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# Forced convection ovens for reheating pre-cooked frozen food

R. B. WALKER AND G. GLEW


## Summary

The importance of food pack thickness in forced convection ovens is shown in relation to production rates. For ovens operated on a batch basis, a pack thickness of 16 mm was recommended, and for ovens operated on a continuous basis, a pack thickness of 10 mm was recommended.

A method for evaluating forced convection ovens was developed and applied for five commercially available ovens which were then compared. The ovens with fans external to the oven cavity and with the air flow ducted across the trays were superior to the ovens with fans built into the oven cavity. The fastest reheating was 25 min for the ducted air type and 35 min for the stirred air type. The most uniform reheating occurred in the ducted air type of ovens.


## Introduction

Forced convection ovens are now established as suitable for reheating a wide range of pre-cooked frozen foods in foil packs, and in Western European countries, in plastic packs (Budelman, Köhl & Wustrau, 1964).

For institutional catering, the full economic benefits of using pre-cooked frozen food cannot be obtained unless: (i) a complete meal, either on a plate or as separate components, is capable of reheating quickly in a single oven, or (ii) full oven utilization is obtained by staggering the meal service (Armstrong, 1968).

To evaluate the commercially available forced convection ovens it was first necessary to develop a suitable test around a satisfactory pack size. Spinell (1963) used a range of commercial packs of food repacked into 127 × 102 × 41 mm foil. Unfortunately his study was limited to studies of commercial products in standard pack sizes. Unpublished work at Leeds University (1967) suggested using 240 × 240 × 40 mm re-usable aluminium trays for hospital use. These trays, together with a carefully chosen test medium, were used to investigate the effect of pack thickness on production rates for a forced convection oven. They were also used in the comparison of commercially available forced convection ovens.

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## Equipment

The following items of equipment were used: (1) five forced air convection ovens; (2) food trays with lids; (3) thermocouples with connections; (4) spiders, for holding the thermocouple in the food; (5) ice in a Thermos flask to provide a reference temperature; and (6) recorder with connection box.

*Five forced convection ovens*

Five forced convection ovens A, B, C, D and E were compared and the following design differences were noted: Ovens A and B were designed with their fans external to the oven cavity with the air flow ducted across the trays. Ovens C, D and E had their fans built into the oven cavity with plates and baffles to guide the air flow around their cavities. Ovens A and B were heated by electricity. Ovens C, D and E were heated by gas, with D being provided with a hot water bath from which hot water vapour was generated.

*Food trays and lids*

The trays used were made from 1·7 mm (15 gauge) aluminium, measured 240 mm square and were notched at one corner to allow the thermocouples wire to pass through. The lids were also of 1·7 mm gauge aluminium and measured 250 × 13 mm deep.

*Thermocouples*

The thermocouples were made from 2-m lengths of copper–constantan 1·0 mm (26 s.w.g.) wire insulated with treble layers of fibreglass (Saxonia Electric Wire Co. Ltd, Greenwich). The junctions of the thermocouples were silver soldered.

*Spiders*

Due to the need for rigid and careful holding of each thermocouple junction during the experiments, the spider shown in Fig. 1 was constructed from a stainless steel welding rod. It has three legs only, with sharpened tips both to cut down excess heat transfer along the legs and to stop sideways movement of the spiders. The arm of the spider is adjustable both in rotation and height so that the thermocouple junction is kept close to the end of the arm for good rigidity, but is kept well away from the three legs to reduce heat transfer interference effects. The weight of the spider (30 g) is concentrated at its centre and is three times heavier than the thermocouples; consequently the thermocouple neither tips nor shifts with the movement of the dangling thermocouples wire. The span of the spider across its legs is restricted to 100 mm; this is due in part to the need for keeping the weight down, in part for rigidity, and in part to overcome effects due to containers with warped or imperfect surfaces.

The thermocouple was clamped to the arm of the spider by means of a hand-

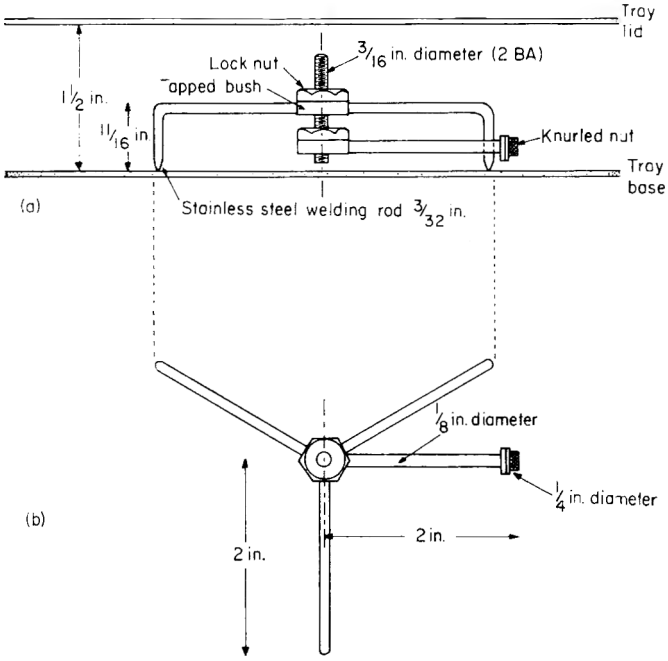


FIG. 1. Thermocouple spider. Evaluation of forced convection oven. (a) Side elevation, (b) plan.

tightened knurled nut. To guard against occasional electrical short circuiting across the nut or arm, fibre washers were used to hold the wires in place and polytetrafluorethylene tape was wrapped around the threads of the arm.

*Recorder*

A sixteen-point multirange, multizero millivolt indicator recorder with a chopper bar action every 5 sec was used (George Kent, Luton).

*Connection box*

Because of unsteady state heat transfer, the thermocouples had to be set up quickly so that a complete record of temperature variation with time was available. Thus a portable connection box was built using wander sockets.

## Materials and methods

Thin packs of test medium were blast-frozen in food trays, depth 40 mm, covered with close fitting lids. The refrigerated air blast was at a constant air velocity of 3 m/sec and at a temperature of $-20°C$. The residence time in the blast freezer was 90 min. After freezing, the trays were stored at $-20°C$ until required. Before reheating, the ovens

were preheated to a standard thermostat setting of 180°C for 25 min. The trays were then removed from the deep freeze, weighed and loaded into the oven under test. Two minutes were allowed for this sequence of operations. The temperature at the geometric centre of the packs was measured by thermocouples of low heat capacity, with the readings recorded automatically on a constant speed time-based chart. The reheat time for each pack was taken as the time required for heating the food from −20°C to the hot service temperature of 80°C.

*Optimum pack thickness for reheating*

Different pack thicknesses were prepared by portioning out various weights of the test medium into trays, and then measuring the thickness on a level surface using a friction slider on a metal rule.

One pack at a time was then reheated in an Elektrohelios oven on the fourth shelf down from the top, so that oven air temperature and oven air velocity remained constant at 180°C and 5 m/sec, respectively. The centre pack temperature during the reheating period was thus recorded for each pack in turn.

*Varying of loads on test ovens*

After preheating, the ovens were loaded with differing numbers of 1·0-kg packs varying from full load (thirty-two packs) down to one pack. Any shelf spaces left after loading were covered with empty trays. If the shelves were somewhat too large, the trays were spread out uniformly onto particular positions which were then used for the subsequent loads. Removable racks were used when provided. These were loaded alongside the ovens for ease of thermocouple connection.

Both preheating and reheating were carried out at the same oven temperature so that thermostat resetting after loading was unnecessary. The heating and preheating times were recorded. When racks were provided, the overall time allowed for transporting and loading of the packs was fixed, and the time that was needed to load the rack was kept to a known minimum.

The packs for the smaller loads were spread out within the units to provide more representative results. For full and part-full loads, any areas of uneven heat transfer were recorded, then for low loads these areas were avoided, and for the single pack loads, an area giving average results was used.

*Choice of test medium*

Most foods were found to vary too much in their individual properties to be of use for testing forced convection ovens. Raw foods that are used for testing natural convection ovens are sponges and Yorkshire puddings, since their rising and browning is a good guide to the evenness of heating within the ovens. Unfortunately sponge and Yorkshire pudding are unsatisfactory for the purpose being considered here.

Pre-cooked frozen foods for use as test media need to display other properties such

as slow freezing and reheating rates. The food chosen as the standard test medium was reconstituted dehydrated potato. It was simple and quick to prepare and was one of the slowest foods to freeze and reheat; therefore, for fast reheating, it was classed as a 'difficult' food. It also gave visual appearance of hot and cold spots and was uniform especially in consistency when made up.

*Preparation of test medium*

Water at 40°C was weighed into a Hobart mixer type AE200. Potato powder (Swel, F.M.S. Products Ltd), was weighed onto the water in the proportion of 1 : 7 dried potato to water. The mixer was then set to slow speed (setting No. 1) for 2 min using the paddle attachment.

The test medium was poured into the tray to within ± 5 g of its required weight and the lid then placed in position.

To ensure uniform thickness of the test medium, a spirit level was used to provide a flat location in the freezer itself.

*Preparation of trays and lids*

Trays and lids were chosen for each experiment and degreased and straightened if necessary. Each tray was weighed individually, and the weight written on the side.

*Preparation of spiders and thermocouples*

The arm of the spider was adjusted both to be just clear of the test medium, and also to be well clear of its legs. The junction of the thermocouples was set horizontally at a height measured by a friction slide on a metal ruler. Coarse height adjustment was by vertical movement of the arm, followed by fine height adjustment to within 0·5 mm by sideways springing of the junction.

The junction was situated at the centre of the tray with the spider leg furthest away from the junction placed nearest the notched corner of the tray. The wire was then crimped over the notch to hold the thermocouples in place. The loose end was coiled up and clipped close to the tray, to prevent unintentional movement of the spider.

*Temperature recording*

The temperature recorder could be used to record temperature above or below freezing by the simple expedient of altering the position of the zero on the chart. The recorder had sixteen separate channels for recording temperatures one of which printed out every 5 sec. One or more channels were used for measuring oven air temperatures. Just prior to their print-out, the sensitivity had to be halved to bring it onto the scale. The other channels were normally connected to thermocouples embedded into the test medium, but if any channels were spare, they were either con-

nected to a channel already in use to provide a more complete recording, or if this was unnecessary, they were short circuited.

After starting each experiment, all connections, especially those of the wander plugs, were checked for good contact, and if necessary rewired. Erratic recorded print-outs were almost always due to dirty or poor wiring of wander plugs. Dirty wires were the most difficult to trace, as the only indication was a slightly reduced temperature.

## Results

*Pack thickness related to reheat time*

The effect of varying pack thickness on reheat time is shown graphically in Fig. 2.

Three test media of varying consistency were used—thick potato mix, thin potato mix and water. The compositions of potato powder to water for the thick mix and the thin mix were 1 : 4 w/w and 1 : 7 w/w, respectively. For water the reheat time increased linearly with increasing thickness of the pack until the trays became too full to manage, and spillage occurred. For both potato mixes, the reheat time increased with thickness to a maximum which occurred for packs of approximately 30 mm thickness. Above this thickness, the reheat times decreased until the trays were full. The maximum occurred when the trays were three-quarters full. After this, the food

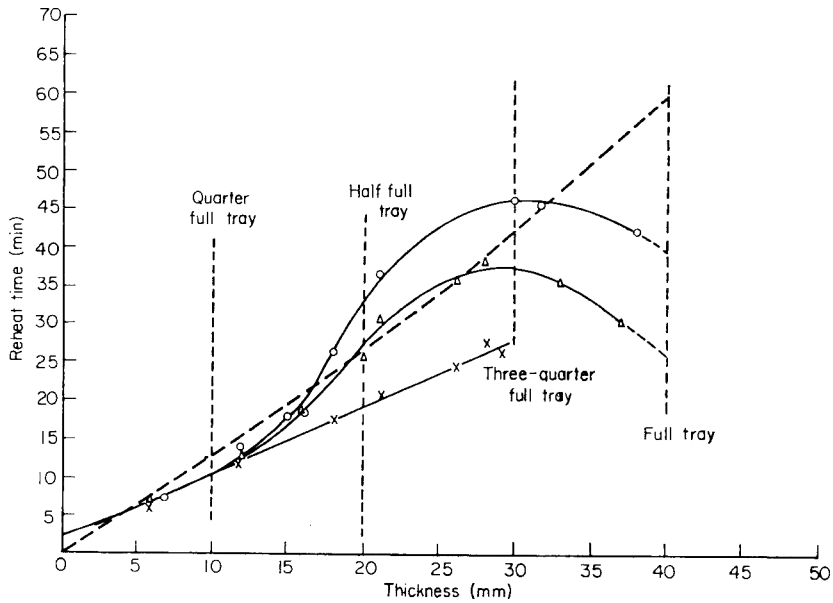


FIG. 2. Variation of food reheat time with pack thickness. ×, Water; △, thin potato mix ○, thick potato mix. The thick broken curve indicates the theoretical curve for thick potato mix.

started touching the lid and the amount of contact between the lid and food increased until with a full tray, it was complete.

For packs thinner than 15 mm the type of test medium had little effect on reheat time. For packs thicker than 15 mm major differences in reheat time occurred with the water reheating much quicker than the potato mixes.

The water and thin mix gave consistently reliable results, whereas, the thick mix tended to suffer from consistency changes which affected the reheat times unless great care was taken.

*Oven comparison*

From Table 1 it can be seen that for ovens A, B, C and E the reheat times were independent of the load, i.e. the number of packs being reheated. For oven D, the reheat time was only independent for small loads; above a loading of six packs, the reheat time increased with increasing load.

TABLE 1. Food reheat times for different ovens varying with food load

| Food reheat time (min) in oven: | | | | | Food load (No. of packs) |
|---|---|---|---|---|---|
| A | B | C | D | E | |
| | | | 52 | 33 | 32 |
| 25 | | 39 | 43 | 36 | 24 |
| 21 | 32 | 41 | 41 | | 18 |
| 25 | 34 | 41 | 29 | 36 | 12 |
| 21 | 32 | 39 | 18 | 34 | 6 |
| 22 | 31 | 39 | 19 | 31 | 2 |

TABLE 2. Uniformity of food reheating* for different oven. varying with food load

| Uniformity of food reheating (min) in oven: | | | | | Food load (No. of packs) |
|---|---|---|---|---|---|
| A | B | C | D | E | |
| | | | 12 | 10 | 32 |
| 12 | | 30 | 9 | 8 | 24 |
| 6 | 11 | 24 | 5 | | 18 |
| 2 | 10 | 15 | 14 | 9 | 12 |
| 3 | 4 | 15 | 15 | 17 | 6 |
| 0 | 0 | 0 | 0 | 0 | 2 |

* The uniformity of food reheating is the time difference for the first and last packs to reach 80°C.

The ovens classed in order of speed of reheating was A, B, E and C, with maximum reheat times of 26, 34, 36 and 41 min, respectively. Oven D with reheat times depending on load could fit anywhere into the classification.

The uniformity of reheating within each load is shown in Table 2 with the uniformity being calculated by subtracting the reheat times for the fastest reheating pack from that for the slowest reheating pack. Ovens A, B and D provided the best uniformity followed by E. Oven C was poor in comparison.

## Discussion

*Heat transfer—theory*

In a forced convection oven, heat is transferred first from the oven air to the surface of the food pack and then to the thermal centre of the pack. The main factors in the transfer of heat from the oven air to the pack surface are oven air temperature, and oven air velocity. The effect of the container material is small (Coulson & Richardson, 1959). Thus, for a given oven, the only ways to increase the heat transferred are to alter the thermostat setting or increase the residence time. For the reheating of the food pack, the following assumptions have been made so that the reheat times can be calculated:

(1) That the air trapped above the food in the trays has a constant effect on the heat transfer.

(2) That the effect of the edges on the temperature at the thermal centre of the pack is very small, due to the geometric shape being a thin slab. Calculations based on National Engineering Laboratory Laboratory data (Dalgleish, 1965) show an effect on centre temperature of approximately 1°C under the conditions of our experiments. Thus, edge effects were ignored so that unidimensional heat flow through the pack could be assumed.

(3) That as the thermal diffusivity of the frozen block is many times that of the liquid phase, and as liquid surrounds the frozen block throughout the thawing stage, the rate controlling phase will be the liquid and not the frozen phase.

The temperature $\theta$ at the thermal centre of the pack with respect to time $t$ can then be found by arranging the physical data into the following dimensionless groups and reading off their interrelationship from charts.

The dimensionless groups are named as follows:

$N$, the Biot number which contains heat transfer properties;

$\Theta$, the reduced temperature; and

$T$, the Fourier number which contains the time factor.

The National Engineering Laboratory provide charts that relate $T$ to $N$ for varying values of $\Theta$. Thus if $N$ is known and $\Theta$ is fixed, $T$ can be read off from the chart and the reheating time then calculated.

The following relationships are used and the calculations are based on S.I. units:

$$\mathcal{N} = \frac{ah \times 10^{-3}}{k},$$

$$\Theta = \frac{\theta - \theta_0}{\theta_1 - \theta_0},$$

$$T = \frac{60 \times kt \times 10^6}{\rho c a^2},$$

where $a$ = half the pack depth (mm),
$c$ = the pack specific heat (J/kg °C)
$k$ = the pack thermal conductivity, W/m² (°C/m),
$\rho$ = the pack density (kg/m³),
$h$ = the suface heat transfer coefficient (W/m² °C),
$t$ = the reheating time (min),
$\theta$ = the temperature at the centre of the pack,
$\theta_1$ = the initial temperature of the pack,
$\theta_0$ = the oven temperature.

The reheating times for thick potato mix were calculated for varying pack depths. The following physical data were used:

$c = 3{\cdot}76 \times 10^3$ J/kg °C $\qquad \rho = 960$ kg/m³
$k = 1{\cdot}06$ W/m² (°C/m) $\qquad h = 14{\cdot}2$ W/m² °C

The values for $c$, $\rho$ and $k$ were taken from existing data (Spinell, 1963; Woodams & Nowrey, 1968); and for $h$ from evaporation rate figures obtained during boiling of water in the trays. The frozen food temperature at the beginning of the reheating time was taken as 0°C due to warming in air during transporting from the deep freeze and loading into the oven.

The food was said to be reheated when the temperature at the centre of the pack reached 80°C:

The oven air temperature was taken as 180°C.

Rearranging: $t = 5{\cdot}67 \times 10^{-2} a^2 T.$

Substituting these values into the above equations:

$$\mathcal{N} = a \times 10^{-3} \times \frac{14{\cdot}2}{1{\cdot}06} = 1{\cdot}39 \times 10^{-2} a,$$

$$\Theta = \frac{80 - 180}{0 - 180} = 0{\cdot}56,$$

$$T = \frac{60 \times 1{\cdot}06t \times 10^6}{960 \times 0{\cdot}90 \times a^2}.$$

For a given pack depth, $N$ could now be calculated. As the values of $N$ and $\Theta$ were then known, the value of $T$ could be read off from the chart and substituted into the above equation to obtain the reheating time $t$.

The reheat times for various pack thicknesses were calculated and plotted on Fig. 2. The theoretical curve is calculated assuming a constant value for $h$, based on a half full tray; for depths of potato around the half full mark the theoretical curve gives quite good agreement considering the assumptions that have been made and that the accuracy of the data is unknown. For fuller trays a possible explanation of the differences between theoretical and actual results is that the air space within the trays is much thinner so the heat transferred through the air space approaches that by conduction alone. Consequently $h$ is reduced and the calculated reheat times are then too short. For full or almost full trays, the potato touches the lid and the value of $h$ is raised so the calculated reheat times are too long.

*Pack thickness related to production rate*

To calculate the production rate for a given pack thickness the delay due to loading and unloading of the food was added to the reheat time (see Fig. 2) to obtain the utilization time. Then the number of times that the oven was utilized in an hour, multiplied by the pack weight in kilograms, gave the production rates in kilograms per hour. Production rates for given pack thicknesses are plotted in Fig. 3.

These production rates are for a very small oven holding one pack only. Similar ovens of larger capacity can have their production rates calculated simply by multiplying by their load expressed as a number of packs.

The delay due to loading and unloading can depend on the particular oven and on the efficiency of the oven operator, but will be less than 5 min as long as a removable rack is used. No delay occurs for a continuous oven.

It can be seen from Fig. 3 that the production rate rises rapidly from zero for zero pack thicknesses, to a maximum for packs between 10 and 15 mm thick. It then falls away rapidly to a minimum at a pack thickness slightly greater than 20 mm because these slightly thicker packs take a disproportionate reheat time; it then climbs away until the tray is filled at 40 mm pack thickness.

For trays less than half full, i.e. packs of less than 20 mm thickness, the delay for loading and unloading can cause a 20% drop in production rate. For trays greater than half full, the effect of the delay is much less marked and is constant. The top curve can only be attained in practice if a continuous forced convection oven is used, but a good batch oven efficiently operated will produce creditable production rates.

Pack thicknesses about 30 mm are impracticable due to surface contact with the lid and consequent burning, and thin packs are impractical due to the large number that have to be handled to provide an adequate production.

Within these working limitations, it can be seen from Fig. 3 that the highest

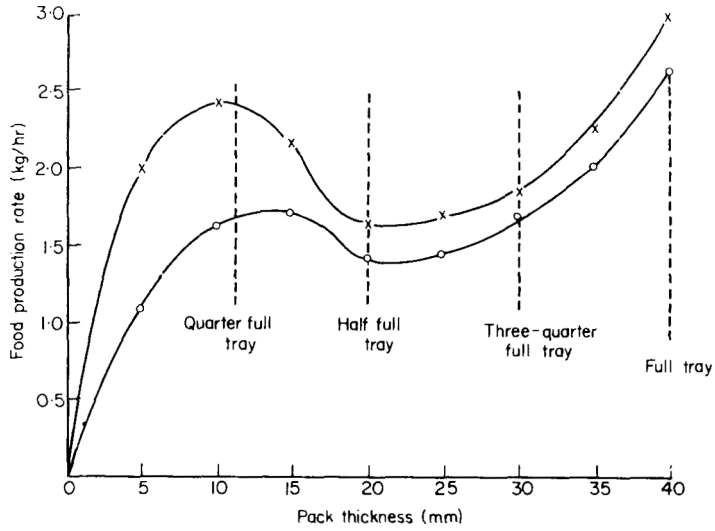


FIG. 3. Variation of food production rate with pack thickness. ×, No delay for loading and unloading (continuous oven); O, 5-min delay for loading and unloading (batch oven.)

production rates are obtained for pack thicknesses varying from 10 to 16 mm thick. For a continuous forced convection oven, using a 16-mm pack, a production rate of 2·0 kg/hr can be obtained.

For a batch forced convection oven using a 16 mm pack, a production rate in excess of 1·7 kg/hr can be obtained. Increasing the 16-mm pack to 20 mm causes a marked drop in production rate of 0·3 kg/hr or 15% due to longer reheat times necessary. Decreasing the 16-mm pack to 10 mm increases the production rate only for the continuous oven. For the batch oven it remains comparatively constant at 1·7 kg/hr.

For large-scale operations continuous cookers coupled to mechanical handling equipment for the packs can be justified economically, so the packs providing the best production rates, i.e. the thin 10-mm pack is recommended. For small-scale operations using batch ovens operated manually, the 16-mm pack is recommended.

*Oven comparison*

The ducted air forced convection ovens provided the fastest reheating and also provided as uniform reheating as the best of the stirred air forced convection ovens, therefore, for reheating frozen food it was decided to use the ducted air models wherever possible.

Prior to testing oven E, the air distribution in the oven was extensively modified to decrease the reheat time to 35 min. It was noted that with this stirred fan type of oven, speeding up the fan decreased the reheat times slightly, but worsened the

uniformity of reheating. The final modification was made at the expense of using a three-phase motor for the fan, which for most applications of a gas oven would be unacceptable as the three-phase supply is not normally available.

Oven D was exceptional, in that the heating was transferred from gas to moist air and from the moist air to the food packs by condensation on the outside of the trays. As heat transfer by condensation is many times more efficient than heat transfer by convection from hot air, all the available heat was absorbed into the packs faster than it was being generated, except for small loads. Also preheating of this oven was not entirely satisfactory, as much of this preheat was lost in the hot water vapour when the oven door was opened. As this oven was a prototype, it was recommended that its heating capacity be upgraded, and that the hot vapour lost when loading the oven be reduced.

## Acknowledgments

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# A mathematical model of the Torry fish drying kiln

P. E. DOE


## Summary

Proposed developments of the Torry fish drying kiln have led to a need for a closer understanding of commercial fish drying processes. In order to investigate the effects on fish drying of air velocity, air temperature and humidity, and fish packing density, a mathematical model of the kiln has been proposed. This model establishes partial differential equations for fish weight, air temperature and humidity. The model is applicable to the drying of other materials. A solution is obtained numerically by standard finite difference techniques.


## Introduction

Fish drying in Britain underwent a change from traditional natural draft dryers to controlled condition mechanical drying following the development at the Torry Research Station, Aberdeen, of the Torry kiln (Fig. 1) around 1940 (Burgess *et al.*,

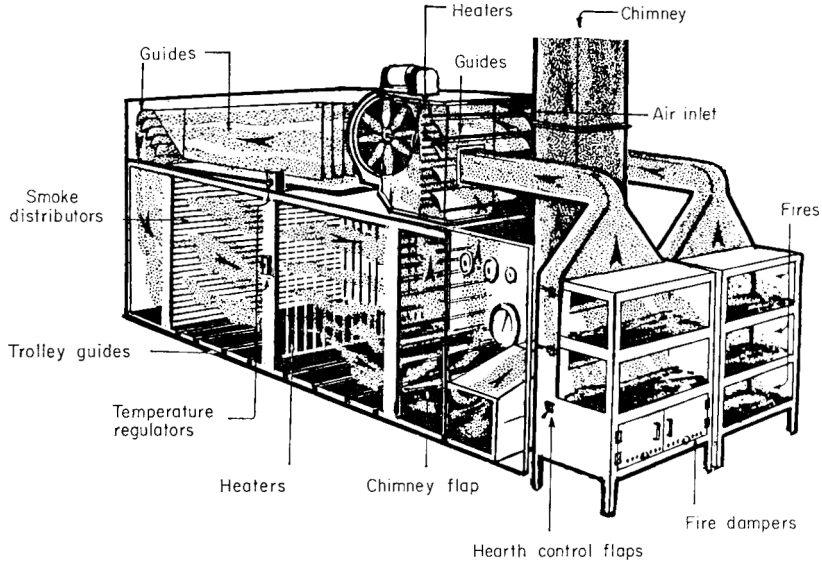


FIG. 1. Cutaway diagram of the Torry Kiln (Crown Copyright Reserved).

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1965a). The Torry kiln in its present form comprises a closed circuit wind tunnel with provision for heating the circulating air, venting to atmosphere and the addition of smoke. The fish is hung in a more or less uniform fashion across the rectangular cross-section of the kiln.

Recently there has been a trend towards automatic operation of Torry kilns as a means of optimizing performance and economy. For this to be successful, a detailed knowledge of the effects of the various variable quantities associated with fish drying, such as air velocity, temperature and humidity, is required.

A considerable amount of investigation into the running of existing kilns has been carried out by the Research Station. This work is of necessity limited to existing operating methods and is subject to uncontrolled variations in atmospheric conditions; furthermore, it is not practicable to perform a long series of controlled experiments on a kiln producing dried fish in commercial quantities. An alternative is to make a scale model of the kiln and investigate the behaviour of the model. This has been done at Torry, but experience has shown that results of studies on models, or even small commercial kilns, do not scale up readily to the larger kilns.

This paper describes the development of a mathematical model to complement the experimental work on model and prototype kilns. The mathematics is general to the forced air drying of materials in which the internal diffusion processes can be described by Fick's laws of diffusion. The model is amenable to computer solution and can predict the separate effects of the various factors on the performance of a kiln. A mathematical model also is capable of easy and rapid modification in order to simulate real behaviour. Thus typical operating data can be input to the mathematical model and the model progressively modified to fit real kiln behaviour.

**Nomenclature**

| *Symbol* | *Significance* | *Equation* | *Units* |
|---|---|---|---|
| $b$ | Breadth of rectangular surface transverse to direction of air flow | 15 | cm |
| $C$ | Shape factor | 17 | — |
| $C_e$ | Equilibrium free water concentration | 23 | g $cm^{-3}$ |
| $C_0$ | Initial free water concentration | 22 | g $cm^{-3}$ |
| $C_s$ | Free water concentration at surface of fillet | 22 | g $cm^{-3}$ |
| $c$ | Half thickness of fillet | 22 | cm |
| $c_{pa}$ | Specific heat of dry air at constant pressure | 7 | cal $g^{-1}$ $C^{-1}$ |
| $c_{pF}$ | Specific heat of fish muscle at constant pressure | 9 | cal $g^{-1}$ $C^{-1}$ |
| $c_{pv}$ | Specific heat of water vapour at constant pressure | 7 | cal $g^{-1}$ $C^{-1}$ |
| $c_{pl}$ | Specific heat of liquid water | 8 | cal $g^{-1}$ $C^{-1}$ |
| $D$ | Effective diffusion coefficient of water in fish muscle | 22 | $cm^2$ $sec^{-1}$ |
| $E$ | Total rate of evaporation from a surface of length $l$ and breadth $b$ | 15 | g $sec^{-1}$ |
| $G$ | Mass flow rate of moist air | 11 | g $sec^{-1}$ |

| *Symbol* | *Significance* | *Equation* | *Units* |
|---|---|---|---|
| $h$ | Enthalpy of $1 + r$ units of mass of moist air | 2 | cal $g^{-1}$ |
| $h_a$ | Specific enthalpy of dry air | 2 | cal $g^{-1}$ |
| $h_g$ | Specific enthalpy of water vapour | 2 | cal $g^{-1}$ |
| $h_A$ | Enthalpy of moist air | 1 | cal |
| $h_F$ | Enthalpy of fish muscle | 1 | cal |
| $k_w$ | Overall mass transfer coefficient for surface of length $l$ | 16 | g $sec^{-1}$ $cm^{-2}$ $atm^{-1}$ |
| $L(\theta)$ | Latent heat of vaporization of water at temperature $\theta$ | 8 | cal $g^{-1}$ |
| $l$ | Length of rectangular surface parallel to the direction of air flow | 15 | cm |
| $M_F$ | Mass of fish muscle in length $dx$ | 5 | g |
| $m_a$ | Mass flow rate of dry air | 3 | g $sec^{-1}$ |
| $m_v$ | Mass flow rate of water vapour | 4 | g $sec^{-1}$ |
| $n$ | Integer | 22 | — |
| $P$ | Pressure of moist air | 24 | atm |
| $p$ | Partial pressure of water vapour | 15 | atm |
| $p_s$ | Saturation partial pressure of water vapour | 15 | atm |
| $r$ | Mixing ratio of moist air, i.e. mass of water vapour per unit mass of dry air | 2 | — |
| $r_0$ | Mixing ratio of moist air entering working space | — | — |
| $t$ | Time | 3 | sec |
| $t_c$ | Time of commencement of falling rate period | 20 | sec |
| $u$ | Air velocity | 15 | cm $sec^{-1}$ |
| $x$ | Distance along kiln | 3 | cm |
| | **Greek symbols** | | |
| $\varepsilon$ | Evaporation flux | 15 | g $sec^{-1}$ $cm^{-2}$ |
| $\varepsilon_c$ | Evaporation flux at end of constant rate period | 23 | g $sec^{-1}$ $cm^{-2}$ |
| $\eta$ | 'Packing density' mass of fish per unit kiln length | 5 | g $cm^{-1}$ |
| $\eta_c$ | 'Packing density' at start of falling rate period | 20 | g $cm^{-1}$ |
| $\eta_e$ | 'Packing density' under equilibrium conditions | 20 | g $cm^{-1}$ |
| $\eta_0$ | 'Packing density' at start of drying | — | g $cm^{-1}$ |
| $\theta$ | Air temperature | 7 | °C |
| $\theta_F$ | Fish temperature | 9 | °C |
| $\theta_0$ | Dry bulb temperature of air entering kiln | — | °C |
| $\xi$ | Surface area of fish per unit length of kiln | 18 | cm |
| $\tau$ | Drying time constant | 20 | sec |
| | **Operators** | | |
| $\delta$ | Increment | | |
| $\partial$ | Partial differential | | |
| $d$ | Increment | | |

## Outline of the problem of air drying in a mechanical kiln

The Torry kiln is basically a closed circuit wind tunnel with a large rectangular working section into which trolleys of fish (usually fillets hung vertically) are wheeled. Air circu-

lation is maintained by a fan and venting is provided which allows humid air to be expelled and dry air or smoke to be admitted. Air temperature is controlled by heaters, and humidity is controlled by venting, steam admission and, in some cases cooling. Larger kilns (750 kg nominal capacity) are provided with a reheater halfway along the working section. Operation is traditionally a batch process with nearly constant air condition maintained at the upstream end of the working section throughout the drying period. There is usually some rearrangement of the fish trolleys in the kiln during drying to compensate for the upstream fish drying more rapidly than those in moister air further along the kiln. Neglecting this rearrangement, the drying process may be described as a stream of air, passing along the kiln through the racks of fish, absorbing water vapour evaporated from the fish and thus becoming cooler and more humid.

If a particular fillet is considered, the factors affecting its rate of drying are the velocity, temperature and humidity of the air stream passing around it, its shape, surface area and moisture content. Below a certain moisture content, the processes of internal diffusion and capillary action within the fillet control the rate of migration of water to the surface of the fillet. This latter state is known as '*falling rate drying*'. Prior to this, where there is no lack of free water at the surface, the drying is known as '*constant rate drying*' (Burgess *et al.*, 1965b).

At some time during the drying, there are fish near the upstream end of the kiln drying at 'falling rate' and fish further down the kiln, less dry, drying at 'constant rate'. The mathematical model of a drying kiln must be sufficiently detailed to provide for this situation.

In all such mathematical studies, the validity of the end result is dependent on the quality of the data and the validity of the assumptions inherent in the establishment of the mathematical model. Most of the relevant information incorporated in the model has been gleaned from a study by Jason of evaporation and diffusion processes in the drying of fish muscle (Jason, 1958) and is thus specifically for the air drying of fish. However, much of the mathematics in this paper is general to other types of drying; indeed to other problems involving the one-dimensional simultaneous heat and mass transfer of water vapour evaporating into air.

## The physical model

Having outlined the 'real' problem of the kiln drying of fish, the first step in obtaining a mathematical model is to make such simplifying assumptions as may be considered justified. This results in a physical model of the real problem. It is hoped that the physical model will be a sufficiently good approximation to the real situation to enable the solution of the derived mathematical model to be of use. The following is a list of simplifying assumptions which describe the physical model:

(1) The working section of the kiln may be considered a rectangular parallelepiped.

(2) There is no preferred direction of air flow other than longitudinally along the

kiln so that the properties of air and fish are at all times constant in planes transverse to the general direction of air flow. Thus the working section is considered one-dimensional.

(3) The evaporation rate from the fillets may be calculated from data of Powell & Griffiths (1935) expressed in equation (18) below. The velocity used may be computed by dividing the air flow rate by the net cross-section of the kiln.

(4) The change in air pressure along the kiln may be neglected.

## The mathematical model

*Heat and mass balances for constant and falling rate drying*

Fig. 2 represents an incremental volume of the kiln of length $dx$. A heat balance over this volume must include:

(1) The change in enthalpy of the air passing through the volume.

(2) The enthalpy of the water vapour evaporating from the fish in the volume.

(3) The enthalpy associated with any temperature change of the fish.

(4) Conduction, radiation and convection of heat through the walls of the kiln. It is assumed that item (4) is negligible when compared with items (1), (2) and (3).

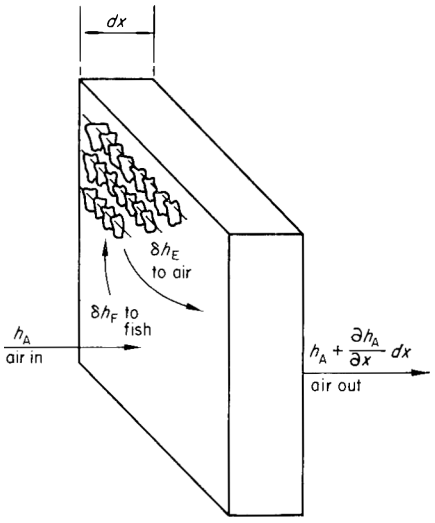



FIG. 2. Heat fluxes associated with a section of the kiln.

In addition to the heat balance in the volume of the kiln there must also be a mass balance which must include:

(5) The increase in the mass of humid air in the kiln.

(6) The quantity of water evaporating from the fish.

(7) The quantity of water condensing or dripping onto the sides of the kiln.

In practice item (7) is negligible in relation to items (5) and (6). Thus, since mass is conserved, the increase in the mass of humid air is equal to the loss of mass from the fish.

Conservation of total enthalpy in the incremental volume requires that:

$$\delta h_A + \delta h_F = 0, \tag{1}$$

where $\delta h_A$ = the enthalpy change of the moist air,
$\delta h_F$ = the enthalpy change of the wet fish.
[$\delta h_A$ is associated with items (1) and (2) and $\delta h_F$ with item (3).]
The enthalpy of $1 + r$ units of mass of moist air may be written (Harrison, 1965):

$$h = h_a + r\,h_v, \tag{2}$$

where $h_a$ = the enthalpy of a unit mass of dry air (specific enthalpy of dry air),
$h_v$ = the enthalpy of a unit mass of water vapour (specific enthalpy of water vapour),
$r$ = the mass of water vapour per unit mass of dry air (mixing ratio).
The change in enthalpy of moist air in a distance $dx$ during the time interval $dt$ resulting from a mass flow rate $m_a$ of dry air is given by:

$$\delta h_A = m_a \frac{\partial h}{\partial x}\,dx\,dt. \tag{3}$$

Putting $m_v = m_a r$, the mass flow rate of water vapour, differentiating both sides of equation (2) with respect to $x$ and substituting in equation (3) gives:

$$\delta h_A = \left(m_a \frac{\partial h_a}{\partial x} + m_v \frac{\partial h_v}{\partial x} + h_v \frac{\partial m_v}{\partial x}\right) dx\,dt, \tag{4}$$

since

$$\frac{\partial m_a}{\partial x} = 0.$$

If a 'packing density' $\eta$ is defined by the expression:

$$\eta = \frac{M_F}{dx}, \tag{5}$$

where $M_F$ is the mass at time $t$ of fish in the incremental length $dx$, then, since the rate of gain of mass of water vapour by the moist air is equal to the rate of loss of mass from the fish (conservation of mass):

$$\frac{\partial m_v}{\partial x} dx = - \frac{\partial M_F}{\partial t}.$$

Therefore:

$$\frac{\partial m_v}{\partial x} = - \frac{\partial \eta}{\partial t}. \tag{6}$$

Let the specific heats at constant pressure of dry air and water vapour be $c_{pa}$ and $c_{pv}$, respectively, and let $\theta$ be the mean temperature in the incremental volume, then:

$$\frac{\partial h_a}{\partial x} = c_{pa} \frac{\partial \theta}{\partial x}, \qquad \frac{\partial h_v}{\partial x} = c_{pv} \frac{\partial \theta}{\partial x}. \tag{7}$$

The specific enthalpy of water vapour may be written as:

$$h_v = \int_0^{\theta} c_{pl} \, d\theta + L(\theta), \tag{8}$$

where $c_{pl}$ is the specific heat at constant pressure of liquid water and $L(\theta)$ is the latent heat of vaporization of water at temperature $\theta$.

By substituting in equation (4) the expressions for $\partial m_v/\partial x$, $\partial h_a/\partial x$, $\partial h_v/\partial x$ and $h_v$ given in equations (6), (7) and (8) and writing:

$$\begin{aligned} \delta h_F &= c_{pF} M_F \frac{\partial \theta_F \, dt}{\partial t} \\ &= c_{pF} \eta \frac{\partial \theta_F}{\partial t} dx \, dt, \end{aligned} \tag{9}$$

where $c_{pF}$ is the specific heat of fish muscle at constant pressure, equation (1) becomes:

$$(m_a c_{pa} + m_v c_{pv}) \frac{\partial \theta}{\partial x} - \left[ \int_0^{\theta_F} c_{pl} \, d\theta + L(\theta_F) \right] \frac{\partial \eta}{\partial t} + c_{pF} \eta \frac{\partial \theta_F}{\partial t} = 0. \tag{10}$$

$\theta$ carries the subscript F in the latent heat term since this relates to fish temperature.

Writing, as the mass flow rate of moist air:

$$G = m_a (r + 1), \tag{11}$$

equation (10) becomes:

$$\frac{G}{r+1}(c_{pa}+r\,c_{pv})\frac{\partial\theta}{\partial x}-\left[\int_0^{\theta_F} c_{pl}\,d\theta+L(\theta_F)\right]\frac{\partial\eta}{\partial t}+c_{pF}\,\eta\frac{\partial\theta_F}{\partial t}=0. \tag{12}$$

It follows from equation (11) that:

$$m_v=\frac{r}{r+1}G, \tag{13}$$

which, on differentiating and substituting in equation (6), gives:

$$\frac{\partial\eta}{\partial t}+\frac{G}{(r+1)^2}\frac{\partial r}{\partial x}=0. \tag{14}$$

*Constant rate drying*

During constant rate drying, convective mass and heat transfer determine the evaporation rate at the fish surface. Powell & Griffiths (1935) in their classical work on evaporation, measured evaporation rates from a saturated horizontal plane rectangular surface and presented the results in the expression

$$\frac{E}{p_s-p}=1{\cdot}61\times10^{-4}\,bl^{0{\cdot}77}\,(1+0{\cdot}121\,u^{0{\cdot}85}), \tag{15}$$

where $E$ = the total rate of evaporation from a surface of length $l$ and breadth $b$ (g $sec^{-1}$),
$p_s$ = the saturation vapour pressure at the wet bulb temperature (atm),
$p$ = the partial pressure of water vapour (atm),
$l$ = the length of the rectangular surface parallel to direction of air flow (cm),
$b$ = the breadth of the rectangular surface transverse to direction of air flow (cm),
$u$ = the air velocity (cm $sec^{-1}$).

Powell (1940) has shown that the presence of ridges on a cylinder can enhance evaporation rates by as much as 50%, while rates of evaporation from the downstream surface of a plane rectangular plate increase as the plate is progressively inclined to the air stream, the increase being 100% in extreme cases. Jason (1958), in confirming that the data of Powell & Griffiths (1935) apply to rectangular slabs of more than a certain length, demonstrated that the rate of evaporation is considerably increased locally by air turbulance generated downstream of the leading edges.

It is impossible with present knowledge to incorporate such effects analytically in

the mathematical model. However, by introducing an empirical shape factor $C$ to allow for the consequences of irregular geometry of the fillets, equation (15) may be written in the form:

$$\varepsilon = k_w (p_s - p), \tag{16}$$

where $\varepsilon$ is the rate of evaporation per unit area (g $sec^{-1}$ $cm^{-2}$) and $k_w$ the mass transfer coefficient for a plane rectangular surface of length $l$ is multiplied by $C$ to give a corresponding value for a fish fillet of:

$$k_w = 2{\cdot}415 \times 10^{-4}\, l^{-0{\cdot}23}\, (1 + 0{\cdot}121\, u^{0{\cdot}85}). \tag{17}$$

[A value $C = 1{\cdot}5$, based roughly on the above considerations, appears to be reasonable when the numerical solution of the equations is compared with real behaviour as shown below.]

The drying rate per unit length of the kiln may be related to the evaporation rate per unit area of fish by the expression:

$$\frac{\delta \eta}{\delta t} = -\varepsilon \xi, \tag{18}$$

where $\xi$ is the surface area of fish per unit length of the kiln.

Equations (16) and (18) give an expression for the drying rate during constant rate drying:

$$\frac{\delta \eta}{\delta t} = -\xi\, k_w (p_s - p). \tag{19}$$

*Falling rate drying*

During falling rate drying, the migration of water within the fish governs the drying rate. Jason (1958) has shown that, whatever the mechanism of diffusion involved, whether capillary flow, thermal diffusion, gaseous diffusion, viscous flow of water vapour, surface diffusion in a porous medium, or molecular diffusion in a solid medium the process can be adequately described by an exponential expression relating the drying rate to the drying time. In the falling rate period this behaviour may be represented by the expression:

$$\frac{\eta - \eta_e}{\eta_c - \eta_e} = \exp\, [-(t - t_c)/\tau] \text{ for } t \geqslant t_c, \tag{20}$$

where $t$ is the time from commencement of drying, $\tau$ is the drying time constant, and the subscripts c and e refer to values at the commencement of the falling rate period and under equilibrium conditions, respectively. Jason has measured $\tau$ for fillets of various sizes and from various species over a wide range of temperature. Differentiation of $\eta$ with respect to $t$ gives:

$$\frac{\delta \eta}{\delta t} = -\frac{\eta_c - \eta_e}{\tau} \exp\left[-(t - t_c)/\tau\right]. \tag{21}$$

*Determination of the end of constant rate drying*

Constant rate drying ends when the processes of internal diffusion of water to the surface of the fish start to control the drying. Jason (1958) has proposed a method of calculating the free water concentration at the surface of a slab of given diffusivity based on an analogous solution in the field of heat transfer (Carslaw & Jaeger, 1947) The difference between the free water concentration ($C_s$) at the surface at time $t$, and the initial free water concentration ($C_0$) at the centre of a slab of thickness $2c$ is:

$$C_0 - C_s = \frac{\varepsilon c}{D}\left\{\frac{Dt}{c^2} + \frac{1}{3} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dn^2\,\pi^2\,t}{c^2}\right)\right\}, \tag{22}$$

where $\varepsilon$ is the flux of water at the surface. $D$ is the effective diffusion coefficient.

Jason then proposes that, at the end of the constant rate period as soon as there is insufficient free water to saturate the air close to the surface, the concentration of water at the surface rapidly approaches a value in equilibrium with the humidity of the air stream. The equilibrium water content of fish muscle has been determined by Jason at various humidities.

If $C_e$ is the equilibrium free water concentration, and $t_c$ is the time at the end of constant rate drying, the evaporation rate at the end of constant rate drying, $\varepsilon_c$, is given by:

$$\varepsilon_c = \frac{D\,(C_0 - C_e)}{c} \Bigg/ \left\{\frac{Dt_c}{c^2} + \frac{1}{3} - \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dn\,\pi^2\,t_c}{c^2}\right)\right\}. \tag{23}$$

At time $t_c$, the flux of water to the surface falls below the critical value $\varepsilon_c$, so that the diffusion of water to the surface can no longer support the rate of evaporation corresponding to the convective mass transfer from a free water surface as given by equation (18).

## Solution of the mathematical model

The solution of the mathematical model requires the solution of the nonlinear partial

differential equations (12), (14), (19) and (21) so that the fish weight per unit kiln length, $\eta$, air temperature, $\theta$, and mixing ratio, $r$, are known for all positions, $x$, along the kiln at any time, $t$.

There are necessarily initial and boundary conditions applying to the equations. The boundary conditions chosen are that the temperature and humidity of the air entering the working space of the kiln remain constant throughout the drying process. That is:

$$\text{at } x=0,\ \theta=\theta_0,\ r=r_0 \text{ for all } t.$$

The initial condition is that the fish is uniformly wet and the kiln is uniformly loaded at the start of drying. That is:

$$\text{at } t=0,\ \eta=\eta_0 \text{ for all } x,$$

where $\eta_0$ is the packing density or weight of fish per unit length of kiln at the start of drying. There is, in addition, a test involving equations (18) and (23) which determines whether the fish is drying under constant or falling rate conditions.

It was found convenient in the solution to use the partial pressure of the water vapour in the moist air $p$ instead of the mixing ratio $r$ as a measure of humidity. These quantities are related by the expression (Harrison, 1965):

$$r=\frac{0{\cdot}622\,p}{P-p}, \tag{24}$$

where $P$ is the total pressure of the air–water vapour mixture.

With the substitution of equation (24), equation (12) becomes:

$$\frac{G(P-p)}{(P-0{\cdot}378\,p)}\left[c_{pa}+\frac{0{\cdot}622\,p}{P-p}c_{pv}\right]\frac{\partial\theta}{\partial x}-\frac{L(\theta_F)\partial\eta}{\partial t}+c_{pF}\eta\frac{\partial\theta_F}{\partial t}=0, \tag{25}$$

it being noted that:

$$\int_0^{\theta_F} c_{pl}\,d\theta \ll L(\theta_F),$$

and equation (14) becomes:

$$\frac{\partial\eta}{\partial t}+\frac{0{\cdot}622\,GP}{(P-0{\cdot}378p)^2}\frac{\partial p}{\partial x}=0. \tag{26}$$

The following two simplifications apply to equation (25):

$$\left.\begin{aligned} \frac{\delta \theta_F}{\delta t} &= 0 \text{ for constant rate drying,} \\ \theta_F &= \theta \text{ for falling rate drying.} \end{aligned}\right\} \tag{27}$$

Equation (25), together with the initial and boundary conditions and the test for the end of constant rate drying (equations 19 and 23), represents the mathematical model in the form chosen as the most convenient for solution.

The solution was obtained by using standard finite difference approximations to the partial derivatives (Carslaw & Jaegar, 1959). The finite difference approximations were chosen so that the computation proceeded in a marching fashion.

The computer program was written in the Algol programming language and run on the Elliott 503 machine at the University of Tasmania. A flow chart of the computation is shown in Fig. 3.

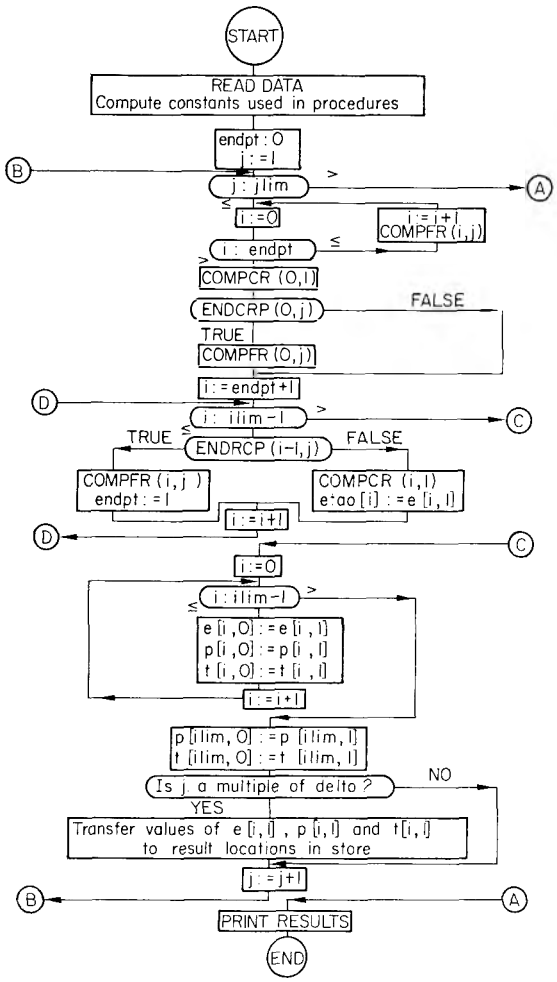
## Convergence of the solution

The author knows of no way to predict the convergence of this solution analytically. That the solution is basically stable is demonstrated by the results obtained. The convergence was assessed by producing a number of solutions with the same data except that progressively smaller time and distance increments were used in the finite difference approximations.

## Effects not included in the model

The evaporation rate during constant rate drying is calculated from the results of Powell & Griffiths (1935) for a flat wet plate. Although no attempt has been made to correct the mathematical model for the effect of proximity of the fish fillets to each other, edge and shape effects and the disordered air flow conditions undoubtedly existing in the kiln, an empirical shape factor $C$ has been introduced, as noted above, to allow for these factors. Although it is admitted that $C$ is chosen to represent typical values encountered when turbulent flow is deliberately introduced, it will be seen below that the results are in reasonable agreement with the only available experimental data.

The assumptions involved in the change to falling rate drying and the application of equation (20), impose a discontinuity on the surface temperature of the fish at time $t = t_c$. In reality there are temperature gradients along particular fillets, with parts of the same fillet drying in the two regimes. The disordered flow conditions in the kiln and lack of detailed knowledge of fish temperature precludes any attempt to include these effects in the model.




List of identifiers and procedures

| | |
|---|---|
| **Identifiers** | |
| Integer | |
| i | Counter for distance increments |
| j | Counter for time increments |
| ilim | Number of distance increments |
| jlim | Number of time increments |
| endpt | Counter to mark end of constant rate drying |
| delto | Number of time increments between results printout |
| Array | |
| 3 [i, j] | Value of fish weight/unit kiln length, $\eta$, after j |
| p i, j | Time increments and i distance increments |
| p [i, j] | Value of partial pressure of water vapour at [i, j] |
| t [i, j] | Value at air temperature at [i, j] |
| etao [i] | Value of $\eta$ at end of constant rate period at [i] |
| **Procedures** | |
| COMPCR (i, j) | Computes values of e [i, j] p[i + 1, j] and t [i + 1, j] during constant rate period from values previously computed |
| COMPFR (i, j) | Computes similar values during falling rate period |
| Type Boolean | |
| ENDCRP (i, j) | Has the value TRUE if the constant rate period is finished, otherwise is FALSE |

FIG. 3. Flow chart of computer program.

The effect of shrinkage is also neglected; but as shrinkage is only significant during the latter stages of falling rate drying, and as drying in this period is computed from measured time constants which must include any effects due to shrinkage, the omission of shrinkage from the model appears justified.

## Results

Computer runs to date have been confined to a study of the drying of haddock fillets (*Gadus aeglefinus*) of a type known as 'golden cutlets'. A close study of the drying in commercial quantities of this fish has been made by Mr R. M. Storey of the Torry Research Station, who has kindly given permission for his data to be used in this

paper. The data used in the computer runs pertaining to the 750-kg Torry kiln and 'golden cutlets' are given in Table 1.

TABLE 1. Data.

| | |
|---|---|
| Drying kiln | |
| Length | 4·00 m |
| Cross-section area (unloaded) | 3·07 $m^2$ |
| Cross-section area (loaded) | 2·22 $m^2$ |
| Normal load of wet fish | 1000 kg |
| Air flow rate | 5·33 $m^3$ $sec^{-1}$ |
| Mean velocity | 2·49 m $sec^{-1}$ |
| Typical condition of air at upstream end of kiln working section | 60% RH at 27·2°C |
| Fish ('Golden Cutlets') | |
| Mean weight | 0·17 kg |
| Approximate size: | |
| Length | 0·23 m |
| Thickness | 0·063 m |
| Width | 0·12 m |
| Mass diffusivity of water in fish | $3{\cdot}25 \times 10^{-10}$ $m^2$ $sec^{-1}$ at 30°C |
| Approximate drying time constant | $5{\cdot}4 \times 10^4$ sec |
| Equilibrium moisture content of fish at: | |
| 10% RH | 4·5 kg $H_2O$/100 kg bone dry solid |
| 20% RH | 7·2 kg $H_2O$/100 kg bone dry solid |
| 30% RH | 8·8 kg $H_2O$/100 kg bone dry solid |
| 40% RH | 11·7 kg $H_2O$/100 kg bone dry solid |
| 50% RH | 14·0 kg $H_2O$/100 kg bone dry solid |
| 60% RH | 17·2 kg $H_2O$/100 kg bone dry solid |
| 70% RH | 22·0 kg $H_2O$/100 kg bone dry solid |
| 80% RH | 31·0 kg $H_2O$/100 kg bone dry solid |

RH = Relative humidity.

Figs. 4 and 5 represent the computer solution with a time increment of 450 sec and a distance increment of 15 cm.

Several somewhat unexpected features emerge from these results. Due to the varying condition of the air further down the kiln following the change to falling rate drying at the upstream end of the kiln, the fish further down the kiln dries rather faster than at its initial constant rate, although 'constant rate' or more strictly 'convection governing' conditions still apply. This is best seen in Fig. 4(a) for $x/l = 1{\cdot}0$. Another feature which is somewhat puzzling at first view is the change in temperatures and humidities at all stations along the kiln at the same time (about 6 hr) (Fig. 4b and c) regardless

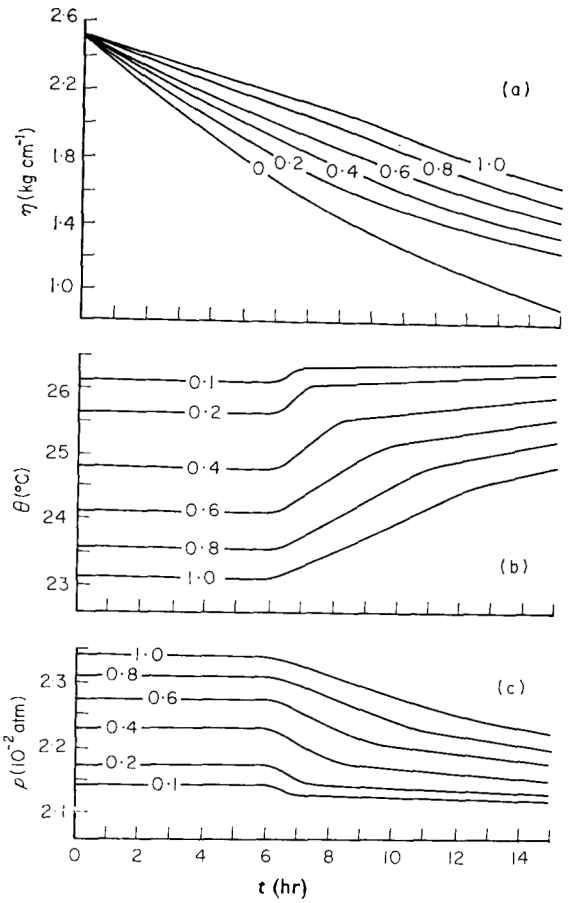



FIG. 4. Variation with time $t$ at various distances $x/L$ along kiln of: (a) fish weight per unit kiln length $\eta$, (b) dry bulb temperature $\theta$, (c) partial pressure of water vapour $p$. Figures on curves indicate values of $x/L$.

of the progressive onset of 'falling rate' drying as indicated in Fig. 4(a). This is explained by the fact that the temperature and humidity at each station remain constant with time only so long as all the fish in the kiln is drying at constant rate. This occurs while the station at the upstream end of the kiln dries at constant rate. After this (i.e. after 6 hr in Figs. 4 and 5) the air reaching stations further along the kiln is rather dryer than previously [indicated by a decrease in vapour pressure in Fig. 4(c) and an increase in temperature in Fig. 4(b)] and so, while these stations are still drying under 'convection governing' conditions, the air properties are changing.

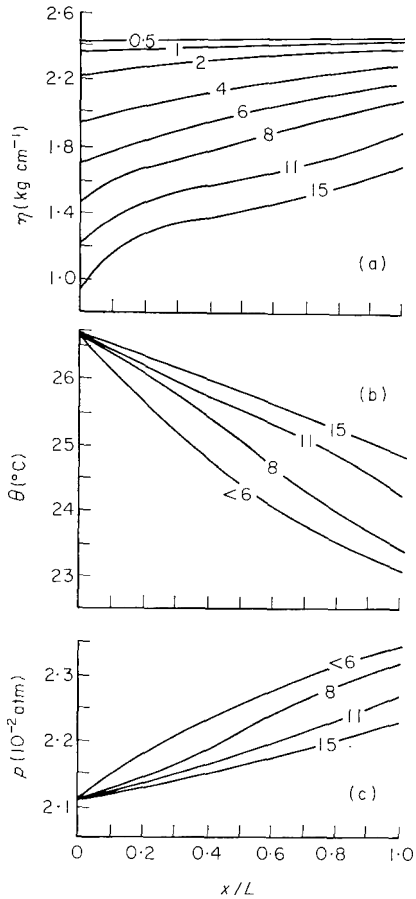



FIG. 5. Variation with distance $x/L$ along kiln at various times $t$ of: (a) fish weight per unit length $\eta$, (b) dry bulb temperature $\theta$, and (c) partial pressure $p$ of water vapour. Figures on curves indicate values of $t$ (hr).

## Comparison with real behaviour

R. M. Storey (1961) in his work on the drying of 'golden cutlets' presents two graphs. One is of the effect on drying rate of variations in mean wet bulb depression (Fig. 6) and the other gives the effect of changes in kiln loading (Fig. 7). Figs. 6 and 7 also show similar curves obtained from the computer solution using the data given in Table 1, together with the appropriate values of upstream humidity and initial loading.

Figs. 8 and 9 show the effect on the drying rate of variations in air temperature and fish thickness. The drying rate is expressed as a percentage of moisture lost per hour and is computed on the basis of a mean 13% reduction in fish weight over the entire kiln, this being roughly the normal weight loss in the drying of 'golden cutlets'.

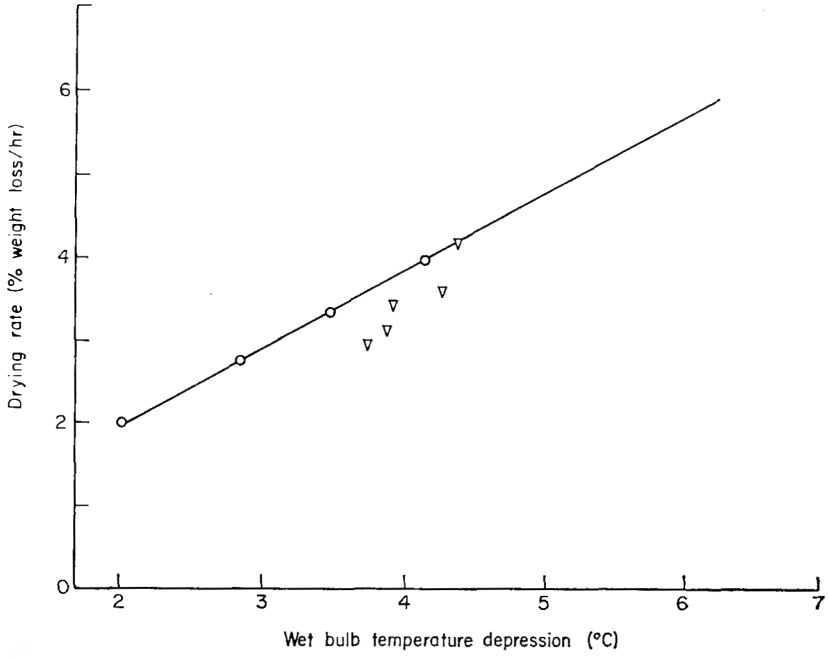



FIG. 6. Variation of drying rate with wet bulb depression. ○, Computed; ▽, measured.

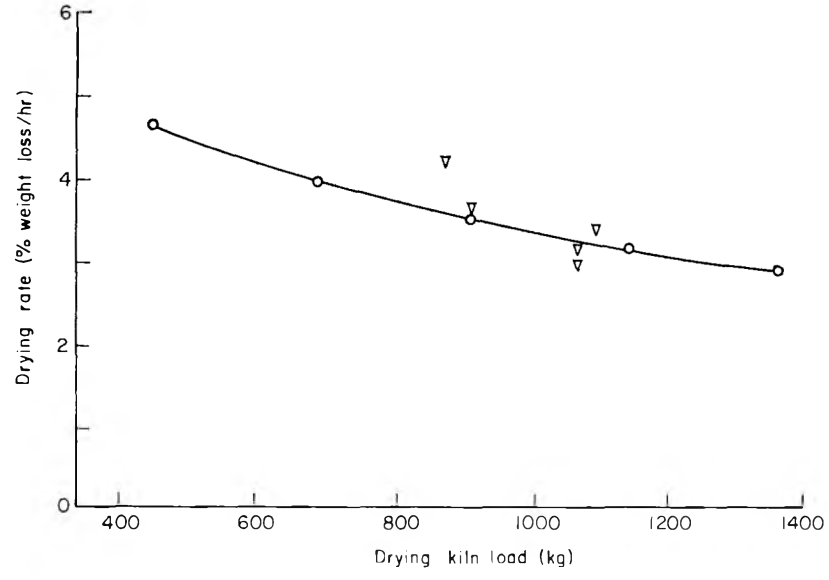



FIG. 7. Variation of drying rate with kiln loading. Key as Fig. 6.

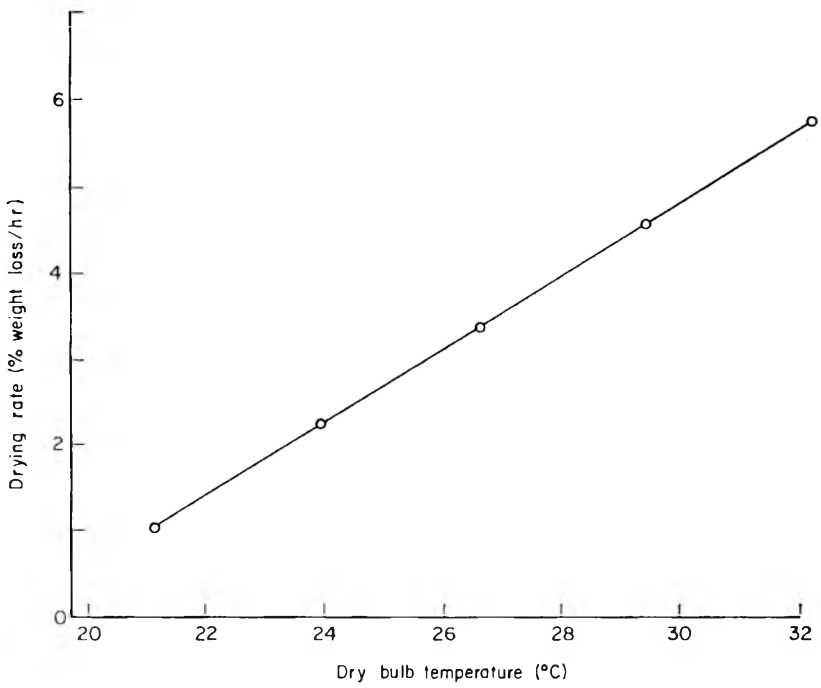



FIG. 8. Variation of drying rate with air temperature.

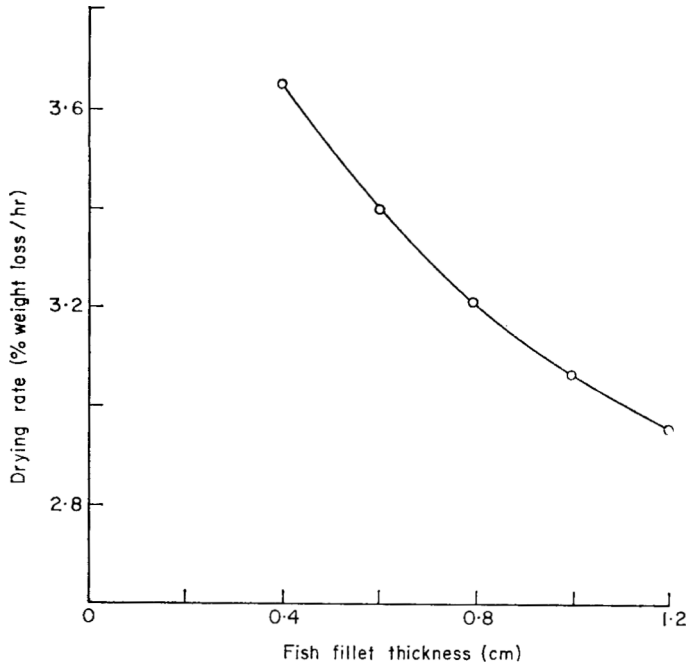



FIG. 9. Variation of drying rate with fish fillet thickness.

## Further development of the model

There are several extensions to the physical and mathematical models which would make the predicted characteristics more realistic. The effects of reheating midway along the kiln, as is practised in larger kilns, and of changing the order of the loaded trolleys within the kiln during drying, could be included. The model could be readily extended to fatty fish by the inclusion of a fat content term in the diffusivity, $D$, Jason (1965). A more complete simulation could be achieved by including the effects of varying upstream conditions during the drying cycle.

All these improvements will probably be necessary before achieving the eventual aim of this study, the selection of optimum operating conditions for automatic control of fish drying kilns.

The facility for varying the temperature and humidity of the air in a kiln throughout the drying cycle has been developed at the Torry Research Station. The immediate application of this model is in the selection of a control program for economical automatic operation of the Torry kiln for particular drying processes.

## Conclusion

The reasonable agreement between the actual and computed behaviour of the drying situation examined gives encouragement that the model will produce a reasonable prediction of many drying processes with similar geometry to that selected for the model.

## Acknowledgments

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# The use of sorbic acid in salted fish

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## Summary

It has been shown that the development of *Hemispora stellata* Vuill and red halophilic bacteria in salted snoek (*Thyrsites atun* Euph.) can be combated successfully by the use of sorbic acid during salting of the fish. Applications of sorbic acid by dipping of the fish in salt–sorbate solutions proved to be more effective than the use of a mixture of salt and sorbic acid in the salting of fish. When the preservative was mixed with the salt, a severe breakdown of sorbic acid, catalysed by fish constituents which migrated into the salt, occurred during salting. In contrast with this the sorbic acid in salted fish was shown to be rather stable.

Though the experiments were confined to limited experimental saltings, and some of the statements might not hold completely for full scale salting, it should be mentioned that in practice the application of dipping in salt–sorbate solutions also gave good protection against development of halophilic moulds and bacteria.


## Introduction

Salted fish with a salt content higher than about 10% can be spoiled by halophilic bacteria and halophilic moulds.

According to Quinta (1968) numerous mould species from different genera isolated from solar salts are osmotolerant and able to grow in media with 20% salt. The mould most frequently occurring in salted fish is the greyish brown *Hemispora stellata* Vuill (synonym: *Sporendonema epizoum* Cda, Cif and Red) which causes the so-called 'dun' although in a few cases *Penicillium stekii* Zaleski, *Aspergillus fumigatus* Fres and *Oöspora halophila* van Beyma have also been found (Lamprecht & Elliott, 1967a).

In hot dry climates in which solar salt has traditionally been available strongly halophilic bacteria may develop on the surface of salted products (Ingram & Kitchell, 1967). The red halophilic bacteria, which are active only at comparatively high temperatures, may cause a cheesy or even putrefactive off-odour and a red dis-

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coloration of salted fish. In contrast with mined salts, solar salts can be an important source of these bacteria (Michaud & VanDemark, 1967). About 70% of 108 samples of South African solar salts, tested for the presence of red halophilic bacteria in the period of 1955–67, were found to be contaminated (Doesburg, Lamprecht & Elliott, 1967). These bacteria, however, are not indigenous only to environments containing high salt concentrations, but are widespread in other environments, e.g. water supplies and soil (Michaud & VanDemark, 1967).

Boyd & Tarr (1954, 1955) showed that sorbic acid (SA) can be used for the control of 'dun', but did not find it to be very effective against red halophilic bacteria. It was also found that SA is rather stable in fish muscle. However, since SA (*trans*-2, *trans*-4 hexadienic acid) is an unsaturated fatty acid and oxidative rancidity is known to occur in salted fish, the study of the effect of SA on red halophilic bacteria and halophilic moulds was combined with some further observations on the fate of SA during the salting and storage of snoek (*Thyrsites atun* Euph.).

## Experimental and results

*Micro-organisms used*

The mould *H. stellata* Vuill was isolated from salted snoek and cultured on the medium of Schoop (1937), which contains 10–12% salt. Red halophilic bacteria isolated from different South African solar salts were grown on skim milk salt (SMS) agar, containing 20% salt (Dussault & Lachance, 1952).

*Determination of sorbic acid*

Determinations of SA were made according to the method of Melnick & Luckmann (1954) using the compact steam distillation apparatus of Schmidt (1960).

In Tables 3–6 the results of determinations of SA in fish which was not treated with the preservative are given in parentheses, since these values may well be due to the presence of interfering substances (Melnick & Luckmann, 1954). In order to make a differentiation between the true and apparent SA contents the blank values of non-treated samples were subtracted from SA readings obtained on the corresponding treated samples.

*Salt*

The salt used in the fish salting experiments was a coarse South African solar salt which was sterilized at 93°C for 2 hr (Lamprecht & Elliott, 1967b).

*Effect of sorbic acid on* H. stellata *Vuill*

The effect of SA on the growth of *H. stellata* Vuill at 20°C was tested by inoculating Schoop's medium to which the equivalent of 0, 0·05, 0·10, 0·15 or 0·20% of SA was added using commercial potassium sorbate of known purity. The effect of these

concentrations was tested at five pH levels of the sterilized medium, i.e. pH 5·0, 5·5, 5·8, 6·0 and 6·5 obtained by adjustment to slightly higher pH values by the dropwise addition of hydrochloric acid or sodium hydroxide solutions before sterilization. The mean recovery of SA was 98·6% before and 94·4% (87–98%) after sterilization of the media. The observations on the development of the mould during incubation for 80 days are recorded in Table 1. In the absence of SA the first visible growth was not affected by a variation of the pH from 5·0 to 6·5, but at the lower pH values sporulation was somewhat retarded. At pH 5·8 and lower, 0·05% SA was sufficient to inhibit mould growth completely. At pH 6·0 and 0·05% or 0·1% SA the first signs of growth were only slightly retarded but sporulation did not occur, and at this pH value no growth took place in the presence of 0·15% SA or more. At pH 6·5 the development was retarded only by 0·20% SA, but no sporulation occurred in concentrations of 0·1% SA and above.

TABLE 1. Effect of sorbic acid in Schoop medium at different pH values on halophilic brown mould

| Concentration of sorbic acid in medium(%) | Incubation time required for first appearance of growth at 20°C (days) | | | | |
|---|---|---|---|---|---|
| | pH 5·0 | pH 5·5 | pH 5·8 | pH 6·0 | pH 6·5 |
| No sorbic acid (control) | 4 (14)* | 4 (12) | 5 (12) | 4 (9) | 4 (9) |
| 0·05 | No growth | No growth | No growth | 9 (no) | 4 (60) |
| 0·1 | No growth | No growth | No growth | 9 (no) | 4 (no) |
| 0·15 | No growth | No growth | No growth | No growth | 6 (no) |
| 0·20 | No growth | No growth | No growth | No growth | 12 (no) |

* Figures in parentheses: incubation time required for sporulation.

*Effect of sorbic acid on red halophilic bacteria*

Equivalents of potassium sorbate in order to give 0·1–0·5% SA were added to SMS agar and the pH values were adjusted before sterilization to obtain pH values of 5·5, 6·0 or 6·5 in the sterilized media. The mean recovery of added SA was 97·1%. The observations on the bacterial growth during incubation for 70 days at 37°C are listed in Table 2. The preservative was fully effective in concentrations of 0·2–0·5% and 0·3–0·5% at pH 5·5 and pH 6·0, respectively.

*Preliminary experiments on fish*

Pieces (each about 60 g) from a commercial sample of lightly salted snoek were subjected to a further Kench salting (Jarvis, 1950; Legendre, 1967) for 14 days at 20°C.

Alternating layers of salt and fish at a ratio of 3 : 10 were packed in wooden boxes (15-cm cubicals), the top and bottom layers being salt. The salt contained nil, 0·05, 0·1 or 0·2% SA (from potassium sorbate), the distribution of the potassium sorbate in the salt having been carefully checked. Six fish pieces per treatment were, after salting,

TABLE 2. Effect of sorbic acid in skim milk salt medium at different pH values on red halophilic bacteria

| | pH 5·5 | | pH 6·0 | | pH 6·5 | |
|---|---|---|---|---|---|---|
| Concentration of sorbic acid in medium (%) | Incubation time (days)* | Amount of growth | Incubation time (days)* | Amount of growth | Incubation time (days)* | Amount of growth |
| No sorbic acid (control) | 6 | Slight | 5 | Fair | 5 | Fair |
| 0·1 | 13 | Very slight | 6 | Slight | 6 | Slight |
| 0·2 | No growth | None | 26 | Very slight | 7 | Slight |
| 0·3 | No growth | None | No growth | None | 19 | Slight |
| 0·4 | No growth | None | No growth | None | 20 | Slight |
| 0·5 | No growth | None | No growth | None | 28 | Very slight |

* Incubation time required for growth at 37°C.

TABLE 3. Characteristics of fish after Kench salting of lightly salted fish and development of mould growth during 6 months storage

| | Characteristics of fish | | | | Observations on mould growth (20°C) | | |
|---|---|---|---|---|---|---|---|
| Concentration of SA in the salt used (%) | SA content (%) | Moisture content (%) | Salt content (%) | pH | Incubation time (days)† | Pieces‡ | Days§ |
| No SA | (0·0012)* | 51·1 | 18·0 | 5·2 | 14 | 6 | 30 |
| 0·05 | 0·0052 | 49·4 | 18·3 | 5·4 | 20 | 6 | 52 |
| 0·10 | 0·0082 | 45·3 | 18·2 | 5·5 | 35 | 5 | 186 |
| 0·20 | 0·0220 | 44·6 | 19·3 | 5·5 | No growth | 0 | – |

* Apparent SA content.
† Incubation time required for first growth.
‡ Total No. of pieces out of six finally showing growth.
§ No. of days required for development.

inoculated with a spore suspension of the brown mould, placed in sterile Petri dishes and incubated for 6 months at 20°C at 75% relative humidity. The results of SA determinations on fish after the salting and the observations on mould growth during storage are given in Table 3. Mould growth was completely suppressed during 6 months only when the fish was treated with salt containing 0·2% SA, giving a SA of 0·02% in the fish and a pH 5·5.

*Kench salting experiments*

The following tests were carried out according to salting procedures used in practice.

Fresh snoek were headed and gutted and the split fish cut into pieces of approximately uniform size (8 × 5 × 1·5 cm) and weight (60 g). According to the normal salting practice the fish were then subjected first to pickle salting (Legendre, 1967) for 36 hr at 20°C; about 18 kg of fish pieces were packed in a polythene-lined container in twenty-four layers, skin up and down alternately, with twenty-five layers of salt. A weight was placed on the lid resting on the upper layer of salt. The ratio of the weights of salt to fish was 1 : 4. After this pickling period about 4·1 kg of drip was formed from 17·9 kg fish. The drip was removed and the drained fish pieces randomly divided into different lots, which were used in the following experiments.

One part was Kench salted by packing the fish in layers with salt in a ratio 7 : 1 in wooden boxes beneath weights as before. The sides of the boxes and the lids were covered with polythene and a square of expanded aluminium was placed at the bottom of each box to assist drainage. The boxes were stored for 14 days at 20°C. The excess salt was then scraped off the fish and the fish was again salted in the same way with fresh salt and stored for 3 weeks at 20°C. During the second Kench salting, salt was used containing nil, 0·05, 0·10 or 0·20% SA or the equivalent amount of potassium sorbate. Six pieces per treatment were then inoculated with a suspension of spores of *H. stellata* Vuill or with a suspension of red halophilic bacteria, and placed in sterile Petri dishes and stored at 20° or 37°C, respectively.

A second batch of pieces from the pickling treatment was Kench salted once only for 14 days at 20°C using salt with the same concentrations of SA or their equivalents as potassium sorbate as just described. The fish were then inoculated and stored in the same manner. The results of the first experiment, the composition of the fish and the development of mould and halophilic bacteria after two Kench saltings, are reported in Table 4. The results of the second experiment are not reported here since they are very similar to those shown in Table 4.

The fate of SA and its distribution during salting was studied further. Two other lots of the pickled fish were used in similar experiments with SA (0, 0·1 and 0·2%) or in equivalent amounts as potassium sorbate, both in the first or second Kench salting. The 15-cm cubical boxes were made from expanded aluminium, the inner sides lined with polythene and with a fine nylon mesh covering the bottom to prevent loss of salt crystals. The filled boxes were placed in a funnel of plastic sheet leading into a bottle

to collect the drip, which was measured and analysed for SA. Drip formation ceased after 2 days in the first salting and no drip was formed in the second. Evaporation of drip was minimized during its collection. After salting the fish were scraped free of salt. The fish and the salt, which was very wet, were weighed and analysed first. The boxes and linings were washed with distilled water, the washings made up to 250 ml and also analysed for SA. The results of the analyses are shown in Table 5.

No consistent difference in the SA contents and pH values of fish treated with equivalent amounts of SA or potassium sorbate were found (Tables 4 and 5). The maximum SA levels of 0·012–0·014% in the fish after the second Kench salting were insufficient to suppress growth of mould or red halophilic bacteria (Table 4). SA contents of the fish when the preservative was applied in a Kench salting just after pickling were lower than for double salting. In the first case 7·6–19·5% of the SA was lost in the drip. The total recovery of SA from the different fractions of the salt stocks varied from 34·0 to 67·5% of the amount added, thus showing a considerable breakdown of SA during the salting procedures. Moreover, only a very small percentage of the added amount of preservative was recovered from the salt fractions (Table 5).

*Dipping experiments*

Pieces of fresh snoek, prepared and pickled as before, were dipped for 1 min in 15% salt solutions, containing 0, 0·5, 1·0, 2·0 or 4·0% potassium sorbate. After draining for 30 min, the pieces were given two subsequent Kench saltings as described earlier, using only salt without SA. Inoculation with mould spores was carried out directly after the pieces were dipped and drained. In order to test the effect of infection at a later stage some pieces were re-inoculated at the end of the salting procedure. Inoculation with red halophiles was carried out with artificially infected salt in the second Kench salting, since it was found in previous experiments that infected salt was a more effective inoculum than a bacterial suspension in a salt solution. Six pieces from each treatment were then stored in Petri dishes as described. Some pieces were re-inoculated with the mould or halophilic bacteria after 3 months storage. The results are shown in Table 6. The SA contents of the fish were rather stable during two subsequent Kench saltings; in most cases there was no, or hardly any, decrease of SA percentage and only in one case a decrease of about 33% was found. No mould growth from initial infections took place in 6 months, even at the lowest SA content (0·01%) in the fish. When pieces from different treatments were re-inoculated after 3 months storage, mould developed $2\frac{1}{2}$ months later only on fish previously dipped in the solution containing 0·5% potassium sorbate. Growth of red halophilic bacteria was prevented for 4 months by dipping in a solution containing 1% or more potassium sorbate. Re-inoculation of red halophiles, also carried out after 3 months storage, caused some growth on some of the fish pieces previously dipped in 0·5–4·0% potassium sorbate solutions. Similar results were obtained in a similar experiment not reported here.

TABLE 4. Characteristics of fish after second Kench salting and microbial development during 9 months storage of fish species

| Concentration of SA in the salt used (%) | Characteristics of fish | | | | Observations on mould growth at 20°C | | | Observations on growth of red halophilic bacteria at 37°C | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SA content (%) | Moisture content (%) | Salt content (%) | pH | Incubation time (days)* | Pieces† | Days‡ | Incubation time (days)* | Pieces† | Days‡ |
| No SA | (0·0030) | 43·8 | 17·1 | 5·6 | 15 | 6 | 28 | 58 | 5 | 70 |
| SA used: | | | | | | | | | | |
| 0·05 | 0·0024 | 39·6 | 16·7 | 5·6 | 21 | 6 | 43 | No growth | 0 | – |
| 0·10 | 0·0056 | 40·1 | 16·2 | 5·5 | 35 | 6 | 43 | 58 | 1 | 58 |
| 0·20 | 0·0140 | 40·1 | 16·2 | 5·4 | 35 | 4 | 266 | 128 | 1 | 128 |
| K-sorbate used: | | | | | | | | | | |
| 0·05 | 0·0022 | 40·5 | 15·9 | 5·4 | 21 | 6 | 42 | No growth | 0 | – |
| 0·10 | 0·0051 | 40·9 | 16·6 | 5·5 | 43 | 6 | 64 | 58 | 4 | 63 |
| 0·20 | 0·0125 | 44·0 | 17·1 | 5·7 | 43 | 6 | 266 | 58 | 1 | 58 |

* Incubation time required for first growth.
† Total No. of pieces finally showing growth.
‡ No. of days required for development.

TABLE 5. Distribution of recovered SA over various fractions after Kench salting

| SA content in added salt (%) | Preservatives used in first Kench salting | | | | | | | Preservatives used in second Kench salting | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | SA content in fish (%) | SA content in salt (%) | % recovery of added SA from fractions of Kench cure | | | | | SA content in fish (%) | SA content in salt (%) | % recovery of added SA from fractions of Kench cure | | | |
| | | | Fish | Salt | Drip | Wash | Total | | | Fish | Salt | Wash | Total |
| SA used: | | | | | | | | | | | | | |
| 0·1 | 0·0035 | 0·0015 | 23·6 | 0·9 | 7·6 | 1·9 | 34·0 | 0·0071 | 0·0010 | 47·7 | 1·0 | 3·0 | 51·7 |
| 0·2 | 0·0148 | 0·0037 | 49·3 | 1·1 | 16·1 | 1·0 | 67·5 | 0·0156 | 0·0027 | 51·6 | 1·4 | 2·3 | 55·3 |
| K-sorbate used: | | | | | | | | | | | | | |
| 0·1 | 0·0065 | 0·0040 | 43·0 | 2·3 | 18·1 | 1·8 | 65·2 | 0·0065 | 0·0060 | 43·2 | 6·4 | 1·5 | 51·2 |
| 0·2 | 0·0101 | 0·0021 | 36·6 | 0·5 | 19·5 | 1·7 | 58·3 | 0·0152 | 0·0084 | 50·4 | 4·3 | 2·3 | 56·6 |
| Control | (0·0027) | (0·0029) | — | — | — | — | — | (0·0049) | (0·0013) | — | — | — | — |
| Average | — | — | 38·1 | 1·2 | 15·3 | 1·6 | 56·2 | — | — | 48·2 | 3·3 | 1·1 | 52·6 |

TABLE 6. Characteristics of fish after dipping and two Kench saltings, and microbial development from initial infections during 6 months storage

| Concentration of K-sorbate in solutions used for dipping (%) | Characteristic of fish: SA content After dipping (%) | SA content After Kench cure (%) | Moisture content (%) | Salt content (%) | pH | Observations on mould growth at 20°C: Incubation time (days)† | Pieces‡ | Days§ | Observations on growth of red halophilic bacteria at 37°C: Incubation time (days)† | Pieces‡ | Days§ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| No sorbate | (0·003) | (0·003) | 43·7 | 16·8 | 5·8 | 22 | 6 | 42 | 38 | 4 | 59 |
| 0·5 | 0·010 | 0·011 | 48·5 | 20·0 | 5·8 | No growth* | 0 | — | 59 | 2 | 73 |
| 1·0 | 0·026 | 0·025 | 46·9 | 18·4 | 5·8 | No growth | 0 | – | No growth* | 0 | – |
| 2·0 | 0·064 | 0·043 | 46·1 | 18·7 | 5·9 | No growth | 0 | – | No growth* | 0 | – |
| 4·0 | 0·115 | 0·107 | 42·5 | 18·0 | 5·9 | No growth | 0 | – | No growth* | 0 | – |

* Growth occurred about 2½ months after re-infection of some pieces after 3 months storage.
† Incubation time required for first growth.
‡ Total No. of pieces finally showing growth.
§ No. of days required for development.

*Sorbic acid content of fish stored at different temperatures*

Fish pieces from a similar dipping-Kench cure treatment, which were dipped in a 15% salt solution containing 1% potassium sorbate, were stored in closed jars at 0°, 20° or 30°C. The air in the jars was refreshed twice a week. The SA content (0·03%) was constant over a period of 158, 103 or 70 days when the fish was stored at 0°, 20° or 30°C, respectively. After 158 days the SA contents of the pieces stored at 20° or 30°C were 0·024 and 0·021%, respectively.

*Mechanism of breakdown of sorbic acid*

According to Tappel (1953) the haeme compounds are the predominant catalysts for oxidation of unsaturated fatty acids in animal tissue. This haematin catalysed oxidation can be inhibited by the presence of $2 \times 10^{-2}$ M KCN (Tappel, 1962), whereas

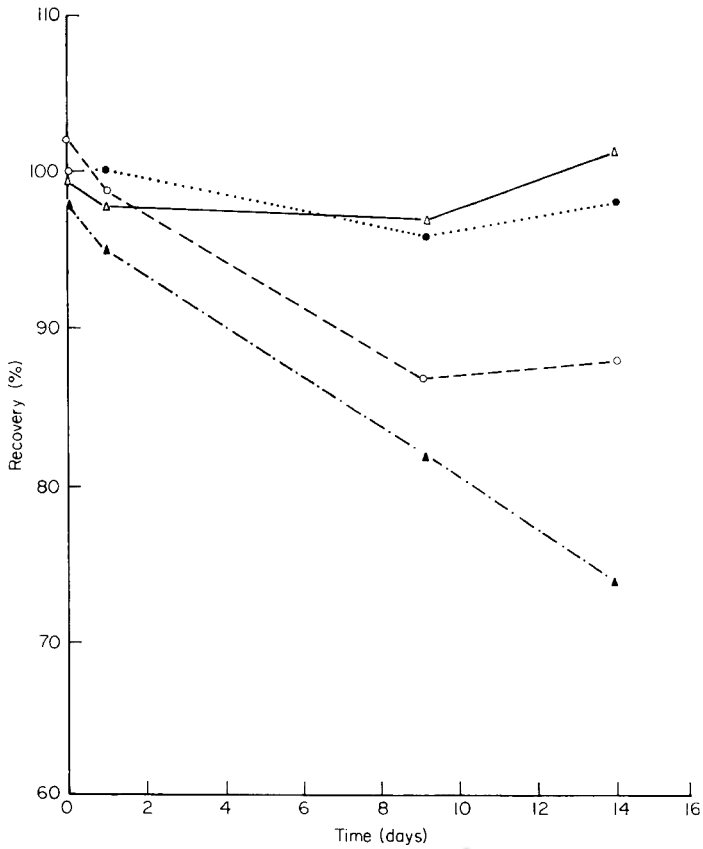


FIG. 1. Percentage recovery of added SA from stored mixtures of salted snoek, water and salt with (○) and without (▲) the addition of 0·03 M KCN, and from water–salt mixtures with (●) and without (△) 0·03 M KCN.

oxidation catalysed by heavy metals (iron and copper) is not, or only very slightly, influenced by cyanide (Chang & Watts, 1950). According to Melnick, Luckmann & Gooding (1954) and Marth *et al.* (1966) the presence of mould may form an additional cause of SA breakdown; this is also inhibited by KCN.

To investigate some aspects of the breakdown of SA during salting of snoek the behaviour of SA was studied in mixtures of salt–water and of minced salted snoek and salt. In some cases 0·03 M KCN was added to the non-salt part of the mixtures. A slurry of 80 g salted snoek and 120 g water was prepared in a Waring blendor. Twenty-five-gram aliquots of this slurry were thoroughly mixed with 218 mg potassium sorbate or with 218 mg potassium sorbate and 50 mg KCN and each aliquot mixed with 300 g of the salt as used as in the previous experiments. One hundred and twenty grams of these mixtures were spread over the bottom of 14-cm Petri dishes and placed at 20–22°C in a desiccator.

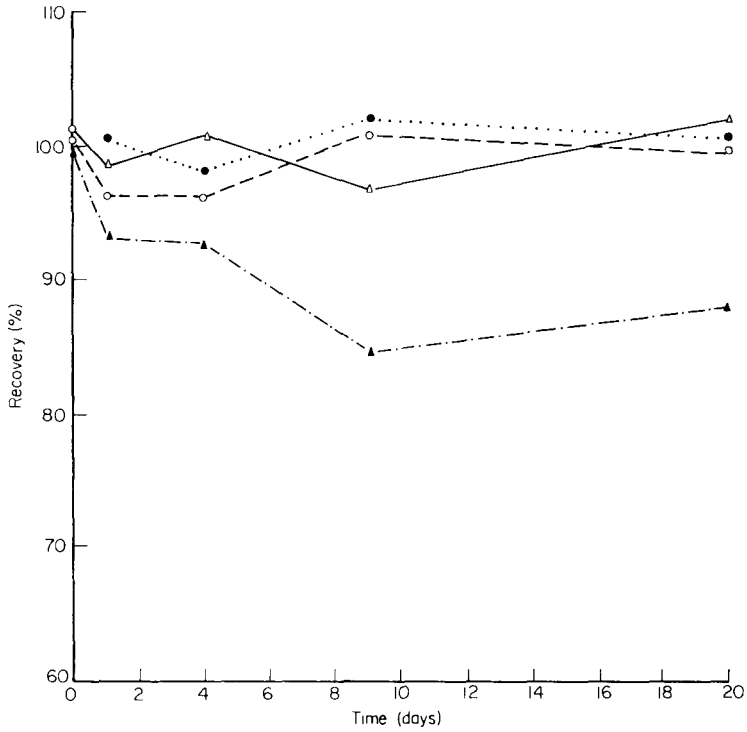


FIG. 2. Percentage recovery of added SA from stored mixtures of salted horse mackerel, water and salt with (○) and without (▲) the addition of 0·03 M KCN, and from water–salt mixtures with (●) and without (△) 0·03 M KCN.

In parallel experiments the snoek was replaced by water with the same salt content as the salted fish. Since the salted snoek used in this experiment was some months old and at that time fresh snoek was not available, fresh horse mackerel (*Trachuris capensis* Cast.) was salted and used in a similar experiment. Samples of the different snoek–salt, horse mackerel–salt and water–salt mixtures were assayed for their SA contents after different periods of storage. The amounts of recovered SA calculated as a percentage of the initial amount of SA are plotted in Figs. 1 and 2. In mixtures of water and salt the amount of SA showed to be constant. In mixtures with salt, water and minced salted fish, however, a breakdown of SA occurred which could be inhibited partially by 0·03 M KCN in the presence of minced salted snoek and completely when minced salted horse mackerel was used.

## Discussion

The ability of various species of moulds to grow at different concentrations of SA varies considerably. According to Marth *et al.* (1966) various *Penicillium* species isolated from cheese were able to grow in the presence of 1800 ppm potassium sorbate (equivalent to 1393 ppm SA) when potato dextrose agar with a pH 5·3–5·5 served as the substrate, and some moulds even developed in the presence of 7100 ppm potassium sorbate (5230 ppm SA). On grapejuice adjusted to pH 5·7 moulds from different genera showed growth in the presence of 745 ppm SA (Dudman, 1963) whereas the growth of *H. stellata* Vuill on the medium of Schoop (1937) adjusted to pH values ranging from 5·0 to 5·8 was completely inhibited by 500 ppm SA (Table 1). The maximum SA concentration at which growth is initiated seems to be species dependent (Marth *et al.*, 1966), but there are several indications that the sensitiveness of micro-organisms (yeasts, *Lactobacillus plantarum*) to SA is increased with an increasing salt content of the culture media (Costilow, Ferguson & Ray, 1955; Costilow *et al.*, 1957; Rehm, 1962). The action of NaCl is synergistic with those of various other inhibiting agents (Ingram & Kitchell, 1967). Therefore, it could be that the high sensitivity of *H. stellata* Vuill to SA as found in Schoop's medium (10–12% salt) is partially due to the high salt concentration and that this sensitivity is even greater at higher salt concentrations such as found in salted fish.

In several cases low average SA percentages (e.g. 0·02%) in foodstuffs were shown to be sufficient for suppression of mould growth, but these percentages are mostly related to initially high surface concentrations, e.g. in cheese. The beneficial effect of the same average percentages is decreased when the surface concentration is diluted by penetration of the preservative into the product (Melnick *et al.*, 1954). This may also apply to salted fish treated with SA. Though the SA content of salted snoek stored at 20°C was shown to be stable for more than 5 months and an initial infection with *H. stellata* Vuill on snoek dipped in a solution with 0·5% potassium sorbate failed to develop, a second infection after 3 months storage caused growth of the mould (Table 6).

As shown by Boyd & Tarr (1954, 1955) the development of 'dun' on salted ling-cod could be prevented by use of 0·1% SA in the salt used for Kench curing with a ratio of salt to fish of 1 : 3·5 (Jarvis, 1950). Unfortunately the corresponding SA percentage and the pH of the fish are not listed; the use of salt with 0·2% SA gave a content of 0·032–0·037% in the fish.

Since good quality salted snoek has a pH lower than 6·0, small quantities of SA in the fish may control the development of 'dun' (Table 1). According to the results listed in Tables 3 and 4 the average SA percentages of 0·008–0·014% obtained by use of SA during Kench salting were not sufficient to inhibit mould growth, but an average percentage of 0·01% obtained by dipping in SA solutions completely inhibited mould growth from an initial infection (Table 6). An average SA content of 0·02% obtained by Kench curing was shown to suppress the development of an initial infection (Table 3).

A discrepancy was also found for SA contents (0·2–0·3%) necessary to inhibit red halophilic bacteria on SMS agar (Table 2), and the effective average SA contents in fish. The low SA values (0·0022–0·0140%) obtained by the application of SA during Kench curing gave some protection against initial infection (Table 4) and 0·025% SA in the fish after dipping caused a full inhibition of an initial infection. However, after re-infection 3 months later, red halophiles developed on fish with an initial SA content of 0·025–0·115% (Table 6). These differences can be explained again by an uneven distribution of SA in the fish and in the total salt stock during Kench curing. During Kench curing the distribution of SA may depend on the ratio salt to fish, the contact between salt and fish, variation of pressure in the salt stock, and the evenness of distribution of salt between the fish. The SA breakdown and loss in the drip (Table 5) may be different at various places in the salt stock. These factors may account for the irregular results in growth of mould and red halophilic bacteria after application of SA during Kench curing (Table 4). Moreover, analyses of individual layers of fish species showed a rather great variation in SA contents. These factors, especially the evenness of distribution of salt, may be expected to play a greater role under practical conditions.

The analyses of SA in various fractions after Kench curing showed that an appreciable loss of the added preservative occurred (Table 5). The SA content of the fish was in most cases higher when the preservative was used in the second Kench salting which can be explained by the extra loss in the drip in the first Kench salting. From the results shown in Figs. 1 and 2 it is clear that breakdown of SA is catalysed by fish constituents, since no breakdown occurred in the absence of fish material. The low recovery of SA from the salt fraction and the higher contents in the fish (Table 5) showed that the breakdown took place mainly in the salt fraction where it appears to be catalysed by fish constituents which migrated into the salt. These results confirmed also that the SA is much more stable in the fish, probably as a result of reduced access of air or protection by fat-soluble antioxidants (e.g. tocopherols) in the fish, which do not migrate into the salt fraction.

In mixtures of minced salted horse mackerel, salt and water (Fig. 2) the breakdown of SA was completely inhibited by the presence of $3 \times 10^{-2}$M KCN and partially in similar mixtures with salted snoek (Fig. 1). Since no mould growth could be detected in the materials used in these tests, this inhibition of SA breakdown indicated that oxidation catalysed by haeme compounds was important. Under practical conditions the degree of bleeding of the fish may be expected to influence the stability of SA in a Kench cure.

The non-inhibited part of the breakdown in the presence of salted snoek might be attributed to oxidation catalysed by heavy metals. It is difficult, however, to account exactly for the differences in the presumed metal-catalysed oxidation in salted snoek and horse mackerel, since fish muscle from different species were found to show considerable differences in the relative susceptibility to rancidity induced by specific metals (Castell & Spears, 1968). These differences may depend on different metal and lipid concentrations and the metal-binding capacity of non-lipid constituents.

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# Rheological characteristics of processed whole egg

S. J. CORNFORD, T. L. PARKINSON AND J. ROBB


## Summary

Flow curves determined with a rotational Viscometer have shown that unfrozen raw and pasteurized liquid whole egg are Newtonian fluids and that thawed frozen whole egg is pseudo-plastic. For the latter a useful value for comparative purposes may be obtained by calculating the apparent viscosity at a selected low rate of shear. Some preliminary results illustrate the very large difference in viscosity between unfrozen egg and thawed frozen egg.


## Introduction

Pasteurized liquid egg is supplied to the bakery trade in the chilled or frozen state for use in flour confectionery. The pasteurization process is as follows: The egg, which may be either freshly broken out shell egg or defrosted frozen egg, is thoroughly well mixed in a holding tank and passed first through a heat exchanger, in which it flows regeneratively against hot pasteurized egg, then through a hot water circulating system where it is raised to the correct pasteurizing temperature (at least 64·4°C, and from which it flows into the holding unit maintained at that temperature. It then passes back through the heat exchanger, then through a section cooled by chilled water. After this it is either filled into cans and frozen or delivered immediately to bakeries as chilled pasteurized egg in bulk tankers or in churns.

A widespread belief exists in the bakery trade that the viscosity ('body') of liquid egg is associated with its performance in the bakery, a 'thin' sample being regarded as inferior to a 'thick' one. However, very little work on the actual measurement of egg viscosity has been reported in the literature, and there is no consensus of opinion on which method of measurement should be employed. Thomas & Bailey (1933) and Pearce & Lavers (1949) used a perforated disc to measure resistance to penetration, and Wertheim (1964) employed a falling sphere viscometer provided with an electrical detector. Payawal, Lowe & Stewart (1946) reported that pasteurization of fresh whole egg caused only a slight increase in viscosity, which they measured with a specially designed capillary viscometer. Sugihara, Ijichi & Kline (1966) used both the Brook-

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field RVT rotating viscometer and the Corn Industries recording viscometer to study the consistency of pasteurized egg that had been frozen and thawed. Only two results obtained with the Brookfield instrument were quoted, all the other results given in their paper having been obtained with the Corn Industries recording instrument. The latter has only one rate of shear and is, therefore, a single-point instrument and cannot be used to obtain flow curves relating shear stress to rate of shear. Such curves would enable the rheological character of the egg product to be determined and would provide information useful for comparing one sample with another. Wachs & Johnsson (1964) used a Haake 'Rotavisko' to obtain flow curves for model systems composed of egg yolk, water and decalin and also presented curves relating 'viscosity' to rate of shear for fresh, preserved and pasteurized egg yolk. A search of the literature failed to reveal any record of flow curves for liquid whole egg although Mayo & Baker (1965), who used a Brookfield Synchroelectric Viscometer, stated that 'fresh whole egg magma fulfils the requirements of a Newtonian fluid while the frozen-thawed egg magma does not'. It was, therefore, considered necessary to make a detailed study of this aspect of the problem.

## Materials and methods

*Egg samples*

'Raw egg' was a sample of unpasteurized melange taken from the float tank of a commercial pasteurizing plant, 'frozen egg' was pasteurized egg that had been frozen, stored in the frozen state and defrosted overnight when required, and 'pasteurized egg' was standard pasteurized raw egg supplied in the chilled state. The 'frozen' samples originated from the same batch but the 'raw' and 'pasteurized' samples were all derived from different batches on different days. All samples were supplied by the British Egg Marketing Board, and all were kept at 21·1°C (70°F) overnight before measurement; in the case of frozen egg, this was defrosted before overnight storage at 21·1°C (70°F).

*Baking tests*

Sponge cakes were made and measured as described by Knight *et al.* (1967) using the 'all-in' method.

*Viscometry*

All measurements were made with an Epprecht-Rheomat 15 Viscometer, manufactured by A. G. Epprecht Ltd (Zurich). This is a rotational viscometer and has been described under the name 'Drage Rheometer' by Van Wazer *et al.* (1963). It is supplied with cups and bobs of various sizes and has a total of fifteen possible speeds. The driving motor, bob, etc., are suspended by a torsion wire and when the motor turns the shaft, viscous drag sets up a reaction which is offset by a torsion spring, the

resultant torque being indicated by a pointer and dial. The dial reading is proportional to shear stress ($\tau$), to which it may be converted by multiplication by a suitable factor. The factor is obtained from tables supplied with the instrument which also give the appropriate rates of shear for each cup–bob–speed combination and factors for calculating the viscosity (of Newtonian fluids) or 'apparent viscosity' (of non-Newtonian fluids). The largest cup and bob combination (System 'A', covering the viscosity range 5–480 cP was used in all cases. The cup has a depth of 135 mm and internal radius of 24 mm, and the bob has an overall length of 98·5 mm with the middle cylindrical section having a length of 57 mm and a radius of 22·8 mm. This means that there is a fall in shear stress of 10% across the gap between bob and cup. It must be pointed out, however, that this is characteristic of all concentric coaxial measuring systems and that this instrument is designed to work over a certain range of shear stresses and not on a single given stress. The viscometer was kept permanently in a constant temperature room maintained at 21·1°C (70°F).

## Results

The various relationships studied are expressed as graphs and it is convenient to classify the results according to the type of graph plotted. Only typical curves are shown for each group.

*Shear stress and rate of shear*

As the dial reading is directly proportional to shear stress, it is convenient to plot the scale reading on one axis and the rate of shear (read off a special scale provided with the instrument) on the other. Results are given in Figs. 1 and 2. The linear relationships shown in Fig. 1(a) and (b) for raw liquid whole egg and chilled pasteurized whole egg are characteristic of Newtonian fluids whereas the curves obtained with thawed frozen pasteurized egg (Fig. 2) are characteristic of pseudo-plastic materials. Consequently, for raw and for chilled pasteurized egg, viscosity is independent of the rate of shear and may be determined by multiplying the scale reading for a given speed setting by the factor for that speed given in the tables supplied with the instrument. Applying the same factors to the pseudo-plastic thawed frozen egg produces a different 'apparent viscosity' for each speed and it has been noted that the 'apparent viscosity' falls as the bob speed increases.

Later examinations of thawed frozen whole egg samples showed that when the speed of rotation of the bob was first increased to a maximum and then decreased, the scale readings on the downward run were lower than those that had been obtained on the upward run, demonstrating the thixotropic nature of this material.

For such materials it is worth examining relationships other than the direct one shown in Figs. 1 and 2 and the plots shown in Figs. 3, 4 and 5, and discussed below, are relationships sometimes used in rheological studies.

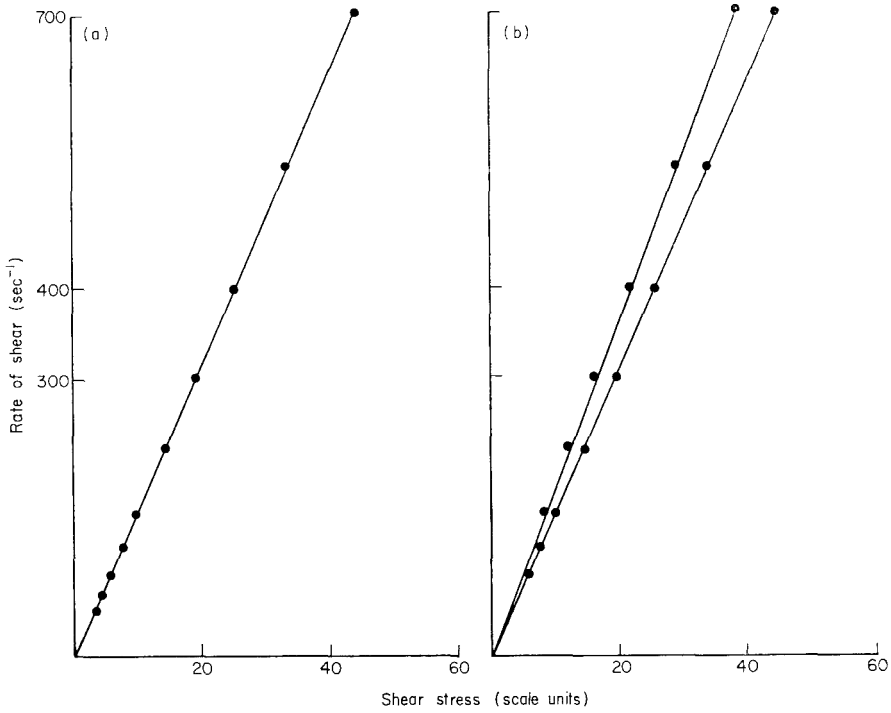


FIG. 1. Flow curves for: (a) raw liquid whole egg, and (b) chilled pasteurized whole egg.

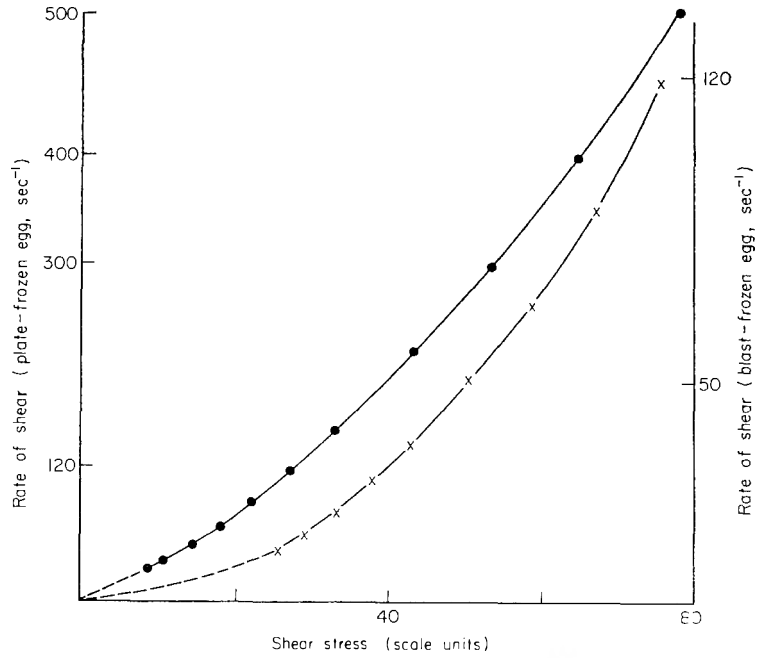


FIG. 2. Flow curves for thawed plate-frozen (●) and blast-frozen (×) pasteurized whole egg.

*log (shear stress)* versus *log (rate of shear)*

For pseudo-plastic materials this relationship should be linear and Fig. 3 shows that this is so for frozen pasteurized whole egg that has been defrosted, irrespective of the method used for freezing the egg. The divergence between the two lines representing blast-frozen and plate-frozen eggs emphasizes the difference in viscosity produced by these two treatments.

*'Apparent viscosity'* versus *log (rate of shear)*

For frozen pasteurized egg, calculation of 'apparent viscosity' for each speed of rotation, by applying the factors given in the table supplied with the viscometer, leads to a set of values that decrease steadily as the rotational speed of the bob increases.

A plot of apparent viscosity against log (rate of shear) for two typical samples of frozen and thawed pasteurized egg is shown in Fig. 4. The curves obtained are non-linear, but show that values of apparent viscosity obtained at a single rate of shear are suitable for making comparisons between different samples. The differences are rather more divergent at lower speeds of rotation and so it is better to choose a low speed for determining the apparent viscosity of these samples.

*Square root of shear stress* versus *square root of shear rate*

When these square roots are plotted against each other, as in Fig. 5, the relationship for blast-frozen egg appears to be linear and to be capable of extrapolation to the base-line to give a pseudo-yield value which is characteristic of the material, but that for the plate-frozen egg is linear only over the range of higher speeds of rotation and deviates from linearity at lower speeds.

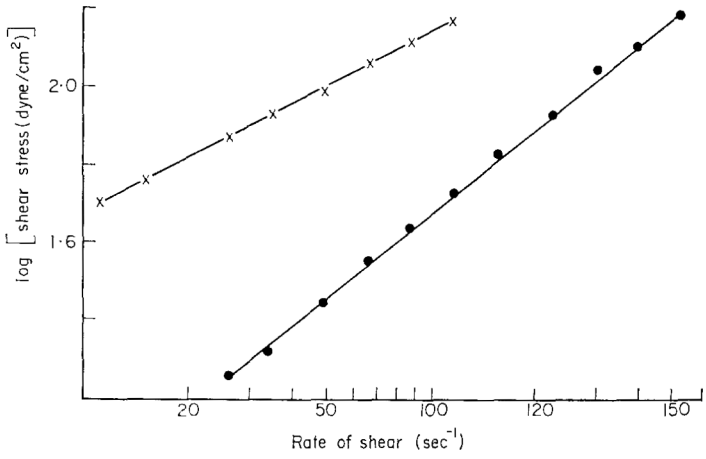


FIG. 3. Relationship between logarithms of shear stress and rate of shear for thawed plate-frozen (●) and blast-frozen (×) pasteurized whole egg.

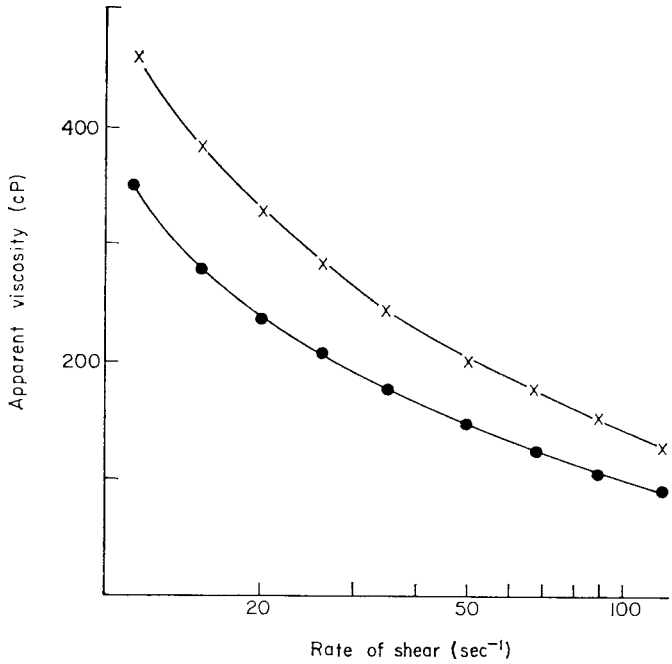


FIG. 4. Relationship between 'apparent viscosity' and logarithm of rate of shear for thawed plate-frozen (●) and blast-frozen (×) pasteurized whole egg.

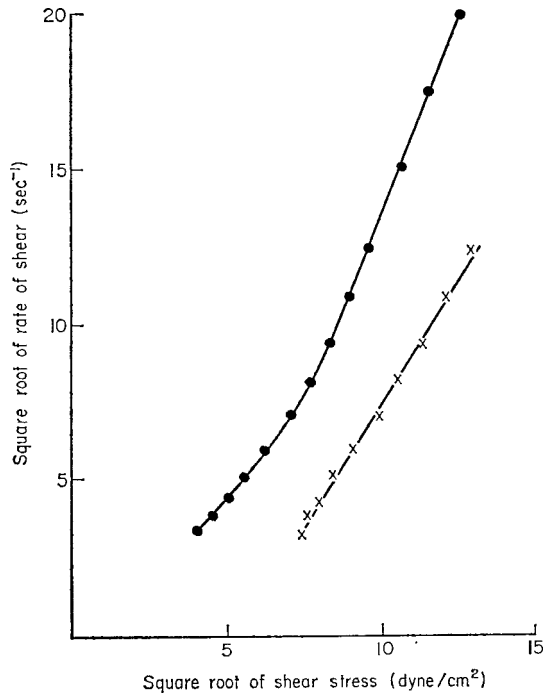


FIG. 5. Relationship between square roots of shear stress and rate of shear for thawed plate-frozen (●) and blast-frozen (×) pasteurized whole egg.

*Results on liquid egg samples*

The viscosity of unfrozen egg, being independent of the rate of shear, was calculated for each speed of rotation used and the mean of these results recorded for each sample. A sample of raw whole liquid egg, taken from the float tank of a pasteurizing plant, had a mean viscosity of 12·3 cP. The results obtained on a series of unfrozen pasteurized whole egg samples are recorded in Table 1, together with the specific volumes of sponge cakes prepared from the same samples.

From the results recorded above for thawed frozen whole egg it was concluded that the 'apparent viscosity' calculated from the scale reading obtained at a low rate of shear would be suitable for comparing the consistencies of such egg samples. Table 2 quotes results obtained on samples of thawed egg that had been frozen by two different methods (plate-freezing and blast-freezing) and then stored at −11·1 to −8·9°C (12–16°F). At intervals during the storage period samples were withdrawn from the cold store, defrosted overnight in running cold water and examined for viscosity and baking quality.

Inspection of the few results given in Tables 1 and 2 indicates that there is probably no correlation between the specific volumes of sponge cakes and the viscosity of the egg used. In fact correlation coefficients calculated for the group in Table 1 and the two groups in Table 2 were 0·05, 0·39 and 0·08, respectively. These suggest an absence of correlation, but it will be necessary to examine many more samples before definite conclusions may be drawn.

TABLE 1. Viscosity determinations and baking test measurements on samples of unfrozen pasteurized liquid whole egg

| Sample code | Viscosity (cP) | Specific volume (ml/g) of sponge cake |
|---|---|---|
| B | 10·5 | 5·75 |
| C | 11·8 | 5·71 |
| D | 11·1 | 5·77 |
| E | 10·7 | 6·14 |
| F | 12·1 | 5·84 |
| G | 10·5 | 6·18 |
| H | 10·8 | 5·95 |
| J | 10·5 | 6·11 |
| K | 11·8 | 5·80 |
| L | 8·8 | 6·07 |
| M | 11·8 | 6·63 |
| N | 12·4 | 5·92 |

TABLE 2. 'Apparent viscosity' determinations and baking test measurements on samples of thawed frozen pasteurized liquid whole egg

| Freezing treatment | Time in frozen storage (weeks) | Apparent viscosity (cP) at shear rate of 26·32 sec | Specific volume (ml/g) of sponge cake |
|---|---|---|---|
| Plate | 5 | 64 | 5·57 |
| | 12 | 97 | 5·45 |
| | 26 | 204 | 5·90 |
| | 43 | 119 | 5·74 |
| | 52 | 138 | 5·97 |
| | 62 | 114 | 5·92 |
| | 68 | 146 | 5·33 |
| | 75 | 187 | 5·78 |
| Blast | 5 | 289 | 5·33 |
| | 12 | 265 | 5·19 |
| | 26 | 380 | 5·93 |
| | 43 | 262 | 5·54 |
| | 52 | 253 | 6·17 |
| | 62 | 261 | 5·82 |
| | 68 | 216 | 5·49 |
| | 75 | 210 | 5·88 |

## Discussion and conclusions

The plots of rate of shear against shear stress revealed a clear distinction between frozen and unfrozen liquid whole egg. Unfrozen egg, whether raw or pasteurized, behaves as a Newtonian fluid, i.e. its viscosity is independent of the rate of shear. Thawed frozen egg, on the other hand, is non-Newtonian and its flow curves are characteristic of pseudo-plastic materials, giving values of 'apparent viscosity' that are high at low rates of shear and that fall off markedly as the rate of shear increases. These values are considerably greater than those normally found for unfrozen egg, often being about forty times as much as typical unfrozen values at the lowest rate of shear and two or three times as much at the highest rate. The present work suggests that for comparative purposes it is reasonable to determine 'apparent viscosities' at a given rate of shear, which should be as low as practicable and should be within the range investigated in the present work.

From the few results quoted only tentative conclusions may be drawn but it appears that the very great difference in viscosity between thawed frozen pasteurized egg and unfrozen pasteurized egg is not related to any difference in the specific volume of baked sponges. It is clear that, from the rheological standpoint, these are two very different materials and any attempt to correlate baking quality with the viscosity of an egg

product must necessarily be confined to a particular type of egg product, defined in terms of its starting material and processing treatment. The results in Table 2 indicate that the apparent viscosity of thawed frozen egg can be influenced not only by the method of freezing but by other factors as well. This observation is in line with the statement of Mayo & Baker (1965) that rate of freezing, rate of thawing and length of storage in the frozen state all influence the viscosity of frozen-thawed egg magma.

## Acknowledgments

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# The morphological changes produced in cauliflower stems during pickling, and their relationship to texture parameters

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## Summary

The changes in morphology and texture which occur during the pickling of cauliflower have been studied using the electron microscope and Instron Universal testing rig.

It has been shown that the marked changes in the texture parameters, hardness, elasticity and cohesion, during the initial 24 hr in brine, correlate with plasmolysis of the tissue and re-organization of cell wall materials. At the end of the 1st week in brine, with the disruption of the protoplast, the only intact organelles were the spherosomes. The cell walls became extremely thin in the pit field regions, and it was to these areas that the spherosomes tended to migrate. The disruption of the spherosomes, during the 4th week in brine, with the possible release of hydrolytic enzymes may have contributed to the further weakening of the cell wall.

The use of electron histochemical stains has permitted the demonstration of the gradual degradation of pectic substances, resulting in enlarged intercellular spaces and a decrease in tissue cohesion. By staining neutral polysaccharides, it has been shown that the cell wall materials are not degraded to a marked extent and hence would add little to the sugars available for bacterial fermentation.

The increase in crispness, said to arise from freshening and acidification, is not just a simple recovery in turgor pressure, since the protoplast plasmalemma quickly loses its semi-permeable characteristics and is later destroyed. However, an enhancement of elasticity and tissue cohesion has been demonstrated by using freshening solutions containing 2500 ppm calcium.


## Introduction

The production of pickled cauliflower is a well established procedure and its technology has been fairly well documented (Morpeth, 1952; Dakin & Milton, 1963; Anderson, 1968; Dakin & Scholey, 1969). In commercial brining of cauliflower the

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salt concentration normally used varies between 50 and 60% saturation as this is optimal for adequate bacterial fermentation and satisfactory quality of the preserved material. There can be little doubt that not only does the salt concentration affect the texture of the brined vegetable, but that even in a given salt concentration the texture considerably alters throughout the complete period of preservation.

The texture of a pickle is an important attribute. Szczesniak (1963) defined texture as the composite of the structural elements of food and the manner in which it registers with the physiological senses. Obviously morphology and chemical structure will be two of the major factors influencing the texture of vegetables (Isherwood, 1960). Thus any changes occurring in chemical composition or cellular organization during the brining and fermentation of cauliflower might be reflected in the final texture of the product.

The object of the present investigation was to study the fine structure of cauliflower stem, and relate the textural changes resulting from brining with alterations to the cellular organization. The use of electron histochemical methods for the demonstration of various functional groups enabled the degradation of cell wall components to be followed.

## Materials and methods

The cauliflowers were trimmed to remove the leaves and surplus stalk. Small florets ($1\frac{1}{2}$–3 in.) were then cut from the heads to facilitate packing into 1-gallon jars. The first brining was carried out in 50° brine at room temperature for 24 hr after which time the solution was replaced with fresh 50° brine (13·25% w/w sodium chloride).

During the first 10 days in brine the containers were agitated at least once a day to prevent stratification of the salt solution (Morpeth, 1952). The brining was allowed to proceed until fermentation had ceased, which occurred after approximately 7 weeks. During the brining process, samples were removed at regular intervals for study with the elctron microscope and for texture measurements. When a jar had two samples removed from it, it was discarded, since surface yeast growth then increased sharply and might have impaired the quality of the stalks.

The fully fermented cauliflowers were freshened by batchwise processing. The concentration of calcium in the washing fluid was varied, the following solutions being used: (a) de-ionized water, (b) tap water containing 250 ppm calcium, and (c) tap water containing 2500 ppm calcium.

After freshening, the cauliflowers were placed in 4% acetic acid, and when equilibrium had been reached the tissue was sampled for electron microscopy and texture measurements.

### *Electron microscopy*

Thin discs less than 1 mm thick were cut 0·5 cm from the exposed end of the cauliflower stem. The discs were then fixed by one of the following procedures: (a) 3%

glutaraldehyde at pH 7·2 for 3 hr (Sabatini, Bensch & Barnett, 1963); (b) as in (a) then followed by post-fixation in 2% osmium tetroxide for 4 hr (Palade, 1952); and (c) 3% glutaraldehyde in 50° saturated brine for 3 hr followed by post-fixation in osmium tetroxide.

Following fixation, the tissue was dehydrated stepwise in an ascending graded ethyl alcohol series and finally embedded in pre-polymerized methyl–butyl methacrylate (40 : 60) or Maraglas (Freeman & Spurlock, 1962). Sections 500–800 Å thick were cut on a Cambridge–Huxley microtome and collected on collodion–carbon covered copper or gold grids. Those sections which were intended for histochemical reactions were supported on the gold grids, since copper grids react with silver solutions. The sections of osmium fixed material were stained with uranyl acetate and lead citrate (Reynolds, 1963). The examination of the sections was carried out using an Hitachi Hs–7s electron microscope operating at 50 kV.

*Electron histochemistry*

The demonstration of esterified pectin was achieved using the hydroxylamine–ferric chloride technique modified by Albersheim & Killias (1963). In order to ensure that any positive reaction was due to the formation of pectin hydroxamic acids, control material was used in which either the alkaline hydroxylamine or ferric chloride was omitted.

The presence of neutral carbohydrates was demonstrated in sections by either a periodate, Schiff, phosphotungstic acid technique (Thiéry, 1967) or periodate, thiocarbohydrazide, silver protein technique (Thiéry, 1967) both modified and adapted for plant tissue (Jewell & Saxton, to be published). Control sections were employed in which: (a) periodate oxidation had been omitted, (b) Schiff reagent or thiocarbohydrazide had been omitted, or (c) phosphotungstic or silver protein had been omitted. To ensure that any positive reaction was due to matrix carbohydrates, samples of glutaraldehyde fixed material were pre-treated with 0·5% ammonium oxalate for 48 hr at 60°C followed by 4% sodium hydroxide for 96 hr at room temperature. Such procedures will remove pectic and hemicellulose materials (Jensen, 1960).

*Texture measurements*

Assessment of texture parameters was carried out using an Instron Universal testing rig.

Throughout the present investigation the definitions of texture profile laid down by Szczesniak (1963) and modified for application to the Instron testing rig by Bourne (1968) have been adopted: (1) hardness is defined as the maximum force required to produce a known compression; (2) elasticity is defined as the extent the material recovers between two applications of the compression load; and (3) cohesion is defined as the ratio of the work done during the compression strokes.

A cylinder of parenchyma tissue 5 mm in diameter was cut from the stem of a cauliflower using a No. 1 cork borer, and trimmed to a height of 6 mm. The sample was placed vertically between two flat plates attached to the load cell and moving cross head. The cross head was set to compress the sample, by a given amount, at constant speed of 1 cm/min. At the completion of the compression stroke the cross head returned to the starting point, prior to commencing its second stroke. Each sample was subjected to two compression strokes. The data from the load cell were recorded on a chart driven at 50 cm/min and using 5 kg full scale deflection. The data obtained from the first compression stroke provide both the maximum force required to compress the material by a given amount, i.e. hardness, and the area under the curve as the work function $A_1$. From the trace of the second stroke the recovery of the tissue after compression was measured as the work function $A_2$; the elasticity is given by the distance along the base line subtending the function $A_2$. The tissue cohesion can be expressed as $A_2/A_1$.

## Results

*Fresh tissue*

The parenchyma cells constitute the bulk of the cauliflower stem and, therefore, have been extensively examined during this investigation. These cells can be characterized both by their size and their large central vacuole. Their protoplasts contain numerous inclusions which are contained within a thin parietal layer of cytoplasm between the vacuole and cell wall (Plate 1a). The nuclei of these cells varied considerably in shape and chromatin aggregation. Numerous mitochondria were observed throughout the cytoplasm. Golgi bodies were also observed, but in general showed no evidence of major synthetic activity. Endoplasmic reticulum was also sparsely distributed throughout the cytoplasm. Chloroplasts or starch granules were not observed during this investigation, and in general the parenchyma cells of cauliflower did not contain plastids having a well-defined function. Throughout the cell cytoplasm aggregations of small (150 Å) ribosomes were found which were intensely stained when fixed in osmium containing fluids. In the majority of the cells in cauliflower stem larger particles were observed and identified as spherosomes (Plate 1b). These particles could be characterized in methacrylate embedded material by their intense reaction with osmium. However, following embedding in 'Maraglas', these particles appeared much less dense, and were often difficult to differentiate from other protoplast inclusions. The spherosomes were usually found in close proximity to the cell wall, separated from it by only the plasmalemma.

The plasmalemma (Plate 1c) was identified as a densely staining membrane in close contact with the cell wall, encompassing and delineating the protoplast. Other unidentified particles were occasionally distributed throughout the cytoplasm, these consisted of a double membrane surrounding electron transparent contents.

The cell wall of parenchyma cells varied greatly in width, the radial walls being much thinner than the tangential walls. Although the size of the walls varied consider-

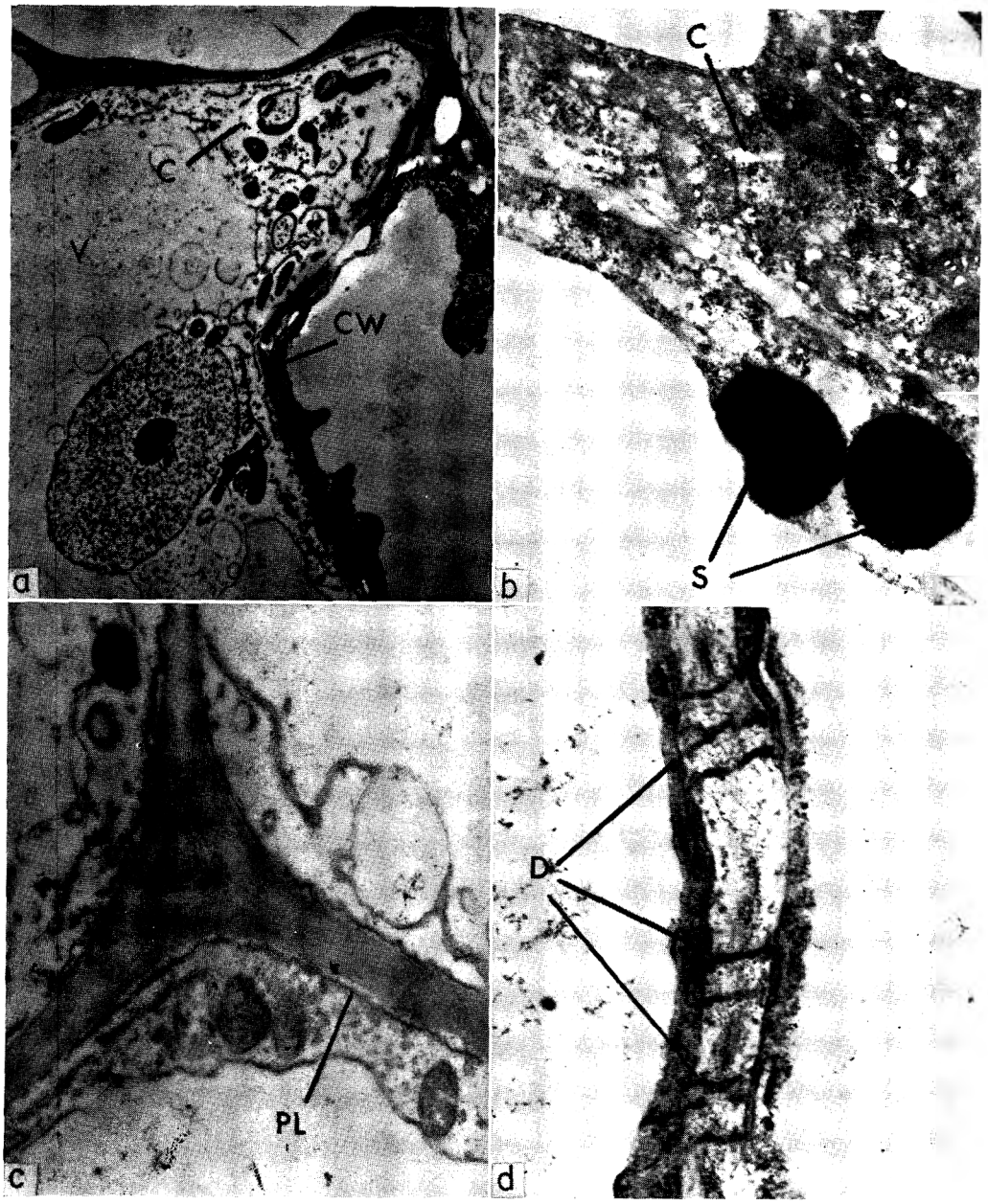


PLATE 1. (a) A parenchyma cell of fresh cauliflower. A prominent nucleus (N) can be seen in the cytoplasm (C). The cell wall (CW) and vacuole (V) are also clearly visible. × 5800. (b) Part of a parenchyma cell of fresh cauliflower. Spherosomes (S) can be seen in the cytoplasm (C). × 19,500. (c) Part of a parenchyma cell of fresh cauliflower. The plasmalemma (PL) and intercellular space (I) can be seen. × 16,000. (d) Part of the cell wall of a parenchyma cell showing plasmadesmata (D). × 42,000.

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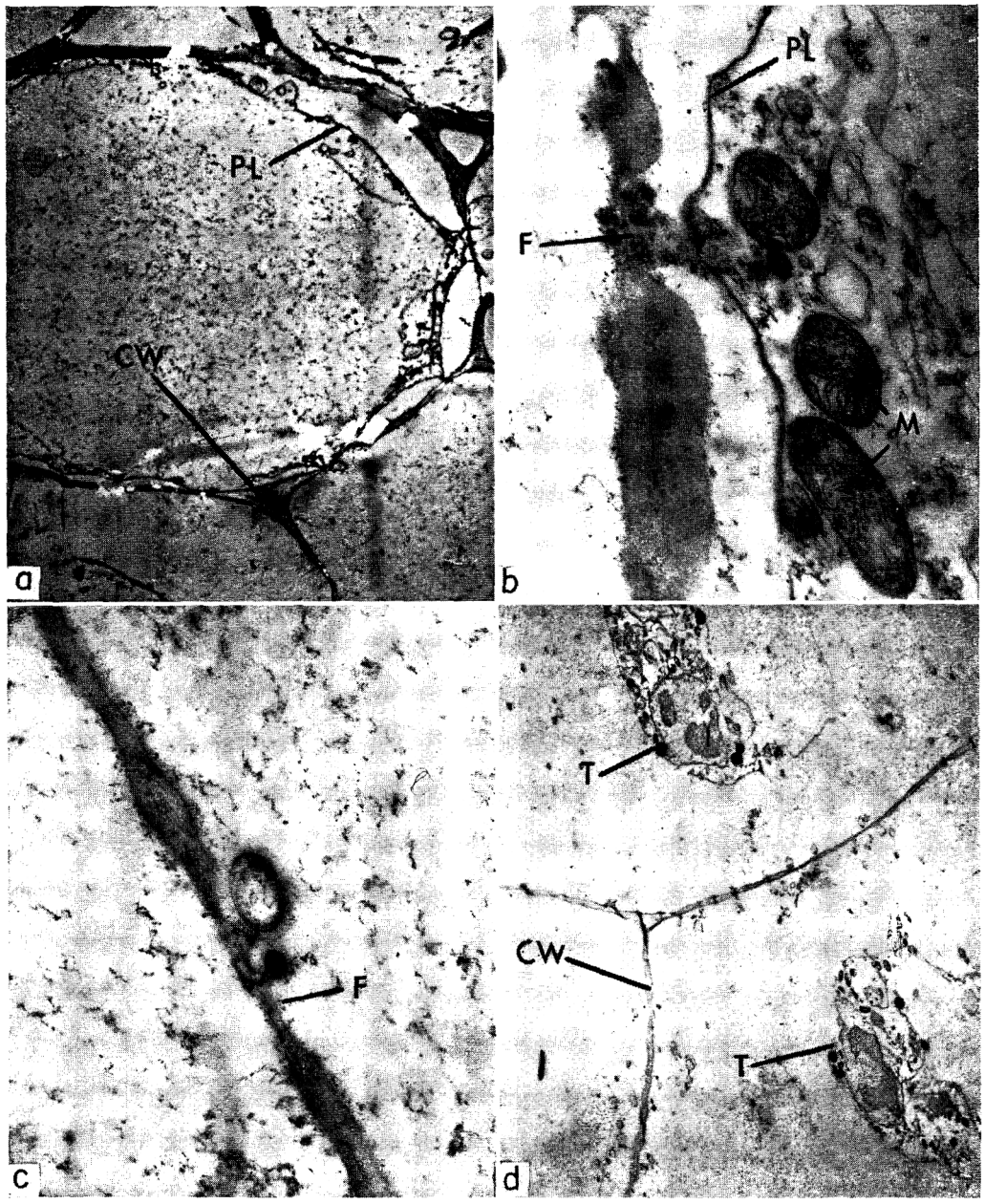


PLATE 2. (a) A parenchyma cell which has been brined for 8 hr. The plasmalemma (PL) is separating away from the cell wall (CW). × 5200. (b) A parenchyma cell which has been brined for 8 hr. The plasmalemma (PL) is attached to the pit fields (F). Several mitochondria (M) can be seen in the cytoplasm. × 33,000. (c) Part of the cell wall of a parenchyma cell brined for 8 hr. The cell wall is very thin in the pit field regions (F). × 19,500. (d) Parenchyma cells which had been brined for 24 hr. The protoplast (T) shows no attachment to the cell wall (CW). × 4000.

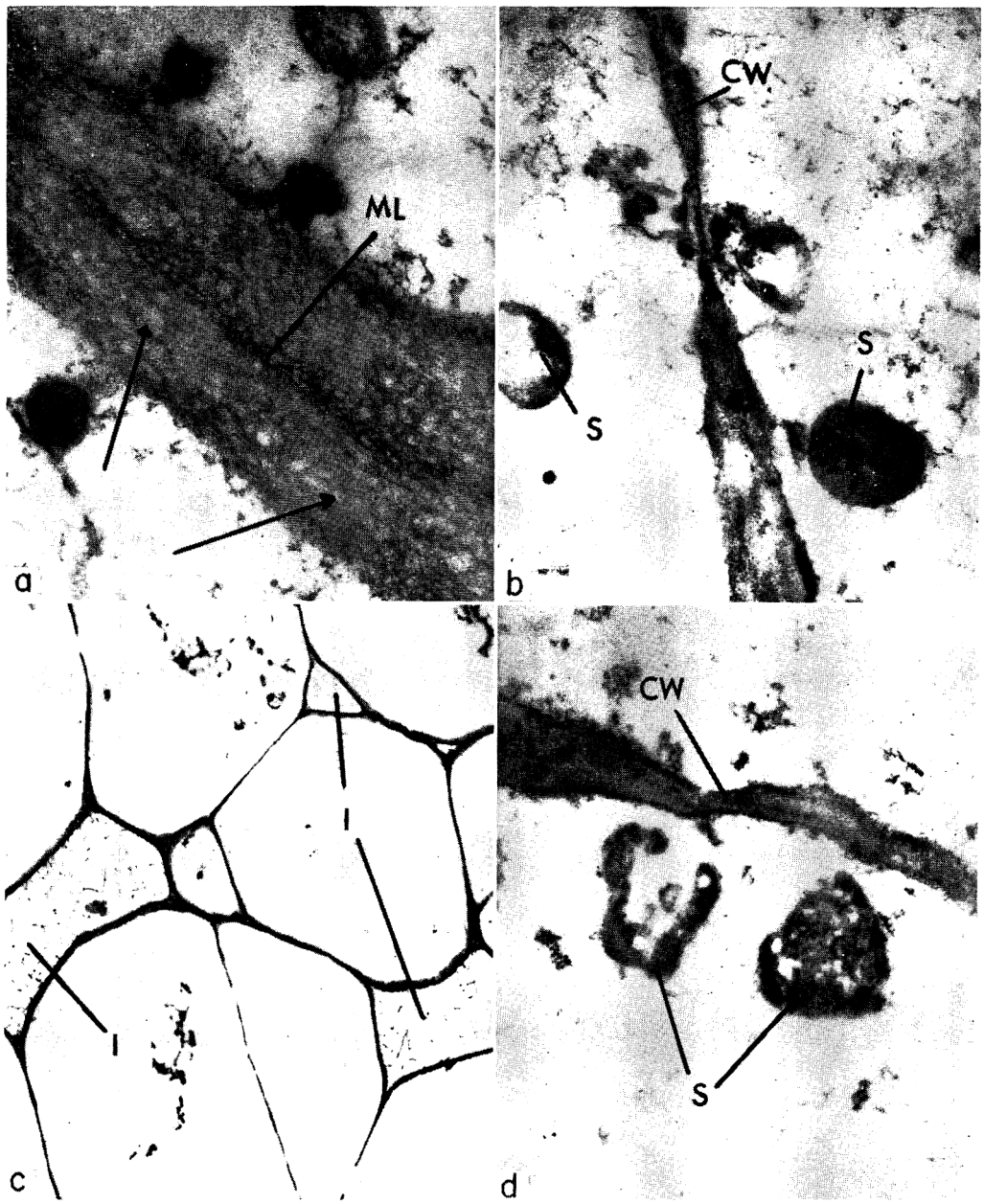


PLATE 3. (a) The cell wall of a parenchyma cell which has been brined for 24 hr. The middle lamella (ML) can be seen, and also clear unstained areas (see arrows). × 46,000. (b) Part of a parenchyma cell which has been brined for 3 weeks. The spherosomes (S) have migrated to the cell wall (CW). × 19,500. (c) Parenchyma cells after 3 weeks in brine, the intercellular spaces (I) have become considerably enlarged. × 4000. (d) Part of a parenchyma cell which has been brined for 3 weeks. The spherosomes (S), which are adjacent to the cell wall (CW), are disrupting. × 29,000.

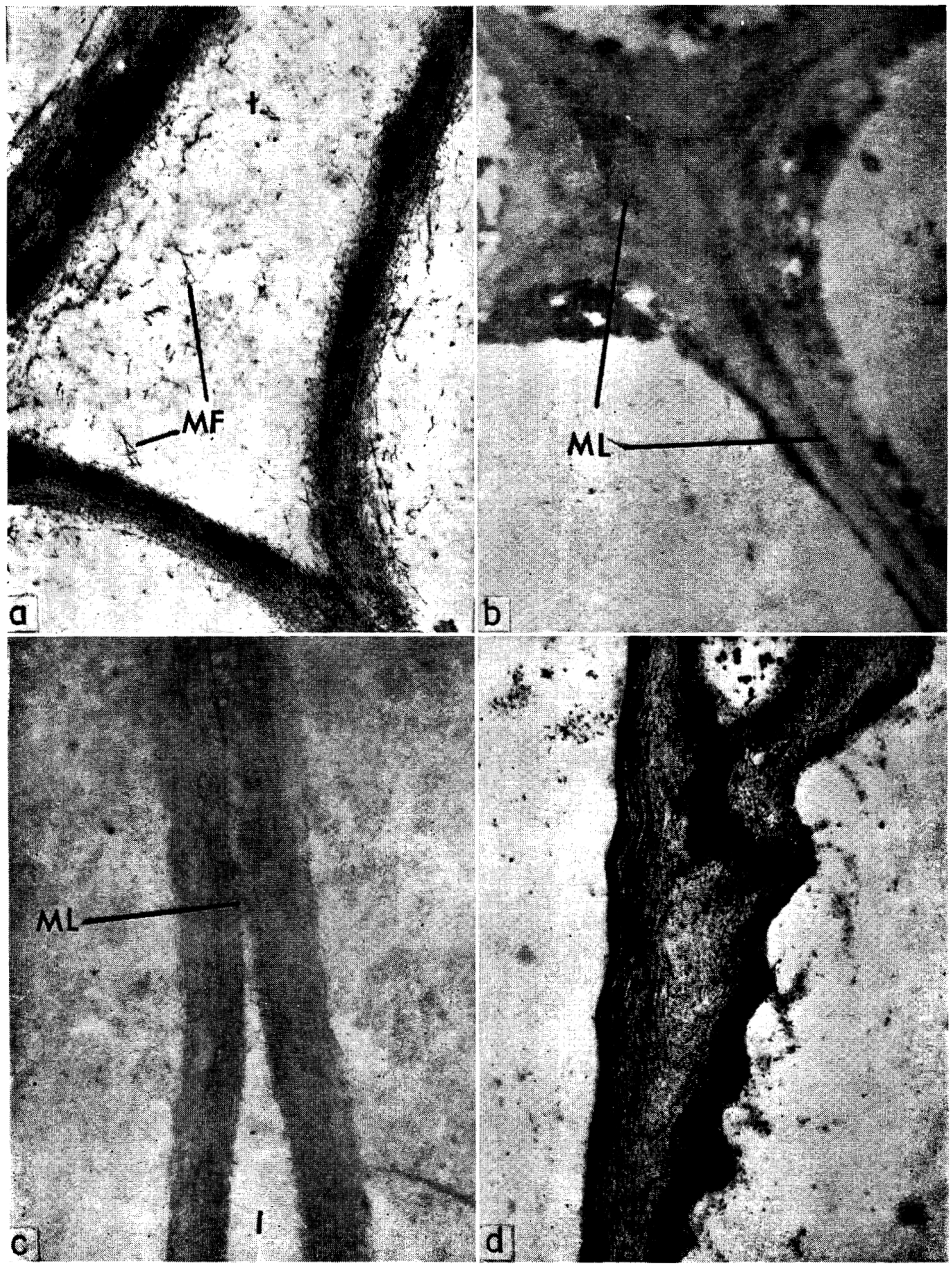


PLATE 4. (a) Part of the cell wall of a parenchyma cell brined for 7 weeks. Micro fibrils (MF) can be seen in the intercellular space (I). × 29,000. (b) Part of the cell wall of a fresh parenchyma cell stained with hydroxylamine–ferric chloride. The pectin can be seen as a granular staining of the middle lamella (ML). × 26,000. (c) Part of the cell wall of parenchyma cell brined for 7 weeks and then stained with hydroxylamine–ferric chloride. A diminished reaction is observed in both the intercellular spaces (I) and middle lamella (ML). × 36,000. (d) Part of the cell wall of fresh parenchyma tissue stained with silver protein. The reactive 1 : 2 glycols are revealed as an electron dense network surrounding electron clear fibrils. × 23,000.

ably, the width of each remained reasonably constant along its length. At the junction of several cells the walls formed a triangle which in some instances enclosed a small intercellular space (see Plate 1a and c). It is often difficult to distinguish between primary and secondary walls by electron microscopy. However, the dimensions of the parenchyma cells walls indicate a primary origin. In general the techniques used in electron microscopy revealed little regarding the structure of the cell wall. The middle lamella was normally an exception to this generalization by showing as a more electron dense region after prolonged staining with uranyl acetate. Elsewhere throughout the wall the lack of apparent structure prevents the cellulose micro-fibrillar orientation and general structural arrangement for being determined. Plasmadesmata were occasionally observed (Plate 1d) as thin cytoplasmic threads traversing regions of the cell wall, in particular those of thinner radial orientation. They were observed as either a single element or more frequently as groups forming regions known as pit fields. It was evident that the plasmadesmata do not necessarily cross the cell wall transversely, i.e. by the shortest route, and oblique forms were encountered. Occasionally part of the endoplasmic reticulum was observed in close proximity to the orifice of the plasmadesma.

*Brined tissue*

The appearance of the parenchyma cells underwent considerable alteration during the initial 8 hr brining, as a result of plasmolysis of the protoplast (Plate 2a). In cells exhibiting slight plasmolysis it was clearly observed that the cell wall and living protoplast separated at the plasmalemma–cell wall boundary. The protoplast, however, was not free within the cell, but remained attached via contact of the plasmalemma with the pit fields (Plate 2b). Serial sections of such attachments revealed that the plasmalemma relationship with the cell wall occurred only at thin isolated areas associated with individual plasmadesma within the pit field. In these regions the cell wall had also been modified. Whereas in fresh parenchyma cells the radial walls were thin but of uniform width, these walls now exhibited localized areas of thinning in the regions of the pit fields (Plate 2c). In such regions the wall was approximately one-sixth the width of the adjacent wall. Traversing that region of the wall were the plasmadesmata which were dimensionally unchanged. Thus in these regions the protoplast was attached to the cell wall via protruding plasmadesmata. The plasmadesmata of the plasmolysed cells were modified during this short period in brine. The electron dense core was surrounded by a thin electron transparent region delineated by a membrane. Between the cell wall and plasmolysed protoplast were observed numerous unidentified vesicles which differed both in size and electron density.

Examination of parenchyma cells after brining for 24 hr revealed that as a result of plasmolysis the protoplast was present as a small compressed body (Plate 2d) in the centre of the cell, with no protoplasmic attachments to the cell wall. The vesicles previously associated with the thinned region of the wall were only occasionally con-

nected to plasmadesmata. In the majority of observations the vesicles were separated from the wall but remained connected via thin elements. There were isolated instances in which plasmadesmata remained attached to vesicles, although the plasmadesmata appeared to be partially extruded from the wall.

The cell walls of cauliflower brined for 24 hr showed considerable alteration in staining characteristics and structure. Staining with uranyl and lead solutions revealed large unstained areas (Plate 3a) in an otherwise electron dense network. Since the diameter of these areas ranged up to 0·1 μ it is probable that they represent reorganization of cellulose microfibrils.

Although the protoplast continued to be bounded by an intact plasmalemma, the cytoplasmic organelles showed symptoms of degeneration. The membranes of the Golgi bodies and cisterns of mitochondria were degraded, in many instances to the extent of complete disruption. The nuclear chromatin was indistinct and ribosomes infrequently distributed throughout the cytoplasm.

The result of brining for 7 days revealed that the protoplast had degenerated considerably during this period. The plasmalemma was completely ruptured in many instances liberating the cytoplasmic contents into the cell space. The only organelles which could still be recognized were the spherosomes. The appearance of the cell wall was similar to that of fresh material, except for the regions of thinning and absence of plasmadesmata.

The effect of prolonging brining to 3 weeks can be seen in Plate 3(b). This period of brining resulted in the complete disintegration of all cellular organelles. The spherosomes which had remained intact during the 'initial' brining period had migrated towards the thinned regions of the cell wall. The intercellular spaces had become enlarged (Plate 3c).

Examination of cauliflower brined for 4 weeks revealed that the spherosome membranes had ruptured. Hitherto the contents of the spherosomes appeared homogeneous, however, on disruption of the limiting membrane several smaller dense inclusions were released (Plate 3d). It was particularly interesting that the spherosomes often were directly opposed on either side of the thinned region of the cell wall.

At the completion of brining, i.e. when fermentation was visually assessed to be complete (7 weeks), little of the original cellular organization remained. Thus, after brining, the tissue was composed of only a network of cell walls permeated by large intercellular spaces. The staining characteristics of the wall were different to those after short brining, as the middle lamella could not be demonstrated by uranyl acetate. This reagent revealed that the composition of the wall had been adversely affected by brining (Plate 4a) so enabling cellulose microfibrils to be liberated into the intercellular spaces. In many instances the intercellular spaces had been enlarged by the removal of the substances composing the middle lamella.

On completion of brining, the cauliflower was freshened using the solutions previously described. Examination of washed cauliflower which had been fixed in glutar-

aldehyde, revealed that the use of washing fluid containing 2500 ppm calcium ions considerably enhanced electron density in the matrix of the wall. Washing brined cauliflower in either tap or de-ionized water had no such effect on wall opacity.

The ultrastructure of the brined, washed and acidified cauliflower showed no differences from the fully brined material, which has been previously described.

*Electron histochemistry*

The control reactions of the technique for demonstrating pectin, revealed that the use of acid ferric chloride on glutaraldehyde fixed cauliflower resulted in increased electron density of the cytoplasm. In addition, the middle lamella of fresh parenchyma cells increased in electron density when the hydroxylamine–ferric chloride reaction was employed (Plate 4b). Since the increased magnification of the electron microscope enabled a more precise localization of reactive sites to be demonstrated it was apparent that, although methylated polyuronides were mainly confined to the middle lamella, the intercellular spaces formed by the junction of cell walls also contained pectin.

The examination of cauliflower, using the hydroxylamine–ferric chloride technique, which had been brined for various periods of time showed that no significant changes in the pectin occurred during the first 3 weeks of brining. After 3 weeks' brining the intercellular spaces had become enlarged. This was associated with a reduction in the intensity with which the pectin stained in these regions, although the intensity of staining of the middle lamella areas was unaffected. Prolonging the brining resulted in a diminished reaction in both the enlarged intercellular spaces and middle lamella regions (Plate 4c).

When fresh material fixed in glutaraldehyde was stained for the demonstration of 1 : 2 glycols, the reactive sites were revealed as an electron dense network surrounding clear microfibrils (Plate 4d). The application of selective extraction procedures demonstrated that the electron clear fibrils were cellulose and that the reactive sites consisted of hemicellulose materials.

The examination of brined material stained for 1 : 2 glycols revealed only a slight reduction in intensity of the staining, thus indicating very little degradation of the neutral 1 : 2 glycols present within the cell wall.

*Texture measurements*

The force–distance curves obtained with the Instron Universal testing rig on cauliflower stem are shown in Figs. 1 and 2. In the former the stem was compressed to one-third its original height and in the latter to two-thirds its height. When the sample was compressed to only two-thirds original height, the force–distance curve (Fig. 2) did not exhibit the sharp drop in load, shown in Fig. 1 which can be attributed to brittle fracture. Trial experiments indicated that brittleness rapidly diminished in-brined material, and this led to difficulties in the interpretation of other texture parameters, i.e. hardness, elasticity and cohesion. The behaviour of these three parameters

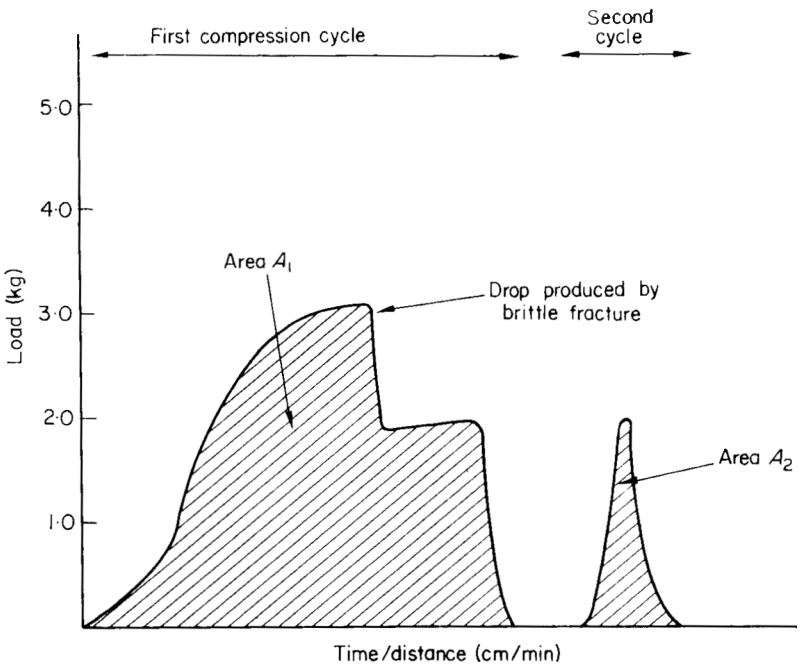


FIG. 1. The force–distance curve obtained when a cylinder of cauliflower stem was compressed to one-third its original height.

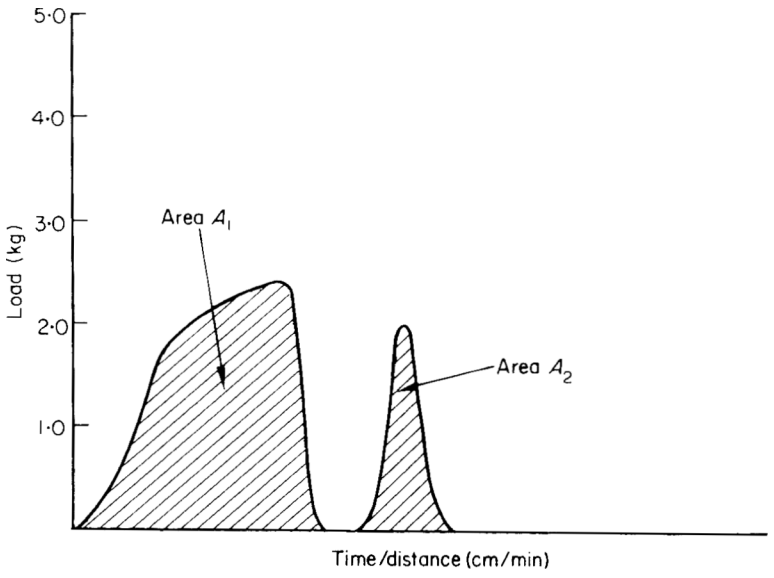


FIG. 2. The force–distance curve obtained when a cylinder of cauliflower stem was compressed to one-third its original height.

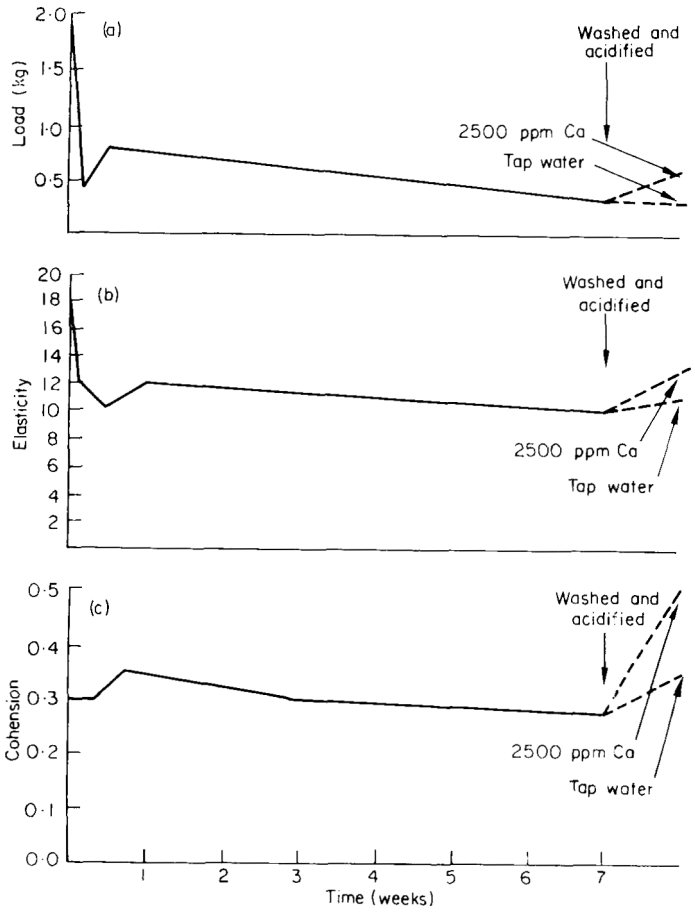


FIG. 3. (a) The variation of hardness during brining, and after freshening and acidification. This was calculated from the total load required to compress the sample to two-thirds original height. (b) The variation of elasticity during brining, and after freshening and acidification. This was calculated from the distance along the base line subtending the function $A_2$ of a sample compressed to two-thirds original height. (c) The variation of cohesion during brining, and after freshening and acidification. This was calculated from the ratio of the work function $A_2/A_1$ of a sample compressed to two-thirds original height.

during the brining process, on the basis of compression to two-thirds original height are shown in Fig. 3. It was apparent that the greatest alteration to hardness and elasticity occurred within the initial 24 hr in brine. During the following 24 hr there was a recovery in hardness and elasticity values, whilst a decrease in cohesion was observed The continuation of brining resulted in the gradual reduction of the values of all three parameters.

The freshening of fully fermented material in solutions of varying calcium concentration, followed by acidification with acetic acid, resulted in marked texture differences (Fig. 3). The use of tap water containing 2500 ppm calcium produced a large increase in both cohesion and elasticity. Tap water containing 250 ppm calcium had less effect on these parameters, whilst deionised water gave a decrease in cohesion.

## Discussion and conclusions

Considering that parenchyma cells constitute the bulk of the tissue of higher plants, surprisingly little information regarding their fine structure has been published. Recently O'Brien & Thimann (1967) have supplied data on coleoptile parenchyma cells. It is obvious from comparing such results with the present investigation that parenchyma vary considerably both between species and with locality in any one plant.

In the cauliflower stem the cells are very simple in cytoplasmic arrangement being devoid of such plastids as starch and chloroplasts. Even more significant, the pit fields and plasmadesmata are considerably less frequent than has been reported for many other cell types (Esau, 1965). Individual plasmadesmata were thinner and devoid of the unstained region surrounding the electron dense core.

The occurrence of densely staining spherosomes in the cytoplasm of plant tissue is not uncommon, although they were not reported by O'Brien & Thimann (1967) as being present in coleoptile cells. It has been shown by other workers (Gahan & Maple, 1966) that spherosomes can contain similar hydrolytic enzymes to those found in animal lysosomes, and which when released into the cell environment have an auto-digestive function. Although no attempt has been made to demonstrate the presence of these enzymes during this investigation, the disruption and release of the spherosome contents at the already thin region of the cell wall may, in part, contribute to further weakening of the wall.

There can be little doubt that the major changes in texture and ultrastructure occur within the initial 24 hr in brine. Plasmolysis has been extensively studied by light microscopy for many years, but as yet has received little attention from electron microscopists. In the present study the morphological appearance of the plasmolysed cytoplasm indicates that during the first 8 hr in brine the protoplast continues to be viable, although the reduction of ribosomes and endoplasmic reticulum suggests that the metabolic state of the cell has been considerably effected. The appearance of vesicles during plasmolysis between the plasmalemma and cell wall provides evidence for the action of reverse-pinocytosis, thereby enabling the protoplast to decrease in content of cytoplasm and plasmalemma. The degeneration of the cytoplasmic connections to the plasmadesmata in the pit fields coincides with the inability of the tissue to regain its turgidity when washed. Although the plasmalemma remains morphologically intact, its function as a semi-permeable membrane has deteriorated with the result that there is no increase in turgor pressure when the material is treated with a de-plasmolysing agent. Because turgor pressure cannot be regained within the cell after 24 hr in brine

it is clear that this factor can play no part in determining the texture characteristics of pickles. This is considered to be an important discovery, because turgor pressure is paramount in determining the texture of fresh vegetable tissue, and by extension had been thought to control pickle texture. This is now shown to be wrong, and thus attention must be directed to the cell wall region.

It was considered by Heyne (1931) that changes in elasticity could arise through alterations in either the amount or quality of the cell wall materials. As wall strength is influenced by cellulose content, hardness is probably a function of the cellulose–matrix relationship. Cohesion is considered by Zaitlin & Coltrin (1964) to be related to pectin content of the wall. Although these three primary texture parameters have been assessed during this investigation, it must be concluded that texture of vegetable material is a complex property and that alterations to any one of the parameters will influence the other characteristics.

The introduction of large areas of re-organization in the wall of cauliflower brined for 24 hr indicated a re-orientation of the cellulose microfibrils within the macrofibril, which probably contributed to the large texture change observed during the initial brining period. Subsequent stabilization of the wall constituents may explain the partial recovery of the texture.

The majority of the matrix, in which the cellulose framework is embedded, consists of a highly hydrated molecular arrangement of polymeric substances, e.g. polysaccharides and polyuronides. Whilst the distribution of methylated polyuronides was similar to that reported by Albersheim & Killias (1963), demonstration of neutral carbohydrates within the wall was particularly significant. It is evident from these observations that, since the cellulose microfibrils and the matrix can be clearly differentiated, the carbohydrates within the matrix are either more reactive or more accessible to the reaction than the glucose units comprising the cellulose. The regions of the cell wall in which pectin is localized exhibited reduced reaction during the demonstration of neutral carbohydrates. This would suggest that under the conditions employed, pectin substances are unlikely to contribute to the reaction. Because the PAS reaction is specific for 1 : 2 glycols, and since it is not possible to have a 1 : 2 glycol on a 1 : 3 linked sugar, the positive PAS reaction indicated that linkages other than 1 : 3 must be present in the matrix. According to Leblond, Glegg & Eidinger (1957) such carbohydrates as galactans and mannans are PAS reactive, and, since these are known to be present in hemicellulose, it is almost certain that some of them are responsible for the positive neutral carbohydrate reaction in this investigation.

Although the result of fermentation is to remove sugars, the relative stability of the reacted neutral carbohydrates in the cell wall indicate that the majority of the fermented material must be derived from the protoplast or vacuole contents. However, since completely brined material shows the release of cellulose from the wall, it is probable that the matrix in these regions has been modified. In addition to the reacted carbohydrates, it is known (Rogers & Perkins, 1968) that 1 : 3 linked carbohydrates and

hemicellulose containing uronic acids are present in the matrix, although histochemically these groups cannot be demonstrated by the techniques used in the present investigation. It is possible, therefore, that these functional groups are associated with the alterations to the matrix, resulting in a release of cellulose microfibrils from the wall.

The foregoing discussion of the various factors assessed during this investigation indicates that some correlation exists between the ultrastructural degradation of the material and the altered textural characteristics caused through brining. Following the initial texture change, associated with loss of turgor pressure due to plasmolysis, the subsequent gradual softening of the material coincides with changes in wall structure. The alteration and partial removal of matrix carbohydrates are reflected by decrease in hardness and elasticity, whilst the reduction in cohesion can be attributed to removal or demethylation of the pectin. Evidence supporting the demethylation of pectin in some regions of the wall is given by the binding of multivalent ions (calcium) during freshening, which will tend to form cross-linkages with free carboxyl groups of the pectic substances. The formation of such a network would increase the cohesion of the tissue, which is reflected in the texture measurement when increased concentrations of calcium are used in the washing water. Such evidence indicates that the increase in 'crispness' on freshening brined cauliflower is related to the calcium content of the washing fluid, since the use of de-ionized water produces an unacceptable spongy product.

## Acknowledgments

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# Studies on the effect of *N*-dimethylaminosuccinamic acid on the ripening of apple fruits

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## Summary

The spraying of apple trees in July with *N*-dimethylaminosuccinamic acid (2000 ppm) (B9) delays both the onset of the respiration climacteric and increased ethylene production in fruit picked near the time of normal commercial harvest by about 10 days. It also reduces the rate of respiration at the climacteric peak by approximately 20%. The rate of ethylene production of fruit from trees treated with B9 is much reduced and may be only 20% of that of fruit from untreated trees. The amount of ethylene produced is, however, still sufficient to initiate the enzyme processes associated with ripening. It is suggested that the action of B9 is to modify the balance of the various hormones which regulate the development and ripening of fruits.

## Introduction

The growth retardant *N*-dimethylaminosuccinamic acid (B9, B995, Alar) when sprayed onto apple trees has a number of beneficial effects on the yield and quality of the fruit borne by the trees. Its effects include prevention of pre-harvest drop of fruit, increase in blossom yield and reduced shoot elongation. In addition, B9 acts in delaying the onset of maturity and ripening of the fruit. It has been shown that it delays (Dilley & Austin, 1967) and reduces (Sharples, 1967) the intensity of the respiration climacteric (Looney, 1967). B9 also affects other parts of the ripening process including the development of red colour, increased firmness, slower rates of chlorophyll breakdown (see Looney, 1967). B9 has been shown in some cases to cause a significant drop in the development of the disorder, scald, during storage (Williams, Batger & Martin, 1964), but treated fruit tends to be more susceptible to another storage disorder, core flush (Sharples, 1967).

In the present work, we have studied the effect on the ripening of the fruit by spraying trees of the Cox's Orange Pippin variety with B9 8 weeks after petal fall (the time at which 90% of the flowers had shed their petals). We have studied particularly the onset of ethylene production and the subsequent increase in the system producing

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ethylene, the onset and intensity of the respiration climacteric and the development of the enzymic system discovered by Neal & Hulme (1958) which controls the decarboxylation of malate in ripening apple tissue.

## Materials and methods

Fruit was picked at intervals from the normal commercial harvest date (25 September 1967 or 18 September 1968) onwards from two groups of Cox's Orange Pippin apple trees on Malling IX rootstocks growing at the Burlingham Horticultural Station, North Burlingham, Norfolk. Two applications of B9 were given to a set of six trees; these trees were sprayed with 2000 ppm B9 in water containing 0·005% wetting agent, on the 10 July 1967 and again on the 17 July 1968. The other group of six trees served to provide the 'control' fruit.

Batches of about twenty fruits from each treatment (control and B9 sprayed) at each picking (see later) were stored at 12°C in desiccators through which a stream of $CO_2$-free air was passed. The $CO_2$ produced by the fruit was measured by the method described by Hulme, Jones & Wooltorton (1963) while samples of the air stream were taken and analysed for ethylene by the gas chromatographic method described by Galliard *et al.* (1968). At intervals during the storage at 12°C, samples of fruit were taken and disks of peel prepared and assayed immediately as described by Rhodes *et al.* (1968) and their ability to decarboxylate added malate measured by the manometric method of Neal & Hulme (1958).

## Results

A comparison of the $CO_2$-production at 12°C of apples picked on the 25 September 1967 from control trees and from those sprayed with B9 is shown in Fig. 1. The main points that arise from these data are that treatment of the trees with B9 not only delays the onset of the respiration climacteric, it also reduces the maximum respiration value attained at the climacteric peak both 'on' and 'off' the tree. Untreated fruit picked on 11 October had already started on the climacteric rise in respiration whereas treated fruit picked on the 25 October was still in the pre-climacteric state. Fig. 2 shows the respiration and ethylene production of treated and control fruit (picked on 25 September) taken from storage in 3% oxygen at 3°C and subsequently stored at 12°C. It is evident that both the samples from the treated and control trees are near their climacteric peak values. However, the ethylene production in the B9 apples is approximately one-third that of the apples from untreated trees.

During the 1968 season, a more detailed study of the effects of B9 on the onset of ethylene production was made, together with a study of the malate decarboxylating capacity of disks produced from the fruit as it ripened. The fruit was picked on successive dates from 18 September, from control and sprayed trees and the results are shown in Fig. 3.

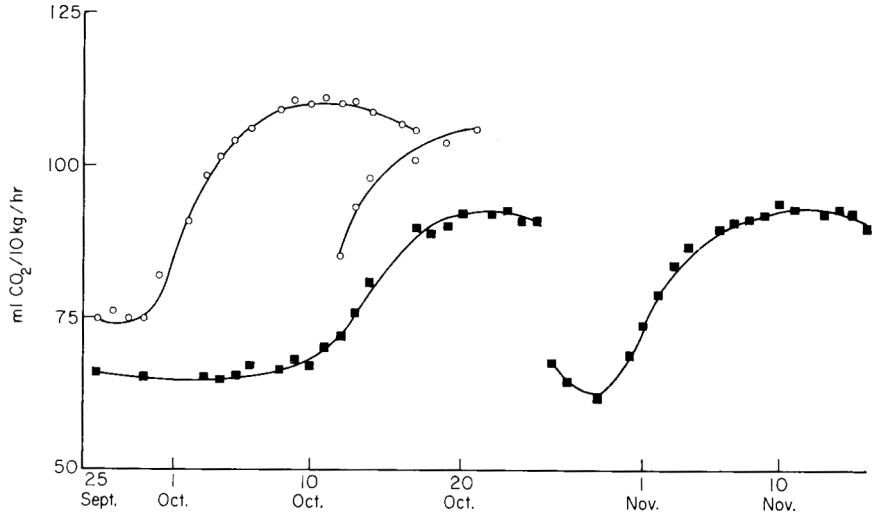


FIG. 1. Carbon dioxide production of apples, stored at 12°C, from control (○) and B9 sprayed (■) trees.

In considering the data for untreated apples, it is clear that, in the first pick, the apples are initially not producing ethylene and there is a delay before the onset of ethylene production (this corresponds with the delay in the onset of the climacteric). In the second pick, the apples are initially producing ethylene and thus the climacteric 'on' the trees has commenced by 24 October. Initials from subsequent picks have increasing rates of ethylene production with a 'climacteric peak' between 5 and 12 November. In all cases, on subsequent storage, the rate of ethylene production rises and finally reaches a maximum steady rate of about 800–1000 μl/10 kg/hr.

In the series of B9 treated apples, the climacteric 'on' and 'off' the tree is delayed compared with control fruit. In comparing the two series of fruits of the first pick the onset of ethylene production (and of the respiration climacteric) in the treated fruit is delayed by 10–11 days. In the later pick (pick 3) on 1 November the treated fruit is still just pre-climacteric (i.e. not producing ethylene) while the controls are near the peak 'on' the tree.

Not only does the spray treatment delay the onset of the climacteric, it also reduces the rate of ethylene production at the climacteric peak. This is particularly dramatic in the first pick when the peak value in the treated apples is about one-fifth of the rate

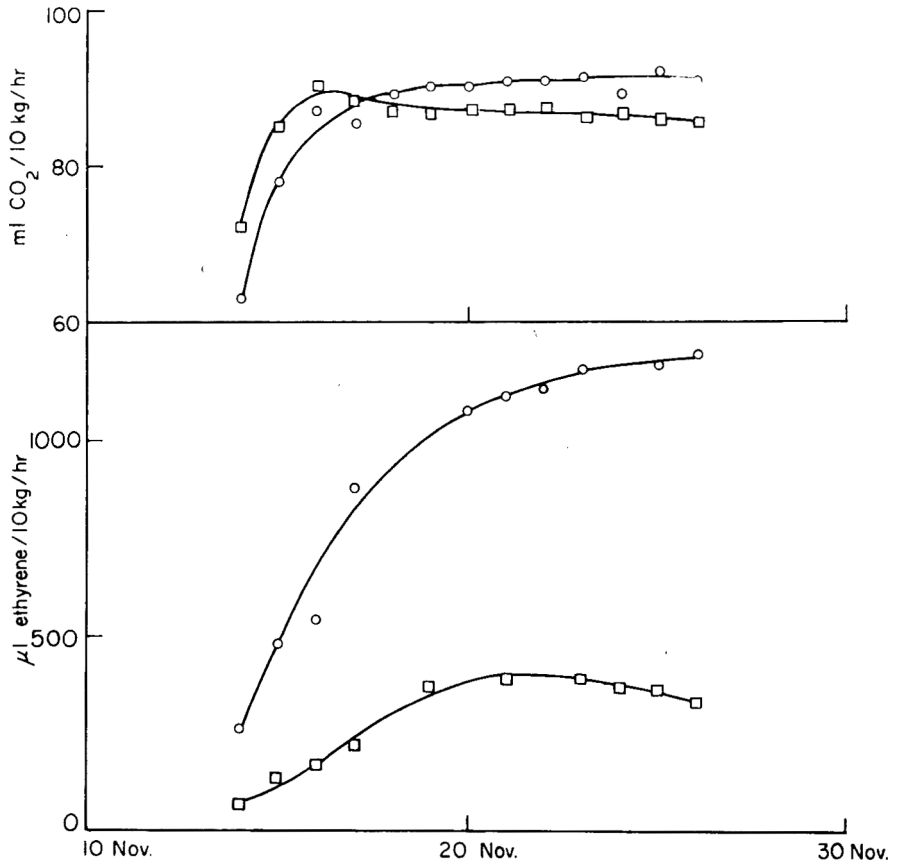


FIG. 2. Carbon dioxide and ethylene production, at 12°C, of fruit from control (○) and B9 sprayed (□) trees, taken from storage in 3% $O_2$ at 3°C.

in the control apples. The effect on the peak production becomes progressively smaller in later picks but the rate in the B9 treated samples is never more than half that in the control samples. This depressive effect is also evident in the initial from each pick as the climacteric 'on' the tree develops in the fruit.

Fig. 4 shows the rates of ethylene production of disks of peel taken from the control and treated fruits of the picks shown in Fig. 3, and also from the apples of each pick subsequently stored at 12°C. The ethylene production of disks taken from the fruit as the climacteric develops closely parallels the changes in the rate of production by the whole fruit. Again the delaying effects of spraying trees with B9 on the subsequent development of ethylene producing capacity and the delay in the development of the climacteric both 'on' and 'off' the tree is clearly seen.

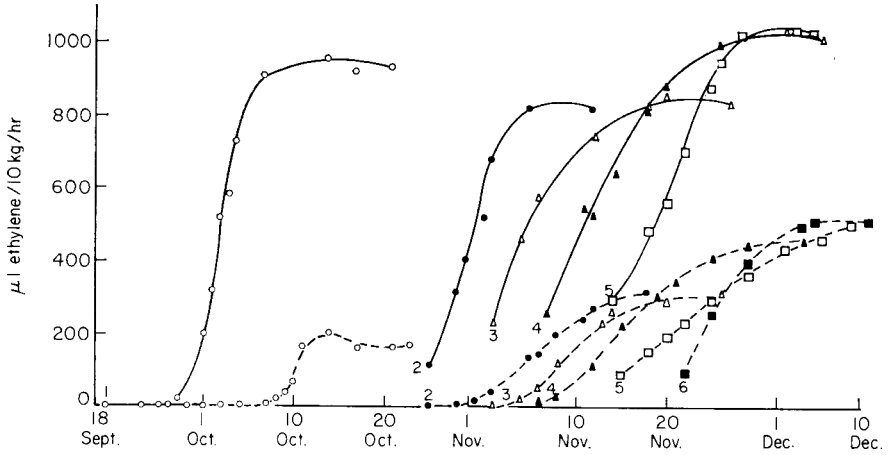


FIG. 3. Ethylene production of whole fruit picked at various dates and stored at 12°C. ——, Control trees; - - - -, B9 sprayed trees.

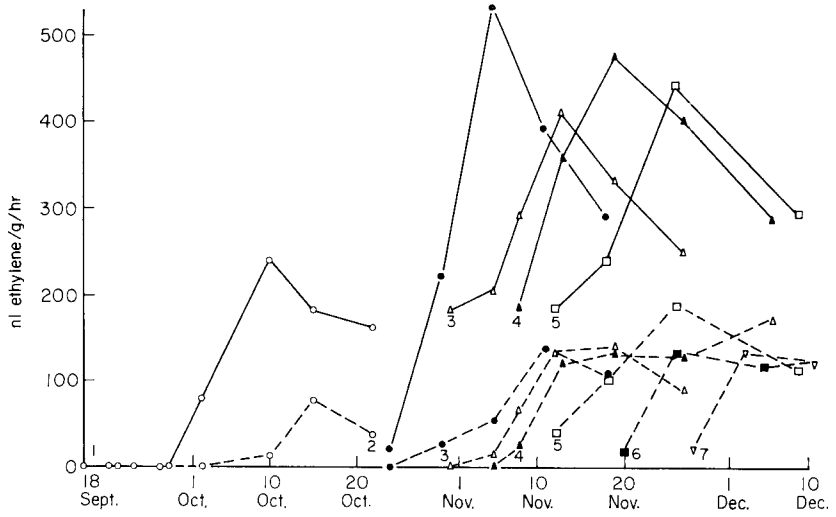


FIG. 4. Ethylene production of disks of peel taken from fruit from control (——) and B9 sprayed (- - - -) trees. Fruit taken at various stages during the development of the climacteric of the whole fruit at 12°C, of the picks shown in Fig. 3.

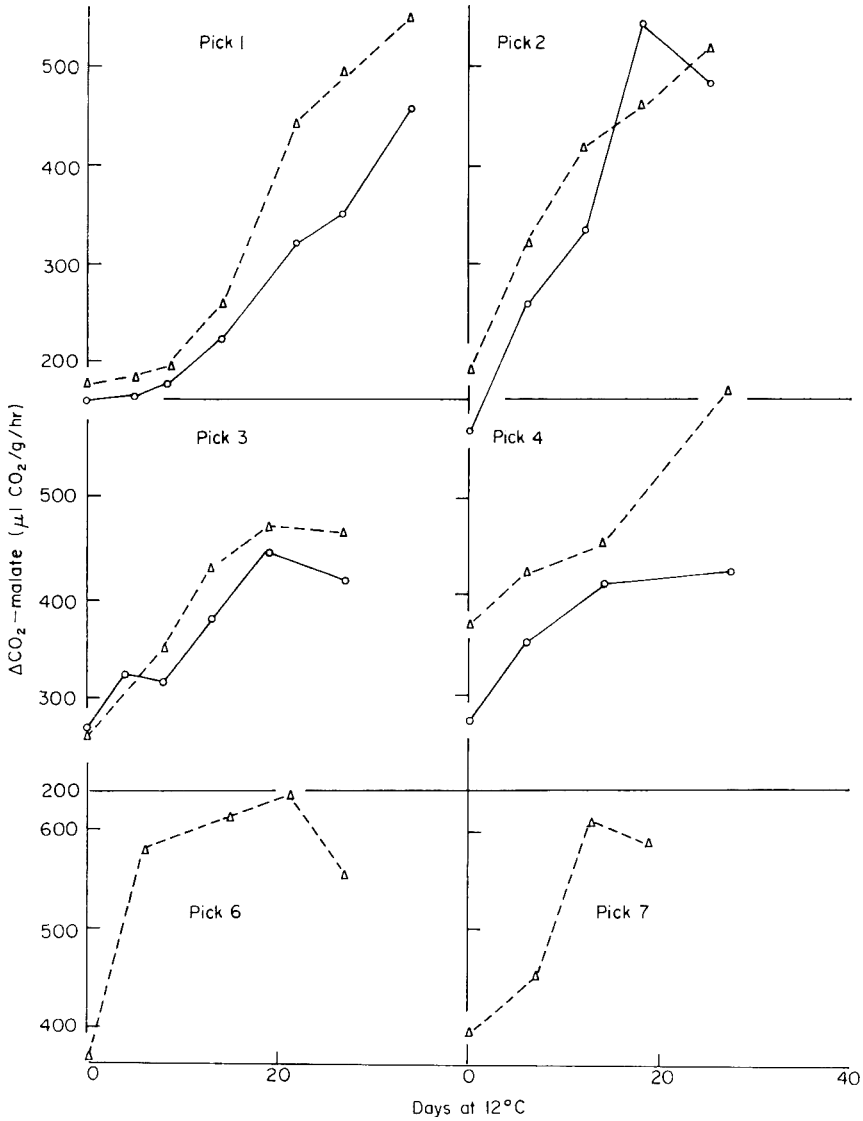


FIG. 5. The development of the malate decarboxylating system in disks taken from fruit from control (○) and B9 sprayed (△) trees of the picks shown in Fig. 4.

Fig. 5 shows the development of the capacity to decarboxylate added malate in disks taken from the control and treated samples given in Figs. 3 and 4. In view of the large effect of B9 in delaying the onset of ethylene production, the fact that the onset of the development of the malate decarboxylation system is hardly affected by B9 is surprising. In comparing the changes in ethylene production of whole fruit (shown in Fig. 3) with the development of the malate decarboxylation system (shown in Fig. 5)

for the control fruit, it is clear that the development of the malate effect lags behind the ethylene production and the rise to the climacteric peak. With the B9 sprayed samples the development of the effect follows closely on the formation of ethylene producing capacity in comparable disks. In the case of the first pick, the malate effect is slowly increasing during the lag *before* measurable ethylene production appears *outside* the fruit (see 'Discussion') then increases rapidly as ethylene appears in the atmosphere above the disks. However, the rate of development of the malate effect is faster in treated fruit than in the controls and the final activity attained is higher. With very late picks of treated fruit, taken after all the fruit had fallen from the control trees, the malate effect increased to very high levels and this may be associated with the late stages of the ripening of the fruit 'on' the tree when it is known the respiration may rise to very high values (Hulme *et al.*, 1963).

Fig. 6 shows the basic respiration of the disks from the 1968 series of picks. The *trends* (but not the absolute amounts) in respiration of the successive samples of disks

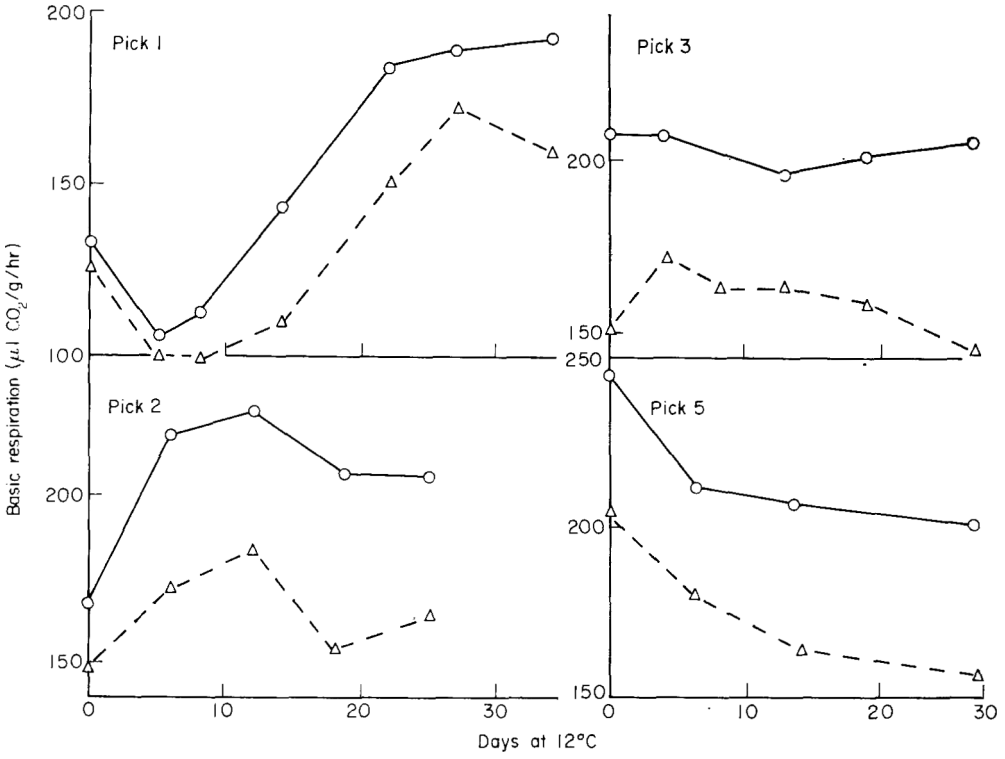


FIG. 6. Basic respiration of disks taken from fruits from control (○) and B9 sprayed (△) trees of the picks shown in Fig. 4.

follow closely the patterns predicted from the rate of ethylene production of the whole fruit. In the first pick, both samples are clearly pre-climacteric at the time of picking and the delay in the onset of the climacteric in the treated apples on subsequent storage is evident. It is seen that throughout the series, the disks from B9 treated fruit have a lower respiration rate than comparable untreated disks.

Fig. 7 shows the data for *initial* samples from each of the picks from the two sets of fruit plotted to show the development of the ripening process 'on' the tree. Close

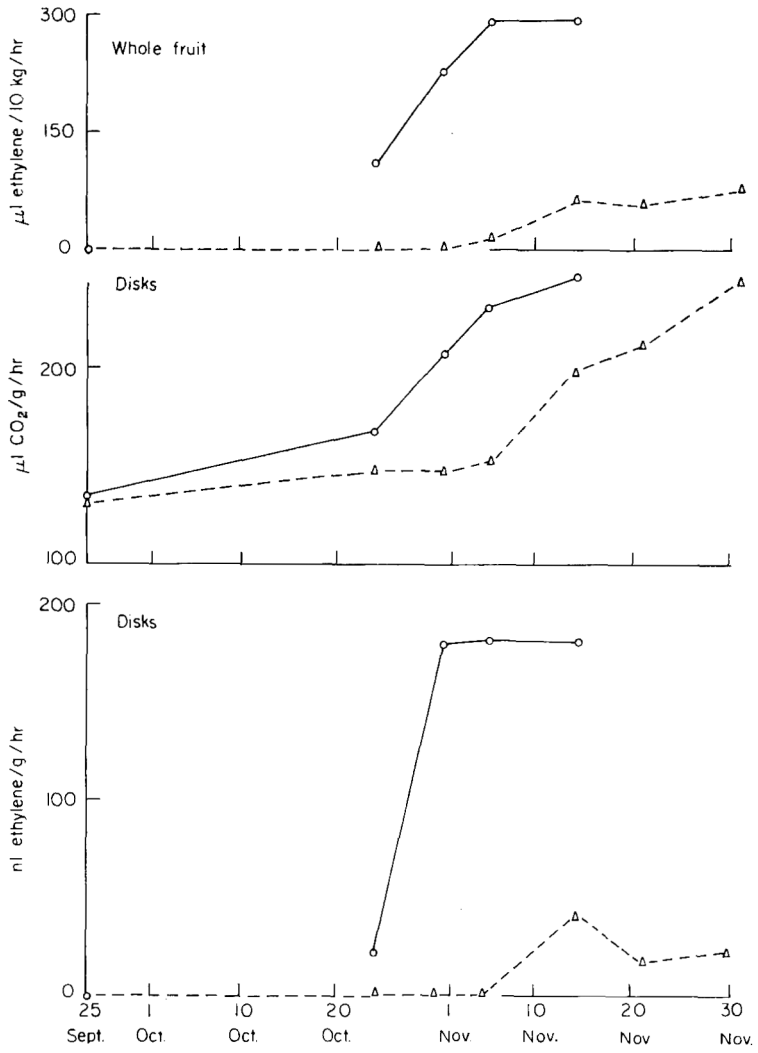


FIG. 7. Ethylene production of whole fruit and ethylene and carbon dioxide production by disks prepared from them for fruit picked at various dates and stored at 12°C.

agreement as to the time of onset of the climacteric in both treatments is shown when the basic respiration or ethylene production of disks is compared with the ethylene production of whole fruit. Again the delaying effect of B9 on the development of the climacteric on the tree is shown together with its suppressive effect on ethylene production once the climacteric peak is reached.

## Discussion

The effect of spraying apple trees with B9 in delaying the onset of the climacteric in the fruit has been confirmed. Spraying trees in July at 2000 ppm delays the respiration climacteric in fruit picked near the normal commercial harvest date by about 10 days. Further, it reduces the respiration of fruit at the climacteric peak by about 20%. The onset of the 'climacteric' in ethylene production is similarly retarded by about 10 days. In addition, spraying with B9 has a marked effect on the maximum rates of ethylene production by disks of peel prepared from the fruit. This is especially evident in the early picks when the climacteric rate of ethylene production of the treated fruit is only 20% of that of the controls. From Fig. 1 it is clear that the climacteric in fruit 'on' the tree is delayed by 3–4 weeks. The ethylene results for 1968 confirm this increased delay in fruit attached to the tree.

It is of interest to consider how far this inhibition of ethylene production can account for certain aspects of the effects of B9 on the fruit since some of the processes affected by B9 are known to be affected by ethylene (i.e. harvest drop and shoot elongation). The mechanism of the growth retarding properties of B9 is not yet understood but it is generally thought that its primary locus of action is on the biosynthesis and functioning of growth substances and in this gibberellins and IAA have been implicated. The intimate nature of the relationship between IAA-function and ethylene production has been described by many workers (Burg & Burg, 1966) and thus the present finding that B9 suppresses ethylene formation in apples fruits is particularly interesting. Looney (1968) showed that the inhibition of apple ripening by B9 is reversible by exogenously supplied ethylene and suggested that B9 retarded either ethylene production or its action. The former of these two possibilities seems more likely in view of the present work and the responsiveness of B9 treated fruit to exogenously supplied ethylene. Looney (1968) further proposed that the site of action of B9 is on the IAA levels in the pre-climacteric tissues. It is known that in some tissues application of IAA will stimulate ethylene production (Abeles, 1966) and some authors consider that the balance between IAA and ethylene regulates many physiological processes in the plant with the threshold for ethylene action decreasing as senescence proceeds (Burg & Burg, 1965).

The mode of action of IAA (Davies, Patterson & Trewavas, 1968) and ethylene (Abeles & Holm, 1966; Holm & Abeles, 1967) involves the stimulation of the production of specific RNA and protein moieties. Thus the effect of IAA in promoting ethylene

synthesis could be via the induction of specific RNAs and enzyme proteins involved in ethylene biosynthesis. This would agree with studies on the development of ethylene producing capacity (using protein synthesis inhibitors) in whole apples and pears (Frenkel, Klein & Dilley, 1968) and in the ageing of disks of pre-climacteric apples (Galliard *et al.*, 1968). The acceleration of the ripening of apples and pears by auxins has been reported (Hansen, 1946) but the present authors have been unable to reproduce this stimulation by application of IAA to disks during ageing (Rhodes, Wooltorton & Hulme, 1969). Very little evidence is available on the changes that occur in IAA and other growth substances during growth and maturation of fruit and thus this discussion must be largely speculative. In particular a breakdown product of B9, 1-dimethylhydrazine, is a powerful inhibitor of diamine oxidase which catalyses the conversion of tryptamine to indole acetaldehyde, a step necessary for IAA synthesis (Reed, 1965). There is evidence that B9 is slowly metabolized by apple tissue (Martin, Williams & Batger, 1964) but the products have not been identified.

Another possible effect of B9 is that it may act as an 'antigibberellin' (Lockhart, 1962; Kuraishi & Muir, 1963) but this seems unlikely in view of the known antagonistic effects of gibberellin and ethylene *action* (not production of ethylene) on ripening fruits and in senescence (Dostal & Leopold, 1967; Scott & Leopold, 1967). Other possible effects of B9 lie in its effects on respiratory processes. For instance, Knypl (1966) has postulated that B9 inhibits the synthesis of certain essential intermediates by acting as a structural analogue of succinic acid. Heatherbell, Howard & Wicken (1966) have shown that B9 at $5 \times 10^{-3}$ to $5 \times 10^{-4}$ M can uncouple oxidative phosphorylation in plant mitochondria. However, from the foregoing discussion, it seems most likely that B9 delays the climacteric and ethylene production by interfering in some way (most probably by affecting the hormonal balance of the tissue) wiith the development of the ethylene producing enzymes.

B9, which has such a marked effect on the onset of the respiration climacteric and the interaction of ethylene biosynthesis during the climacteric, has no marked inhibiting effects on the onset of the development of the malate decarboxylation system which has been shown to be associated with ripening in some fruits (Neal & Hulme, 1958; Hulme *et al.*, 1968). In the series of control fruits the development of the decarboxylation system lags behind the development of the climacteric while in the B9 treated fruits, this follows closely on the onset of the ethylene production and it in fact preceeds slightly the development in the control fruit. This difference may be more apparent than real since Burg & Burg (1962) have shown that physiological levels of ethylene inside the tissue may be reached before measurable amounts appear in the atmosphere outside the fruit. For example, the initial disks of pick 1, although producing no measurable ethylene into the ambient atmosphere in the 1st hour of incubation were, after 5 hr, producing – control fruit 4·8 and B9 treated fruit 2·1 nl/ethylene/g/hr. This, on the minimum conversion factor deduced by Burg & Burg (1962) represents 4·8 and 2·1 ppm, respectively, *within* the fruit. Since the threshold value for ethylene to

have a physiological effect on apples lies between 0·1 and 0·2 ppm (Burg, 1968) there may well still be sufficient ethylene within the B9 (as well as the control) fruits to initiate enzyme processes (e.g. malate effect) soon after picking. It appears that B9 may have a direct inhibitory effect on enzyme systems since we have found, that if disks of pre-climacteric fruit are 'aged' for 24 hr (see Rhodes *et al.*, 1968) the 'normal' development of the malate decarboxylating system is almost completely suppressed.

Our results agree with the suggestion of Blanpied, Smock & Kolles (1967) that B9 seems to be having a differential effect on various aspects of ripening and as such may prove to be a useful tool in studying the interrelationships between the various processes involved in ripening.

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# Uptake of salt in the kippering of herring

A. AITKEN AND C. R. BAINES

## Summary

The effects of several factors on the uptake of salt during the brining of herring for kippering have been studied. The most important factors were the brine concentration, the brining time and the rate of stirring. The orientation of the fish (skin up or skin down on the brine surface), the oil content and the size of the fish were less important.

## Introduction

Kippers are a semi-traditional British product prepared by light salting and mild smoking of split herring (*Clupea harengus*) (Burgess & Bannerman, 1963). Salting, to a level of 2–3% of the final smoked weight, is invariably carried out by immersion in a concentrated brine to which a dye is normally added. In the traditional process the herring are brined batchwise in tubs and the control of brining time and brine strength is usually rather limited. In addition, several layers of fish may be floating on the surface of the brine, with inevitable lack of uniformity of salt uptake. Large processing factories are now introducing continuous briners which have only a single layer of fish on the brine surface and allow closer control of operating conditions: the present investigation was carried out to give information on the factors controlling salt uptake for possible application to design of future briners. A factorial design was chosen for the experiment and as many controllable factors as possible were varied within the limits of normal commercial practice.

## Experimental

*Design*

The design was a split-plot one-sixth replicate of a $2^2 \times 4 \times 3^3$ factorial, the factors and levels being listed in Table 1. Two fish were sampled at each condition.

In addition to these controllable factors, the size and oil content of the fish varied continuously over a fairly wide range. Thickness (a measure of size) and oil content were treated as covariates.

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TABLE 1

| Factor | Level 0 | 1 | 2 | 3 | Alteration of levels |
|---|---|---|---|---|---|
| Brine concentration (°B)* | 70° | 85° | 100° | – | Between tanks |
| Brine temperature (°C) | – | 10° | 20° | – | Between days |
| Brining time (min) | 2 | 5 | 10 | 16 | Within tanks |
| Stirring | None | Moderate | Vigorous | – | Between tanks |
| Position in tank | – | Skin up | Skin down | – | Between days |
| Temperature history of fish | Fresh | Iced for 2 days | Frozen | – | Between days, within tanks |

* Brine strength is usually measured in degrees Brineometer (or Salinometer) and is the percentage by weight in the brine of saturated brine; 70°, 85° and 100° are equivalent to 210, 263 and 318 g NaCl/l, respectively.

*Procedure*

Herring, split for kippering, were obtained from a commercial splitting machine. (For kippers, herring are split down the back from snout to tail and the back-bone is not removed.) The fish were supplied within 36 hr of being caught and had been iced during most of this period. Six batches, each of seventy-two fish, were obtained on 2 successive days of 3 separate weeks. Thirty-six fish were brined when received, eighteen were frozen immediately and eighteen were iced for a further 2 days before treatment. Thirty-six fish were brined each day (all fresh or eighteen iced and eighteen frozen), six fish being brined at each of six sets of conditions. Before brining, the length (snout to tip of tail), thickness (at thickest point on bone and boneless sides) and weight of each split fish were measured. The frozen fish were thawed in water initially at 25°C.

Brining was carried out in stainless steel tanks 60 × 60 × 30 cm deep, in brine adjusted to the required concentration and temperature. To achieve vigorous stirring a 50-cm wide paddle was rotated at about 60 rev/min; the fish were fully immersed and continually turning over in the brine. The 'position in tank' factor does not operate at this stirring rate, which is probably as high as can be allowed without damaging the fish. For the 'no stirring' and 'moderate stirring' cases the fish were floating in a single layer on the surface. In 'moderate stirring' the brine was agitated by a small laboratory stirrer running at about 1000 rev/min and the fish were prevented from rotating with the brine. After brining, the fish were tentered (i.e. hung on hooks fixed to wooden bars), allowed to drip for 10 min and weighed (in the groups of six fish treated identically). After 30–60 min all fish were smoked to about 15% weight loss in a controlled fish-smoking kiln (Burgess & Bannerman, 1963). After smoking, the kippers were cooled for ½ hr, their external appearance noted, packed individually in plastic pouches and frozen until required for analysis.

*Analysis*

Two fish from each group of six were analysed. Each fish was weighed; since the original weight before kippering was known, it was possible to refer measurements to the original weight. These corrected values can be taken to apply with little error to the fish after brining but before smoking, as the weight change during brining is small. The tail and head but not the bone or skin were removed and the fish was cut lengthwise into the bone and boneless sides which were then weighed. Each side was minced and samples taken for chloride analysis. The two sides were then mixed and the moisture content measured. The oil content was determined on occasional samples.

Chloride was measured (Official Methods of Analysis of the Association of Agricultural Chemists, 1960) by nitric acid digestion in presence of excess standard silver nitrate followed by back titration with thiocyanate. Moisture was determined by heating at 105°C for 48 hr and oil either by the method of Bligh & Dyer (1959) applied to the wet mince or the dried residue or by Soxhlet extraction with ether of the dried material. Salt, moisture and oil contents are quoted as percentages (by weight) of the unbrined, unsmoked split fish. Thickness is in millimetres.

Fig. 1 shows the linear relationship between moisture content and oil content, the latter measured by the two methods mentioned. Oil contents not directly measured were derived from the moisture content using this line. The corresponding line obtained by Brandes & Dietrich (1953) for the edible portion of herring is shown and is in close agreement.

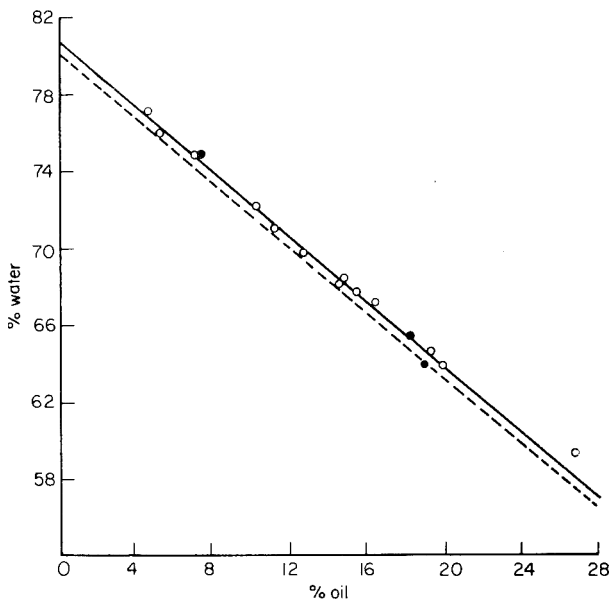


FIG. 1. Relationship between oil and water content: oil measured by Bligh & Dyer (1959) method (O) and Soxhlet extraction (●). ————, Present data; - - - - -, data of Brandes & Dietrich (1953).

*Statistical analysis*

The results for the bone and boneless sides of the kipper were treated separately. From the duplicates at each set of conditions, the linear regression of salt uptake on oil content and thickness was calculated. The effects of all the controlled factors and their standard errors were derived by standard least-squares procedures.

## Results

*Oil content and thickness*

In the equation:

$$\delta s = b_f\, \delta f + b_t\, \delta t, \tag{1}$$

where $\delta s$ is the change in salt content due to changes $\delta f$ and $\delta t$ in oil content and thickness, the regression coefficients $b_f$ and $b_t$ have the following values (standard errors in parentheses):

Bone side $\begin{cases} b_f = -0{\cdot}025\ (0{\cdot}007); \text{ significant at } 1\%, \\ b_t = -0{\cdot}016\ (0{\cdot}015); \text{ insignificant,} \end{cases}$

Boneless side $\begin{cases} b_f = -0{\cdot}051\ (0{\cdot}018); \text{ significant at } 1\%, \\ b_t = -0{\cdot}165\ (0{\cdot}054); \text{ significant at } 1\%. \end{cases}$

TABLE 2

| | Effect | Symbol | Estimate and standard error: Bone side | Estimate and standard error: Boneless side |
|---|---|---|---|---|
| Grand mean | | | 1·7537 (0·0135) | 3·0345 (0·0364) |
| Main effects | Brine strength (linear) | $b_L$ | 0·2509 (0·0171) | 0·4626 (0·0452) |
| | Brining time (linear) | $d_L$ | 0·2960 (0·0114) | 0·5282 (0·0298) |
| | Stirring (linear) | $s_L$ | 0·3964 (0·0166) | 0·9314 (0·0445) |
| | Stirring (quadratic) | $s_q$ | 0·2694 (0·0291) | 0·6120 (0·0783) |
| Interactions | Brine strength (linear) × stirring (linear) | $b_L s_L$ | 0·1096 (0·0228) | 0·3112 (0·0592) |
| | Brine strength (linear) × stirring (quadratic) | $b_L s_q$ | 0·2511 (0·0501) | 0·3651 (0·1251) |
| | Brining time (linear) × stirring (linear) | $d_L s_L$ | 0·1020 (0·0134) | 0·2090 (0·0360) |
| | Brining time (linear) × stirring (quadratic) | $d_L s_q$ | 0·0732 (0·0234) | 0·1464 (0·0630) |
| | Stirring (linear) × position in tank | $s_L P$ | 0·0770 (0·0226) | 0·1378 (0·0606) |

*Controllable factors and interactions*

Of the main factors, two were found not to have a significant influence on the salt uptake; these were the brine temperature and the temperature history of the fish. The numerical values of the significant effects and interactions, after eliminating the effects of oil content and thickness, are given in Table 2. These are expressed as increase in salt content per unit level, where the levels (0, 1, 2 and 3) are given in Table 1. The standard errors are given in parentheses. The level of significance is 1% in all cases except the interactions $d_{LSq}$ and $s_{Lp}$ for the boneless side which are significant only at the 5% level.

*Weight change during brining*

The mean change in weight of fish during brining was − 0·47%, i.e. a loss of weight, but the variability was high, both losses and gains being recorded. The total range was 2·38% to − 3·88%. Previous work on cod (*Gadus callarias*) at the Torry Research Station (1962) suggested that the brine strength would most influence the weight change: grouping of the data and recalculation of mean weight changes gave the following results:

| | Brine concentration | | |
|---|---|---|---|
| | 70° | 85° | 100° |
| Mean weight change (%) | 0·16 | − 0·52 | − 1·04 |
| Standard deviation | 1·11 | 0·97 | 1·13 |

The linear regression of weight change on brine strength proved to be highly significant; the variability is still very high and the effect of brine strength is unlikely to be noticeable in commercial practice.

The change in weight during brining is the net effect of salt uptake and change in water content of the fish. Since salt uptakes are all positive, the change in water content must account for the variation with brine strength of the direction of the weight change.

*Change in water content during brining*

The change in water content is simply obtained as the difference between the change in weight and the salt uptake. All changes were negative, i.e. all fish lost water to the brine. As in the previous section the data were grouped according to brine strength.

| | Brine concentration | | |
|---|---|---|---|
| | 70° | 85° | 100° |
| Mean change in water content (%) | − 1·79 | − 2·77 | − 3·63 |
| Standard deviation | 0·98 | 1·19 | 1·46 |

Again there is a significant association between loss of water and brine strength but the variability is high and further analysis of the data was not warranted. As might be expected, the water loss from the fish increased with increasing brine concentration.

*Appearance of the smoked fish*

The quality of smoked fish is judged commercially mainly on its appearance, though this is in fact not a sound indicator of quality. It is commonly said that fish for smoking should not be brined in saturated brine as this may lead to the absence of the desirable surface gloss on the smoked fish. In the present experiment it was observed that poor surface gloss was not necessarily associated with the use of saturated brine but rather with a salt content of over 3% (expressed as the mean salt content of the whole kipper).

## Discussion

The experiment described was intended to demonstrate the factors of commercial importance in the brining of herring. Had the intention been to examine the underlying mechanisms of brining a different approach would have been required and experiments of this kind have been carried out at the Torry Research Station (1962) and by Del Valle & Nickerson (1967). The present experiment is unlikely to reveal any fundamental underlying principles but some of the results can be examined and interpreted in the light of the more basic studies.

*Oil content*

The earlier work had shown that, in well stirred brine, the uptake of salt is a process of diffusion into the fish. Since diffusion will take place only in the aqueous phase of the tissue, an increase of oil content and the consequent reduction in water content (Brandes & Dietrich, 1953) would lead one to expect a decreased rate of salt uptake as observed in practice. This effect has long been recognized in commercial curing.

It is possible by making certain assumptions to calculate the effect on the salt uptake of change of oil content near the mean of 16·6%. It is known that for diffusion controlled processes the initial uptake at a given time is proportional to the square root of the diffusion coefficient (e.g. Crank, 1956, Fig. 4.6). If we assume that the apparent diffusion coefficient is directly proportional to the water content, it can be calculated that a 1% change in oil content would cause a change in the mean salt uptake by the bone side of 0·014 and by the boneless side of 0·023, values which are below the experimental ones, 0·025 and 0·051, respectively. The latter values are, however, subject to considerable uncertainty, as shown by the rather large standard errors, and the agreement may in fact be not unsatisfactory. On the other hand, there are reasons for believing that the calculations are of doubtful validity; in particular, it is known that the distribution of oil within the fish is far from uniform, being much higher near the skin so that the variation of apparent diffusion coefficient with oil content is not easily estimated.

*Effect of size*

The work already referred to on the uptake of salt would lead one to expect that, other things being equal, the uptake would vary with the smallest dimension, namely the thickness, of the fish and it was for this reason that the regression on thickness was carried out. To a first approximation the percentage salt uptake should be inversely proportional to the thickness. At the mean thickness of the boneless side, a change in thickness of 1 mm should lead to a change in salt uptake of 0·276 on average, which is considerably more than the experimental value 0·165; as before the uncertainty of the experimental value is considerable.

A related question is the difference in the salt uptakes of the bone and boneless sides. By a simple calculation one would expect the bone side, with a mean thickness of 15·3 mm, to have a mean salt content of 2·18%. The actual mean is 1·75%: the difference is most unlikely to be due to experimental error in either value. It is clear that the presence of the bone has reduced the salt uptake by a greater amount than would be anticipated from the increased thickness, perhaps by reducing the surface area across which transport of salt is taking place.

*Effects of controlled variables*

Discussion will centre on three aspects: (a) why are some effects not significant, (b) are the magnitudes of the significant effects in accordance with expectation, and (c) can any interactions of main effects be explained?

(a) It had been expected from previous work that the brine temperature would have a small but noticeable influence on the rate of salt uptake. It must be concluded that the effect is too small to be detected in the present experiment.

Neither keeping the fish in ice for 2 days nor freezing affected the salt uptake and there is no obvious reason why they should do so. There is certainly a belief in the industry that spoiling fish and frozen fish pick up salt more rapidly than fresh fish but there is little evidence to substantiate this. The effect, if real, is clearly quite small in the range covered by the present experiments. A much longer period in ice or extended storage in the frozen state might show significant effects.

(b) The significant main effects are the brine concentration, the brining time and the stirring rate.

It would be reasonable to expect the salt uptake to be directly proportional to brine concentration and this appears to be approximately borne out by the other studies quoted. In the present experiment, however, although the relation was found to be linear, with a rate of increase dependent on the stirring rate, there were marked deviations from strict proportionality at particlar levels of the other factors. The results thus do not afford any evidence that uptake is proportional to brine concentration.

The influence of brining time is again complicated by interaction with the stirring rate. Previous work on the mechanism of brining which showed that, in well stirred

solutions, the uptake is controlled by diffusion within the fish, would lead one to expect that in the present experiment the uptake would be proportional to the square root of time, at least in the vigorously stirred condition and probably also with moderate stirring. In fact in no set of conditions was the uptake proportional to the square root of time. No explanation can be offered for this unexpected behaviour.

The magnitude of the stirring effect is roughly in accordance with expectation; as the levels of stirring are purely descriptive no quantitative calculation can be made of the anticipated effect of altering the stirring rate.

(c) The interactions between the different factors all involve the stirring rate. Thus the effects of brine strength and brining time depend upon the level of stirring rate being considered. No obvious explanation of these interactions can be suggested. The effect of position, skin up or skin down, appears as an interaction mainly because the position factor necessarily does not apply to the vigorous stirring condition. The effect is to be expected in so far as the resistance to diffusion of both the skin and the oily layer beneath the skin leads to a lower uptake in the skin-downward position. The effect was perhaps smaller than might have been expected and is probably not of commercial importance.

*Variability of results*

Despite the careful control of experimental conditions in the present investigation, the variability of the results was quite high; the coefficient of variation was 9·3% for the bone side and 14·4% for the boneless side. The reason must lie in the variability of the raw material, the split fish. (The within-fish variability, resulting from sampling and analytical error, is at least an order of magnitude lower.) The fat content is the best known aspect of the biological variability of herring and account of this was taken, but there are possibly other factors such as nutritional status, pH and many others which might marginally affect the subsequent brining behaviour. Apart from biological variability, the treatment of the fish must introduce some minor influences which are either beyond control or impossible to quantify. These might include mechanical damage during catching and subsequent handling and variation introduced by the splitting process.

The variability is unlikely to be any less in commercial practice since, even when continuous mechanical briners are used, the control of the known controllable factors is unlikely to be as good as in the present experiment.

*Simplification of uptake equation*

The salt content of a kipper under any combination of conditions within the limits used in the present experiment can be estimated by averaging the salt contents of the bone and boneless sides indicated separately in Table 2, the average being weighted to take into account the different weights of the two sides. The mean weight ratio of the bone to the boneless side was 1·49 with a standard deviation of 0·101. To be of

practical use, a simple equation is required for predicting the salt content of a kipper. Since it is not possible in practice to ensure that the fish in a batch or in a continuous briner are brined all skin up or all skin down, the average of these conditions must be taken as an approximation. For the mean fat content of 16·6% and the mean boneless side thickness of 11·0 mm the mean salt uptake of a kipper can be predicted from:

$$\text{Salt}_k\ (\%) = 0{\cdot}0163\ B + 0{\cdot}3230\ \sqrt{D} + S\ (2{\cdot}2696 - 0{\cdot}0269\ B - 0{\cdot}0698\sqrt{D}) - S^2\ (1{\cdot}5967 - 0{\cdot}0198\ B - 0{\cdot}1190\sqrt{D}) - 0{\cdot}4661, \qquad (2)$$

where $B$ is the brine strength in degrees Brineometer, $D$ is the duration of brining in minutes and $S$ has the values 0, 1 and 2 for unstirred, moderate and vigorous stirring, respectively. Numerical values of the uptake predicted by this equation are shown on three graphs (Fig. 2a, b and c) for the three levels of brine concentration. The equation has not been tested outside the present range of conditions.

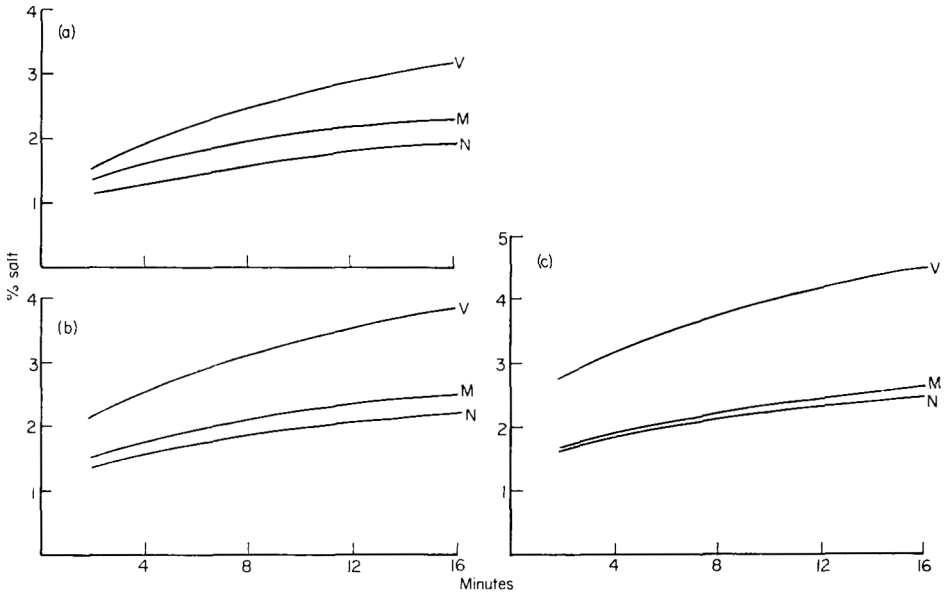


FIG. 2. Predicted salt uptake by herring as function of time for (a) 70°B brine, (b) 85°B brine and (c) 100°B brine. V, vigorous stirring; M, moderate stirring; N, unstirred.

Differences of the oil content and thickness from the means can be taken into account by equation (1) using weighted mean values of the regression coefficients $b_f$ and $b_t$. Thus:

$$\text{Change of salt content} = 0{\cdot}035\ (16{\cdot}6 - F) + 0{\cdot}066\ (11{\cdot}0 - T), \qquad (3)$$

where $F$ is the percentage oil content and $T$ is the maximum thickness of the boneless side in millimetres. The salt content is here expressed in terms of the weight of the original fish and a further correction will be required to take account of the weight loss during processing.

No wide generality can be claimed for the above equations, since they strictly refer only to herring caught in a fairly limited area at a particular season.

The traditional kipper has in recent years been giving way to the boneless kipper; this product differs from the traditional one by being slit along the belly and by having the head and backbone removed. Fish split in this manner are likely to approximate quite closely in their brining behaviour to the boneless side of a kipper-split fish, in which case the data of the present paper can be used.

## Acknowledgment

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# The xerophilic mould, *Xeromyces bisporus*, as a spoilage organism

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## Summary

Some spoilage outbreaks resulting from the growth of the obligate xerophilic mould *Xeromyces bisporus* are described. Methods and media are suggested for the isolation of the mould, and observations are given on the tolerance to $CO_2$. Data are given on the heat resistance of its ascospores. The spoilage characteristics of the mould are discussed with relevance to the findings.


## Introduction

*Xeromyces bisporus* Fraser was first recorded by Fraser (1953), who also gave a full description of the morphological and growth characteristics of this xerophilic mould. It was originally discovered by Scott in 1946, in Australia, growing on mouldy stick liquorice, and is of great interest due to its strict xerophilic requirements. Scott (1957) showed that growth did not occur at water activities ($A_w$) above about 0·97, with an optimum of about 0·93. Studies by Pitt & Christian (1968) on the minimal water requirements for the germination of spores of this mould showed that the aleuriospores germinated at a $A_w$ of 0·605 and ascospores at 0·644. The organism was probably first observed in the United Kingdom in 1959, when investigation in the Authors' laboratory revealed it as the causative spoilage agent of packaged table jellies. Reference to this particular spoilage outbreak was made by Bunker (1967).

Since this outbreak of spoilage of table jellies in 1959, five other instances of the occurrence of *X. bisporus* causing spoilage on substrates of low water activity have been observed in this laboratory. The following is a brief description of these spoilage incidents:

In 1960, *X. bisporus* was isolated from dried prunes which had been imported from the South of France. The prunes were covered with a fine film which closely resembled the initial stages of sugar migration but which, on microscopic examination and subsequent culturing, was identified as the growth of *X. bisporus*.

Two spoilage incidents due to mould were investigated in tobacco flakes (nominal $A_w$ 0·86) from two different tobacco manufacturers. In each case *X. bisporus* appeared

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to be the sole mould present. White mycelial growth of the mould was observed closely adhering to the surface of the tobacco flakes.

In 1967, mould growth on a sample of currants purchased from a shop was confirmed as *X. bisporus*. The currants had been packaged in high density polythene film and the mould appeared as a restricted white growth on the fruit surface. Microscopic examination revealed the presence of the typical fusiform ascospores of *X. bisporus* and this mould was recovered on culturing. The approximate $A_w$ of the currants was 0·66–0·67.

Recently (1968) a further case of spoilage due to mould growth was observed in a chocolate sauce ($A_w$ 0·77) packaged in polythene–cellulose laminate pouches. The sauce was cloudy due to mould growth and *X. bisporus* was the only organism recovered on culturing.

Recorded references to this mould would appear to be rare and the following details concerning the spoilage, isolation methods used and general observations on the mould are given as being of commercial as well as of general scientific interest. Spoilage incidents due to the growth of *X. bisporus* have apparently so far not received the attention of food scientists in this country, but this is believed to be due mainly to the fact that it has not been detected since it requires special isolation methods. It is also possible that packaging techniques of relatively recent origin may create environmental conditions under which this mould is more likely to develop.

## Materials and methods

The media used for isolation purposes and for the various studies reported here were those described by Fraser (1953) and additionally the following, all of which will readily support the growth of osmophilic moulds:

50% *sucrose malt extract agar* (50% SMEA)
- 500 g Sucrose ('Analar'),
- 50 g malt extract agar granules (Oxoid),
- 500 ml distilled water.

60% *sucrose malt extract agar* (60% SMEA)
- 600 g Sucrose ('Analar'),
- 60 g malt extract agar granules (Oxoid),
- 400 ml distilled water.

60% *sucrose malt extract broth* (60% SMEB)
- 600 g Sucrose ('Analar'),
- 20 g malt extract broth granules (Oxoid),
- 400 ml distilled water.

45% *dextrose yeast-extract agar* (DYEA)

| | |
|---|---|
| 450 g | Dextrose ('Analar'), |
| 5 g | yeast extract, |
| 20 g | Difco agar, |
| 550 ml | distilled water. |

In each case the above media are 'sterilized' at 100°C for 30 min.

Isolation from mould infected natural substrates was made using one or other of the solid media listed above.

On substrates where other osmophilic (or osmotolerant) micro-organisms were present, suspensions of the infected material were made in sterile 65% sucrose solution. In an attempt to eliminate the unwanted flora the suspension was then heated for 10 min at 65°C and portions plated in 50% SMEA. This technique proved successful in these studies.

*Preparation of ascospores suspension*

A suspension containing 1000 ascospores/ml was prepared in 60% sucrose solution. This suspension was heated at 70°C for 5 min to inactivate mycelial fragments. The ascospores were harvested from a 5-week culture on 60% SMEA. Counts were made microscopically.

*Determination of heat resistance*

One hundred millilitres of inoculum were mixed with 400 ml of 60% SMEA at 50°C. Ten-millilitre aliquots of this mixture were dispensed into sterile plugged tubes. These tubes were immediately heated in a water-bath for the required times and temperature (45 sec were allowed for coming up to temperature). The tubes were then water cooled and the agar solidified as long slopes and subsequently incubated for 28 days at 30°C.

*Tolerance to* $CO_2$

Pure cultures of the following moulds were inoculated onto prepared slopes of 50% SMEA: *X. bisporus* and three strains of *Aspergillus* spp. selected for their tolerance of substrates of low $A_w$. The inoculated tubes were suspended over saturated potassium bromide in 1-litre flanged 'Quickfit' culture vessels fitted with multisocket flat flange adapters. The required gas mixtures were prepared from the individual gases and the concentrations checked by gas chromatographic analysis, initially and at intervals during, ensuring 25°C incubation.

## Results and discussion

*Xeromyces bisporus* would appear to be a spoilage organism in various situations where

the growth of other moulds is completely inhibited or severely restricted. It seems likely that, due to its unusual growth requirements, this mould might be overlooked in normal examination procedures. In order to confirm its presence culturally, it is necessary to use media of low $A_w$, possibly in conjunction with a selective heating process (e.g. 10 min at 65°C).

Our observations, which have shown that a number of foodstuffs and other low $A_w$ materials are able to support growth of the mould, have been confirmed by Pitt & Christian (1968) in their studies of the water relations of xerophilic fungi isolated from prunes. When *X. bisporus* ascospores are present on the surfaces of such substrates, germination will occur, with subsequent outgrowth, if the prevailing relative humidity (RH) is sufficiently high. Once surface mycelial growth has commenced, and this may not easily be discernible on close scrutiny, growth may continue even when the prevailing RH falls below that necessary to initiate growth if hyphal penetration of the substrate has occurred.

Studies made by Scott (1957) and Pitt & Christian (1968) indicate that growth on low $A_w$ substrates is slow and, therefore, that spoilage of foodstuffs of low $A_w$ by *X. bisporus* may only become evident after prolonged storage.

Ascospores of the mould appear to be quite heat resistant, (Table 1) though somewhat less so that those of *Byssochlamys fulva* which are stated to survive 30 min at 85°C and 10 min at 87·7°C (Gillespy & Thorpe, 1962). However, this heat resistance may possibly have been influenced by the high sugar content of the suspending medium used in this study.

The mould would appear to be very tolerant of high $CO_2$ concentrations, at least in the presence of oxygen (see Table 2) and this could conceivably allow it to grow competitively in some situations in which other moulds would be restricted or completely inhibited. Variations in the micro-climate in any situation can produce changes in microflora, e.g. a build-up of $CO_2$ produced by one micro-organism may produce changes in, or be inhibitory to, others, giving rise to an ecological succession (Waid, 1968). Situations of this type have been discussed by Griffin (1963), although in a different context, for soil substrates of high moisture content but it could also be the

TABLE 1. Heat resistance of ascospores in 60% SMEA (approximately pH 5·4) (2000 ascospores/heating)

| | |
|---|---|
| At 75°C ascospores survived for | 36 min but not for 40 min |
| At 80°C ascospores survived for | 9 min but not for 12 min |
| At 85°C ascospores survived for | 4 min but not for 6 min |
| At 90°C ascospores survived for | 2 min but not for 3 min |

Results were recorded after 28 days incubation at 30°C.

TABLE 2. $CO_2$ tolerance of *Xeromyces bisporus* compared with other osmophilic mould species grown on 50% SMEA

| % gas concentration | | | Moulds | |
|---|---|---|---|---|
| $CO_2$ | $N_2$ | $O_2$ | *Xeromyces bisporus* | *Aspergillus* sp. |
| 70 | 29 | 1 | + | + |
| 85 | 12 | 3 | + | + |
| 85 | 14 | 1 | + | — |
| 95 | 4 | 1 | + | — |

+, Growth; —, no growth.
Results recorded after 5 months at 25°C.

case for substrates of low $A_w$ where $CO_2$ is evolved due to chemical activity of a product such as occurs in some packaged materials.

In view of the increasing use of pre-packaged foodstuffs and other materials in flexible and other types of package more frequent occurrence of spoilage due to outgrowth of *X. bisporus* is possible and, therefore, stricter attention to packaging conditions of vulnerable materials may be required.

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# Copper–flavonoid complexes in acidic solutions

K. A. HARPER


## Summary

Amperometric titration was used to detect complexing of cupric ions by flavonoids in solutions more acid than pH 4·5. Strongest complexing ability was shown by the 3-hydroxy-4-carbonyl system although the 5-hydroxy-4-carbonyl system also complexed with copper in acid solution. The *o*-diphenolic grouping did not form complexes under the conditions used. Complexing ability was enhanced by the presence of hydroxyl groups in conjugation with the carbonyl group. Quercetin was the only flavonoid tested capable of complexing copper at pH 2·3. The significance of these results to the anti-oxidant action of flavonoids in fruit juices is discussed.


## Introduction

The ability of flavonoids to form complexes with cupric ions has an important bearing on the anti-oxidant activity of these substances in the copper-catalysed oxidation of ascorbic acid in natural fruit juices (Harper, Morton & Rolfe, 1959). To date, studies on complex formation between flavonoids and cupric ions have been mainly concerned with considerably less acid conditions than those in such products as blackcurrant juice in which ascorbic acid is remarkably stable (Clegg & Morton, 1968). The role of copper–flavonoid complexes in human physiology (Clark & Geissman, 1949; Detty, Heston & Wender, 1955) and in fat autoxidation (Kelly & Watts, 1957; Crawford, Sinnhuber & Aft, 1961) was studied in weakly acid or neutral conditions, and in investigations of complex formation between cupric ions and crude and purified apple phenolics (principally catechin) Timberlake (1957a) did not use solutions of pH below 3·25. This note reports the study of the interaction between cupric ions and several pure flavonoids under acidic conditions such as exist in natural blackcurrant juice.

## Experimental

The techniques used were a modification of the amperometric titration method (Detty *et al.*, 1955) employed to study copper–flavonoid complexes at moderate pH. Copper sulphate solutions ($2 \times 10^{-4}$ M, 12·7 ppm) were prepared in buffers based on sodium

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acetate and hydrochloric acid with pH values of 2·3, 3·1 and 4·5; gelatine (0·005%) was added to inhibit maxima effects. The solutions were de-oxygenated by the passage of nitrogen and immediately titrated with the flavonoid solution (0·01 M in ethanol). The current flowing between a dropping mercury cathode and the mercury pool anode was measured with a spot galvanometer ($7 \times 10^{-3}$ μA/mm) in a simple polarographic circuit. Polarograms of each system showed that 0·60 V applied across the electrodes allowed the measurements to be made on the plateau of the copper wave without interference from the flavonoid reduction wave.

The resulting titration curves showed a constant current when no complex was formed, and a decrease in current when the addition of flavonoid resulted in complex formation. The point of inflexion of the titration curve indicated the ratio of copper to flavonoid in the complex. The decrease in current during titration was a measure of the amount of copper involved in complex formation and this value at the point of inflexion was expressed as a percentage of the initial current to give an approximate measure of the percentage of copper in complex form. The results obtained with various phenolic substances of increasing hydroxyl substitution are shown in Table 1.

TABLE 1. Percentage complexing of copper with polyphenols in acid solutions

| Polyphenol | pH 2·3 | pH 3·1 | pH 4·5 |
|---|---|---|---|
| Flavone | 0 | 0 | 0 |
| Catechol | 0 | 0 | 0 |
| D-Catechin (3,3′,4′,5,7-tetrahydroxyflavan) | 0 | 0 | 0 |
| Tectochrysin (5-hydroxy-7-methoxyflavone) | 0 | 0 | 9 |
| Chrysin (5,7-dihydroxyflavone) | 0 | 25 | 25 |
| Robinetin (3,3′,4′,5′,7-pentahydroxyflavone) | 0 | 50 | 76 |
| Kaempferol (3,4′,5,7-tetrahydroxyflavone) | 0 | 59 | 95 |
| Quercetin (3,3′,4′,5,7-pentahydroxyflavone) | 18 | 69 | 95 |

## Results

Although all 3-hydroxyflavones formed complexes of comparable stability at pH 3·1 and 4·5, only the quercetin complex was stable at pH 2·3, probably as a result of additional contributions to the resonating system arising from the presence of 4′, 5 and 7 hydroxyl groups. The variation in the extent of complex formation shown by the 3-hydroxyflavones (robinetin and kaempferol) compared with the 5-hydroxyflavones

(tectochrysin and chrysin) can be explained in similar terms; Jurd & Geissman (1956) had previously suggested that such resonating systems were responsible for the differing stabilities of aluminium–flavonoid complexes with different hydroxylation patterns. The 3-hydroxyflavone system clearly formed more stable complexes with cupric ions in acid solution than did the 5-hydroxyflavone system; a similar observation has been made with respect to aluminium complexes by Jurd & Geissman (1956).

The 3′,4′-dihydroxyflavonoid system, either alone or in combination with other substituents on the flavonoid nucleus, did not form complexes under the conditions used. Thus catechin formed no copper complexes at all at pH 2·3–4·5, and the polyfunctional flavonoids only formed complexes with a ratio of two moles of flavonoid to one mole of copper. Timberlake (1957b, 1959) working with simple polyhydroxyphenolics above pH 3·0 and Detty *et al.* (1955) working with flavones and flavanones above pH 5·0 had obtained similar results, reporting that *o*-dihydroxyphenols only formed stable copper complexes at higher pH levels. The inactivity of this system towards copper ions in acidic solutions was also observed in cyanidin chloride, even though such a group will form complexes with aluminium ions (Harborne, 1958); the inability of anthocyanins to react with the bivalent ions of transition metals has been noted previously (Bayer, 1966).

These findings are significant in the study of fruit juices such as blackcurrant juice, in which the anti-oxidant activity of polyphenols is often attributed to their ability to sequester trace metal catalysts. Even those flavonoids like quercetin which are capable of forming complexes with copper at low pH do so to only a limited extent in acetate buffer and no complexing could be demonstrated in citrate buffer at pH 2·3. The activity of flavonoids as anti-oxidants in acid solutions cannot, therefore, be considered due to their sequestering ability, especially when acids such as citric and malic are present which are themselves capable of sequestering metal ions (Parry & Du Bois 1952; Timberlake, 1960).

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# Book Reviews

**Recent Advances in Food Science.** Volume 4: **Low Temperature Biology of Foodstuffs.** Ed. by J. HAWTHORN and E. R. ROLFE.
Oxford: Pergamon Press, 1969. Pp. 458. £6.

This volume records the proceedings of a NATO advanced study institute held at the University of Strathclyde in September 1966, and includes papers by a number of specialists in Europe, America and Canada, covering advances in low temperature biology with a wide range of topics.

The papers in the first half of the book are concerned with the behaviour of plant and animal cells, water content, nucleation and the growth of ice crystals in water, the behaviour of the ice phase and ice formation. Professor Luyet's paper on ice formation contains some excellent photographs, together with data on the behaviour of the ice phase in aqueous solutions.

An account of the freezing of fruits and vegetables, low temperature injury, post-mortem changes in meat, thaw rigor, and the effects of freezing on the protein of fish muscle in the second half of the book is followed by papers on deterioration and storage life of fish, the effect on microbial populations of foodstuffs, and objective tests for frozen food quality.

Undoubtedly this well-illustrated volume brings together many different facets of the subject, and makes stimulating reading. There are contributions from twenty-three authors in all, and each paper concludes with a long list of up to date references. The editors are to be congratulated on producing an interesting and useful addition to the series, *Recent Advances in Food Science;* it contains very valuable reference material and will be essential for those working in this field.

D. E. VERRIER

**Clinical Toxicology of Commercial Products.** By R. E. GLEASON, R. P. GOSSELIN, M. N. HODGE and H. C. SMITH.
Baltimore: Williams & Wilkins; Edinburgh: Livingstone, 1969. Pp. xii + 1432. £11 10s.

The purpose of this book, as stated in the Preface, is to assist the physician in dealing quickly with acute poisoning through the misuse of commercial products. The original edition was published in 1957 and the need for a third edition within 12 years undoubtedly testifies to its predecessors having enjoyed a good reception, as well as to the rapidly changing nature of the subject. The authors truly represent a high level of

expertise in the field of toxicology and the work is certainly comprehensive and authoritative.

The lay-out has been carefully designed to facilitate rapid reference in poisoning emergencies. Sections dealing with, for example, first aid, ingredients of branded products and manufacturers' addresses are identifiable at a glance and each section is also planned for quick searching. The listed commercial products are representative of the U.S.A. market and the value of such data is naturally rather limited for the U.K. reader. There is, on the other hand, an enormous wealth of general information on the toxic properties of a wide range of typical ingredients and formulations, which transcends national boundaries.

Product brands deemed by the authors to merit inclusion comprise a variety of packaged commodities possibly capable of giving rise to accidental or other forms of poisoning hazard. They include proprietary medicines, cosmetics, household products and horticultural aids among others. Where available, lists of the constituents of branded items are given. Typical formulations for similar products are shown in another section, as a further aid to the physician who needs a quick indication of likely causes of poisoning. The book does not, as the title might perhaps suggest, give a dossier of probable lethal doses for the branded products; a wealth of information concerning toxicity ratings is, however, given in the extensive 'Ingredients Index'. Toxicity ratings follow the pattern of the original Hodge & Sterner classification, but are derived only in part from laboratory animal oral $LD_{50}$ findings. Where available, actual experience of human exposure takes priority as the basis for the toxicity rating. The ratings range from 1 (practically non-toxic), indicating that the probable human lethal dose will exceed 15 g/kg and equivalent to a dose of more than 1 quart for an adult, to 6 (super toxic), with a lethal dose below 5 mg/kg, equivalent to less than 7 drops consumed by a 70-kg man. There are theoretical and practical objections to a simple scheme like this, but the physician with a dangerously ill poisoning case will doubtless be willing to accept the somewhat restricted validity of an empirical approach.

This review may suggest some of the ways in which the book in question could be of value beyond its primary target readership. It will not, for example, serve as a major reference source on the safety of food additives but it does offer a great mass of supplementary or 'fringe' information which might take much longer to locate elsewhere.

N. J. VAN ABBÉ

**Practical Meat Inspection.** By ANDREW WILSON.
Oxford and Edinburgh: Blackwell Scientific Publications, 1968. Pp. vii + 196. £2.

This book contains a great deal of sound practical advice, but needs firmer editing, as much of its merit is lost through apparently illogical presentation and the use of technical terms which are not explained, e.g. foramen, fungiform and vallate papillae, lesion,

metazoa, multinucleated giant cells. A greater degree of consistency in description is particularly required and more emphasis should be given to the prevalence and relative importance of the pathological conditions dealt with, as the student meat inspector cannot be expected to be familiar with these most important aspects of the subject.

Some shifts of emphasis would also be advantageous. For example, although an increase in the amount of tuberculosis found in cattle can be expected to follow the reduction in frequency of tuberculin testing in some areas of Britain, it is questionable whether description of the disease now merits two and a half pages.

Specimens chosen for illustrations have no doubt been most carefully selected, but, in common with many works on pathology, poor colour reproduction unfortunately limits their value for instructional purposes. There are useful diagrams showing the differentiation of organs from various species and also illustrating the lymphatic systems of the ox.

An Appendix lists enactments of particular importance to the meat inspector and then summarizes certain sections of the Food and Drugs Act, 1955. Since it is essential for the student to study the legislation in detail, it is suggested that this Appendix would be more valuable if the summarized sections of the Act were replaced by a few lines covering the major provisions of each enactment listed. This would help the student to refer to the law relating to any aspect of the subject.

The book is well produced, is of convenient size and there are very few printing errors, but proof reading needs greater attention. The definite or indefinite articles have been omitted in several places and the resulting passages read like lecture notes, although this style has not been consistently adopted.

T. M. LEACH

**Post-Process Sanitation in Canneries.** Technical Manual No. 1. By R. H. THORPE and J. R. EVERTON.
Chipping Campden, Gloucestershire: Fruit and Vegetable Preservation Research Association, 1969. Pp. 188. £5 5s.

This is the first of a series of technical manuals being published by the Fruit and Vegetable Preservation Research Association, Chipping Campden, Gloucestershire. The use of hydrostatic sterilizers has increased considerably in recent years and has led to some unexpected microbiological problems. This book has arisen largely as a result of the efforts of the two authors in finding solutions to these problems. Apart from users of hydrostatic sterilizers, users of batch sterilizers and simpler continuous sterilizers would find this book of considerable interest.

After some introductory chapters, the authors go on to discuss bacteriological standards, recommendations for can cooling water systems, recommendations for the sanitation of post process can handling equipment, and recommendations for personal

hygiene of operatives handling processed cans. There are six useful appendices ranging from determination of chlorine residuals in can cooling water to a suggested syllabus for training operatives.

Throughout the approach is a practical one aimed at supervisors of all levels. The only criticism that I can make is that some of the recommended concentrations of chlorine solutions and quaternary ammonium compounds are rather higher than I should have thought desirable.

H. D. G. ROPER

**Practical Canning.** Third edition. By ARTHUR LOCK.
London: Food Trade Press 1969. Pp. xvi + 415. 14 4s.

The qualifying adjective in the title is appropriate, for this book contains much practical advice for canners of fruit and vegetables, based on the author's 50 years' experience, acquired the hard way. An experienced canner may, with discrimination, glean useful information from it, but the beginner should not take it all for gospel.

The scientific bases of food preservation are not discussed; indeed, the author seems to have little time for science and technology, apart from a brief reference to the possible value of employing a food chemist or technologist in the cannery. The text is virtually the same as in the second edition of 1960, apart from a few amendments and additions, such as a couple of pages on the canning of new potatoes. There are, however, nearly three times as many illustrations of machinery and equipment, mostly modern. Attempts to bring the text wholly up to date have not been thorough, and it is disconcerting to come across references to practices during the war 25 years ago, to obsolete can sizes and to such a statement as 'the usual working pressure of retorts on vegetables is 10 to 11 lb. per sq. in. and the low-pressure main should be set at 20 lb. per sq. in. . . .'. Other instances could be given of out-of-date methods described and of references to information which has been superseded.

In the chapter on retort operation much of the advice is sound, but a glaring omission is any emphasis on the vital matter of efficient venting. The recommended practice could be dangerous, especially when divider plates were in use. The important matter of hygiene and sanitation in canneries is barely mentioned, and measures to minimize infection by leakage are not discussed. The index has been much extended compared with the former editions, but is very poorly compiled, headings and subheadings being lifted from the text to the index with the initial word, in most cases, having little relevance to the subject matter of which the reader seeks information.

In spite of these criticisms readers of this book may rely on much of the advice given on canning and cannery operations, though they will have to look elsewhere for an understanding of the technological processes involved.

T. G. GILLESPY

## Books received

**Edible Fats and Oils.** By NORMAN E. BEDNARCYK.
U.S.A.: Noyes Development Corporation, 1969. Pp. 404. $35.

**Protein-Enriched Cereal Foods for World Needs.** Ed. by MAX MULLER.
U.S.A.: American Association of Cereal Chemists Inc., 1969. Pp. x + 344. $7.50.

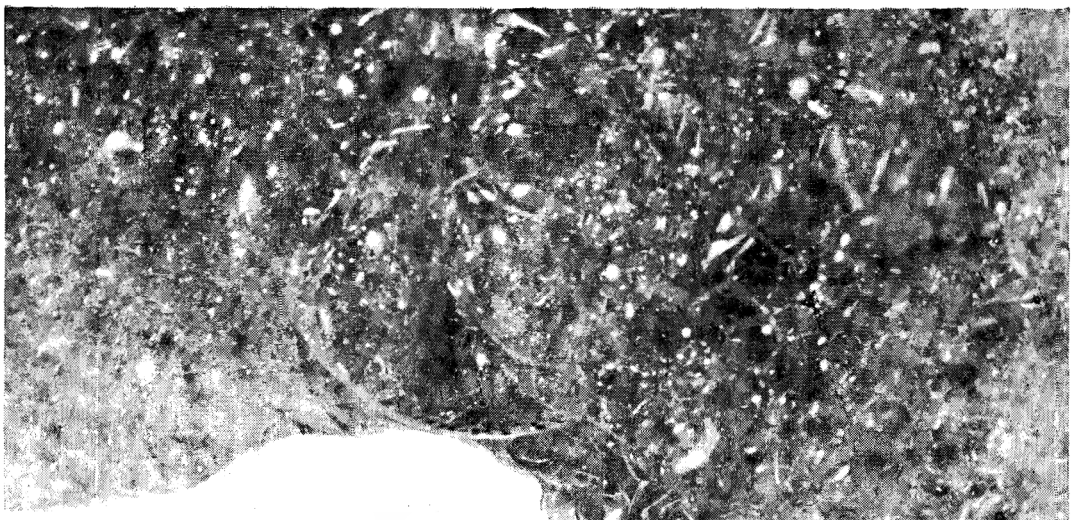
**Ernahrung und Atherosklerose.** Ed. by J. C. SOMOGYI.
Basel: Karger, 1969. Pp. 144. £4 15s.

## Addendum

HARPER, K.A., MORTON, A.D. & ROLFE, E.J. (1969). The phenolic compounds of blackcurrant juice and their protective effect on ascorbic acid. III. The mechanism of ascorbic acid oxidation and its inhibition by flavonoids. *J. Fd Technol.* **4**, 255.

The authors wish to point out that the work described in this paper was initiated and financed by the Department of Food Science of the University of Strathclyde and would like to acknowledge their indebtedness to Professor J. Hawthorn of that Department.

# AUTHOR INDEX TO VOLUME 4



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# CONTENTS

## Volume 4, Number 1, March 1969



## Volume 4, Number 2, June 1969

## Volume 4, Number 3, September 1969

## Volume 4, Number 4, December 1969

Book Reviews

# JOURNAL OF FOOD TECHNOLOGY: NOTICE TO CONTRIBUTORS

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**Standard usage.** The *Concise Oxford English Dictionary* is used as a reference for all spelling and hyphenation. Verbs which contain the suffix ize (ise) and their derivatives should be spelt with the z. Statistics and measurements should always be given in figures, i.e. 10 min, 20 hr, 5 ml, except where the number begins the sentence. When the number does *not* refer to a unit of measurement, it is spelt out except where the number is greater than one hundred.

**Abbreviations.** Abbreviations for some of the commoner units are given below. The abbreviation for the plural of a unit is the same as that for the singular unless confusion is likely to arise.

| | | | |
|---|---|---|---|
| gram(s) | g | second(s) | sec |
| kilogram(s) | kg | cubic millimetre(s) | $mm^3$ |
| milligram(s) | | millimetre(s) | mm |
| ($10^{-3}$ g) | mg | centimetre(s) | cm |
| microgram(s) | | litre(s) | l |
| ($10^{-6}$ g) | µg | millilitre(s) | ml |
| nanogram(s) | | pound(s) | lb |
| ($10^{-9}$ g) | ng | gallon(s) | gal |
| hour(s) | hr | milliequivalent | mEq |
| minute(s) | min | $R_F$ values | $R_F$ |

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## Contents



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