These light scattering measurements offer revealing insights into the decrease in viscosity of egg white (usually referred to as "thinning") observed on storage of eggs. The time-dependent changes in M_w of aggregated ovomucin which take place at pH 11.5 can be accounted for by the alkaline degradation process alone, suggesting that, at this pH, disaggregation is a much slower process than degradation. However, since the degradation process is very slow at pH 7.9, the observed difference in M_w of ovomucin at pH 6.2 and 7.9 (270×10^6 and 40×10^6) is probably due to disaggregation. Since thinning occurs between pH 7.6 and 9.7 (Sharp and Powell, 1931), much of the thinning might be produced by disaggregation of gel-like aggregates of ovomucin in the thick portion of the egg white, rather than by alkaline degradation of disulfide bonds. It appears possible to resolve this question by other physical techniques, and such studies are now underway in this laboratory.

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Water Vapor Sorption Hysteresis in Dehydrated Food

Max Wolf,* John E. Walker, and John G. Kapsalis

Determination of the 40 and 100°F adsorption and desorption isotherms of a variety of dehydrated foods revealed the presence and extent of hysteresis as a characteristic of food type, represented by the sorption patterns of apple, pork, and rice. The integrals of hysteresis, obtained by plotting desorption–adsorption values at water activity intervals of 0.05 for these foods were, respectively, at 100°F: 0.08, 0.70, and 2.13; and at 40°F: 2.79, 0.90, and 3.72. Distribution of hysteresis along the isotherm had a distinctive pattern. The effect of increase in temperature was to decrease the amount of hysteresis and to limit its extent along the isotherm. The effect of storage was to increase the area of the hysteresis loop, due mainly to a decrease of the adsorptive capacity of the material. These findings suggest the possibility of using the changes of hysteresis as an index of quality deterioration.

The key to understanding the water sorption properties of food is the water vapor sorption isotherm, which is schematically represented in Figure 1. The shape of the isotherm reflects the manner in which the water is bound. Up to a water activity, A_w, of about 0.30, where the first inflection appears, water is held on polar sites of relatively high energies. This is the "monomolecular region." Between about A_w 0.30–0.70 there is a "multi-layer region." Above A_w 0.7 the water approaches the condition of "condensed water"; it is relatively free and the isotherm reflects solution and surface capillary effects.

Food Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760.

The moisture sorption isotherm has many practical as well as theoretical applications in food. Rockland (1969) re-

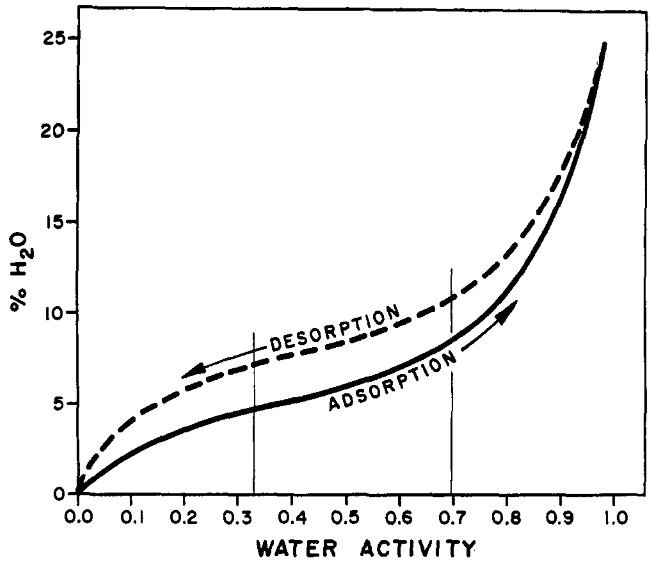

Figure 1. Schematic representation of a water vapor sorption isotherm

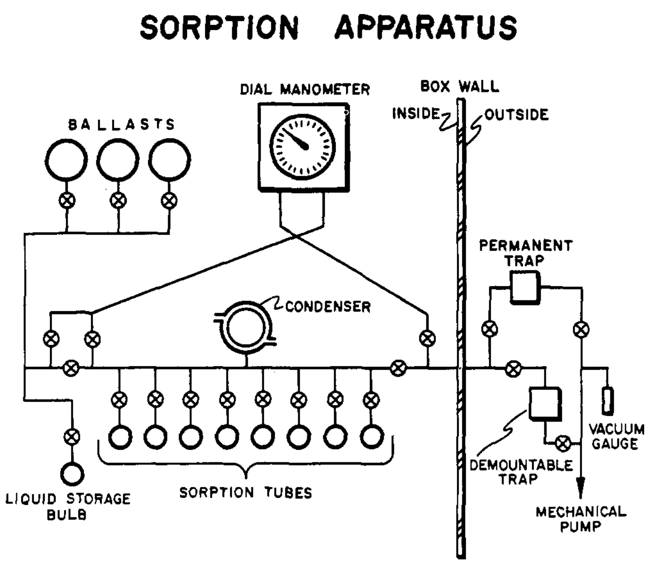

Figure 2. Diagram of sorption apparatus

viewed the effects of water activity on storage stability. Kapsalis *et al.* (1969) discussed the relationship of the isotherm to textural properties. Labuza (1968) reviewed the theoretical and practical aspects of water sorption.

Figure 1 shows that in certain cases the amount of water at any one A_w value depends on whether a desorption or adsorption process is involved. This difference between desorption and adsorption is called *hysteresis.* A large volume of work has been published on the theoretical interpretation of the cause(s) behind this phenomenon in different types of adsorbent and adsorbate materials. Arnell and McDermot (1957) considered hysteresis in relation to three types of solid sorbents: rigid and porous, where capillary condensation of the sorbate appeared to be the usual cause of hysteresis; rigid nonporous, where chemisorption and other effects were of primary importance; and nonrigid solids, where structural effects of the sorbent in interaction with the sorbate were implicated. More recently, Everett (1967) presented a critical review of the thermodynamic and other aspects of hysteresis.

In biological materials, Bettelheim and Ehrlich (1963) and Bettelheim *et al.* (1970) studied the relationships between

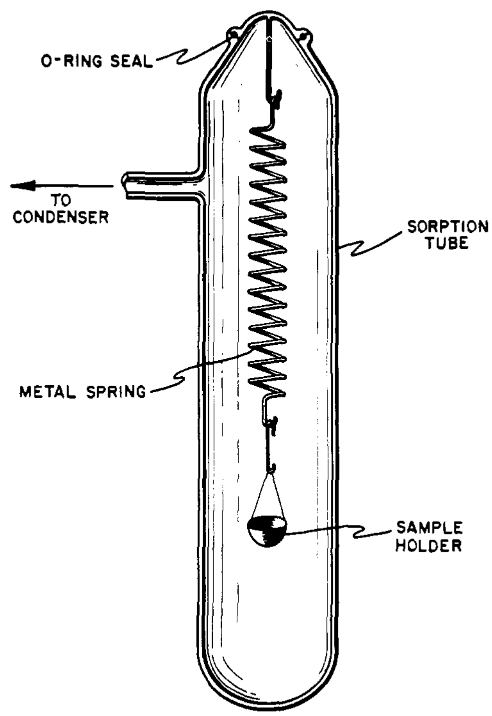

Figure 3. Diagram of sorption tube details

molecular structure and irreversibility as exhibited by the hysteresis, together with other aspects of the sorption process of polysaccharide materials. Rao (1941) studied hysteresis of water and carbon tetrachloride in rice and other grains, and advanced an interesting theory of the swelling of organo gels. Taylor *et al.* (1961) showed that in dextrans and wheat starch the water vapor sorption hysteresis depends on the conditions of adsorption and on crystallization changes of the adsorbent. Young and Nelson (1967) and Chung and Pfost (1967) discussed several theoretical aspects of hysteresis on cereal products.

Recently in our laboratories Strasser (1969), using a sorption isobar technique, observed that quality changes upon storage of cooked freeze-dried beef could be detected by the corresponding changes in sorption hysteresis. In relation to this and subsequent work, our literature search indicated that knowledge was scarce with regard to the presence and extent of hysteresis in different types of dehydrated food products, and the effects of temperature and storage on both the magnitude as well as the distribution of the hysteresis loop along the isotherm. The present paper is an effort to provide this information as a prerequisite to further work on the use of hysteresis as an "index of quality" of Army rations, and of dehydrated foods in general.

EXPERIMENTAL

To study the effect of composition on hysteresis, the dehydrated foods tested were selected from the four classes which Salwin (1963) suggested could be distinguished on the basis of their adsorption isotherms. These foods included: apple slices and orange juice; carrot, peas, and tomato; beef, pork, cod, and haddock; and rice, potato, and flour.

To study the effect of temperature, the adsorption and desorption isotherms of these foods were determined at 40 and 100°F.

To study the effect of storage, beef, haddock, potato, and carrots (items of high military importance) were stored at 100°F for 6 months. For each of these foods the adsorption

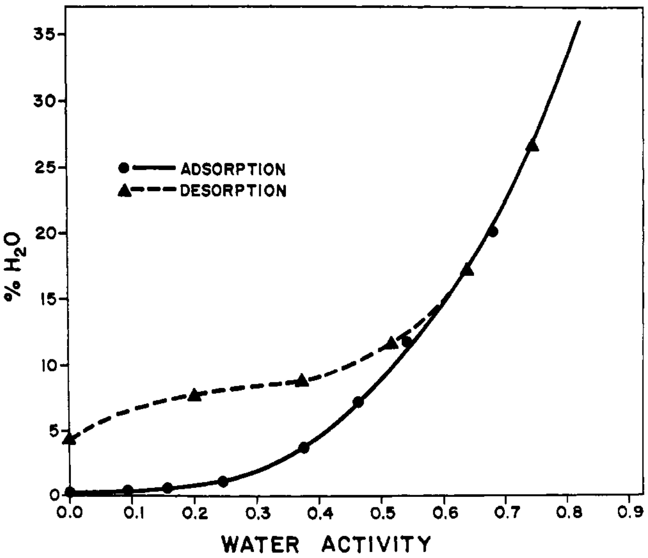

Figure 4. 40°F water vapor sorption isotherm of air-dried apple slices

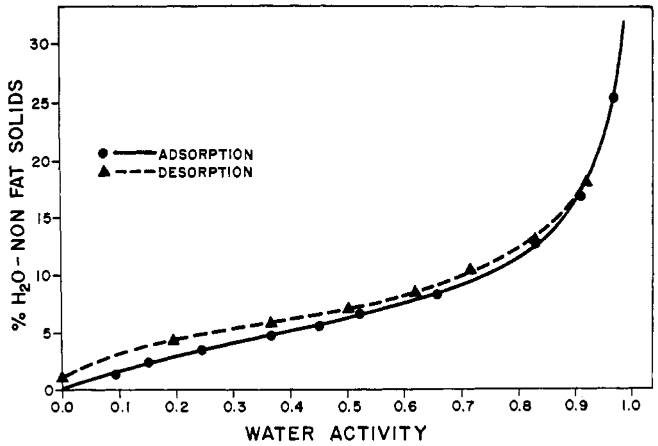

Figure 5. 40°F water vapor sorption isotherm of freeze-dried cooked pork

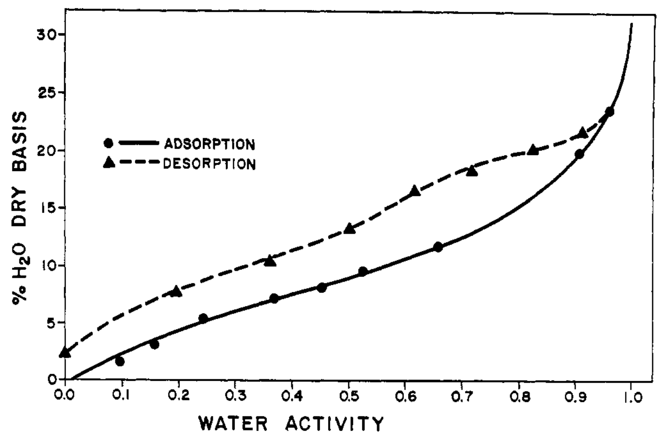

Figure 6. 40°F water vapor sorption isotherm of freeze-dried rice

and desorption isotherms were determined at 45°F, initially and after storage.

A modified McBain–Bakr sorption apparatus was used for the determination of the water vapor sorption isotherms (Figure 2). This apparatus consists of sorption tubes, manometer, vacuum system, and a condenser to control water vapor pressure. Sample temperature was controlled to within a maximum of ±0.4°F in the range of 40 to 100°F, by enclosing the sorption system in an insulated thermostatically controlled cabinet. Details of the sorption tube are shown in Figure 3. The sample was held in a quartz bucket suspended from a metal spring (nickel-span-C of 5 mil diameter) which had a constant of about 1.5 mg per mm extension, with a standard deviation of 0.01 mg per mm. The changes in spring length due to the adsorption or desorption of water by the food were determined with a cathetometer to ±0.05 mm. In operation, the food sample was subjected to a vacuum at 0.005 Torr until there was no further change in the extension of the spring. This reading was taken as the weight of the sample at zero A_w. The water vapor sorption pressure of the system was then set by adjusting the temperature of the water condenser, while the sample temperature was thermostatically controlled in the insulated cabinet. After weight equilibration at this pressure, the condenser temperature was increased to a new vapor pressure equilibrium point. The desired number of points on the adsorption isotherm in increments of A_w 0.10–0.15 were thus obtained. Because reproducibility of the desorption isotherm depends on starting at A_w above 0.9, the test samples were exposed at A_w above 0.95 prior to desorption. The desorption branch of the isotherm was obtained immediately after the adsorption by reversing the above procedure. The resulting isotherms are characteristic of the dehydrated material.

Results were evaluated by comparing the shape of the adsorption and desorption branches of the isotherm, defining the intervals of water activity within which hysteresis occurred, and expressing the hysteresis loop in terms of relative "hysteresis units." For this purpose the adsorption values were subtracted from the desorption values at A_w intervals of 0.05, and the resulting differences were plotted *vs.* the corresponding water activity. Graphical integration of the area under this curve between the A_w limits of 0.025 to 0.975 gave the hysteresis units.

RESULTS AND DISCUSSION

The results plotted as isotherms showed that composition of the food, isotherm temperature, and conditions of storage affected the water vapor sorption hysteresis.

Effect of Composition. Although the total amount of hysteresis, distribution relative to water activity, and temperature dependency varied widely for the different foods, three general hysteresis patterns could be distinguished. These patterns are represented by the 40°F isotherms of apple, pork, and rice in Figures 4–6.

In the dry apple, which is a high pectin and sugar-containing food, hysteresis occurs predominantly in the monomolecular region (Figure 4). Although the total hysteresis is large (2.79 units), there is no hysteresis above 0.65 A_w. This indicates that the food possesses a surface free of capillarity, and that condensation of water on this surface takes place in association with solution effects. The change from an isotherm of type III for the adsorption branch to an isotherm of type II for the desorption branch (Brunauer classification, 1945) indicates a definite change in surface structure. As shown in Figure 4, below A_w 0.65, the desorption isotherm no longer shows the convex-to-the-abscissa characteristic of a typical crystalline surface. Since 4% water remains at zero vapor pressure even after prolonged pumping-down for 3 days in the sorption tube, a hydrate formation of much lower crystallinity is suggested.

In cooked freeze-dried pork, which is a high-protein content food, hysteresis begins in the capillary condensation region, at about A_w 0.85 (Figure 5). The total hysteresis is

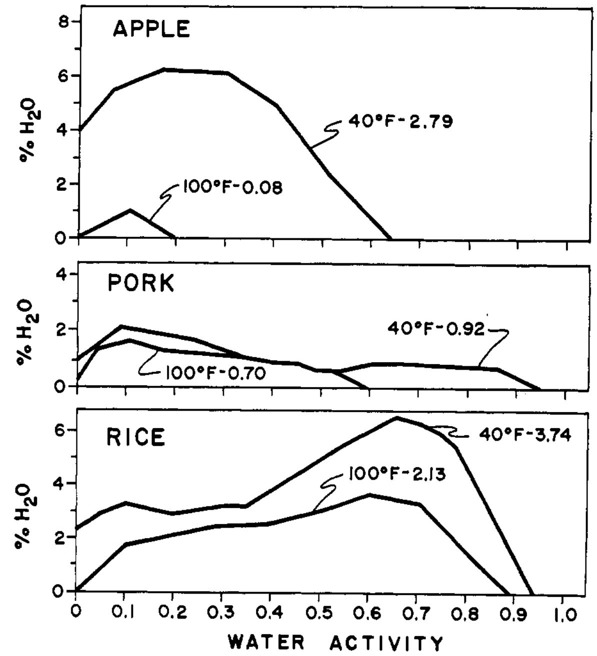

Figure 7. The 40°F and 100°F hysteresis values plotted for apple, pork, and rice against water activity

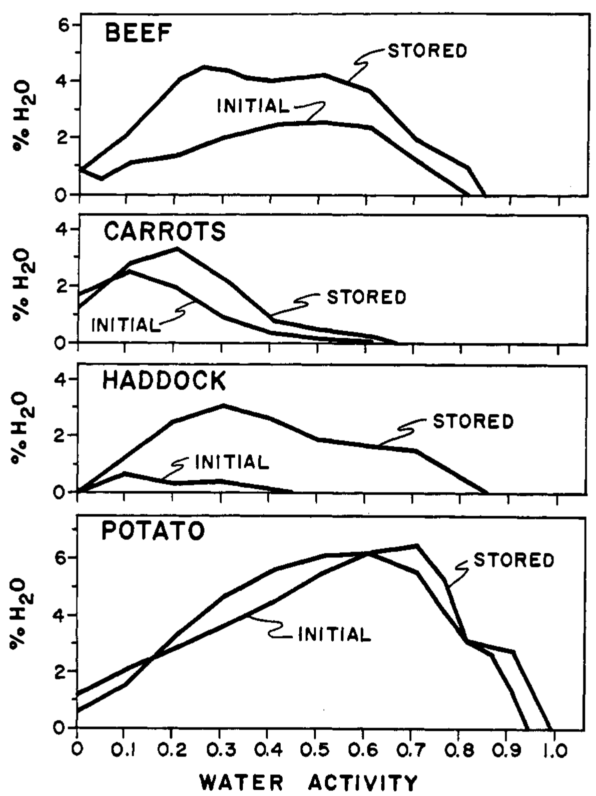

Figure 8. The 45°F hysteresis values of beef, carrots, haddock, and potato plotted against water activity, initially and after storage of samples at 100°F for 6 months

moderate (0.92) and it is fairly evenly distributed along the isotherm, except for a slight maximum at about A_w 0.15. Both branches of the isotherms have the sigmoid shape which is typical of proteins.

In rice, which is representative of starchy foods (Figure 6), the total amount of hysteresis is large (3.74) and a maximum occurs at about A_w 0.65, which is within the capillary condensation region. A surface capillary structure is indicated by the retention of water during desorption in accord with the "ink bottle" theory of McBain (1935). As the desorption proceeds within the multilayer region, the water may also be bound by sorption sites which were made available by prior exposure of the sorbent to high water vapor pressures. The apparent deviation of the desorption branch from the typical sigmond shape indicates that the desorption processes are the result of competing as well as overlapping processes.

Table I. Comparison of Integrals Before and After Storage of Hysteresis, Adsorption, and Desorption Branches of the Isotherm

	Hysteresis		Initial minus storage	
	Initial	Storage	Adsorption	Desorption
Beef	1.32	2.11	2.38	1.50
Carrot	0.615	1.006	0.649	0.049
Haddock	0.115	1.374	1.715	0.455
Potato	3.50	3.60	0.15	0.17

Effect of Temperature. The effect of increasing isotherm temperature was to decrease the total hysteresis and to limit the span of the loop along the isotherm (Figure 7). By increasing the isotherm temperature from 40 to 100°F, the total hysteresis was reduced in apple from 2.79 to 0.08, in pork from 0.92 to 0.70, and in rice from 3.74 to 2.13. The beginning of hysteresis was shifted in apple from A_w 0.65 to 0.20, in pork from 0.95 to 0.60, and in rice from 0.94 to 0.88. The amount of water retained at zero vapor pressure was also greatly reduced.

The above results are in variance with the hysteresis behavior of bovine serum albumin reported by Seehof *et al.* (1953). These workers found that in this protein the amount of hysteresis was virtually independent of temperature and almost constant over the entire range of relative pressures. The small temperature differential used in the experiments of Seehof and the presence in pork of nonprotein components may account for the differences.

Effect of Storage. Storage at 100°F for 6 months resulted in a general increase of the area of the hysteresis loop (Figure 8). This effect was pronounced in beef and haddock (high-protein foods), whereas it was relatively small in carrots and potato.

Expressed as hysteresis units, the 40°F hysteresis of the pre-storage samples were, respectively, 1.32, 0.62, 0.12, and 3.50 for beef, carrot, haddock, and potato; it was 2.11, 1.01, 1.37, and 3.60 for the same foods stored at 100°F for 6 months. The increase was 0.79 for beef, 0.39 for carrot, 1.25 for haddock, and only 0.10 for potato. As shown in Table I, in foods which showed a large change of hysteresis upon storage there was a marked decrease of adsorption relative to desorption, resulting in an apparent increase of the desorption–adsorption difference. In the case of potato there was little change in either.

Examination of the stored samples by a small group of researchers revealed decreases in several quality attributes. In the beef, haddock, and carrots, the color, taste, and rehydratability showed appreciable deterioration. In the potato quality changes were moderate. As a sequence of these observations, planned future work in our laboratories will aim at the assessment of the correlation between changes in hysteresis and objective and sensory changes of quality upon storage.

The use of hysteresis as a quantitative index of quality for certain dehydrated foods appears a promising possibility if practical methodology can be developed. The present procedure for determining the complete isotherm requires from 10 to 20 days, and is therefore impractical. It is necessary, however, to use this or a similar procedure to establish the normal sample variation, and to obtain reference isotherms for the foods of interest. Once this is done, simplified procedures can be developed. The hysteresis characteristics may then serve to evaluate remaining shelf-life in warehoused products, or it may be used to evaluate quality of ingredients used in the manufacturing of multi-component foods.

CONCLUSIONS

The total amount of water vapor sorption hysteresis, its distribution relative to water activity, and the effect of isotherm temperature varied widely for different dehydrated foods. Three patterns of hysteresis were recognized. These were associated with high sugar, high protein, and high starch content foods. Thus, hysteresis is an important feature of the water vapor sorption behavior of the different foods, and it provides information which is not available from consideration of either the adsorption or desorption isotherm alone.

In general, storage conditions which produced marked changes in the quality of foods were associated with definite changes of the water vapor sorption hysteresis. Specifically, a large decrease in the adsorption branch of the hysteresis loop (indicating a decrease in sorptive capacity) combined with a much smaller decrease of the amount of sorbed water in the desorption branch produced a net increase of hysteresis. In some cases the distribution of the hysteresis loop relative to water activity also changed. The above marked effects of storage suggest that hysteresis changes could be used as an index of quality deterioration of many foods. Further work toward this objective is planned in our laboratories.

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