Finally it might be mentioned that the relatively weak flavour which is usually obtained when so-called instant mashed potato products are made according to the manufacturers' instructions (e.g. by adding hot water or hot milk) is probably due to the fact that the degradative reactions leading to the volatile constituents of flavour only occur weakly, if at all. This observation and the experiments with baked potatoes support the suggestion that the desirable aroma of cooked foods is due to such degradative reactions.

Conclusions

The results reported are to be regarded as exploratory and only comparative within each group, and the observed differences are not necessarily true for all varieties of potato. Nevertheless, the following points have been established.

(1) There are distinct differences in the flavour volatile components between the potato varieties so far examined.

(2) New potatoes are notable for their lower concentrations of volatile substances rather than for the appearance of characteristic different constituents.

(3) The effect of storage is markedly to alter the flavour 'spectrum'.

(4) The soil types in which the potatoes are grown appear to affect the volatile substances produced but much more work will be necessary to explore this effect.

(5) Simple alterations in cooking procedures may produce marked changes in the flavours produced.

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The environment for chemical change in dried and frozen foods

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The primary object of the main methods of food preservation is to maintain the food in a wholesome condition during prolonged periods of storage. Ideally the storage life of the food should be unlimited, a goal which can only be achieved if it is possible to attain absolute stability. Though some types of change may in particular instances be considered desirable, conditions that permit them to occur

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must inevitably make possible other changes of a less desirable nature. Indeed, if one accepts the fresh food or its cooked counterpart as representing a standard of top quality, any departure from this standard must be regarded as detrimental. This, of course, applies particularly to those foods in which the preservation process itself does not cause a major alteration in the properties of the material as finally prepared for eating. Most dehydrated and frozen products would fall in this general category.

Dehydration and freezing, though very different as processes, have features in common. Not the least of these is the fact that most of the water originally present in the food is either actually removed, as in dehydration, or effectively removed, as in freezing, so that it is no longer available as a medium within which chemical reactions can take place during storage. There are, of course, reactions occurring in dried and in frozen foods in which water need play no part, for example oxidations involving atmospheric oxygen. We shall confine ourselves here to a consideration of the conditions necessary for those changes in which water is involved as a reaction medium.

The low temperatures at which frozen foods are stored do not of themselves completely prevent chemical change, but merely depress the rate of such change. Considerations other than temperature determine whether reactions are possible and, with regard to the types of change with which we are concerned, it is the availability of water that is the overriding factor. The proportion of the original water content removed during drying or freezing determines the effectiveness of the preservation process. A relatively small reduction in available water merely increases the concentration of potentially reactive substances in the aqueous phase, and can increase rather than decrease the rate of deterioration. At the other end of the scale, a complete removal of water is impracticable, certainly in a commercial process. Is there a particular point between these extremes, which is not just a convenient compromise, but which has a fundamental significance and, at the same time, can be regarded as a useful target for the processor and handler? Our knowledge of the condition of water in foods and of its relationships with the solid constituents leads us to believe that there is indeed such a point.

The water contained in a food material can be divided into a number of fractions, one of which is thought to be completely immobilized owing to its firm association with the solid constituents, in particular those of high molecular weight (Kuprianoff, 1958). This fraction is difficult to remove either by drying or by freezing and its properties are quite different from those of ordinary liquid water; for example its vapour pressure is relatively very low. The water relations of foodstuffs and of pure macromolecular constituents are conveniently illustrated by means of sorption isotherms, in which the moisture content, at equilibrium, is plotted against the relative humidity or water vapour pressure of the surrounding atmosphere. The shape of such isotherms is normally sigmoid (Fig. 1), the first steep part of the curve representing the sorption of that part of the water that is very firmly bound. Stitt (1958) shows water sorption isotherms for a range of foodstuffs. Several workers have applied the equation of Brunauer, Emmett & Teller (1938) to their data for the

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sorption of water by pure constituents of foods (for a review of this work see McLaren & Rowen, 1951). This equation generally fits the data well over the lower range of relative humidity and can be used to calculate a value of moisture content corresponding to one complete layer of adsorbed water molecules. The number of molecules present in this layer is inadequate completely to cover the macromolecular surfaces and adsorption appears to occur at specific sites (Bull, 1944; Shaw, 1944). This interpretation has been supported by the demonstration of a reasonably close agreement between the numbers of water molecules comprising the monolayer and the respective numbers of potential binding sites for water, such as the polar side-chains of proteins and the hexose residues of polysaccharides (the hydroxyl groups attached to the number 6 carbon atoms) (Pauling, 1945; McLaren & Rowen, 1951). There has been some discussion as to whether, in proteins, the peptide groups themselves play a part in water binding, and it has been found necessary for a stoicheiometric relationship in some instances to assume that a certain proportion of peptide groups is binding water molecules. Indeed, some workers (Riedel, 1961; Nemitz, 1961) consider that these groups play a major role.

Most foodstuffs are of course complex mixtures and, though a few macromolecular constituents generally predominate, each such constituent has its own characteristic sorptive capacity. Moreover, the salts present can have an appreciable effect on the hydration characteristics of the material (Nemitz, 1961). The significance of monolayer values calculated from sorption data for complete foods is therefore less clear and, for a given product, differences arise owing to minor variations in composition and in the degree of crystallinity of the components of high molecular weight (Table 1). Nevertheless, Salwin (1959) has pointed out the close agreement between such calculated values and the respective moisture contents at which a number of dehydrated products have been shown to have the greatest stability.

The amount of water contained in this first adsorbed layer lies within the range of approximately 4–10 g/100 g dry solids. To what extent can water in excess of this small fraction be bound and rendered unavailable? The theory of Brunauer *et al.* (1938) envisages the formation of several successive layers of adsorbed molecules over the same sites. There is also the possibility, with proteins and polysaccharides, of additional binding sites, of lower affinity for water, becoming effective at higher relative humidities. However, McLaren & Rowen (1951) calculate that, for collagen, 84% of the total heat of sorption is accounted for during adsorption of the monolayer. Moreover, Hamm (1960) points out that, according to the multilayer theory of Brunauer *et al.* (1938), the forces holding the second and subsequent layers would be too small to confine the molecules to specific sites.

Some intermediate degree of immobilization does, however, appear to be characteristic of a certain proportion of water in excess of the first 10%. The application of other techniques to determine the content of bound water in foods has yielded much higher values. Most of these have been obtained by freezing methods, the most recent work in this field having been carried out by Riedel (1956, 1957, 1960, 1961). Riedel finds that, for a number of animal products, the amount of water remaining unfrozen at temperatures of between $-25°$ and $-40°$ (and even down to $-70°$),

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Table 1. *A comparison of calculated monolayer values (obtained with the equation of Brunauer* et al. 1938) *with values of bound water, determined by freezing, for a range of foodstuffs*

	Monolayer water (g/100 g dry solids)		Bound water (g/100 g dry solids)	Temperature used (°C)	
Material	Value	Reference	Value		Reference
Peas	3·64*	Gane (1950)	4·1–32·08	−20	Daughters & Glenn (1946)
Green beans	4·21*		10·98–68·49		
Rhubarb	5·71*		3·8		
Strawberries	4·78*		17·15–49·05		
Raspberries	2·14*		31·03		
Lima beans	5·37	Salwin (1959)	4·57		
Potato	5·46				
	7·2–9·6	Duckworth (1962)			
	7·7	Görling (1958)			
Starch	5·68	Salwin (1959)			
(potato)	6·85	Duckworth & Smith (1963)	38·0–40·0	−40	Riedel (1960)
	7·92	McLaren & Rowen (1951)			
Cellulose	10·44				
Meat	6·19	Salwin (1959)	43·0	−40	Moran (1934)
	4·0–5·0	Hamm (1960)	40·0		Riedel (1957)
			22·5	−180	Riedel (1961)
Fish	4·92	Duckworth & Smith (1963)	38·5	−40	Riedel (1956)
Chicken	5·48	Salwin (1959)	35·0		Riedel (1957)
Egg-white	6·78*	Gane (1943)	25·0	−30	Nemitz (1961)
Egg albumen	4·97–6·15	Dunford & Morrison (1954)			
Gelatin	8·73		53·0	−20	Moran (1934)
			49·0–58·0		Mennie (1932)

*Value not given in the original, but calculated from the author's data.

per unit weight of solid constituents, is similar for samples showing a wide range of initial total water content. If the total water content is first reduced, by drying, below the level corresponding to this same amount of unfrozen water, then no freezing takes place. There appears then to be a definite fraction of the water which is bound against freezing over this range of temperature. Some earlier results of Daughters & Glenn (1946) for a range of plant materials cooled to −20° are also available (Table 1). With few exceptions, these values for bound water determined by freezing are much higher than corresponding monolayer values calculated from sorption data. However, it is known that some water continues to freeze out at temperatures below −40° (see p. 189). Indeed, there are indications that if extremely low temperatures are used, down to −180°, water directly and firmly bound to the macromolecular surfaces can be removed as ice.

Let us examine these results more closely in relation to the known composition of food materials. Salwin's (1959) calculated monolayer value for beef (on a fat-free basis) is 6·19%. Hamm's (1960) figures for meat are between 4 and 5%, and our

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own value for haddock is 4·92%. Expressed as moles water/100 g dry solids, the corresponding range is 0·22–0·34. The main structural proteins of muscle tissue—actin, myosin and tropomyosin—yield values for the content of polar side-chains of between 0·49 and 0·54 moles/100 g. Collagen, with values of between 0·33 and 0·61 cannot modify the range greatly for meat as a whole, nor will other proteins present in smaller amounts have any major effect on an overall value (see Hamm, 1960). In this example then, the number of moles of water comprising the monolayer can be little more than half the number of polar side-chains. Riedel (1961), as a result of his freezing experiments on meat, gives a value for bound water of 22·5 g (1·25 moles) water/100 g dry material, corresponding to about two molecules of water per polar side-chain. However, he relates his values to the nitrogen content of the material and calculates that, on average, one molecule of water is bound by each amino-acid residue or peptide bond. A similar correspondence between the numbers of bound water molecules and of nitrogen atoms is claimed by Nemitz (1961), working in the same laboratories, to occur in desalted egg-white. In this instance, the value for the content of bound water obtained by freezing is supported by the results of other experiments on the heat denaturation and water sorption of similar material. The temperature at which denaturation occurs is unaffected by changes in moisture content until the latter is reduced below 25 g/100 g dry solids—the amount of water remaining unfrozen at −30°. Moreover, the heat of binding calculated from the results of sorption experiments falls rapidly from an initially high value in dry material to reach zero at this same moisture content of 25 g/100 g dry solids. Nemitz also points out that, if the central linear portion of the sorption isotherm is extrapolated to 100% r.h., the corresponding moisture content at this point would be close to this same value.

Other figures given in Table 1 show that, for plant materials also, there are large discrepancies between published values for monolayer water and for water bound against freezing. (For cellulose and starch the moles water sorbed per 100 g in the monolayer are 0·58 and 0·44 respectively, as against 0·62 moles of glucose residues in each substance (McLaren & Rowen, 1951). Is this intermediate fraction of water really immobilized and unavailable as a medium for reactions in solution?

Our own approach to this problem has been to study the ability of simple soluble constituents to diffuse within food materials at these intermediate moisture levels, and at different temperatures of storage in the frozen state.

Many tests have been carried out in which both plant and animal products, treated locally with ^{14}C-labelled glucose, have been stored in equilibrium with atmospheres of different relative humidity to give moisture contents over a suitable range. The materials have been used both in the form of pieces and of thin sections (generally 10 μ thick). The latter are particularly suitable for the detection of diffusion over short distances by counting methods, and also for the application of fine autoradiographic techniques for the study of the distribution of the diffusing tracer in relation to the histochemical structure of the material. Sections have been brought to equilibrium at the desired moisture levels both by sorption of water from the dry state and by desorption from the original water content, and, since no difference

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in behaviour has been found, it is concluded that hysteresis effects have had little or no influence on the diffusion processes. Various counting techniques have been used to detect and measure the extent of diffusion (Duckworth & Smith, 1963). Autoradiography with X-ray film has also proved very useful for demonstrating the diffusion of small quantities of tracer, when detection by counting techniques would have involved unduly long periods of counting.

The two materials most exhaustively studied have been potato and fish (haddock). A consistent feature of the results has been that a demonstrable degree of migration of labelled glucose has occurred (during storage periods of 2–3 months) at moisture contents of as low as 6·6 and 6·3% (dry weight basis) respectively, both of which figures are only slightly in excess of the calculated monolayer values for the corresponding materials (5·11 and 4·92) (Duckworth & Smith, 1963).

It has been pointed out above that the amount and condition of the water present within different structural elements of a tissue, at a given overall moisture content, may differ owing to chemical and physical differences between the structures concerned. For this reason, the route along which a solute diffuses can follow a characteristic pattern. We have shown, for example, that the diffusion of glucose through sections of potato starch gel, in equilibrium with an atmosphere of given relative humidity, is relatively slow as compared with its diffusion through sections of scalded potato tissue and of similar tissue from which the starchy contents of the cells have been removed enzymically. This finding suggested that in the complete tissue at intermediate levels of moisture, glucose diffuses predominantly along the network of cell walls. Autoradiographic evidence in support of this conclusion has been obtained (Duckworth & Smith, 1963).

An examination has been made of the distribution of adsorbed water in relation to the structural elements of potato tissue, by allowing initially dry sections to reach equilibrium over saturated solutions of salts in tritium-labelled water of high specific activity (100 mc/ml). After hydration, these sections were set up in contact with stripping film emulsions and exposed at −78·5°. It has not so far been possible to demonstrate any marked difference in the content of tritium-labelled water between the cell-wall network and the starch gel inside the individual cells. A large difference is not, however, to be expected and the degree of immobilization of water associated with particular components will not necessarily be the same, even when the actual water content is of a similar order. This technique is currently being applied to other tissues.

The facility with which solutes can move in the remaining water would be expected to have an influence on the electrical conductivity of the materials. Accordingly, measurements have been made of the resistance of some dehydrated materials at moisture contents over the ranges used in the diffusion experiments. These measurements show that there is a fairly sharp increase in resistance as the moisture content falls below the levels found to be limiting for solute diffusion. The curve in which the log of the electrical resistance is plotted against moisture content is, indeed, almost a mirror image of the sorption isotherm for similar material. The results of these various experiments, for potato, are summarized in Fig. 1.

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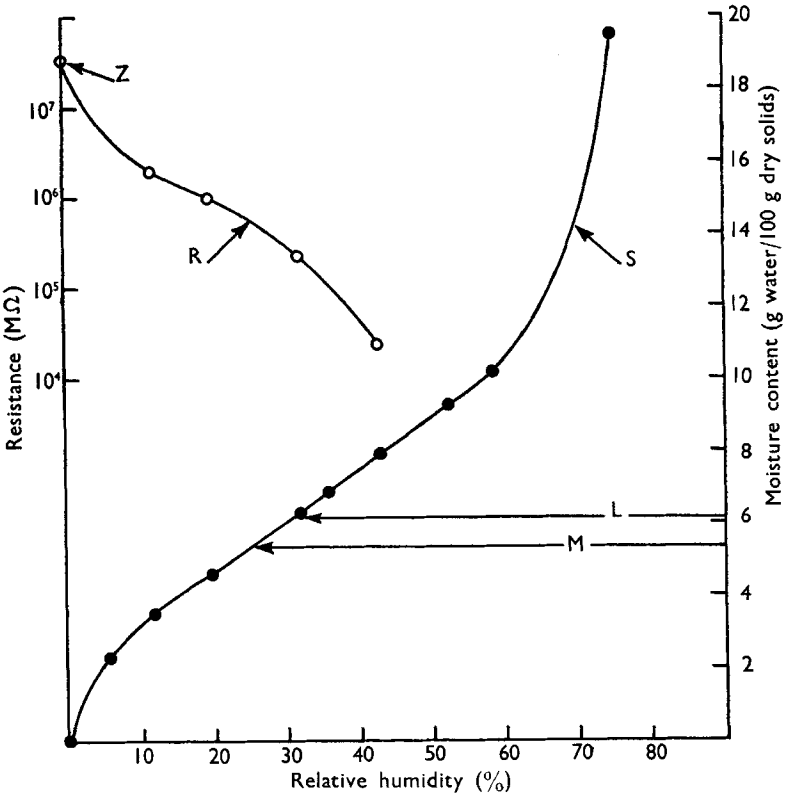

Fig. 1. Comparison of the sorption isotherm for dehydrated potato (S) with the curve for the electrical resistance (R) of similar material brought to equilibrium at the same relative humidities (all readings taken at 37°). M, the monolayer value, 5·28 g/100 g dry solids (Brunauer *et al.* 1938); L, the lowest moisture content, 6·09 g/100 g dry solids, at which the diffusion of glucose was detected in similar material; Z, this point is taken from the insensitive part of the scale of the instrument and lies very close to the limit of this scale, which corresponds to infinite resistance.

This picture, which has emerged from the study of dehydrated material, one would expect to be applicable, in its general aspects, to the conditions in frozen foods, in which most of the water is removed as ice. Frozen foods are not generally stored at temperatures below 0°F (−17·8°C). The results of Riedel (1956, 1957, 1960, 1961) and of Daughters & Glenn (1946) therefore suggest that, during the storage of frozen foods, water will be present in considerable excess of the amount shown to be necessary for solute diffusion. In order to test this assumption, a series of diffusion experiments, similar to those described above, but using frozen materials and frozen sections, has been carried out over a range of temperatures between −5 and −20°. The results show that glucose can diffuse more or less readily through foods of both plant and animal origin over this full range of temperature. The effect of a decrease in temperature over this range, as for a decrease in moisture content (above the limiting values), has merely been to depress the rate of movement. With frozen foods, however, as was expected on theoretical grounds, the limiting conditions for solute diffusion were not reached within the range of temperature employed.

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Measurement of the electrical resistance of food materials held at −20° has given values (between 50 and 500 MΩ) which, though spread over a complete order of magnitude, even for a single material, are all relatively low when compared with those for corresponding dehydrated products (between 20 000 and 2 000 000 MΩ). If the temperature of frozen materials is depressed below −20°, the resistance continues to rise steeply until, at between about −50 and −60°, it is similar to that of material of the same kind dried to a water content near to the monolayer value. It is interesting to recall that, in attempting to define the temperature at which the freezing out of water in food materials is complete, various authors have given values of between −40 and −60° (Moran, 1934, −40 to −60° for meat; Kallert, 1926, −55° for meat; Heiss, 1933, −59° for muscle; Taylor, 1926, −59° for fish; Birdseye, 1929, −57° for haddock). This suggests that in order to approach, in frozen foods, the degree of non-availability of water achieved by drying to a moisture content near the monolayer value, storage temperatures of well below −20° would be necessary. It appears likely therefore, that at temperatures between −20° and about −50° some solvent water will still be present, and that reactions in solution must still proceed, leading to a slow but progressive change in the quality of the materials.

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