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The techniques for the transport by sea of chilled and frozen beef are of great importance to Australia and New Zealand, which export beef, and to the United Kingdom, which imports large quantities.

The Overseas Transport of

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***The procedures described in this article* apply chiefly to the trade in chilled and frozen beef before 1939. Investigations now being actively pursued at Cannon Hill, Q., by C.S.I.R.O. in collaboration with workers from the United Kingdom may lead to further improvement in the quality of the beef reaching the United Kingdom. These investigations will form the subject of an article in a later number of the* Food Preservation Quarterly.**

The development of the import trade in chilled and frozen beef into the United Kingdom nearly 50 years before World War II may be gauged from the accompanying table.

Importation of Beef into the United Kingdom

Year	Thousands of Quarters			Chilled (% of Total)
	Chilled	Frozen	Total	
1891	1049	—	1049	100
1901	1934	789	2723	70
1911	2255	1095	4350	52
1921-25 (average)	3743	1979	5722	65
1932-38 (average)	4896	1225	6121	80

CHILLED BEEF

Development of Trade

Beef in this form was first exported from North America and later from the Argentine. Between 1934 and 1939 Australia and New Zealand developed the trade to such an extent that in 1938 about 26 per cent. of the export beef from Australia and 60 per cent. from New Zealand was shipped in the chilled form. Overseas transport of chilled meat over long distances is limited to beef.

Preparation and Cooling

The following procedures apply chiefly to Australia and New Zealand before 1939. The experimental basis for these procedures and for overseas transport is described in detail in publications, listed at the end of this article, by the Australian Council for Scientific and Industrial Research, now C.S.I.R.O. (Empey and Scott 1939; Scott and Vickery 1939), and by the British Department of Scientific and Industrial Research (Callow 1932; Coyne 1933; Haines 1933; Moran, Smith, and Tomkins 1932; Tomkins 1932).

Since the storage life of chilled beef is limited chiefly by the onset of spoilage by bacteria, moulds, and yeasts, it is essential for long storage that during the preparation of the beef microbial contamination of the carcass surfaces be reduced to a low value. This figure, expressed in terms of microorganisms which grow well at 0°C, is found in practice to be of the order of 150 organisms per sq. cm.

The major source of contamination is the hair of the hides and the accompanying soil. Other sources which may at times be important are the water used for washing the beef, slaughter-floor equipment such as wiping cloths, brushes, knives, and saws, and also the hands, arms, and clothing of the operatives. The air of the slaughter-floor is seldom a serious source of contamination.

In order to reach the low population of 150 organisms per sq. cm., a number of stringent hygienic precautions must be observed. They

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Chilled and Frozen Beef

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include the following:

- The installation of vigorous forced water sprays in the cattle races leading to the slaughter-floor. These sprays must be arranged so as to subject all areas of the hide and feet of the animal to a thorough washing.
- The sterilization of carcass washing water by heat or by chlorination.
- Frequent, thorough cleansing of the floors and walls of the slaughtering and dressing sections of the meat-works.
- The provision of special vessels containing hot detergents for cleaning and sterilizing saws, cleavers, knives, and steels.
- The provision of steam sterilizing equipment for brushes and cloths used for dressing the beef.
- The provision of specially designed basins where the operatives may frequently clean their hands and arms.
- The issue of freshly laundered clothing each day to every operative.

The slaughtering and dressing operations should not occupy more than 45 minutes, after which the sides of hot beef should be placed immediately in the chilling rooms. At the completion of the dressing operation the surfaces of the sides should be free from excess moisture and blood.

Further microbial contamination during the cooling of the sides of beef to approximately −1°C must be prevented by thorough cleansing of the chilling rooms, by washing walls, floor, ceiling, rails, etc. with a hot detergent solution followed by fumigation with formaldehyde gas. Sawdust, a source of heavy contamination, must not be used on the floors.

Large increases in the microbial population of the beef surfaces during chilling often occur. Such increases can, however, be prevented by ensuring a rather extensive degree of desiccation in surface layers (1-2 mm thick) of the meat.

About 24 hours are required to reduce the temperature of the superficial tissues of the thickest portions of the sides of beef to −1°C. To produce the required surface desiccation, two conditions are essential:

- A minimum air speed over the beef of about 80 cm per second, which is equivalent to 45-80 changes of air per hour, depending on the method of distribution.
- A high rate of cooling, with a reduction of air temperature to −1°C within 10 hours of the completion of the loading of the chilling room.

During the subsequent period of 48 hours required to reduce the "bone" temperature of the thickest portions of the meat to −1°C, a fairly high drying power of the air must be maintained. This may be achieved by various combinations of speeds and relative humidities of the air. For instance, for a speed of 15 cm per second over the beef, the appropriate relative humidity is 72 per cent., but for 65 cm per second a relative humidity not exceeding 87 per cent. must be maintained. Such conditions not only prevent microbial growth, but also aid materially in the maintenance of the good "bloom" or appearance of the beef during the long period of shipboard transport. During the cooling period of 72 hours, the loss of moisture from the beef subjected to the above conditions will amount to 2.3-2.5 per cent. of the hot weight.

At the completion of the 72-hour period of cooling, it is usual to cut the sides into quarters and to wrap them in stockinette and hessian, which must be previously heat-sterilized.

During the period of storage in the meat-works while awaiting shipment, an air temperature of −1°C and the drying power of the air mentioned above must be maintained.

Transport to Ship

Unless the meat-works is situated adjacent to a deep-sea loading berth, transport to the ship is generally effected by refrigerated railway cars in which the meat is hung. These cars are pre-cooled and the bunkers filled with lump ice prior to loading.

For short journeys of less than 12 hours, warming during loading of the cars is generally the most important factor. Consequently, rapid loading through trunkways is highly desirable.

FROZEN MEAT

Preparation

The conditions to be observed in the slaughtering and dressing of meat which is to be frozen are less stringent than for chilled beef. Reasonable cleanliness must be observed in all operations and the meat surfaces should be free of blood.

Chilling

It is usual to subject only beef sides to chilling for 24-48 hours prior to freezing in order to "set" the meat sufficiently to permit cutting down into quarters to be effected without appreciable slip of the meat over the bone. The sides are placed in the chilling rooms within 45 minutes of slaughter and the speed of cooling is such that the bone temperature of the thickest portion—the buttock—should be reduced to 15°C or below within 24 hours.

Freezing and Storage

The freezing chambers are usually cooled convectively or by forced air circulation using direct expansion of ammonia in piping on the walls and ceiling. Lamb, mutton, and pork carcasses are usually placed directly into these chambers within six hours of slaughter, whereas the commencement of freezing of beef quarters occurs after the period of 24-48 hours' cooling in chillers. After the chambers are filled, the air temperature is reduced as rapidly as possible to between −14 and −18°C. The time required to reduce the "bone" temperature of the thickest portion to about −10°C varies from 36 hours for lamb carcasses to 4½ days for beef quarters.

Temperatures in the range −12 to −14°C are commonly employed during storage before shipment and at these temperatures the growth of microorganisms is completely inhibited. Serious loss of "bloom" or appearance through surface desiccation may occur if the storage temperature is not steady or if the relative humidity of the air is not maintained at a high value. The way in which high relative humidity is maintained in frozen stores is to construct them with thick insulation and a high ratio of surface area of refrigerating piping to air volume, thereby achieving a low rate of heat leakage into the space and a minimum temperature difference between the produce and the pipe surface.

Transport to Ship

If the refrigerated railcars are loaded rapidly, and if undue exposure of the meat to atmospheric temperatures is avoided, it is generally unnecessary to cool the cars artificially by such means as ice and salt if the transport period does not exceed about 16 hours. For longer periods without ice and salt the average temperature rise is excessive. In warm climates, at least, the use of ice and salt mixtures in the car bunkers is generally essential for transport periods exceeding about 16 hours. An endeavour is usually made to arrange transport and handling conditions so that the highest bone temperature of the meat at the time of loading in the ship does not exceed −6.5°C. If meat is loaded at a temperature much above this value there is the danger of staining due to partial thawing and of distortion of meat when under load in the holds.

OVERSEAS TRANSPORT OF CHILLED BEEF

The temperature for the carriage of chilled beef was generally −1.4°C, and since small changes of temperature in this region have a marked effect on the ice formed in muscular tissue (ice begins to form at about −1°C and at −3°C more than 68 per cent. of the water is frozen out as ice) it is important to control the temperatures throughout the spaces within narrow limits.

The average duration of voyages for chilled beef shipments varied from 18 to 24 days for the Argentine and from 40 to 60 days for the Australian trade.

The latter trade was established as the result of researches mentioned in the first part of this report and of other research work at the Low Temperature Research Station, Cam-

bridge, which showed that carbon dioxide in the atmosphere surrounding the meat in concentrations of the order of 10 per cent. produced an inhibitory effect on the growth of certain microorganisms which commonly cause meat to deteriorate at chilled temperatures.

Ships designed especially to carry chilled beef have deck spaces to give just sufficient head room for hanging a hindquarter of beef. Other 'tween-deck spaces up to nine feet in depth were, however, in common use. Before they are filled these spaces are cleaned and disinfected by a method similar to that used for cleansing chilling rooms in meat-works.

When it is necessary to render cargo spaces gas-tight so as to be able to maintain a 10 per cent. concentration of carbon dioxide in the atmosphere, it is usual to select spaces in the form of lockers at the end or sides of a 'tween deck.

The spaces between deck plates and frames or stiffeners which are normally filled by cement chocks are closed by welded steel sheets, and pipes, cables, or fan-spindles passing into the space are fitted with gas-tight glands.

In contrast to the older type of spaces cooled by wall and roof grids, much of the modern construction employs air circulation over batteries of pipes.

The meat must be hung so that the stow is tight enough to prevent undue bruising and chafing of the meat from the movement of the ship. On the other hand, the stow must also be sufficiently open to allow for a reasonable circulation of air through the cargo.

Chilled beef stows at the rate of about 120 cubic feet per ton; the corresponding figure for frozen beef is about 95 cubic feet per ton.

Condition on Arrival in U.K.

The results of six years' experience (1934-39 inclusive) of experimental and commercial consignments could be summed up as follows:

- Except for a few very long voyages there was very little trouble due to mould and bacterial slime.
- The appearance of considerable quantities of the beef was poor. This loss of "bloom" showed up as a dull greyness of the fat instead of the red-yellow colours which are typical of good "bloom". Large areas of cut muscle such as the "wing end" and aitchbone of hindquarters and the brisket and neck areas on crops also showed bad discoloration of a deep red-brown or grey-brown nature.
- "Chafing" of the meat due to movement of the ship was sometimes serious.
- Loss of "bloom" was generally more serious on beef of poorer quality. A good uniform covering of fat such as that found on beef of prime quality seemed generally to retain the fresh colour of the meat.

OVERSEAS TRANSPORT OF FROZEN BEEF

Temperatures in the range of −9 to −11°C are commonly employed during the storage and overseas transport of frozen meat. At these temperatures the growth of micro-organisms is completely inhibited. There are some advantages in storing carcass meat (especially pork) at lower temperatures, since the onset of rancidity in the fat is thereby delayed. The advantages do not generally, however, justify the extra cost unless the period of storage is very long.

If the relative humidity of the air is too low, surface desiccation of carcass meat and especially of offal may occur. The use of wrapping materials resistant to the transfer of water vapour is one practical method of overcoming this problem.

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HEADSPACE GAS

Earlier articles in this series appeared in the **Food Preservation Quarterly**, *Volume 13 (1953), pages 3-8 and 21-31, and Volume 14 (1954), pages 8-18 and 26-31.*

A KNOWLEDGE OF THE COMPOSITION OF THE gas in the headspace of a spoiled canned food is frequently a valuable aid in the diagnosis of the cause of spoilage. However, even in a normal, sound can the headspace gases differ in composition from air; generally there is a loss of oxygen, an increase in nitrogen content, and an accumulation of carbon dioxide.

LOSS OF OXYGEN

Immediately after a canned product is sealed, oxygen commences to disappear from the headspace gases; in plain cans of acid products its disappearance is complete in 10-20 days, and in 4-6 weeks in lacquered cans (Baker 1912*b*; Horner 1933-34). Most of the oxygen is consumed in corrosion reactions at the internal tinplate surface. Some is absorbed by the product, for instance by reducing agents such as ascorbic acid or by unsaturated oils in fish packs (Jarvis 1943). As a result of the disappearance of the oxygen the vacuum in the can may increase by as much as 4-5 inches during a short period after canning.

When the oxygen is removed the proportion of nitrogen in the headspace gases becomes greater than in air.

ACCUMULATION OF CARBON DIOXIDE

Commencing immediately after canning, an accumulation of carbon dioxide is observed in the headspace gases of normal cans of all types of canned foods. A number of processes probably contribute to this production of carbon dioxide, for instance:

- The intracellular gases in fruits are high in carbon dioxide as a result of respiratory activity. During processing these gases are liberated by the heat treatment in partial vacuum and find their way into the headspace (Horner 1933-34).

- Carbon dioxide may be evolved in reactions between carbohydrates and amino acids or other organic acids. Such reactions ("browning reactions") occur in a wide variety of foodstuffs and are responsible for changes in colour, flavour, and physical properties, but their fundamental chemistry is imperfectly understood (Lewis, Esselen, and Fellers 1949; Hodge 1953).

- Carbonates and bicarbonates in hard waters may contribute carbon dioxide. Higher carbon dioxide contents have been demonstrated in the headspaces of canned fruits containing hard water than in packs containing soft water (Horner 1933-34).

- Incipient microbial decomposition in fish prior to canning causes a high carbon dioxide content in the canned product (Clough, Shostrom, and Clark 1925).

Thus in normal cans of most canned foods the headspace gases are composed of nitrogen together with up to about 15 per cent. of carbon dioxide; small amounts of hydrogen may also be present (see below) but oxygen is usually absent.

HEADSPACE GASES IN SWELLED CANS

When a swelled can is spoiled by micro-organisms, the gas in the headspace is mainly carbon dioxide except when spoilage is due to some rare organisms which produce mixtures of carbon dioxide and hydrogen. It is seldom necessary to examine the headspace gases in

Critical comments on the procedures described, and suggestions for modified or alternative methods found to be useful in practice, will be welcomed.

COMPOSITION

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such cans since the microbial spoilage is usually quite evident. But when a swelled can shows no sign of spoilage by microorganisms, a headspace gas analysis is an important step in investigating the cause of spoilage.

If the can has become a springer or a soft swell because of loss of vacuum the headspace gases will be normal in composition. In many instances, however, characteristic abnormalities in headspace gas composition are observed which enable the swelled can to be classified as a hydrogen swell, a carbon dioxide swell, or a nitrite swell.

Hydrogen Swells

As soon as all the residual oxygen in a can is used up, hydrogen begins to be produced in reactions between the contents and the tinplate container. Hydrogen evolution is extremely slow in most products, but in some fruit packs it is sufficiently rapid to produce a positive pressure and to swell the can within a fairly short storage period at moderate temperatures. In cans which reach this stage the headspace gases usually contain more than 60 per cent. hydrogen.

The majority of the hydrogen swells examined in the Homebush Laboratory have been in packs such as berries, berry jams, cherries, and beetroot, in lacquered cans. Products containing red anthocyanin pigments are packed in internally lacquered cans to minimize pigment changes caused by corrosion reactions, notably a blue discoloration due to dissolved tin and a gradual bleaching by reduction. But in lacquered cans, severe localized corrosion may occur at discontinuities in the lacquer film, at scratches, and along the side and end seams, and lead to rapid hydrogen swelling. In the common Australian canned fruits, such as peaches, apricots, pears, and pineapple, the incidence of hydrogen swells is very low under normal marketing conditions, but serious outbreaks have occurred in the fruit canning industry in Great Britain in such packs as plums, berries, and cherries (Adam and Dickinson 1944; Hirst and Adam 1945).

In the course of examinations of Army foodstuffs during the war years, hydrogen swells were encountered in a number of packs not usually regarded as subject to this form of spoilage, for example, tomatoes, parsnips, and meat pastes (Finlay, Hansen-Lowe, and Hicks 1945). Factors which probably contributed to cause these outbreaks were: lightly coated tinplates (nominal 1.25 lb per base box), long storage (12-18 months) in Army dumps in warm areas, and low initial vacuums.

Carbon Dioxide Swells

Sometimes swelled cans which show no evidence of microbial spoilage are found to have headspace gases composed almost entirely of carbon dioxide. Spoilage of this nature has been reported in orange-juice concentrate (Continental Can Co. 1945; Veldhuis 1945) and has also been encountered at the Homebush Laboratory in a fruit spread held for a few months at 100°F. It is most likely that the carbon dioxide is produced in these products by browning reactions.

Coffee packs are also known to develop carbon dioxide swells but in this instance the most plausible explanation is that carbon

dioxide in large amounts is adsorbed in the coffee during roasting and then slowly released after packaging (Bredt 1934; Rector 1934).

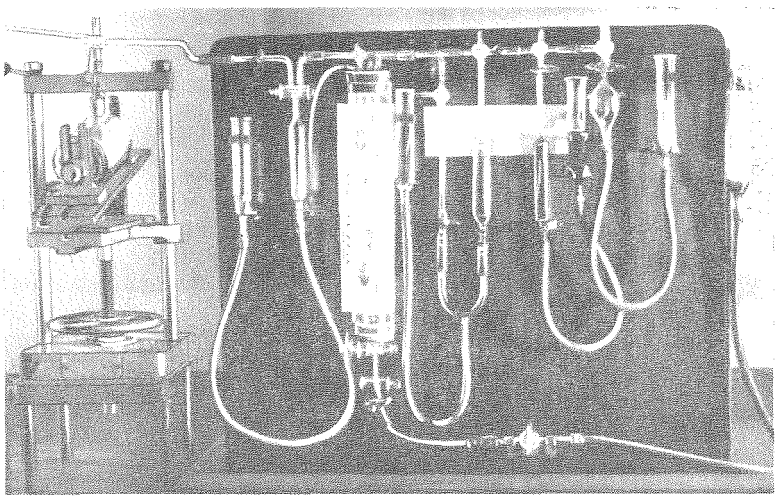
Nitrite Swells

Cured meat packs containing amounts of nitrite of the order of 1000 p.p.m. have been found to develop hard swells during retort processing, owing to the evolution of nitrogen and oxides of nitrogen (Empey 1951; Morris 1952). Nitrite contents of this order are grossly excessive and are likely to be reached only when accidental addition of excess nitrite has occurred or when dry curing ingredients have not been uniformly mixed into a batch. About 20 p.p.m. of nitrite are sufficient for complete conversion of the myoglobin of muscle tissues to nitrosomyoglobin, the pink pigment in cured meats, and the amount added need never exceed 100 p.p.m. (0.01 per cent.).

ANALYSIS OF HEADSPACE GASES

The equipment required for analysing headspace gases consists of a device for puncturing the can and sampling the gases in the headspace and a gas analysis apparatus.

Many types of gas-collecting clamps have been described (Anon. 1944; Baker 1912*a*; Behre 1952; Cartwright 1946; Clough, Shostrom, and Clark 1925; Fuller 1928; Horner 1933-34; Møller *et al.* 1948; Morris 1947; Neuman and Slosberg 1948; Strachan and Embree 1944; Taylor and Danforth 1952; Thiel, Hills, and Scharp 1947). In the Homebush Laboratory, the Campden manometer (Kefford 1954) is used for this purpose by connecting the three-way tap of the manometer by means of a capillary tube to a gas analysis apparatus, as shown in the illustration below and the diagram on the opposite page.



Headspace gas analysis apparatus.

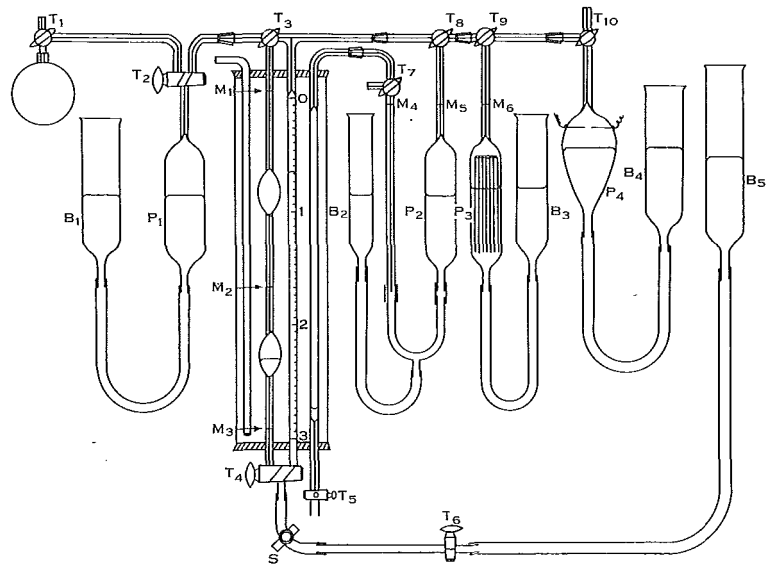
GAS ANALYSIS APPARATUS

The gas analysis apparatus illustrated is of the Haldane type (Haldane and Graham 1935) but it incorporates modifications suggested by Sleigh (1937). It consists of two measuring burettes and a compensating burette surrounded by a water jacket to maintain a uniform temperature. The water jacket is provided with an air tube passing to the bottom for stirring. One measuring burette has two bulbs each with a capacity of 3 ml and the other has a total volume of 3 ml graduated in divisions of 0.01 ml. Thus in the two burettes any volume of gas up to 9 ml can be measured to 0.005 ml or better. This arrangement overcomes a major disadvantage of the original Haldane apparatus in which the absorption of more than 30 per cent. of a gas mixture took the reading off the scale.

The gas burettes are connected through a capillary manifold and a series of three-way taps to a sampling pipette (P_1), two absorption pipettes (P_2 and P_3), and a combustion pipette (P_4), each pipette having a levelling

bulb. The pipettes P_1 and P_4 contain mercury and the pipettes P_2 and P_3 contain appropriate absorbents (see below). The combustion pipette P_4 is provided with two platinum electrodes connected to an induction coil for creating a spark. The several components are connected by ground-glass joints along the manifold and are supported by metal clips on a board.

Other types of gas analysis apparatus, e.g. the Orsat apparatus, are also suitable for analysing headspace gases provided a sufficiently large sample can be withdrawn from the can under examination. For the determination of oxygen only, instrumental methods based on the measurement of the magnetic susceptibility of the headspace gases may be used (Taylor and Danforth 1952). A portable headspace analyser using this procedure has recently been described (Crown Cork and Seal Co. 1954). For analysing very small samples of headspace gases an apparatus of the Blacet and Leighton type (Lewis 1949) has been used in the Homebush Laboratory.



Details of headspace gas analysis apparatus.

PROCEDURE

The procedure of headspace gas analysis described refers to the modified Haldane apparatus illustrated. For detailed operating instructions and precautions the analyst should consult Haldane and Graham (1935) and Sleigh (1937).

A little dilute sulphuric acid is introduced into the compensating and measuring burettes to avoid variations in water vapour pressure in a gas sample during an analysis and to neutralize alkalinity derived from the glass.

The pipette P_2 is filled with a 50 per cent. solution of potassium hydroxide for the absorption of carbon dioxide and the pipette P_3 contains an alkaline pyrogallol solution for the absorption of oxygen. The exposed surfaces of the potash and pyrogallol reagents in the levelling bulbs of the absorption pipettes are protected from the atmosphere by layers (approx. $\frac{1}{2}$ in.) of liquid paraffin.

The pyrogallol absorbent is prepared by dissolving 15 g of pyrogallic acid in 10 ml of hot water and adding it to 100 ml of 80 per cent. potassium hydroxide solution. Since the absorption of oxygen in this reagent is comparatively slow it is advantageous to pack the pipette P_3 with pieces of glass tubing to increase the gas-liquid contact surface.

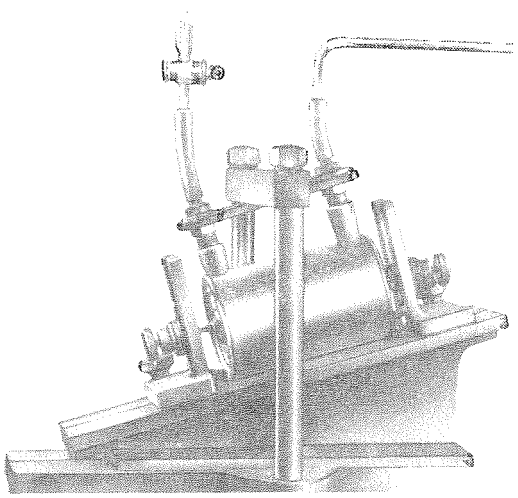
For the absorption of nitric oxide, when examining suspected nitrite swells, the following absorbent is suggested (Moser and Herzner 1924): 15 parts ferrous sulphate, 15 parts 54 per cent. sulphuric acid, and 70 parts water by weight.

Drawing a Gas Sample

Before drawing a sample of headspace gases from a can under test, it is necessary to remove air from the connexions between the tap T_1 and the gas burettes. By manipulating the taps T_1, T_2, and T_3 and the levelling bulb B_1, the capillary between taps T_2 and T_3 is evacuated and the capillary between taps T_1 and T_2 is filled with mercury.

The rubber gasket around the puncturing needle is moistened and the can under test is brought up to the needle and punctured. Then the bulb B_1 is lowered to draw a sample of the headspace gases into the pipette P_1.

When the test can is flat, with a high internal vacuum, the volume of headspace gas may be very small. However, by applying a high vacuum by means of the levelling bulb



Apparatus for sampling headspace gases by displacement with water.

B_1 it is usually possible to obtain an adequate sample. An alternative procedure is to puncture the can in two places and allow water to enter the can at the lower puncture to displace the headspace gases which are withdrawn through the upper puncture (Baker 1912*a*; Horner 1933-34). A modified can puncturing device which permits this procedure to be followed is illustrated above.

Analysis for Carbon Dioxide and Oxygen

Before a gas sample is analysed the connexions in the apparatus must be filled with nitrogen remaining from a previous analysis or prepared from air by removal of carbon dioxide and oxygen. It is advisable to store a supply of nitrogen in the pyrogallol pipette for use in subsequent analyses. When expelling the nitrogen prior to taking in a sample it is important to raise the mercury level in the burettes in a steady flow, avoiding up and down movements which may draw in air.

At the commencement of an analysis, the potash and pyrogallol solutions are adjusted to the reference marks M_4, M_5, and M_6. First, the compensating burette is brought to atmospheric pressure through the tap T_7, then this tap is closed to the atmosphere throughout the analysis. The potash is brought to the mark M_4 by adjusting the bulb B_2 and to the mark M_5 by manipulating the bulb B_5 and taps T_4, T_6, and T_8. Similarly the pyrogallol is brought to the mark M_6 by adjustments through the tap T_9. Then taps T_8 and T_9 are closed to the pipettes. A screw-clip S on the rubber tube adjacent to the tap T_4 assists in making fine adjustments of the solutions to the marks.

At this stage the mercury in the large burette should be near the mark M_1 and slightly below zero in the small burette. The mercury in the large burette is brought to M_1 and the volume of the small residue of nitrogen in the small burette is measured with reference to marks M_4 and M_5.

Now, with tap T_8 closed again to the potash pipette, a sample of headspace gases is drawn into both burettes by manipulating taps T_2, T_3, T_4, and T_6, and the bulbs B_1 and B_5. For samples of 6-9 ml the mercury in the large burette is adjusted to the mark M_3, for samples of 3-6 ml to mark M_2, and for samples less than 3 ml to mark M_1. The same adjustments apply when measuring gas volumes after absorption.

The volume of gas in the burettes is measured to 0.005 ml and this volume less the volume of residual nitrogen gives the volume of sample taken.

By raising the mercury level, the portion of the sample in the small burette is transferred into the potash pipette P_2. Then the total sample is passed back and forth between the potash pipette and the large burette, through taps T_3 and T_8, until the absorption of carbon dioxide is complete as indicated by constancy in volume. About five passes are usually required.

Oxygen is absorbed in the pyrogallol pipette by a similar procedure, by-passing the potash pipette. The complete absorption of oxygen requires two or three times as many passes as the absorption of carbon dioxide.

Determination of Combustible Gases

For the estimation of hydrogen and any other combustible gases that may be present, a fresh sample of the headspace gases is taken and mixed with air to provide the oxygen necessary for combustion. The original sample is rejected through the tap T_{10} and the connexions in the apparatus, including the capillary leading to the potash pipette P_2, are thoroughly flushed out with air drawn in and rejected through the tap T_{10}. A volume of air, approximately 8 ml, is then drawn in and freed from combustible gases and carbon dioxide by sparking and absorption in potash to constant volume.

Now a sample of the headspace gases, approximately 1 ml, is taken and measured accurately and the total volume of gas is transferred to the combustion pipette. A spark is passed several times while the bulb B_4 is raised and lowered to move the gas sample through the spark, until combustion is complete as shown by constancy in volume. The reduction in volume is measured, and measured again after passing the gas through the potash pipette to absorb any carbon dioxide produced by combustion of hydrocarbon gases. In cans examined at the Homebush Laboratory hydrocarbons have never been present; hydrogen has been the only combustible gas detected. The volume of hydrogen present is equal to two-thirds of the reduction in volume after combustion.

Interpretation of Results

From the volume of the original sample and the observed reductions in volume, the percentage composition of the headspace gases is calculated, nitrogen being estimated by difference. The composition found may be typical of the headspace gases in normal cans or it may show abnormalities which permit the cans under test to be identified as hydrogen swells, carbon dioxide swells, or nitrite swells. It should be noted that it has been possible to detect nitric oxide only in nitrite swells opened shortly after processing. At a later stage nitrite swells appear to show abnormally high nitrogen contents in the headspace gases.

ROUGH TESTS FOR HYDROGEN SWELLS

Hydrogen swells may often be identified by using one of the following tests:

The test can is punctured under water and the headspace gases are collected over water in a stout test-tube held above the puncture. The test-tube is held to a naked flame and if a high proportion of hydrogen is present the gases ignite with a sharp report.

The so-called "popping test" is even more simple. The can under test is punctured and a naked flame is applied to the puncture as the gases issue. If the can is a well-advanced hydrogen swell, a faint report may be heard or the gases may burn for an instant with a blue flame.

When a positive result is obtained in either of these tests, the can may be regarded with reasonable certainty as a hydrogen swell, but a negative result does not exclude the possibility that it is a hydrogen swell.

CALCULATION OF INITIAL VACUUM

Another useful application of information on headspace gas composition is the estimation of the original vacuum in a can (Morris and Bryan 1931). For this calculation it is also necessary to determine the headspace volume in the can and the total volume of gas present in the headspace. The can is weighed and then punctured under water and the headspace gases are collected over water in a calibrated gas burette. All the gas in the can is expelled and displaced by water by alternately pressing and releasing the lower end of the can. The gain in weight in the can gives the headspace volume. The total volume of headspace gases at atmospheric pressure is measured in the gas burette. The gases are analysed and the original vacuum is calculated by assuming that all the nitrogen found is derived from original air.

Estimations of original vacuum by this method are probably not closer than $\pm$ 2-3 in. Hg (Adam and Dickinson 1944) because of a number of sources of error, e.g. solution of the gases, notably CO_2, in water during collection, uncertainty as to the original position of the can ends, and higher nitrogen percentages in intercellular air in the product at the time of canning. Cans which have been "breathers" through seam leaks will also show high nitrogen contents.

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ANSWERS TO INQUIRIES

PICKLING OF ONIONS

How are pickled onions prepared?

Overseas a number of varieties of onion are used for pickling, but it is doubtful if any of these is grown commercially in Australia. Several Australian varieties have, however, been successfully processed — the most popular is Early Hunter River White, another is Winter Pearl. Size is very important: crops of small onions of fairly uniform size are obtained by sowing closely and harvesting at early maturity.

Only fresh onions are suitable for processing; stored material is quite unsatisfactory.

The purity of all materials used in processing, particularly for salting, is of great importance. Impure salt impairs curing and generally speaking, salt containing lime or sulphates in excess of 0.5 per cent. should not be used. Insoluble calcium salts such as the sulphate may form a white sediment or make white spots on the pickles. Iron salts bring about discoloration by reacting with tannin or oxygen. Salt should also be free from alkalis, for a pH greater than 7 may induce spoilage by neutralizing the acid produced during fermentation.

The pickling process is carried out in stages:

Preparation.—The first step is to trim and peel the onions. Peeling is generally done by hand but may be accelerated by blanching 2-3 minutes in boiling water to loosen the outer skin. Abrasive peelers may also be used. Root and stem ends must be removed to give a good appearance and to reduce the possibility of discoloration.

Salting.—It is usual to soak the onions in several changes of water for 3-4 days to reduce the strong flavour and to remove the objectionable juice which sometimes causes the brine to become dark and putrid. When soaking is complete the water is run off and replaced by fresh water containing 4 lb salt to each bushel of onions. The salt continues to leach out the strong flavour and makes the onions whiter. Sulphur dioxide is often added to the brine to increase its bleaching action. The Pure Food Regulations limit the sulphur dioxide content of the pickles when sold to 5 grains per pound in some States of Australia and to 2 grains in others.

After four days the onions are drained and covered with a 60-degree salinometer brine (15.9 per cent. salt). Salt is added from time to time to keep up the strength of the brine. Should the storage period be protracted the brine concentration should be increased to 80 degrees (21 per cent.).

Processing.—The onions are removed from the brine and covered with fresh water to each 40 gallons of which has been added 1 lb alum or $\frac{1}{2}$ lb calcium chloride. They are then heated to 90°F and allowed to stand overnight. The heating plumps the onions and further reduces the strong flavour. The temperature of 90°F should not be exceeded, higher temperatures may cause the layers to loosen and break apart.

To keep the onions fresh and free from spoilage they should not be held in cold water for more than two days. If they are to be held for any length of time they should be covered with vinegar.

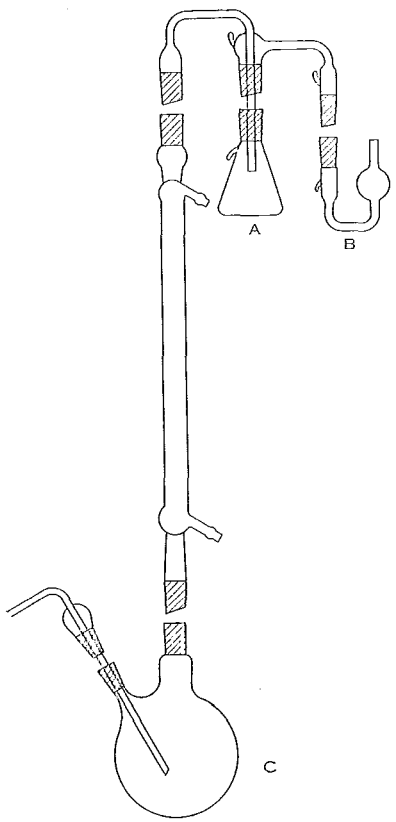
One ounce of sodium sulphite is added to each $12\frac{1}{2}$ gal. of the water used in the final processing in order to whiten the onions.

Finishing.—After the salt has been leached out the onions are placed in 50-grain vinegar for about 5 days. They are then covered with an unspiced sweet liquor containing 8 lb sugar to 1 gal vinegar. The onions are held in this liquor for 5-7 days, after which it is replaced by a spiced sweet liquor containing 12 lb sugar, 1 gal vinegar, and $\frac{1}{2}$ gal water. After remaining in this liquor for about one week, the onions are ready for bottling.

The author examines proposals made in the literature for the modification of the Monier-Williams method of determination of sulphur dioxide. The examination is followed by an outline of an analytical method developed at the C.S.I.R.O. Homebush laboratory and used there for over five years.

Estimation of Sulphur

THE EXTENSIVE USE OF SULPHUR DIOXIDE, AS the gas or in the form of sulphite solutions, for the preservation of foodstuffs has led to a variety of methods for its quantitative estimation (Monier-Williams 1927; Nichols and Reed 1932; Bennett and Donovan 1943; Prater, Johnson, Pool and Mackinney 1944; Reifer and Mangan 1945). The Monier-Williams method, based on the oxidation of liberated sulphur dioxide with three per cent. hydrogen peroxide and titration of the resultant sulphuric acid with standard alkali, has been adopted as an official method by the Association of Official Agricultural Chemists (A.O.A.C.) (1950). Several authors (Nissen and Petersen 1943; Thompson and Toy 1945; Morris 1947) have suggested modifications to improve particular points in the method, but there appears to have been no critical examination of the procedure as a whole.



Distillation apparatus for determination of sulphur dioxide.

Study of Experimental Procedure

The following aspects of the A.O.A.C. (1950) method were critically examined:

Apparatus.—The apparatus described by the A.O.A.C. was found to be susceptible to leaks and difficult to manipulate. To overcome leakages an all-glass apparatus was devised and to facilitate handling it was set up vertically. This apparatus, which has performed satisfactorily, is illustrated at left. Nichols and Reed (1932) preferred electric heaters to gas-burners, claiming that they heated more uniformly and reduced foaming. This claim has been confirmed: a 400-watt Gilmer-type electric heater proved quite satisfactory.

Gas-flow.—The A.O.A.C. method uses carbon dioxide as the carrier gas. However, it was observed at Homebush, and it has also

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Dioxide in Dried Foods

been reported by Thompson and Toy (1945), that carbon dioxide prevents a sharp end-point to the titration. The use of nitrogen overcomes this. Complete recovery of sulphur dioxide is dependent on the flow rate of the carrier gas. The volume of carrier gas must be sufficient to sweep all liberated sulphur dioxide into the traps within the refluxing time. With the apparatus used in these experiments a flow rate of 6-12 bubbles per minute through the tube (6 mm O.D.) of trap *A* has been found adequate for a refluxing time of 30 minutes. The nitrogen used was approximately 99.7 per cent. pure. No oxidation by the small amount of oxygen present has been detected.

Hydrogen Peroxide.—Nissen and Petersen (1943) found that hydrogen peroxide solutions neutralized with barium hydroxide to the bromophenol blue end-point contained free barium ions. This observation has been confirmed. The same authors suggested neutralization with sodium hydroxide, but it has been found satisfactory to use unneutralized hydrogen peroxide and to correct the results by a blank titration, as described by Morris (1947).

Use of Air-free Water.—Theoretically the presence of air in the refluxing medium, or in the atmosphere in the apparatus, could lead to oxidation of the sulphur dioxide. Hence the A.O.A.C. method requires the water-acid mixture to be boiled while a stream of carbon dioxide is passed through the apparatus. Nichols and Reed (1932) were unable to detect any oxidation when unboiled water was used. In our experiments water aerated by bubbling air through it for two hours had no effect on the recovery of sulphur dioxide from a wide range of foodstuffs.

Time of Refluxing. — The A.O.A.C. procedure recommends refluxing for one hour, or 1½ hours for dried fruit. With finely-ground or minced samples it has been found that recovery of sulphur dioxide is complete in 30 minutes. On the other hand, 15 minutes' refluxing gave variable results with a mean recovery of 93 per cent. sulphur dioxide.

Heating of Condenser at the End of Refluxing.—Thompson and Toy (1945) reported that this step could be omitted for dehydrated vegetables. The point has been checked by using a thin-walled Liebig condenser or the Davies double-surface condenser in determinations on a range of dehydrated vegetables and

Comparison of A.O.A.C. Method and Proposed Method

Sample	Sulphur Dioxide (p.p.m.)	
	A.O.A.C. Method	Proposed Method
Dehydrated peach	843	838
Dehydrated peach	836	832
Dehydrated potato	1869	1863
Dehydrated potato	292	284
Dehydrated potato	279	275
Dehydrated cabbage	2358	2381
$NaHSO_3$ solution*	850	850
$NaHSO_3$ solution*	960	960

* The recovery of sulphur dioxide from the sodium bisulphite solutions was quantitative. The solutions were standardized against iodine.

fruits, and on cordials and sulphite solutions. Heating of the condensers failed to increase the recovery of sulphur dioxide from any of the foodstuffs used.

Comparison of Methods. — The proposed method was compared with the A.O.A.C. procedure, using in each case the apparatus shown in the diagram on page 54 with nitrogen as the carrier gas. The results obtained are set out in the table on page 55, each figure representing the mean of three analyses.

The reproducibility of the proposed method was determined by a series of 18 analyses on a thoroughly minced sample of dehydrated peaches. The mean value was 421 p.p.m. with a standard deviation of ± 8 p.p.m.

Recommended Method of Analysis

Reagents.—The reagents recommended are:

3 per cent. hydrogen peroxide,
10N hydrochloric acid,
0.1N sodium hydroxide (standardized with bromophenol blue),
bromophenol blue (0.1 g dissolved in 1.5 ml 0.1N NaOH and diluted to 25 ml).

Apparatus.—As shown in the diagram on page 54.

Procedure.—Dried foodstuffs, other than fruits, are ground quickly to pass through a fine mesh (20-30), being heated as little as possible. Dried fruit is thoroughly minced in a household food mincer. All prepared samples are kept in sealed containers until subsampled.

Fifteen ml and 5 ml of 3 per cent. H_2O_2 are added to traps *A* and *B* respectively; the latter are then assembled and connected to the condenser. Four hundred ml H_2O and 20 ml 10N HCl are measured into flask *C*, and the nitrogen lead tube connected. An accurately weighed amount of the prepared sample, containing 3-15 mg SO_2, is introduced into flask *C*, which is immediately connected to the condenser. Nitrogen is allowed to flow through the system at such a rate that 6-12 bubbles per minute are observed in trap *A*. The sample is then refluxed in the acid solution for 30 minutes. The traps are disconnected and the contents of trap *B* transferred to the 150-ml Erlenmeyer flask of trap *A*, in which the titration against 0.1N NaOH is carried out. Three drops of bromophenol blue are used as an indicator. The free acid in the 3 per cent. H_2O_2 is determined by a blank titration on 20 ml of the reagent, and results of the analysis are corrected accordingly (1 ml 0.1N NaOH = 3.2 mg SO_2).

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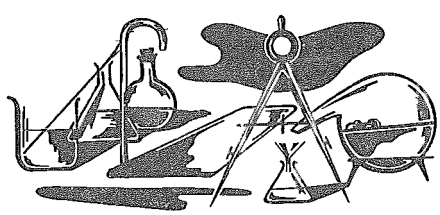

Address delivered to the fourth Annual Convention of the Institute of Food Technologists (Australian Regional Sections) at Leura, N.S.W., May 29, 1954.

Prediction of Shelf Life of Food Packages

By E. W. Hicks

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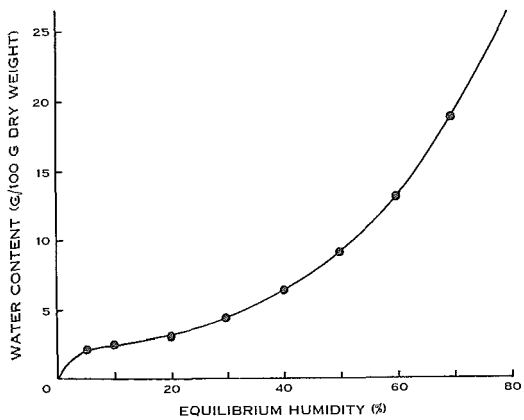
IT IS CLEARLY NECESSARY, IN ORDER TO predict the shelf life of a particular food package, to have information on the properties of the foodstuff packed as well as on the package itself. Cornflour is commonly packed at a water content such that it is nearly in equilibrium with the average relative humidity of the storage atmosphere and change in its water content by a few per cent. would probably have little effect on its storage life. Consequently the permeability to water vapour of its container is generally of little importance. On the other hand, dried milk is very hygroscopic, that is, it is packed with an equilibrium humidity well below the humidity of the storage atmosphere, and absorption of quite a small amount of water will decrease its storage life seriously. Consequently the permeability of the container to water vapour is the most important property to consider for dried-milk packages. The following account deals mostly with packages in which uptake of water vapour is the main factor affecting the shelf life.

In considering such packages we need to know two properties of the food inside, namely how hygroscopic it is and how much water it may be allowed to absorb. The hygroscopic nature of a foodstuff is best expressed by its humidity isotherm.

HUMIDITY ISOTHERM

A sample of foodstuff with a particular water content will be in equilibrium with air at a particular relative humidity. It will lose water to air with a lower relative humidity and absorb water vapour from more humid air. Thus a sample of foodstuff has a definite equilibrium humidity at each water content. A plot of equilibrium humidity (E.H.) against water content yields a definite curve which is called a humidity isotherm. Most foodstuffs have humidity isotherms of the form shown in the accompanying figure.

The curves are called isotherms because they are strictly valid at one temperature only. However, the variation with temperature is quite small and may generally be neglected in package design calculations.



Humidity isotherm at 15°C for a dried meat and vegetable soup mixture. (Data obtained at Low Temperature Research Station, Cambridge, by Dr. R. Gane.)

The data available on humidity isotherms are adequate for most purposes though many of them have been published in out-of-the-way places. Not every food pack one may wish to consider has been studied but it is usually easy enough to derive estimates for an unlisted food either by using the figures for a product of similar composition or by interpolating between the data for other foods.

The other property of the food required for calculations is an estimate of the amount of water uptake which may be permitted. This is often hard to arrive at. Most of the values we use are only intelligent guesses. To obtain precise estimates we should have to know the relation between the water content and the rate of deterioration of the food as well as the amount of deterioration which may be permitted. The first of these is hard to determine precisely and the second must be somewhat arbitrary. Opinions will always differ on the specification of the end of the storage life.

Lack of precise data on the amount of water uptake which may be permitted is the chief factor affecting the real accuracy of shelf life predictions. However, this does not mean that it is not worth while doing calculations. A great deal of time and money would have been saved in Australia in the last 15 years if more people in the food industries had been able and willing to sit down and do a little simple arithmetic before adopting or recommending particular packages. With the existing data, packages can generally be classified as hopeless, doubtful, promising, or extravagant. The application of these data in the past would have eliminated a surprising number of small packages as hopeless before money was spent on them, and a number of others as too extravagant for the less sensitive foods.

PERMEABILITY OF PACKAGES

For design calculations it is necessary to express the permeability to water vapour of a package in some such units as grams water transmitted per square metre per day per millimetre of mercury vapour pressure difference. We may then write the general equation:

$$E = P.A.t.\delta p, \quad \ldots\ldots \quad (1)$$

where E is the weight of water absorbed,
P is the permeability to water vapour of the packaging material,
A is its area,
t is the time, and
δp is the appropriate mean difference in vapour pressure between the foodstuff and the storage atmosphere.

In many cases the seal is the weakest part of a package and some materials are adversely affected by folding. Consequently it is sometimes essential and generally desirable to determine the product PA in equation (**1**) from measurements with complete packages. In dealing with hygroscopic materials the change in equilibrium humidity which can be permitted is usually small compared with the difference between the equilibrium humidity of the food and the relative humidity of the storage atmosphere, so that the arithmetic mean of the initial and final vapour pressure differences may be used for δp. Thus we may write,

$$\delta p = \frac{p_s}{100} [h_a - \tfrac{1}{2} (h_1 + h_2)] \quad \ldots \quad (2)$$

where p_s is the saturation vapour pressure of water at the storage temperature,
h_a is the relative humidity of the storage atmosphere,
h_1 is the initial E.H. of the food, and
h_2 is the E.H. of the food after it has absorbed the permissible amount of water.

If the foodstuff can approach equilibrium with the storage atmosphere this method of averaging, which amounts to using a concentration average, may lead to serious errors. It is wrong because the rate of water absorption decreases substantially as time goes on. In cases where the relevant part of the humidity isotherm can be treated as a straight line, the mathematically appropriate form for δp is the logarithmic mean of the initial and final vapour pressure differences. It is sometimes necessary and often desirable to use this form.

Cases in which neither the arithmetic nor the logarithmic mean is accurate enough do not often arise but they may be encountered at times, particularly with materials which may be allowed to approach fairly close to equilibrium with the storage atmosphere. Oswin* has given a reliable analytical method of dealing with some such cases, and also of increasing the precision of calculations in cases

*Oswin, C. R. (1946).—*J. Soc. Chem. Ind., Lond.* **65**: 419.

in which the simpler methods outlined above are usually adequate. There will remain some cases for which numerical integration of the differential equation corresponding to equation (1) is necessary, but they are rare.

Thus in most cases in which the storage life is limited by water uptake the arithmetic of shelf life prediction is very easy and within the capacity of any food technologist.

UPTAKE OF OTHER GASES AND VAPOURS

Questions are often asked about the transfer of other gases and vapours through packaging materials so it is desirable to say a little about these. The principles governing the transfer of these materials are exactly the same as for the transfer of water vapour but for most of them data are not available to permit calculations.

It is important to prevent the access of oxygen to some foodstuffs, as in gas packing dried milk or dried vegetables. Data are available on the permeability to oxygen of some of our better packaging materials and calculations for oxygen transfer in certain types of package can be made in the same way as for water transfer. As a rule a few milligrams of oxygen are enough to destroy the value of gas packing, whereas several grams of water are usually needed to do much harm. It is perhaps not surprising, therefore, that these calculations indicate that even the best single, flexible packaging films are quite unsatisfactory for gas packing if oxygen can diffuse freely in air spaces inside the wrapper. Something almost equivalent to gas packaging can, however, be obtained with some foodstuffs by using a packaging material which can be shrunk tightly on to the food leaving virtually no air spaces between the foodstuff and the wraps. Presumably when wraps of this type are effective, many tiny areas of the surface of the food are exposed to oxygen, but these form only a very small proportion of the total surface. Little or no oxygen can reach other parts of the surface because there are no air spaces through which it can diffuse rapidly.

The permeability to oxygen of some laminated films is much lower than that of the best single films, and we may in the near future have composite films available which are suitable for gas packing in the ordinary sense. However, the requirements for gas packing are very stringent and it will probably remain difficult to fulfil them with flexible films under commercial conditions.

NEWS from the Division of Food Preservation and Transport

WORK OF THE MICROBIOLOGY SECTION

The Microbiology Section, which is located at the central laboratories of the Division at Homebush, comprises at present three research officers, three technical officers, and four laboratory assistants.

The Section is engaged in studies of the various microorganisms which may grow in foods. These organisms are very varied in their requirements for growth and their resistance to controlling or destructive agencies such as heating, freezing, disinfectants, and preservatives. They include types which will grow at temperatures below the melting point of ice, and others which will grow rapidly at the temperatures in pig-scalding vats. Some are readily destroyed at 100°F, others may resist heating for a few minutes at 250°F. Some grow under very acid conditions, others in concentrated syrups or brines. Some need rich diets complete with many of the vitamins required by man, others grow in water containing traces of a few simple substances, and others again can thrive on some foods containing only about 10 per cent. of water. Knowledge accumulated about the various microorganisms may be applied to predict their reactions under specified conditions of processing or storage. When this knowledge is available answers to particular problems may be obtained without resort to costly and time-consuming experiments with the foodstuffs concerned.

The projects at present receiving attention are studies of the heat resistance of bacterial spores, the water requirements for the growth of various microorganisms, and the survival of organisms dried from the frozen state. The Section also handles a continuing flow of requests for the diagnosis of the cause of spoilage in foods.

PERSONAL

Mr. J. H. B. CHRISTIAN, a Research Officer of the Division, has been granted a C.S.I.R.O. Studentship to enable him to undertake research overseas on the water relations of bacterial cells. He will work in Dr. M. Ingram's laboratory at the Low Temperature Research Station, Cambridge. Mr. Christian left Sydney by the *Strathaird* on August 25, 1954, and will be absent for two years.

PUBLICATIONS BY STAFF

THE PHYSIOLOGY OF GROWTH IN APPLE FRUITS. VI. THE CONTROL OF RESPIRATION RATE AND SYNTHESIS. *Judith A. Pearson and R. N. Robertson Aust. J. Biol. Sci.* **7**: *1-17(1954).*

Experiments are described which test the hypothesis that the rate of respiration is controlled by the phosphate carrier system in apple tissue. The effects of 2,4-dinitrophenol and adenosine triphosphate on the respiration of cut tissue are consistent with the hypothesis that a more rapid utilization of energy-rich phosphate at a critical stage could result in the climacteric rise. The interrelations of starch, organic acid, and nitrogen metabolism and respiration are discussed. An increase in the activity of extracted respiratory enzymes at the time of the climacteric rise has been demonstrated.

* * *

STUDIES IN THE PRESERVATION OF SHELL EGGS. VII. THE EFFECT OF PASTEURIZATION ON THE MAINTENANCE OF PHYSICAL QUALITY. *W. J. Scott and J. R. Vickery. Aust. J. Appl. Sci.* **5**: *89-102 (1954).*

The effects on physical quality of those combinations of time and temperature of immersion in water or oil which eliminated bacterial rotting but did not produce detectable coagulation of the white adjacent to the shell membranes, were studied by observing the amount and retention of thick white, yolk index values, losses of weight during storage, candling quality, and the quality of sponge cakes.

Studies by Funk (Mo. Agric. Sta. Res. Bull. No. 362 (1943)) were extended to a wider temperature range for various times of immersion, and his results concerning immediate increase of thick white following pasteurization and the stabilization of the thick white during storage were confirmed. Pasteurization at the lower temperature sometimes caused deterioration of the egg white. Yolk index values, weight losses during storage, and functional properties of eggs used as ingredients in sponge cakes, were not affected by pasteurization.

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STUDIES ON THE ANAEROBIC DECOMPOSITION OF ASCORBIC ACID. *F. E. Huelin. Food Res.* **18**: *633-9 (1953).*

When canned foods are sealed they contain little free oxygen, and what little is present disappears entirely within one month. Nevertheless, ascorbic acid loss continues steadily throughout the storage life. This loss must be due to anaerobic destruction of the ascorbic acid. It was studied at 30°C and 100°C from pH 2.2 to 6.0.

In citrate-phosphate buffer the reaction proceeded most rapidly at pH 3-4. It was accelerated by fructose, fructose 6 phosphate, and fructose 1.6 diphosphate, the effect increasing with pH. The effect of sucrose appeared to be due to liberation of fructose, as it was equal to that of fructose up to pH 3 and much less at higher pH.

The results are considered in relation to the retention of ascorbic acid by fruit and vegetable products.

Furfural and carbon dioxide were the main products of decomposition at high temperatures or acidities. With lowering of temperature or acidity other products become important.

Copies of the papers mentioned above are available from the Librarian, Division of Food Preservation and Transport, Private Bag, P.O., Homebush, N.S.W. (Telephone: UM 8431, UM 6782.)