor- and time-intensive and, if not collected in a timely manner, can contribute to pest problems within a facility. Unbaited sticky boards can be used for stored product insect monitoring as well, and these may be either suspended vertically in the air or laid flat on surfaces. Because many walking insects will detect sticky surfaces and avoid them, they work best for insects that land or fall on the surface.

Incorporation of an attractant such as a pheromone or food odor can improve the efficiency of a trap. Pheromones are chemical cues produced by one individual that are used to communicate with another individual of the same species. There is a wide range of different functions for pheromones, but the two most important from a monitoring perspective are sex pheromones, which elicit a response in the opposite sex, and aggregation pheromones, which elicit responses from both sexes. Pheromones have been isolated and lures are available commercially for many stored-product insects (Chambers, 1990; Phillips *et al.*, 2000b). Several traps designed specifically for stored-product insects are available commercially (Collins and Chambers, 2003; Mullen, 1992; Mullen and Dowdy, 2001; Vick *et al.*, 1990). There are two general types of pheromone traps. Traps targeted for flying insects typically use a sticky surface on the inside of the trap where a pheromone lure is placed and insects become trapped when they land near the lure or a funnel and bucket combination that reduces the ability of the insect to escape after entering the bucket to find the pheromone source. Traps that target walking insects are placed on the ground and generally use some type of pitfall to capture insects that walk up to the lure.

Pheromone traps have been demonstrated to be effective at capturing stored-product pests, primarily moths in the family Pyralidae, in anthropogenic ecosystems (Bowditch and Madden, 1996; Mankin *et al.*, 1999; Pierce, 1994; Soderstrom *et al.*, 1987; Vick *et al.*, 1986). Pheromone trap use is increasing in commercial facilities (Phillips *et al.*, 2000b). However, many questions remain about the use of these monitoring tools, from the very practical issues such as how many traps are needed and which types work best, to the fundamental issues concerning the relationship between pheromone trap captures and actual pest population density, distribution, and level of product infestation (Arbogast and Mankin, 1999). Research into the relationship between pheromone trap capture and the absolute number of insects present in a structure [i.e., "representative" trap interpretation (Arbogast and Mankin, 1999)] has focused on developing relationships between released insects or insects present in the air and trap capture (Hagstrum and Stanley, 1979; Leos-Martinez *et al.*, 1986; Mankin *et al.*, 1983; Rees, 1999; Wileyto *et al.*, 1994).

Food odors are also important as attractants for traps both on their own or in combination with pheromone lures as synergists or additive attractants. Food odors can be used to improve the capture of species that do not have commercially available pheromone lures, of females that do not respond to traps with sex pheromones, and of immature stages. In a number of situations, pheromones combined with food odor are more attractive then either alone (Landolt and Phillips, 1997; Phillips *et al.*, 1993; Trematerra and Girgenti, 1989). Food odor has an advantage over food bait packs because typically the insect is unable to develop on the chemical fraction containing the attractant in contrast to food bait packs. The effectiveness of food attractants can be diminished in environments that contain other food odors.

Some studies have addressed the temporal and spatial patterns to stored-product pest abundance in bulk grain storage containers (Arbogast *et al.*, 1998; Brenner *et al.*, 1998), flour mills (Doud and Phillips, 2000), food processing plants (Rees, 1999), warehouses (Campbell *et al.*, 2002), and retail stores (Arbogast *et al.*, 2000). The application of geostatistical techniques for understanding insect spatial distribution is also increasing in pest management (Arbogast *et al.*, 1998; Brenner *et al.*, 1998; Liebhold *et al.*, 1993). Techniques such as contour analysis graphically portray spatial data in a way that is quickly understood and can be used to visualize the sources of insect distribution. It is difficult to get a general picture of what is happening in the entire facility simply from observing the number of insects in each sample or trap. Comparing maps of trap captures over time can also show how distributions spread or contract, where new foci develop, and how populations respond to human intervention. Contour mapping is becoming more widely used by the pest management industry.

Contour mapping of spatial data is a three-step process. First, data from each sample point are assigned x and y coordinates to indicate the location on a two-dimensional surface. Second, a denser grid of data points is generated using interpolation algorithms and there are a number of them that can be used. Finally, this denser grid is used to draw contour lines that join points with equal values. An example of a contour map from a flour mill is presented in Figure 2, with the increasingly dark regions indicating increasing estimated numbers of insects that would be captured. As a practical tool, contour mapping helps plant managers visualize and incorporate spatial distribution information into pest management programs. However, it is also important to take into account the assumptions behind this approach and to set up monitoring programs that will generate data of sufficient quality to address the questions needed. For example, the number of traps and degree of spatial autocorrelation among traps strongly influence our ability to make accurate contour maps (Nansen *et al.*, 2003). In addition,

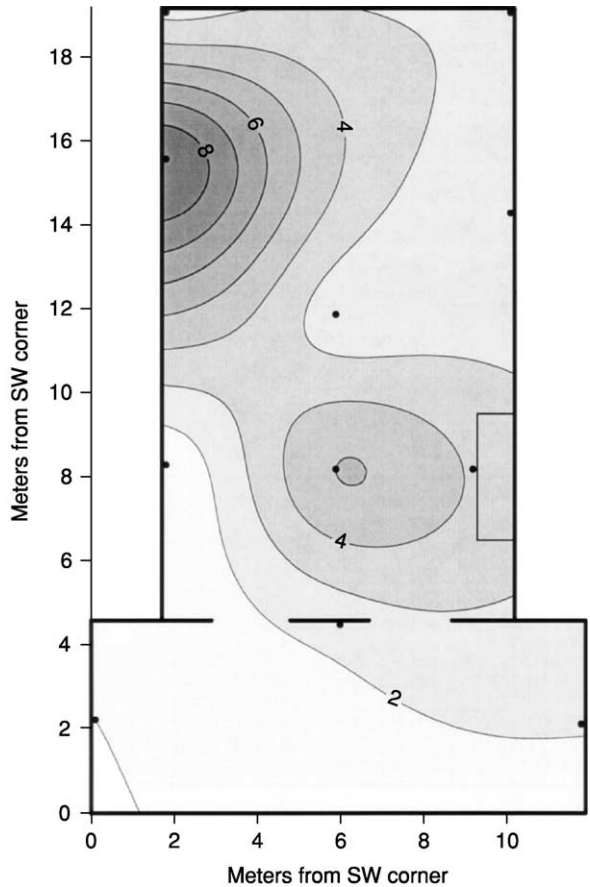

FIG. 2 Contour map of the spatial distribution of red flour beetle, *Tribolium castaneum*, pheromone trap captures in a flour mill (J.F. Campbell and R.T. Arbogast, unpublished data).

insect movement behavior and the environment around each trap can influence trap capture in ways that do not reflect the true distribution of infestation (Campbell *et al.*, 2002).

VII. MANAGEMENT TACTICS FOR STORED-PRODUCT INSECTS

Sanitation includes housekeeping, inspection, physical and mechanical methods, chemical methods, and biological methods (Mills and Pedersen, 1990) and is critical for the production, manufacture, and distribution of

clean and wholesome food (Gould, 1994). Housekeeping can be defined simply as cleanliness and orderliness and is most important in reducing the ability of pests to become established. Inspection involves the examination of raw materials, processes and processing equipment, facilities, and finished products for infestation. Physical measures include the use of various types of barriers, including packaging and controlled temperatures and humidity; mechanical methods include traps, irradiation, etc. Pest exclusion relies heavily on physical barriers and fits well into an integrated sanitation management (ISM) program where reduced pesticide use is emphasized. An emphasis has been placed on the reduced use of pesticides; however, situations exist where contact insecticides and fumigants can and are used safely to protect food products. Biological pest control agents such as parasites and predators show some promise in the control of insects, and pheromones have proven effective in monitoring for pest insects and may have some efficacy in pest suppression.

A. HOUSEKEEPING AND EXCLUSION

Housekeeping and pest exclusion are the foundation of food product protection, whether in the storage and transportation of raw agricultural commodities or in the processing, manufacturing, storage, or distribution of finished food products. Housekeeping involves cleaning spillage, removing or sealing damaged packages, and removing out-of-condition products. Because insect populations can build up in refugia in the structure of the building in which food material is stored, eliminating these food habitat patches can have a dramatic impact on the ability of pest populations to establish and persist. The degradation of food material and the presence of moisture can lead to pest problems that would not occur under good housekeeping conditions.

Many aspects of food processing facility design, modification, and repair concern the prevention of pest (birds, rodents, and insect) entry. Pest exclusion involves two major components: reducing the number of external sources of insects and preventing their entry into the facility. For new facilities, site selection can have an important influence on the potential for infestation. Imholte and Imholte-Tauscher (1999) indicated that selection of a plant location requires economic considerations balanced with product safety considerations. Items that fall within this category include smoke, dust, odors, and other sources of contaminants that may originate from the environment and/or nearby manufacturing or other industries. Parking areas and vehicle access ways should be hard surfaced to eliminate the potential for dust being blown into a facility. Other food processing and grain storage facilities in the vicinity can also impact the potential for infestation.

A "buffer" zone surrounding the actual facility is a desirable feature that can be planned for new facilities but may not be present around existing food plants. A properly maintained space surrounding a food plant can reduce greatly the potential for the entry of rodents, birds, and insects. Maintaining the area surrounding a food processing plant free of tall weeds and grass; accumulations of junk or debris and/or unused equipment; accumulations of standing water; or other conditions that favor the attraction and development of rodent, bird, and insect populations is an effective way of "excluding" these pests from close proximity to food processing facilities. Shrubbery or other vegetation adjacent to a plant facility can provide an attractive harborage for rodents as well as a roosting place for birds. Flowering plants can also serve as a source of attraction for certain insects that are attracted to or infest food products. By avoiding these types of situations, the resulting environment tends to exclude pests from close proximity to the processing facility. Exclusion of birds and rodents from the perimeter of buildings may also reduce the potential infestation from stored product insects because many species can also exploit rodent and bird nests.

Because many insects are attracted by lights, part of an exterior exclusion program involves the proper placement of lighting. Exterior lighting at a food processing plant should be placed at the perimeter of parking areas away from the plant rather than being mounted on the building so that insects are attracted away from the plant rather than toward the facility. Sodium vapor lights should be used instead of fluorescent and mercury vapor lights that produce ultraviolet light to which some insect species are attracted (Imholte and Imholte-Tauscher, 1999).

Structurally, food processing plants should be designed to "exclude" pests. For exterior walls, solid concrete construction is preferred over concrete block or sheet metal. Preformed wall sections of solid concrete require proper sealing to effectively exclude rodents and insects. Openings such as windows, doors, loading docks, track-wells, and intake and exhaust vents are pest entry points that must be constructed and maintained properly to safeguard against pest entry. Modern processing facilities minimize the use of windows; where they may be needed for ventilation, they should be screened. Standard window screen will exclude most insects, but heavier mesh screen is needed at ground level to exclude rodents. Screens should be so constructed and installed that they can be removed and cleaned. Intake and exhaust openings should be protected with heavy mesh screen. Intake vents should be fitted properly with filters that are appropriate for the type of plant operation.

Entry and exit doors should be fitted so that no more than 1/8 to 1/4-in. spaces are at the top, bottom, and sides of the door. This should exclude rodents from entering. Insects and dust can enter very small openings. Nylon

bristle brush protectors are available to minimize the entry of insect and dust through cracks around doors. Because rodents can gnaw wooden doors, they should be fitted with metal flashing along the door bottom to minimize the opportunity for damage and entry. In most cases, metal doors are preferred. Insect and bird entry during loading operations can be minimized by using strip doors or air curtains that allow fork truck passage. Air curtains can be effective in excluding dust and flying insects. Air velocity is a major factor in the effectiveness of air curtains. They are also affected by other factors: prevailing wind velocity, internal building pressure, and air temperatures. For example, warm air and food odors from internal positive plant pressure may be a strong attractant to flies and other insects.

The roof area of a processing plant is often overlooked as a source of pest entry into the plant. Insects may be attracted to product spillage or dust accumulations on roofs from leaking equipment, such as bucket elevators and cyclones. These accumulations can also provide a breeding area for product-infesting insects as well as microorganisms. Because the air supply for plant ventilation sources is often located on roofs, it is important to keep these areas free of product residues and to protect ventilation equipment so that pests are excluded from the plant by this route. Odors emitted from roof ventilators can be attractive to potentially invading insect pests. Proper equipment and good housekeeping are necessary adjuncts to excluding pests from entering the plant by way of the roof. These criteria apply not only to food processing facilities but also to distribution facilities.

To prevent pests from entering a facility, it is necessary to have an effective monitoring program to assure that products are pest free when they arrive at the site. Raw materials (i.e., ingredients, packaging, and equipment) should be inspected to assure that they do not serve as vehicles for pest entry. Truck and/or railcar unloading sites are possible sources of insect entry into the facility.

Cracks, holes, or loose joints in interior walls, floors, and overhead areas must be sealed so that they do not become harborages for insects or rodents. Equipment used for transporting, processing, and packaging food products should also be designed to minimize the buildup and/or accumulation of food materials within the interior of the equipment.

B. PACKAGING

Packages are designed to protect food products from the point of manufacture to the point of consumption. Packages are usually tailored to fit the product being protected and no one package will provide the protection needed for all products, under all conditions, and against all pests. Infestation of packaged products is a function of the package design; package

handling during manufacture, shipping, and storage; and time exposed to potential infestation. The protection of food is not the only concern in package design and needs to be balanced against consumer desires, manufacturing practices, shipping and storage constraints, and ultimately cost. For example, sealing all foods in metal containers would reduce the chance of insect infestation to essentially zero, but would definitely cause problems with the other factors. Almost all nonperishable food package designs have openings that can allow insects to enter due to manufacturing specifications, flaws in manufacturing, or damage that occurs during shipment and storage (Mowery *et al.*, 2002; Mullen, 1994).

A complete understanding of insect-resistant packaging must begin with the pests that most commonly attack packaged foods and the methods that they use to enter packages. Highland (1984, 1991) separated package pests into two categories: "penetrators," which are capable of chewing through one or more layers of flexible packaging materials to enter packages, and "invaders" which enter packages through existing openings. Insects such as the lesser grain borer, *Rhyzopertha dominica*; the cigarette beetle, *Lasioderma serricorne*; the warehouse beetle, *T. variabile*; the rice weevil, *Sitophilus oryzae*; and the rice moth, *Corcyra cephalonica* (Stainton) are known to be good package penetrators. Species classified as invaders include the red flour beetle, *T. castaneum*; the confused flour beetle, *T. confusum*; the sawtoothed grain beetle, *O. surinamensis*; the Indianmeal moth, *P. interpunctella*; and the almond moth, *Cadra cautella* (Walker). These are not mutually exclusive categories, however, as most penetrators will also enter packages through existing holes and some species classified as invaders do occasionally chew into packages. For example, under some circumstances, larvae of the Indian meal moth and the almond moth penetrate packages (M. Mullen, personal observation).

Most infestations are the result of invasion through seams and closures, and rarely through penetrations (Mullen, 1997). Insect pests enter packages through existing openings that are created from poor seals, openings made by other insects, or mechanical damage. For example, the adult sawtoothed grain beetle has been shown to enter packaging through openings less than 1 mm in diameter, and the adult red flour beetle can enter holes in packaging that are less than 1.35 mm in diameter (Highland, 1984). Stored product pests can be attracted to the food odors coming from holes in packages and lay eggs near the holes (Barrer and Jay, 1980; Mowery *et al.*, 2002, 2003). Females may actually insert eggs through openings that are even smaller in size then those through which they could enter the package. The sawtoothed grain beetle has been demonstrated to insert their ovipositor through packaging flaws 0.4 mm in diameter that preclude adult entrance and lay eggs under the packaging film (Mowery *et al.*, 2002). The small early

instar larvae that hatch from eggs laid near holes in packaging may enter packages through extremely small openings. Mowery *et al.* (2002) found that first-instar saw-toothed grain beetle larvae would enter holes in packaging film in response to food odors escaping thorough the holes. Packages with holes as small as 0.27 mm can be infested by first-instar larvae of the saw-toothed grain beetle. Many insects prefer to lay eggs in tight spaces such as those formed when multiwall paper bags or paperboard cartons are folded to create closures, and newly hatched larvae would be in a good position to invade packages.

Some products and packages are more susceptible to insect infestation than others. These products can serve as insect reservoirs, leading to the infestation of other products (Highland, 1984). For example, dry pet foods packed in multiwall paper bags are generally not very insect resistant because they lack adequate seals and closures, whereas bird seed packages often contain ventilation holes that can allow insect entry.

There are a variety of improvements in packaging design that can reduce the chance of insect infestation. Seals and closures can often be improved by changing glue patterns or the type of glue used. Generally, a glue pattern that forms a complete seal with no channels for the insect to crawl through is the most insect resistant. Insect resistance can also be improved by overwrapping the packages with materials such as oriented polypropylene films. To maximize the effectiveness of overwraps, they should fit tightly around the package and be sealed completely to prevent insects entering at the corners of the folded flaps. Another means of discouraging insect infestation is through the use of odor barriers (Mullen, 1994). Food odors may be prevented from escaping the package through the use of barrier materials, resulting in a package that is "invisible" to invading insects. Coating the package with materials such as acrylic, polyvinylidene chloride, or EVOH can improve odor retention. However, any flaw in the package will negate the odor-proof qualities of the package (Mowery *et al.*, 2003). Studies reported by Mullen (1997) have shown that when odor barriers were used to protect a commodity, only those packages with flaws became infested.

C. INSECTICIDES

Insecticides that are used in food processing facilities can be sorted into three general groups. (1) Fumigants are insecticides that are toxic in the gaseous phase; two common fumigants used worldwide are methyl bromide (MB) and phosphine. Modified or controlled atmospheres are also toxic as gases and usually involve lowering oxygen concentrations through the addition of carbon dioxide or nitrogen. (2) Aerosols are applied as mists or fogs in small droplets ranging in size from 5 to 30 μm. They can have vapor and contact

toxicity. (3) Surface treatments are applied directly to flooring and wall surfaces and may be applied to cover surfaces or be limited to specific areas, such as cracks, crevices, wall baseboards, or as spot treatments to defined target areas. They have contact toxicity and generally give some degree of residual control.

Currently there are only a few insecticides in all three of these classes that are registered in the United States for use in food processing facilities and they are discussed in detail. This section focuses on the insecticides used as fumigants, aerosols, and contact insecticides. An exhaustive list of labeled products is not presented, and specific insecticides are discussed primarily to present concepts and ideas. Also, labeling and registrations of insecticides are constantly changing, and products may be removed from the stored-product market as a consequence of regulatory actions and interpretations. Specific labels and label directions should always be consulted and followed when applying insecticides.

1. Fumigants and modified atmospheres

Methyl bromide has historically received extensive use as a whole-plant structural treatment to mills and processing facilities (Taylor, 1994). It is a highly effective fumigant and penetrates into bulk and bagged commodities, packaging, and can disperse throughout a structure to kill hidden insects and immature states. Quarantine treatments are usually done with MB because it kills quickly compared to phosphine, and whole-plant fumigations are often done during a weekend or holiday period to reduce idle or down time for production facilities. Because fumigants give an immediate kill and offer no residual protection, reinfestation is a constant threat for any structural facility.

Methyl bromide has been identified as an ozone-depleting substance and is being gradually removed from world markets. Current legislation and plans call for the elimination of methyl bromide in most industrial countries by 2005, with possible exemptions for quarantine (UNEP, 1996). Currently there is an extensive search worldwide for products that are alternatives to methyl bromide (Kawakami, 1999). These alternatives are broadly defined and include components of management plans such as sanitation, monitoring, contact insecticides, heat treatments, and modified atmospheres, in addition to new fumigants (Batchelor, 1998).

Phosphine gas is registered in the United States for use inside food processing facilities. Currently, it is used primarily for fumigation of bulk stored grain. While there are several reports of phosphine resistance in stored product insect populations in Asia (Subramanyam and Hagstrum, 1996), there are few published data regarding resistance in the United States.

Low levels of resistance have been reported for some populations of Indian meal moth, almond moth, and red flour beetle populations in stored peanuts in the southeastern United States (Zettler *et al*., 1989), but no assessments are available for phosphine resistance in insect populations in mills, warehouses, processing plants, and other structural facilities. Phosphine can be corrosive to metals, particularly copper, electrical wiring, and electronic equipment (Bond *et al*., 1984), which limits its application in food processing facilities and warehouses. A new formulation of phosphine, in which phosphine gas is combined with carbon dioxide and released from a cylinder, alleviates some but not all of the corrosive effects of phosphine and is labeled for use as a structural treatment.

Research is being conducted for fumigants that can possibly replace methyl bromide for use in food processing facilities. The fumigant sulfuryl fluoride appears to be the most likely candidate for replacement of MB (Schneider and Hartsell, 1998) and has recently been registered within the United States. It is effective against adult stored-product insects, but longer exposure times are required to kill eggs compared to methyl bromide (Bell and Savvidou, 1999). Carbonyl sulfide has also shown effectiveness as a fumigant for stored-product insects (Weller and Morton, 2001; Zettler *et al*., 1997).

Modified atmospheres are known to have toxic effects toward stored-product insects (Adler *et al*., 2000; Rameshbabu *et al*., 1991). A low-oxygen atmosphere can be created by replacing oxygen with nitrogen, thereby causing insect mortality from a lack of oxygen. Toxic conditions can also be created by producing atmospheres high in carbon dioxide, regardless of the oxygen content; however, the oxygen is usually reduced somewhat from normal levels. High-oxygen atmospheres are also lethal, but are not generally used for insect control.

Modified and controlled atmospheres have been used with some success to control insects in stored bulk grains (Adler *et al*., 2000). However, they are not generally used by the milling and processing industry as whole-plant treatments because they are expensive compared to methyl bromide, extensive monitoring and sealing are required for effective control, and there are potential problems with contamination (White and Leesch, 1996). However, modified atmospheres, vacuum sealing, or low-pressure treatments may be useful for small-scale or specialty applications (Mbata and Phillips, 2001). With the impending loss of methyl bromide, there may be more opportunities for using modified atmospheres inside food processing facilities.

The efficacy of fumigants and modified atmospheres can be influenced by factors such as insect species and life stage, physical environments, and environmental conditions (Adler *et al*., 2000). Insect species and life stages vary in susceptibility (Weller and Morton, 2001). Generally, eggs and pupae

are the life stages that are more difficult to kill with conventional fumigants (White and Leesch, 1996) and modified atmospheres (Adler *et al.*, 2000). Diapause may also affect tolerance, as the duration of diapause increased in larval Indianmeal moth, *P. interpunctella*, and almond moth, *C. cautella*, tolerance to MB also increased (Bell and Savvidou, 1991). The efficacy of fumigants and modified atmospheres generally increases as temperature increases, and shorter exposure intervals are required to give equivalent levels of mortality (Adler *et al.*, 2000; Bell and Savvidou, 1999; Locatelli and Daolio, 1993; White and Leesch, 1996). However, there are critical temperature thresholds and fumigations are prohibited if temperatures are outside of the specified range. Temperature requirements are generally given on the product labels.

2. *Aerosols and space sprays*

Aerosols and space sprays are targeted primarily at exposed insects that are flying or walking on a surface. They are dispensed from an aerosol fogger, often through a timed application system, and have low persistence and offer very little residual production. There are few products that can currently be used inside food processing facilities as space sprays, and the insecticide labels will generally give directions for application of a specific amount of product per volume area of space, such as ft^3 or m^3. Synergized pyrethrins, a natural product, and the organophosphate dichlorvos are two insecticides that have historically been used for aerosol applications inside processing facilities and in food warehouses. In the United States, all registered pesticides are being reviewed for compliance with the 1996 Food Quality Protection Act (FQPA), and the continued registration and usage of dichlorvos is uncertain. Some insecticides and formulations are restricted to empty facilities, whereas others can be used only if food material is covered. A venting or release period after application is also required after dichlorvos application.

Pyrethroids are a class of synthetic chemicals that are similar in structure to natural pyrethrins. They have been used in field crops and urban pest management for nearly 30 years, and within the last 5 to 10 years new products have been registered for specific use against stored-product insects. Resmethrin is labeled for use as an aerosol in food plants, mills, and warehouse facilities, but could have potential side effects such as discoloration of surfaces and odor contamination and may be more appropriate for use in empty facilities. Labels generally state to cover any food prior to application. The pyrethroids esfenvalerate (Conquer) and prallethrin (Etoc) are also labeled for use in some situations as an aerosol space treatment in

food processing facilities. Laboratory studies indicate the efficacy of new pyrethroid aerosols (Arthur, 1993; Arthur and Gillenwater, 1990), but there are few recent studies whereby efficacy has been assessed in field situations. All aerosols will have restrictions, and each product label must be consulted for precise regulations regarding usage.

An aerosol formulation of the insect growth regulator hydroprene (Gentrol) was labeled several years ago for use in the United States. There are no research reports with hydroprene aerosol, except for Bell and Edwards (1998), which describe a study conducted in Great Britain. In this study, aerosol applications of hydroprene (Protrol) prevented the development of eggs of the red flour beetle, *T. castaneum*, the confused flour beetle, *T. confusum*, and the almond moth, *C. cautella*, that had been placed in exposed dishes with food media.

The status of resistance of stored-product insects to any of the aerosols used in the United States is uncertain, and no new assessments of resistance have been conducted in recent years. Indianmeal moth, *P. interpunctella*, and almond moth, *C. cautella*, populations in peanut warehouses in the southeastern United States showed low levels of resistance to dichlorvos (Arthur *et al.*, 1988), but reflected an increase relative to earlier studies (Zettler, 1982). In other studies, 24% of red flour beetle and 64% of confused flour beetle populations collected from flour mills were resistant to dichlorvos (Zettler, 1991).

3. Surface treatments

Currently there are few insecticides registered as surface treatments to control stored-product insects. For years the organophosphate insecticide malathion was used as a surface treatment for structural facilities, but stored-product insects throughout the world have developed extensive resistance to malathion (Subramanyam and Hagstrum, 1996). Most of the resistance reports were generated from studies with bulk grains, but in the United States, resistance has been documented for field populations of the red flour beetle, *T. castaneum* (Herbst), and the confused flour beetle, *T. confusum* (DuVal), collected from flour mills (Arthur and Zettler, 1991, 1992; Zettler, 1991). Populations of the Indianmeal moth, the almond moth, and the red flour beetle collected from bulk peanuts and empty warehouses were also highly resistant to malathion (Arthur *et al.*, 1988; Halliday *et al.*, 1988).

Today one the most common insecticidal surface treatments is the pyrethroid insecticide cyfluthrin (Tempo). It is available as an emulsifiable concentrate (EC) or as a wettable powder (WP), but the WP is much more

effective than the EC when applied at the high application rate (19.0 g of 20% [AI] WP in 1 gal of water to cover 1000 ft^2) to concrete (Arthur, 1994, 1998). Resistance to cyfluthrin and other pyrethroids has been reported for the red flour beetle in Australia (Collins, 1990). In the United States, cyfluthrin resistance has been reported in the German cockroach, *Blatella germanica* L. (Cochran, 1996), but has not been reported for stored-product insects. Other insecticides labeled as surface treatment include the pyrethroid prallethrin, but there are no reports on chemical efficacy for this insecticide. The IGR hydroprene is also labeled for use as a general surface application and has activity against red flour beetle and confused flour beetle larvae (Arthur, 2001).

Commercial formulations of the inert dust diatomaceous earth (DE) are also labeled for general surface application inside mills, warehouses, and other indoor structures. DE is a natural product composed of the fossilized cell walls of diatoms, and deposits of this material are found worldwide (Fields and Korunic, 2000). DE is abrasive and damages the insect cuticle, but also interferes with the lipid layer and inhibits water absorption, and the eventual result is death through dessication (Glenn *et al.*, 1999). Some researchers attempt to define DE as "physical control" because neurotoxic mechanisms are not involved, but regulatory agencies such as the US-EPA define DE as a reduced-risk low-toxicity insecticide, often with the acronym GRAS (generally regarded as safe). Most of the research with DE has been conducted on bulk grains (Golob, 1997; Korunic, 1998), and there is comparatively little information regarding actual effectiveness as a surface treatment. In one test in which adult red flour beetles and confused flour beetles were exposed directly to DE, efficacy was inversely correlated with relative humidity and directly correlated with temperature (Arthur, 2000). Mortality was also slower for DE compared to other surface treatments. A 48- to 72-hr exposure period was required to kill both *Tribolium* species with DE, compared to a 2- to 3-hr exposure to the high label rate of cyfluthrin WP (Arthur, 2000).

Several organophosphate, carbamate, and pyrethroid insecticides are labeled as crack-and-crevice treatments inside milling and processing facilities. These include, but are not limited to, the carbamates propoxur and bendiocarb; the organophosphates dursban, diazinon, and acephate; and the pyrethroids fenvalerate, λ-cyhalothrin, and resmethrin. Most of these insecticides cannot be used when the plant is in operation. Cyfluthrin is also labeled as a crack-and-crevice treatment, and some labels permit use when the plant is operational. Also, registrations are changing as a result of regulatory restrictions, and some carbamates and organophosphates are being withdrawn from the market.

D. PHEROMONES

Pheromones are used primarily for monitoring pest populations, but their use as pest suppression tools has also been proposed. These alternative uses include mass trapping, mating disruption, and lure and kill. Although these approaches have been tried with varying levels of success in field and orchard crop systems, they have had limited application for the management of stored-product insects.

The concept behind mass trapping is simple: place a large number of traps in a small area and the product will be protected because a high proportion of the pests will be removed from the population. However, the impact of this approach may be limited because only males are attracted to sex pheromone lures, low trap efficiency, high populations can lead to trap saturation, and high-density trapping can be costly to set up and maintain (Howse *et al*., 1998). In food processing and warehouse environments, moth species such as the Indianmeal moth appear to be the most suitable candidates for population suppression using mass trapping. However, one male Indianmeal moth is capable of mating with up to 10 females (Brower, 1975) so a very high proportion of males would have to be removed before significant population reductions are achieved. Roelofs *et al*. (1970) calculated that for some moth species as many as five traps will be needed for every calling female before a 95% reduction can be achieved. The ability to mass trap is also reduced by the high mobility of male moths and their ability to immigrate from other locations, even from outside the facility (Campbell *et al*., 2002).

Evaluation of the efficacy of a mass trapping program can be difficult. Because of variation among facilities it is difficult to replicate mass trapping programs and compare them to controls. Thus, it is difficult to prove that it is the mass trapping that is causing changes in populations. This can be addressed only by performing long duration studies with alternating periods of mass trapping. An additional problem is that using pheromone traps to monitor the effectiveness of a pheromone mass trapping program can be misleading, as only the male population is measured and not the females or the level of product infestation. Despite these difficulties, there have been some long-term studies that have reported success using mass trapping. Pierce (1994) did mass trapping for the Indianmeal moth, *P. interpunctella*, in a food warehouse using trap densities of one trap per 210 m^3 and reported a 96% decrease in trapped moths for one season. Long-term mass trapping of the cigarette beetle, *Lasioderma serricorne*, over a 9-year period reduced populations (Pierce, 1999).

Mating disruption involves the use of artificially produced high pheromone concentrations in a confined area to impede the ability of males to

detect and locate females. This results in fewer matings and ultimately lower pest populations and a decrease in damage (Carde and Minks, 1995). We are not aware of this approach having been used in commercial food facilities. A problem with its application in food facilities is that harborages such as packaged commodities, wall voids, and even locations outside the building exist where mating disruption is not occurring, which may limit efficacy.

Lure and kill is a modification of mass trapping in which the insect is lured by a synthetic pheromone to a location where it is exposed to a pesticide or pathogen that eliminates it from the population. This approach, also known as "attracticide" or "attract and kill," has shown some promise for control. It is an IPM approach for stored product moths that was first described by Trematerra and Battainia (1987). They used a combination of mass trapping and insecticides to control the Mediterranean flour moth *Anagasta kuehniella*. In a similar study, Trematerra (1988) reported that the combination of trapping and pesticides kept population levels below economic levels for 1 year. However, the moths were not eradicated and improved sanitation at the mill may have impacted populations significantly. Shapas *et al*. (1977) used a combination of the protozoan pathogen *Mattesia trogodemae* and pheromone trapping to reduce populations of the dermestid beetle *Trogoderma glabrum*. Vail *et al*. (1993) demonstrated that granulosis virus picked up in pheromone-baited traps by male Indianmeal moth was spread to other individuals. The lure-and-kill technique probably has the greatest potential for the suppression of pest species in commercial facilities, especially if the cost of each killing station is low so that large numbers can be set up.

E. HEAT

With the impending loss of the fumigant methyl bromide, heat treatments are receiving increased attention as a whole-plant structural treatment for insect control (Dowdy and Fields, 2002; Wright *et al*., 2002). Although the idea is not new (Dean, 1911, 1913), new technologies and advances in heating equipment and design are contributing to the renewed interest in using heat for insect control. Heat can be generated through electrical, diesel, or propane heaters or through an internal steam system, and the goal is to produce temperatures of at least 45 to 55 °C and holding those temperatures for 24–48 hr. Thermal requirements for mortality are known for most of the economically important stored product insects (Fields, 1992; Howe, 1965b; Wright *et al*., 2002). Many private companies are already actively using heat as a part of their management strategies (Heaps, 1988), but data regarding effectiveness are largely proprietary and not published in the public domain. Most of the recent published research involves tests

conducted in experimental situations or facilities. Heat combined with desiccant dusts (DE) effectively reduced the temperatures necessary to kill stored-product insects (Dowdy, 1999; Dowdy and Fields, 2002). In another test, high temperatures typically attained during a heat treatment had no deleterious effects on contact insecticides such as cyfluthrin WP and hydroprene and may have even enhanced the toxicity of cyfluthrin WP (Arthur and Dowdy, 2003). Other research studies have shown that during a heat treatment the temperatures within a facility often are not uniform (Dowdy and Fields, 2002). Contour mapping can be used to plot the temperature accumulations and identify those areas that may not reach target temperatures, which could then allow some insects to survive.

F. BIOLOGICAL CONTROL

Insect populations are regulated by top-down (e.g., natural enemies that feed on the insect) or bottom-up (e.g., availability of food) processes and insects can become pests when this regulation is disrupted. Insects have a suite of natural enemies such as parasites (e.g., parasitoid wasps, nematodes), pathogens (e.g., bacteria, fungi, viruses, protozoa), or predators that exploit the insect as a resource and in the process cause disease and mortality. Biological control uses natural enemies to reduce or maintain pest populations below damaging levels. There is a long history of research into the biological control of stored-product pests and the topic has been reviewed multiple times (e.g., Arbogast, 1984; Brower *et al.*, 1995; Burkholder and Faustini, 1991; Haines, 1984; Schöller and Flinn, 2000). Some experimental successes using biological control have been reported for both whole and processed commodity storage situations, but the use of biological control as a component of IPM in the food industry remains very limited. Although not well documented, natural enemies occur in food facilities and can impact pest populations, even if they are not suppressing populations dramatically due to either intrinsic factors or constraint by other management tools. The incorporation of biological control as a component of IPM may increase in the future with the reduction in the use of broad-spectrum insecticides and better pest monitoring.

There are multiple biological control approaches: conservation, classical introduction, augmentative, inoculative, and inundative. Using conservation biological control, conditions are manipulated in ways that attract, retain, or enhance the effectiveness of natural enemies that are already present in the environment. For example, Flinn's (1998) study on the effect of grain temperature on parasitoid wasp *Theocolax elegans* (Westwood) suppression of *R. dominica* populations in wheat indicated that aeration of the grain bin could increase the effectiveness of the parasitoid. Other ways to conserve

natural enemies include using safer chemical pesticides and modifying storage structures (Haines, 1984) and providing additional shelter and food/hosts (Arbogast, 1984; Hagstrum, 1983). Classical biological control is used against pests that are not native to an area and lack effective natural enemies in their current location. It involves releasing natural enemies that have been collected from the pest's geographic region of origin. Because most stored-product pests have been widely distributed throughout the world for a long period of time, the classical approach is often not feasible. A notable exception is the larger grain borer *Prostephanus truncatus* in Africa where a natural enemy (a predatory beetle *Teretriosoma nigrescens* Lewis) has been identified from central America, screened and tested in the laboratory, and released in Africa (Böye *et al*., 1994; Rees, 1991). Augmentative biological control involves the release of commerically produced natural enemies to supplement and enhance a natural enemy population already present, but not present in sufficient numbers at the optimal time to provide the desired level of pest suppression. Inoculative biological control involves a single release of natural enemies to establish them in an area where they are not currently present. Inundative biological control involves the release of large numbers of commercially produced natural enemies to reduce the pest population below the economic injury level and is similar to using natural enemies as a biological insecticide.

1. Insect pathogens

The use of pathogens (e.g., fungi, bacteria, protozoa, viruses) for stored-product pest management has been limited primarily to basic research and rarely have they been used in IPM programs (Moore *et al*., 2000). This is due to a variety of reasons, including their cost and concerns about pathogens becoming contaminates of the final food product. There is little evidence that consuming food with microbial insecticides presents a health hazard (Burges, 1981; Siegel and Shadduck, 1990), but the use of pathogens, even if specific for insects, around human food does present challenges in terms of public perspective. Despite this relatively dim outlook, some pathogen species have been registered for use on stored-products and some species occur naturally in stored-product pest populations and storage environments where they may impact pest population dynamics (Burges and Hurst, 1977; Krieg, 1987; Morris *et al*., 1998; Oduor *et al*., 2000). The emphasis on insect pathogen use has been on inundative releases, but as a single control tactic, insect pathogens are unlikely to be suitable substitutes for chemical insecticides. However, as part of an IPM program using reduced chemical pesticide applications they have potential. A particularly promising area is autoinoculation releases using food and pheromone baits

to attract insects that pick up the pathogen and then disseminate it through the environment (Shapas *et al.*, 1977; Vail *et al.*, 1993; Vega *et al.*, 1995) [see Moore *et al.* (2000) for a more in-depth review of insect pathology and stored-product insects].

Many bacterial species are associated with insects and most often they need to be ingested for an insect to become infected. *Bacillus thuringiensis* (Bt) is the most significant bacterial biological control agent: it is formulated and applied like many chemical pesticides. *B. thuringiensis* var. *kurstaki* isolate HD-1 has been registered in the United States for application to grain, seeds, peanuts, soybeans, and tobacco to control some lepidopteran pests, but is not widely used. Bt can be effective at reducing Indianmeal moth populations in wheat, corn, and peanuts (McGaughey, 1982, 1985a). It is harmless to vertebrates, including humans, and is exempt from residue tolerances on raw agricultural commodities in the United States (Dales, 1994). Unfortunately, resistance to Bt has been reported to develop quickly in stored-product moths (McGaughey, 1985b; McGaughey and Beeman, 1988).

Fungi typically infect host insects by spores on the cuticle germinating and growing through the insect cuticle until they enter the insect hemocoel where further growth results in mortality. There are many species of fungi, but most stored-product work has focused on *Beauveria bassiana* (Balsamo) Vuillemin and *Metarhizium anisopliae* (Metchnikoff) Sorokin. A number of laboratory studies have demonstrated that some species and isolates can cause significant mortality in stored-product beetles (Adane *et al.*, 1996; Rodrigues and Pratissoli, 1990). Different formulations have also been tested that may reduce contamination of food and increase efficacy (Dales, 1994; Hluchy and Samsinakova, 1989). *B. bassiana* formulated with food pellets with pheromone has been tested for management of the larger grain borer *P. truncatus* (Smith *et al.*, 1999). *B. bassiana* has a registration that permits its use on stored products, but is not widely used. Research indicates that synergistic interactions can be achieved by combining *B. bassiana* with DE to control stored-product beetles (Lord, 2001).

Viruses are cellular parasites that spread through the insect's body, typically starting with the gut cells, causing the cessation of feeding within a few days, reduced fertility, and ultimately death. The virus can also be transmitted from the adult female to her eggs (Vail *et al.*, 1993). A number of viruses have been isolated from stored-product insects [e.g., nuclear polyhedrosis virus (NPV), granulosis virus (GV), cytoplasmic polyhedrosis virus], most often from Lepidoptera, and they tend to be highly host specific. Most baculoviruses (NPV and GV) are found in the environment protected inside occlusion bodies that, after insect ingestion, are dissolved, releasing the infectious baculovirus particles. A *P. interpunctella* GV has been identified

and is the most widely studied virus of stored product insects. Use of GV has been successful experimentally in stored almonds (Hunter *et al.*, 1977) and raisins (Vail *et al.*, 1991) and as a surface treatment in grain (Cox and Wilkin, 1996). Simple GV production and formulation methods were developed and patented (Vail, 1991), but this virus is not used commercially.

Protozoa are single-celled organisms that parasitize primarily the insect fat body and digestive system. They enter an insect by ingestion of spores or can be passed from females to their eggs. Protozoa occur widely in stored product Coleoptera and Lepidoptera and are one of the most extensively studied groups of stored product pathogens in terms of their biology, but research on their use as biological control agents is more limited (Moore *et al.*, 2000). Protozoan infections tend to be slow acting and chronic, causing reduced survival to the adult stage, deformities, reduced fecundity, and mortality, but they can function in regulating insect populations (Brooks, 1988). Protozoan infections can also increase susceptibility to chemical pesticides (Khan and Selman, 1984; Rabindra *et al.*, 1988) and other stressors such as starvation (Dunkel and Boush, 1969). Protozoan safety and ability to persist in stored product environments suggest that they may have potential as part of IPM programs (Moore *et al.*, 2000). The neogregarine protozoan *Mattesia trogodermae* Canning attacks several species of *Trogoderma*, including the Khapra beetle, and has been demonstrated to suppress *Trogoderma glabrum* (Herbst) populations in a simulated warehouse using pheromone lures to facilitate spore dissemination (Brooks, 1988; Shapas *et al.*, 1977).

2. *Parasites and predators*

A suite of parasites and predators are associated with stored-product insects and they have received considerable experimental research, but relatively little field study. Schöller (1998) reported that 58 species of parasitoids and predators that attack 79 species of stored-product pests have been studied in at least 900 published articles. Most species are widely distributed geographically and are often found associated with human storage of food. These species are variable in the host species utilized, the life stage attacked, and their degree of specificity. Some species are specialists and attack only a single or a few closely related species and some are generalists that attack a wider range of not closely related species. Because most food storage environments have multiple pest species, host specificity is an important consideration. The ability of these natural enemies to find insects in hidden and poorly accessible areas such as cracks and crevices and under shelving is an important attribute.

Parasitoid wasps are the most widely studied group of insect parasites. Female wasps lay an egg(s) on or in an insect and the progeny develop utilizing that insect as their sole food source, eventually killing the host. Female parasitoids tend to be host specific and typically exploit a specific host immature life stage (e.g., egg, larvae, or pupae). Most parasitoid wasps are relatively small. Females actively seek out multiple hosts and can find and parasitize host insects in cryptic habitats. There is a wide range of species that attack stored-product insects and a considerable body of research on these natural enemies, only some of which are covered here [see Godfray (1994) for more information on parasitoids and Brower *et al.* (1995) and Schöller and Flinn (2000) for reviews of information specifically on stored product parasitoids].

Internal feeding grain pests are susceptible to parasitoid species that are able to move through bulk grain, detect seeds that are infested, drill through the seed, sting the larvae inside the seed, and lay an egg. Some of the major parasitoid species are *Anisopteromalus calandrae* (Howard), *Lariophagus distinguendus* Förster, *Pteromalus cerealellae* (Ashmead), and *Theocolax elegans* (Westwood). These species tend to be facultative and attack multiple internally feeding species. For example, *A. calandrae* can attack *Sitophilus* spp., *Rhyzopertha dominica, Prostephanus truncatus, Callosobruchus* spp., and *Sitotroga cerealella*, among others (Brower *et al.*, 1995). The parasitoid *Anisopteromalus calandrae* has been demonstrated to reduce rice weevil infestations in wheat spillage by 90% (Press *et al.*, 1984) and to reduce infestation of bagged wheat (Cline *et al.*, 1985).

The immature stages of externally feeding stored-product pests are also susceptible to attack by parasitoids. The eggs of several important stored-product moths are susceptible to attack by tiny wasps in the genus *Trichogramma*. For example, the species *T. pretiosum* Riley and *T. evanescens* Westwood attack the eggs of *Plodia interpunctella, Ephestia elutella*, and *Cadra cautella* (Brower, 1983a,b). *Trichogramma* spp. have been reported from peanut storage environments (Brower, 1984) and weekly releases have reduced moth populations in ishell peanuts (Brower, 1988). *Trichogramma evanescens* Westwood has been used commercially in Europe for the management of stored-product moths in retail facilities (Schöller and Flinn, 2000).

Lepidoptera larvae are also attacked by a suite of parasitoids. *Habrobracon (Bracon) hebetor* is a larger braconid wasp that stings, paralyzes, and lays eggs on late-instar larvae that are searching for pupation sites (Hagstrum and Smittle, 1977). *Venturia canescens* is an ichneumonid wasp that parasitizes pyralid moth larvae, including *P. interpunctella*, and has been recovered from flour mills and other food storage facilities (Carlson, 1979). This species attacks a range of larval instars, which are only temporally

parasitized while eggs are laid internally. In simulated warehouses, the parasitoid wasps *H. hebetor* and *V. canescens* are capable of reducing *C. cautella* infestation in food spillage and reducing subsequent infestation of packaged commodities (Cline and Press, 1990; Cline *et al*., 1984, 1986). As discussed by Cline and Press (1990), the combination of packaging that reduces infestation and parasitoid wasps to reduce pest populations in the structure of the building may be an effective approach in certain situations.

Beetle larvae are also susceptible to attack by parasitoids. For example, wasps in the genus *Cephalonomia* attack a range of stored product beetles. *Cephalonomia waterstoni* Gahan attacks several *Cryptolestes* species. Females follow the chemical trails left by wandering larvae and when they find a suitable host they sting and paralyze it permanently before laying eggs (Howard and Flinn, 1990). Natural populations of *C. waterstoni* may be able to reduce populations of *C. ferrigineus* in wheat bins (Hagstrum, 1987). *Cephalonomia tarsalis* (Ashmead) parasitizes larvae of the sawtoothed grain beetle.

Nematodes are another group of insect parasites that have been studied extensively as biological control agents for a wide range of insect pests and crops (Georgis, 1992). They are sometimes considered to be pathogens, but because of their ability to actively seek hosts they are more like parasites (Campbell and Lewis, 2002). Entomopathogenic nematodes (Steinernematidae and Heterorhabditidae), the most studied group of nematodes, are small (<1 mm) round worms that infect only insects. These nematodes have been used primarily as a biological insecticide (i.e., inundative biological control), but they also have the potential to establish and persist in soil environments. Entomopathogenic nematodes have a long list of attributes that make them effective biological control agents (Gaugler and Kaya, 1990; Kaya and Gaugler, 1993): they have the ability to actively seek out insects in cryptic habitats and infect and quickly kill a wide range of insect species, they are not toxic to vertebrates and are exempt from EPA regulation, they can be mass produced and a number of species are available commercially, and they can be applied using conventional pesticide spray equipment. Entomopathogenic nematodes also generally have a good tolerance to various kinds of chemical pesticides and can be tank mixed with many pesticides (Kaya, 1985).

Laboratory studies have shown that a wide range of moth and beetle stored-product pest species and life stages are highly susceptible to entomopathogenic nematodes (Geden *et al*., 1985; Laumond *et al*., 1979; Morris, 1985). A key limitation on the use of entomopathogenic nematodes in bulk stored grain or food products is the requirement for moisture or high relative humidity. This limitation may be reduced when using nematodes to treat

refuge populations of insect pests (e.g., crack and crevice, empty bin, outside spillage) rather than the bulk commodity (Brower *et al*., 1995). Nematodes are applied suspended in water like many chemical pesticides and this moisture could generate, temporarily, conditions that will enable the nematodes to move and locate insects to infect.

Many predators can utilize stored-product insects as a food resource, but not all can persist in commodity storage facilities and suppress pest populations effectively. The Hemipteran predator *Xylocoris flavipes* (Reuter), the warehouse pirate bug, is probably the most studied predator that persists in commodity storage facilities such as peanut warehouses and grain bins and can effectively suppress pest populations (Arbogast, 1978). This bug attacks the egg and early instar stages of many externally feeding stored product beetles and moths (Jay *et al*., 1968). Laboratory and small-scale field trials have indicated that this species can reduce pest populations, dramatically, especially external feeding beetles (Arbogast, 1976; Brower and Mullen, 1990; Brower and Press, 1992; LeCato *et al*., 1977; Press *et al*., 1975). The wide host range of this species is an advantage in food environments where multiple species typically occur, but not all species and stages are attacked readily (e.g., late-instar larvae and adults of larger species and internal feeding insects), although Donnelly and Phillips (2001) reported that *X. flavipes* could locate and kill *R. dominica* larvae inside wheat kernels. Combining *X. flavipes* with parasites that specifically target moths and internal feeding pests might be a more effective approach, but has not been tested (Brower *et al*., 1995). A variety of Coleoptera species are facultative predators of stored product pests, but a number of these species (e.g., *T. castaneum*) are also directly damaging to grain or processed commodities (LeCato, 1975). An exception is *Teretriosoma nigrescens*, which is an obligate predator and has been used as a biological control agent of the larger grain borer (Rees, 1987). Although many mite species are pests of stored commodities, some species found commonly in food storage situations are in fact predators of insects or of pest mite species. Mites are commonly found associated with stored product insects and they can cause disease and mortality and some species can be quite effective as egg predators. Predatory mites may be most effective at suppressing populations of other mites. The mite *Cheyletus eruditus* (Schrank) has been found to provide high levels of control of pest mite species such as *Acarus siro* L. in small-scale trials in bulk grain or empty bins (Pulpan and Verner, 1965; Zdarkova and Horak, 1990). Application of mites as biological control agents in bulk grain and food facilities is likely to be limited because some species may also attack humans [e.g., *Pyemotes tritici* (Schrank), straw itch mite or grocer's itch mite (Moser, 1975)] and potentially have negative impacts as human allergens.

VIII. CONCLUSIONS

A wide range of monitoring and management tools are available for stored-product pest management in the food industry, but often the effectiveness of these approaches and how best to integrate them are not well understood. Even as some tactics are being lost, new ones are being developed and tested, and older approaches that have not been used extensively due to the reliance on tactics such as fumigation are being revived. The difficulty for the food industry from an IPM perspective has been how to integrate these various tools into a coherent and effective program. Often there is reluctance or lack of interest on the part of the food industry to move away from calendar-based pesticide treatments to a more integrated approach. In large part this is due to a justifiable concern about making mistakes with pest control in an industry with an extremely low pest threshold. From a scientific perspective, there is also a shortage of experimental data from real world situations with which to make recommendations. With the pending loss of major management tools, such as methyl bromide and organophosphate insecticides, due to government regulations and market demands directly from consumers, there will be increasing pressure to develop IPM programs to keep our food supply safe from insect infestation and a need for the scientific community and the food industry to work together to find these solutions.

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