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Concentration processes for liquid foods containing volatile flavours and aromas

H. A. C. THIJSSEN

Summary

Three concentration processes are technically feasible for the selective dewatering of liquid food, viz. evaporation with aroma recovery, freeze concentration and reverse osmosis.

Concerning quality preservation the freeze concentration is superior to the other two processes. The process is not yet developed to full technical maturity, however. It seems likely that in the coming years it will deprive the established evaporation process of its monopoly position. Reverse osmosis has not yet passed the laboratory scale stage. Because membranes with acceptable permeabilities are not very selective, it can be expected that their technical application in dewatering aroma-containing liquid foods will remain restricted to some specialties.

The costs of concentration are about the same for evaporation and freeze concentration. The higher investment costs of the latter process are partially offset by lower costs of energy. Depending upon the capacity and yearly operation hours the costs vary between \$5 and \$15 per ton water removal. Reverse osmosis may become competitive at more than 100 operation days per year.

Introduction

Aroma-containing liquid foods like fruit juices and coffee and tea extract are very complex aqueous mixtures of organic compounds. The water content is usually about 90% by weight with extreme values generally being between 75 and 94%. In order to reduce the storage and transportation volume or to increase keeping qualities the greater part of the water has to be expelled. The concentration of liquid foods, however, is a delicate affair, as they are very sensitive to thermal treatment. Even at moderate temperatures many of their components prove to be unstable. At temperatures between 40 and 70 °C enzyme catalysed reactions can alter juice properties within a few minutes. In order to destroy enzyme action juices must be inactivated by a heat

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treatment, e.g. by keeping it a few seconds at 110 °C. To obtain a good product sanitary conditions must also meet high standards; microbiological processes affect product properties between 0 and 60 °C. The quality is moreover strongly dependent on the concentration and composition of odorous compounds. All flavour and aroma components are naturally volatile and can be lost by evaporation. Thus for obtaining high quality concentrates the following conditions must be fulfilled:

1. Low process temperature and short residence time in the process apparatus, this especially at high temperatures.
2. Nearly sterile operation.
3. Selective dewatering, the major proportion of all components except water being retained in the concentrate.

Either to prevent excessive thickening during and after concentration or for obtaining clear concentrates, it is for some fruit juices necessary to depectinize the juice before the concentration.

Aroma retention

The characteristic flavour of a juice or extract is caused by a specific multi-component mixture* of volatile compounds with boiling points between −150 °C and +250 °C A typical low boiling component in the coffee aroma is methyl mercaptan (BP 6 °C) and a typical high boiling component in grapes is methyl anthranilate (BP 225 °C).

Most of the volatiles are present in the ppm range. Nearly all aroma components, even the high boilers, have at low concentrations a volatility relative to water greater than 1. The relative volatility $\alpha_{j\,w}$ of aroma component j to water is defined by

$$\alpha_{j\,w} = \frac{C_{g,j}/C_{g,w}}{C_{l,j}/C_{l,w}} \tag{1}$$

where $C_{g,j}$ and $C_{g,w}$ denote respectively the concentration of component j and water in the gas phase (g) being in phase equilibrium with the liquid phase (l) in which the concentrations of the components are $C_{l,j}$ and $C_{l,w}$ respectively. The relative volatilities of some aroma components at infinite dilution in water of 100 °C are presented in Table 1.

At equilibrium evaporation of liquids (evaporation rate of the components not limited by a resistance to mass transfer in liquid or gas phase) there can be derived for the retention of a volatile component

$$R_j \equiv \frac{W_{jt}}{W_{jo}} = \left[\frac{W_{wt}}{W_{wo}}\right]^{\alpha_{j\,w}} \tag{2}$$

where W_o is the amount of the component originally present in the mixture and W_t

* Aromas generally comprise of over 100 volatile components.

TABLE 1. Relative volatilities of some aroma components at infinite dilution in water and their retentions after evaporation of 80% of the water

Aroma component	Boiling point (°C)	Relative volatility (α_{jw})	Retention (%)
Methyl mercaptan	5·8	>500	$10^{-3\cdot48}$
Acetaldehyde	20·2	210	$10^{-1\cdot15}$
Acetone	56·5	46	10^{-30}
Methylacetate	57·8	113	10^{-77}
Methanol	64·7	8	$10^{-3\cdot6}$
Ethanol	78·4	12	$10^{-1\cdot1}$
N. propanol	97·8	16	$10^{-9\cdot2}$
Pyridine	115·4	3	0·795
N. butanol	111·7	27	$10^{-16\cdot9}$
Acetic acid	118·1	0·73	31
N. pentanol	138	32	$10^{-20\cdot4}$
Methyl anthranilate	255	3 3	0·49

is the amount left behind after time t. The subscript j and w refer again to the components. Retentions of some aroma components present at infinite dilution in water after equilibrium evaporation of 80% of the water are also given in Table 1. A real equilibrium evaporation is approximated in boiling systems where there is an intimate and large contact area between vapour bubbles and liquid.

There are four essentially different processes possible for the concentration of liquid foods containing volatile flavours and aromas:

1. evaporation with cut back of fresh juice to the concentrate.
2. evaporation with aroma recovery.
3. reverse osmosis.
4. freeze concentration.

In evaporation processes where the liquid has to be concentrated fourfold or more the volatile flavours are lost nearly quantitatively with the vapour, see Table 1. The quality of the 'bouquet' can be partly restored by adding fresh juice to the concentrate. The resulting dilution makes it impractical to obtain products above fourfold of the original strength. By diluting a 57% solids concentrate with fresh juice containing 10% dissolved solids a fourfold concentrate of 40% is obtained. Yet this concentrate contains only 10% of the volatile flavours of the original juice.

Much higher aroma retentions can be obtained by separating in a distillation column the volatiles from the water vapour which escapes from the evaporator and feeding this aroma concentrate back to the concentrate of non-volatiles. The recovery and concentration by distillation is not possible of course for aroma components with a relative volatility near to one.

In reverse osmosis the water is removed from the liquid food through a selectively permeable membrane. The driving force for the water removal is here the pressure difference over the membrane. This process requires neither phase change, such as occurs in evaporation, nor elevated temperatures. Thus by choosing membranes of the right selectivity, if available, it is *theoretically* possible to concentrate food liquids without any loss of aromas. Due to the low process temperature, 20–30 °C, also thermal damage is negligible.

In freeze concentration the water is removed from the concentrate in the form of ice crystals. Down to the eutectic temperature the ice crystals are of a very high purity. Theoretically, then, freeze concentration may be considered as the most selective dewatering process. Moreover, due to the concentration operation at freezing temperatures, the quality of the product is not adversely affected at all.

Evaporation processes

A short review will be given of the evaporation processes and the different aroma recovery systems.

The evaporative concentration of liquid foods

Evaporation is considered the best developed and economically most favourable technique for the concentration of liquid foods. The capital costs of evaporation are relatively low and by applying multi-effect evaporation the energy costs can be reduced to as little as one dollar per 1000 kg of water removal. Serious disadvantages, however, are the heat damage of the product and the fouling of the heated surface in the evaporator.

Heat damage

The heat damage, which is caused by a chemical conversion of the heat sensitive components, is at low conversions nearly directly proportional to the residence time of the molecules in the process apparatus and exponentially dependent on the process temperature. The conversion C or heat damage is expressed by the equation

$$C = kt \tag{3}$$

where t is the residence time and k the conversion rate constant. The temperature dependence of k is expressed by the activation energy E in the Arrhenius equation

$$k : : e^{-E/RT} \tag{4}$$

where R is the gas law constant, T the absolute temperature and e the base of natural logarithm.

According to Burton & Jayne-Williams (1962), for non-enzymatic browning reactions, E amounts to about 20 kcal/mole and for vitamin (riboflavin) destruction about 15. Generally E lies for thermally sensitive liquid foods between 10 and 30. This means that at a constant residence time in the apparatus an increase of the process temperature by 10 °C results in an increase of the thermal decomposition by a factor 1·7–5·0.

Thermal degradation is always the result of a number of subsequent or consecutive reaction steps e.g. A–B–C–D etc. The farther the reaction proceeds the stronger its adverse effect upon quality. A 10% conversion of the original component A into D can be much more detrimental than a 10% conversion of A into B. In order to reduce these consecutive reactions to a minimum the residence time distribution of the liquid in the evaporator has to be as small as possible. This can be realised by a single pass (no recirculation) treatment in evaporators in which the liquid flow approximates plug flow. Plug flow is best approximated in film evaporators like wiped film evaporators (Samba, Luwa), centrifugal film evaporators (Centritherm), climbing film evaporators and down flow long tube film evaporators.

In order to reduce the absolute conversion also the mean residence time and process temperature have to be minimized. According to Perry (1963) the heat transfer coefficient in evaporators varies with the liquid viscosity to the power $-0{\cdot}25$ to $-0{\cdot}7$. The energy of activation of the reciprocal of the viscosity of liquid foods varies between 5 and 15 kcal/mole. Consequently to the heat transfer coefficient can be attributed an E value between 1·5 and 6·7. The mean residence time t_{mean} of the liquid for a given amount of water removal per unit mass of feed and constant ΔT can be calculated from the relation

$$t_{mean} : : \frac{V}{Ah} \tag{5}$$

where V is the liquid content of the evaporator, A is the total heat exchanging surface and h the overall heat transfer coefficient.

The value of t_{mean} is the smallest in film evaporators and has a minimum value in the centrifugal film evaporators.

Because the activation energy of the thermal degradation reactions is higher than that of the heat transfer coefficient a decrease of the process temperature or a decrease of the absolute pressure in the evaporator will always result in an increase of product quality. That notwithstanding the fact that a lowering of the process temperature results in a decrease of the heat transfer coefficient and thus in an increase of the mean residence time. Summarizing it can be stated that thermal degradation will be minimal at a short resistance time and a small residence time distribution of the liquid in the evaporator and a low process temperature.

Fouling

The fouling of the heated surface in the evaporators is mainly caused by the physico-chemical decomposition of protein material. Denaturation reactions of proteins have very high E values, these generally being between 40 and 70 kcal/mole. Morgan (1967b) found for the fouling of evaporator tubes by tomato paste E values varying between 50 and 70. Fouling of the heated surface by decomposition of insoluble matter results in a decrease of the heat transfer rates and thus in a decrease of the capacity of the evaporator. Due to the high E value fouling will increase strongly with increase in temperature of the heated wall. In order to maintain a low heated wall temperature at a given evaporation rate the following conditions must be fulfilled:

1. low temperature of the evaporating liquid (deep vacuum)
2. complete wetting of the heated surface
3. only a thin laminar and stagnant liquid layer near the heated surface
4. low viscosity of the liquid (depectinization of juices)

A new application of the first three concepts is the expanding tube design of a single pass upflow evaporator, see Fig. 1. Another totally different and more revolutionary design is the Wurling evaporator, Morgan (1967a), and Carlson *et al.* (1967). It consists,

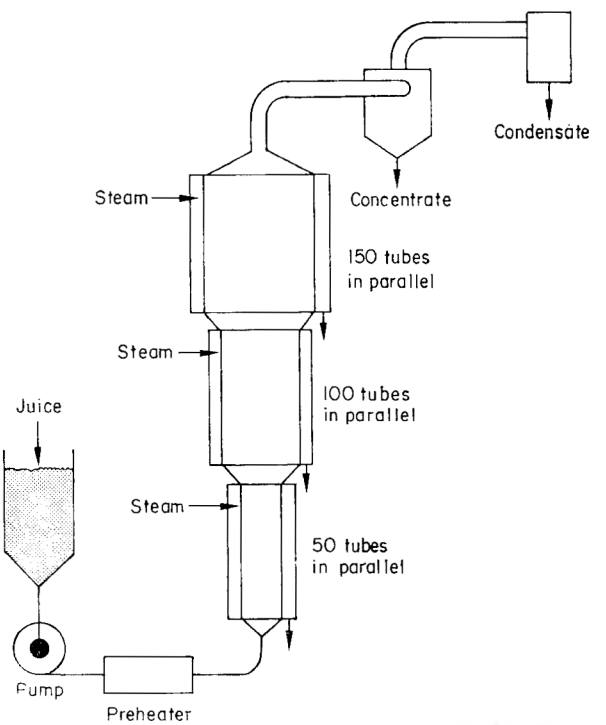

FIG. 1. Single pass upflow evaporator according to Morgan (1967b).

see Fig. 2, of a steam-heated coil rapidly rotating in a pool of liquid food boiling in vacuum. The overall heat transfer coefficient for cold break tomato paste with 50% solids is reported to be 500 btu/hr ft^2 °F compared with a value of 34 in an agitated thin-film evaporator.

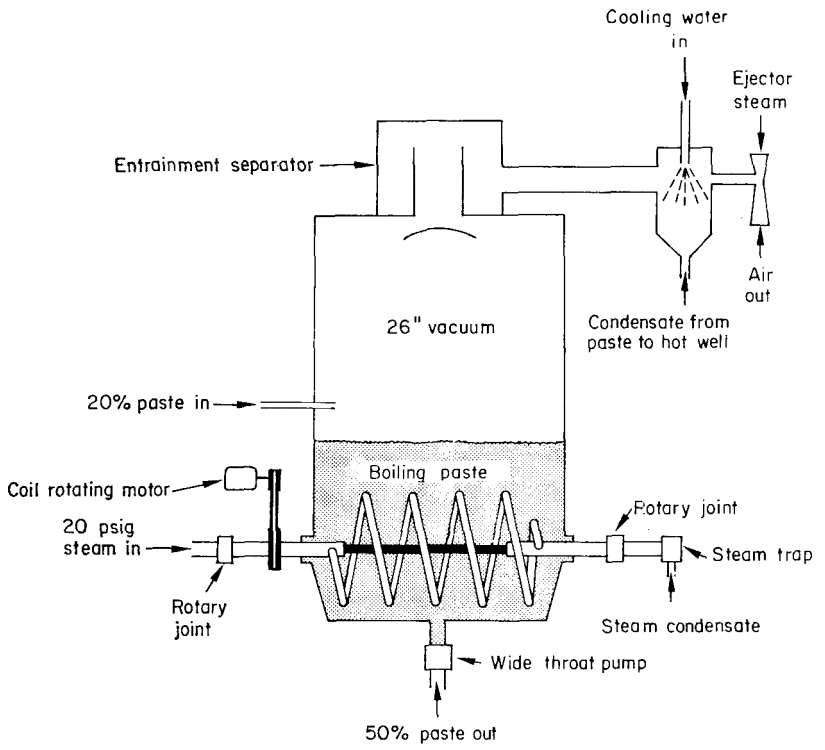

FIG. 2. Wurling Evaporator.

Energy consumption

The energy consumption of single effect evaporators (excluding pumping) amounts to about 1·1 ton of steam per ton of water removed or about $3/1000 kg water. With vapour recompression the energy consumption becomes 0·6 ton steam/ton water and in a double and triple effect evaporator respectively 0·60 and 0·35 ton steam ton water.

The aroma recovery in evaporation processes by distillation

The volatile aromas can be recovered by removing them from either the liquid food before the evaporation or from the vapour produced in the evaporator. These dilute aqueous aromas can be concentrated by distillation or freeze concentration and are thereupon returned to the concentrate of non-volatiles from the evaporator(s).

The most efficient way is steam stripping of the aromas from the fresh liquid food

in a counter-current vapour liquid contacting device such as a sieve plate column or a packed column. For not too small a number of plates in the stripping column the amount of strip steam required to remove 90% of the aromas is about $1/\alpha_e$ ton of steam per ton of feed. Here α_e is the effective relative volatility of the aromas. It is common practice to concentrate the aroma-rich vapour leaving the stripper by distillation. The steam stripping in counter-current and subsequent distillation is schematically illustrated in Fig. 3. A far more complete concentrate, however, can be obtained by freeze concentration of the aqueous aroma.

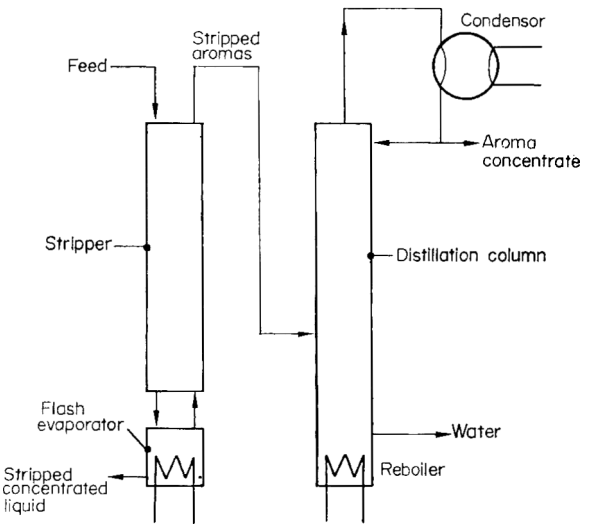

FIG. 3. Stripper with distillation column.

The aromas can also be removed from the fresh juice by flash-evaporating a part of the water and feeding these vapours directly to a distillation column, see Fig. 4. According to relation (2) about $1{\cdot}0{\cdot}1^{\,1/\alpha_e}$ ton of water has to be evaporated per ton of water originally present in the liquid in order to remove 90% of the aromas. The flash evaporation process is described extensively in the literature, Morgan (1967), Eskew & Redfield (1951), Eskew & MacPherson (1951), Eskew & Phillips (1951), Eskew & Redfield (1952), Eisenhardt *et al.* (1958) Claffey *et al.* (1958), Eskew *et al.* (1959), and Moyer & Saravacos (1968).

For the very dilute aqueous feed to the distillation column the energy consumption of the reboiler in the distillation columns amounts to about $1/(\alpha_e - 1)$ ton steam per ton feed. Thus the total energy consumption S of a strip column and distillation column for 90% removal of the aromas and concentrating it to about a 500-fold essence becomes:

$$S = \frac{1}{\alpha_e} + \frac{1}{\alpha_e(\alpha_e - 1)} \quad \text{ton steam/ton feed} \tag{6}$$

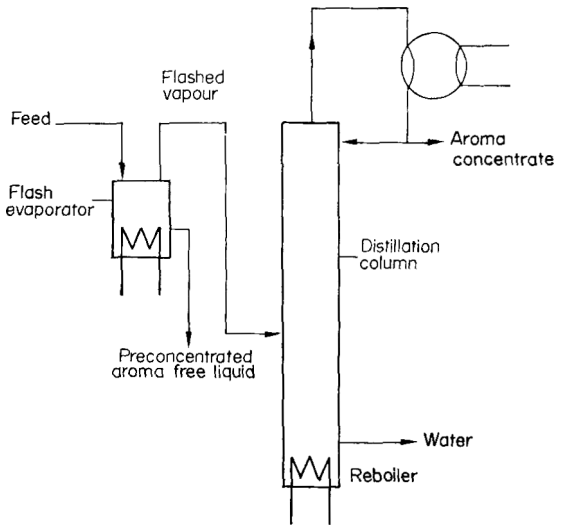

FIG. 4. Flash evaporator with distillation column.

For partial vaporization (flashing) of the feed and subsequent distillation to about 500-fold essence the relation becomes

$$S = (1 - x_F)\left[(1 - 0{\cdot}1^{1/\alpha_e}) + \frac{(1 - 0{\cdot}1^{1/\alpha_e})}{\alpha_e - 1}\right] \text{ ton steam/ton feed} \quad (7)$$

where x_F is the dissolved solids concentration of the fresh liquid food.

The first term in both equation (6) and (7) is the energy required for the liquid evaporators. The energy spent in these evaporators has to be charged to the evaporation process and not to the aroma recovery. The steam consumption according to the second term in equation (6) and (7) for recovering 90% of the aroma as a 500-fold essence is presented for several values of α_e in Table 2.

According to Pilnik & Zwikker (1962) about 90% of the volatile aroma of apple juice is removed by evaporating 30% of the water. Eisenhardt *et al.* (1958) report for blackberry, blueberry, red raspberry, and strawberry respectively 40%, 50%, 40%, and 20% evaporation. With equation (2) we calculate from these values for the effective relative volatilities of apple juice, blackberry, blueberry, red raspberry, and strawberry respectively 6·45, 4·50, 3·33, 4·50, and 10·3. The main aroma component in concord grape juice is methyl anthranilate. Roger & Turkot (1965) reports for this component at infinite dilution in water a relative volatility of 3·33.

From the relative volatilities given above and Table 2 it can be deduced that the energy consumption needed for the distillation column is negligible compared with that needed for the evaporators. Because a strip column increases the capital costs of the

TABLE 2. Effect of effective relative volatility upon steam consumption of the distillation column for recovering 90% of the aromas from a liquid food containing 90% water

α_e	Steam consumption distillation column (ton per ton feed) in combination with	
	Strip column	Partial flash evaporator
1	∞	∞
2	0·500	0·615
3	0·166	0·241
4	0·083	0·131
5	0·050	0·083
10	0·011	0·020
20	0·003	0·005

concentration plant it is evident that for α_e values well above three the flash process is more economical than the stripping process.

The distillation column

Roger & Turkot (1965) were the first to apply the principles of distillation to the design of an aroma recovery distillation column. Their work is extended by Bruin to multi-component mixtures (1969). The residence time of the aromas in the distillation column is directly proportional to the column diameter. The diameter in turn is inversely proportional to the root of the absolute pressure. The absolute pressure, or vapour pressure of the water increases with temperature and has an activation energy of about 10 kcal/gmole. The residence time consequently has a negative activation energy of $\sqrt{10}$. The activation energy of the thermal degradation reaction rate constant amounts to minimally 10 kcal/gmole. It can be deduced from equation (3) that the energy of activation of the thermal degradation is the sum of the activation energy of the residence time and the activation energy of the degradation rate constant. Because the sum remains positive it is obvious that a decrease in the operating pressure always results in an increase in quality.

Aroma recovery by liquid-liquid extraction

Aroma components with a relative volatility smaller than about 1·5 can not be economically recovered by stripping or flashing and subsequent distillation. These aromas, however, can at least in theory be concentrated by other separation processes

such as liquid-liquid extraction. Schultz & Randall (1969) describe a process for the extraction of aromas from liquid foods with liquid carbon dioxide. The energy consumption is about equal to that of distillation. Liquid-liquid extraction, however, is much more difficult to perform than distillation.

Reverse osmosis

Reverse osmosis is a membrane process for the selective de-watering of aqueous solutions at room temperature. By applying a pressure difference over the selectivity permeable membrane larger than the osmotic pressure of the solution the water is forced to flow through the membrane from the side in contact with the liquid with the high dissolved solids concentration to the side in contact with the liquid having a low or even zero dissolved solids concentration, see Fig. 5. The success of the process for the concentration

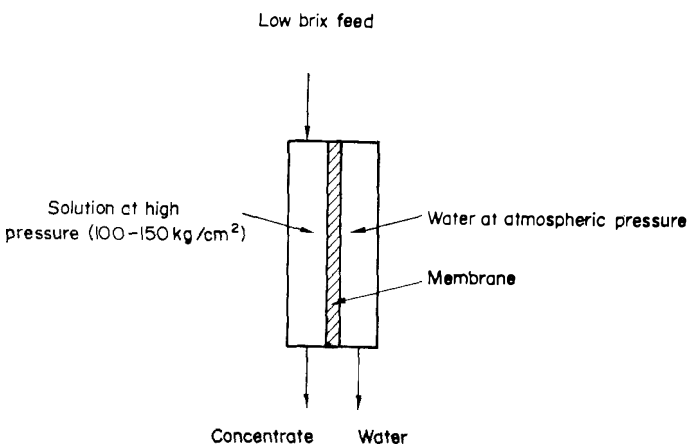

FIG. 5. Schematic presentation of a permeation cell.

of liquid foods depends upon the selectivity of the membrane and upon the rate of water removal. Selectivity is the ability of the membrane to pass water but reject all other components present in the liquid to be concentrated; it is primarily determined by properties of the membrane and the size of the solute molecules. The rate of water removal or permeation rate depends upon membrane properties and net pressure driving force. The net driving force is the pressure difference over the membrane less the osmotic pressure of the film of concentrated liquid bordering the membrane. The most successful membrane from the standpoint of both permeation rate and solute retention is the cellulose acetate membrane developed by Manjikian (1967). Reverse osmosis has been primarily developed for obtaining drinking water from brackish-water and sea water.

Selectivity

The selectivity of the membrane increases with a decrease of the intrinsic water permeability. Intrinsic refers to the permeability for pure water. Merson (1968) measured the aroma retention of Loeb membranes as a function of the intrinsic water permeation rate at 1000 p.s.i. The values for ethyl butyrate, malic acid and dextrose are presented in Fig. 6. For the retention of 60% of the model aroma component

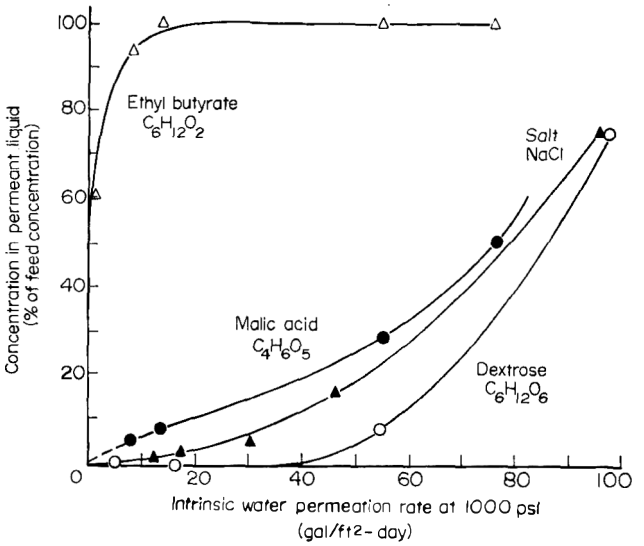

FIG. 6. Aroma loss through cellulose acetate membranes.

ethyl butyrate the intrinsic water permeation rate at 1000 p.s.i. has to be as low as 1 gal/ft²/day. At 2000 p.s.i. or 140 atm. which is about the maximum allowable working pressure the corresponding intrinsic water rate is less than 2 gal/ft²/day. Merson, Ginetti & Morgan (1969) report for strawberry juice an overall aroma retention of about 25% for an intrinsic membrane permeability of 16·5 gal/ft²/day at 1000 p.s.i. Some loss of flavour can be allowed, however, without impairing the quality too seriously. The selectivity of the same membrane is reported to be quite good for the larger water-insoluble aromas like turpenes.

Water permeability

Due to the net water flux through the membrane a positive concentration gradient towards the membrane develops, resulting in a considerably higher dissolved solids concentration at the membrane. This effect is called concentration polarization. The local flux φ is given by the relation

$$\varphi = C(\Delta P - \Delta\pi_l) \tag{8}$$

where ΔP is the pressure difference over the membrane, C is the permeability of the membrane and $\Delta\pi_i$ is the difference in osmotic pressure of the solution in the liquid film at the membrane and the osmotic pressure of the permeant (water) at the other side of the membrane. The osmotic pressure of fruit juice can be calculated approximately with the empirical equation

$$\pi = 132 \frac{C}{(1-C)} \text{ (atm)} \tag{9}$$

where C is the dissolved solids concentration in weight fraction. At a given value of ΔP the higher the concentration C_i at the membrane, the smaller the water flux.

Ginetti & Merson (1969) developed a mathematical model of the membrane permeation. According to this model, at exit concentrations above 10% solids and intrinsic permeabilities above 20 gal/ft²/day at 1000 p.s.i. the flux appears to be completely limited by the concentration polarization. This case is illustrated by Fig. 7. If the

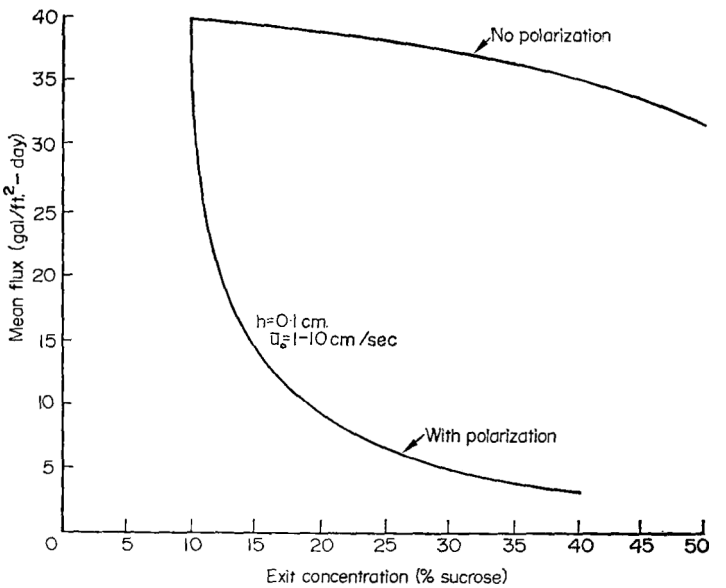

FIG. 7. Effect of concentration polarization upon mean flux, distance between membranes 0·1 cm, liquid velocity 1–10 cm/sec.

liquid in the channel should be completely mixed the flux at 30% exit concentration and a ΔP of 100 atmosphere would be 38 instead of 4·2 gal/ft²/day. At the very low intrinsic permeabilities required for high flavour retention the dewatering capacity is primarily determined by the membrane itself. With the present day membrane casting technique the practically attainable capacities for dewatering aroma-containing food liquids vary between 0·5 and 4 gal/ft²/day.

Energy consumption

In concentrating 1500 kg of feed from 10% to 30% solids 1000 kg of water has to be removed. If the operating pressure is 100 atm., the theoretical energy requirement is 4·1 kwh. Estimating motor and pump efficiency to be 80% each, the actual energy requirement becomes 6·4 kwh per 1000 kg dewatering. If we assume an energy rate of 1·7 cent/kwh the energy costs become \$0·109/1000 kg dewatering.

Freeze concentration

Freeze concentration is the crystallization of a part of the water from an aqueous solution followed by the separation of the ice crystals from the concentrate. Water forms an eutectic mixture with the other components present in liquid foods. Down to the eutectic temperature, therefore, the water segregates in the form of ice crystals upon cooling.

Experimental freezing curves of some juices and a coffee extract are presented in Fig. 8. It can be seen that by the freezing of apple juice with 10% dissolved solids to a temperature of −4·6 °C, the solid content of the liquid phase becomes at equilibrium 30%. Consequently 74% of the water segregates as ice crystals.

The crystallizer is usually designed as a stirred vessel in which the driving force for

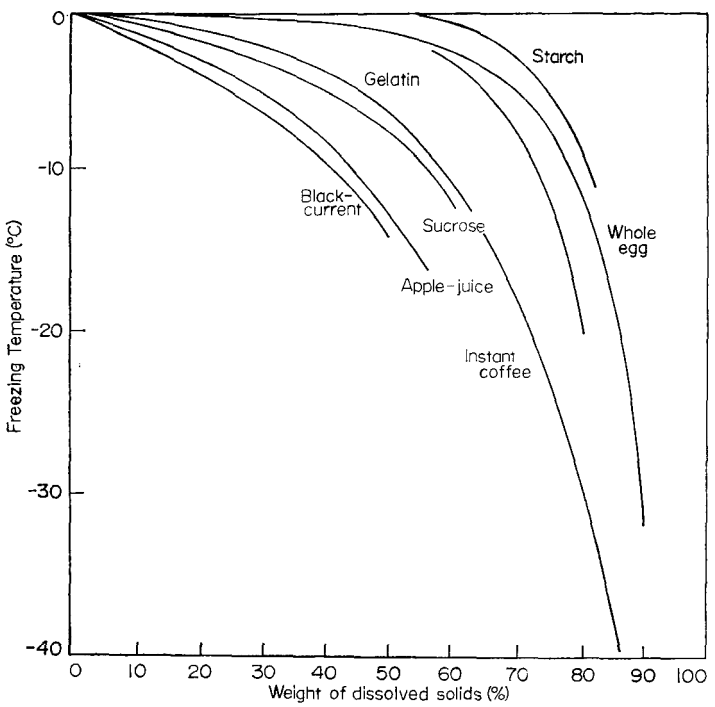

Fig. 8. Freezing curves of sucrose, coffee extract, and some fruit juices.

crystallization can be provided by a feed stream containing small crystals, a supercooled crystal free feed stream, or by an indirect cooling of the ice suspension in the crystallizer. If small crystals are fed to an ice suspension in the crystallizer containing relatively large crystals the large crystals will grow at cost of the smaller ones which eventually disappear.

Ice crystals grown from a solution are of a very high purity. Theoretically, then, freeze concentration may be considered as the most selective dewatering process. In practice, however, the dewatering may deviate from ideality. In the separation of the ice crystals from the concentrate, part of the mother liquor is occluded by and adheres to the crystals. Consequently the selectivity of the concentration is completely determined by the quality of the ice-liquid separation. The separation can be performed in a centrifuge, a press, a wash column or a combination of these devices.

For a maximum phase separation in basket centrifuges and wash columns the specific surface area of the ice crystals must be as small as possible. In presses the sharpness of separation is insensitive to crystal size, and crystal shape. The capacity of all these separator devices, however, sharply increases with an increase in the size and uniformity of the crystals.

A review of the state of the technique is given by Thijssen (1969a, b). The best, also economically attractive, process is the combination of an externally cooled crystallizer with a wash column as developed by the Phillips Petroleum Company. The external

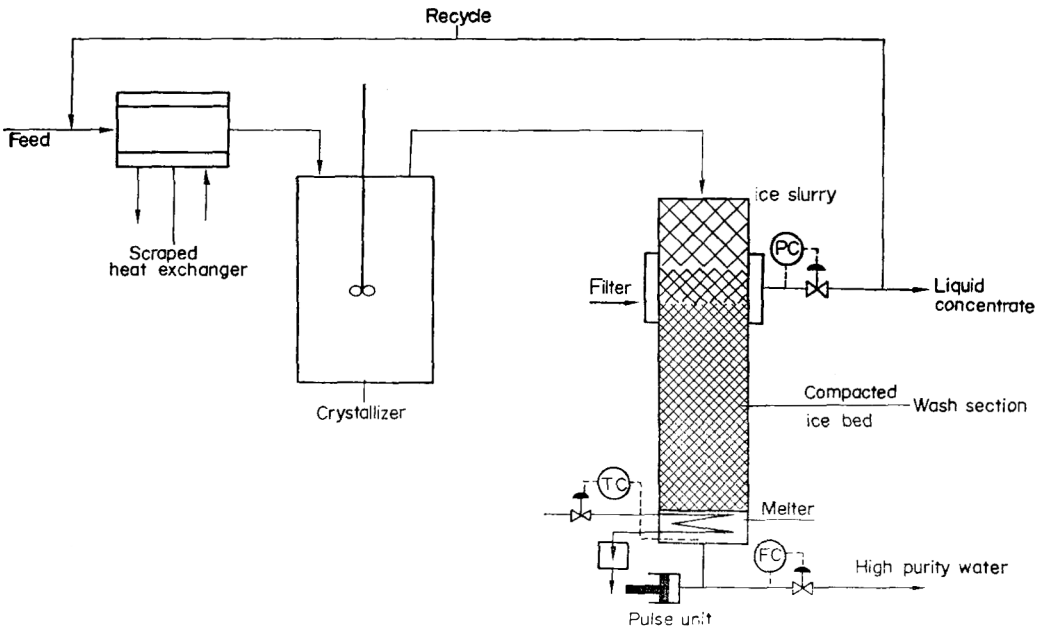

FIG. 9. Schematic representation of a freeze concentration process with scraped heat exchanger and Phillips wash column.

cooling of the crystallizer can be performed in a scraped heat exchanger. The process is schematically presented in Fig. 9. In the crystallizer nearly spherical crystals can be grown with a mean diameter well above 0·5 mm. If the wash column is properly dimensioned the loss of dissolved solids with the ice (or melted ice) can be smaller than 0·1%.

Compared to evaporation and reverse osmosis freeze concentration exhibits exceptional quality-preserving properties. The dewatering can be almost completely selective and the process temperature is so low that chemical or biochemical reactions play almost no role. A restriction is that only clear or colloidal solutions can be processed. In concentrating nectars obtained by mincing whole fruit the insoluble coarse cellular material gets lost with the ice. However, if the non-dissolved material is separated from the melted ice in, for example, a helical cone centrifuge and thereupon fed back to the concentrate, this restriction of the applicability of the process has been eliminated.

Energy consumption

Without any cold recovery the process requires about 110 kcal per kg of water removal. At an evaporation temperature of the refrigerant of -30 °C and a condensation temperature of + 30°C the energy requirement is $0{\cdot}655 \times 10^{-3}$kw per kcal. At a price of 1·7 cent/kwh the energy costs become \$1·23/1000 kg water removal.

Concentration costs

The costs of concentration will be based upon a plant to concentrate 1400 kg of liquid food per hour from 10 wt% dissolved solids to 35 wt% solids. The dewatering capacity is 1000 kg per hour. These costs are exclusive handling costs of the concentrate, costs of floor space, contractor fee, engineering, mounting, and costs of labour.

The plant will operate continuously 60 days per year for fruit juices or continuously 220 days per year for extracts like coffee and tea. The costs of steam, cooling water and electricity are estimated at \$2·75/1000 kg, \$0·03/m^3 and \$0·017/kwh respectively. The economical and technical life of the evaporator with aroma recovery, the reverse osmosis installation and the freeze concentrator are taken to be 10 years. The interest is estimated at 10% over the non-depreciated capital. This results in a total yearly cost of 15%.

Cost specification evaporation with aroma recovery

The effective relative volatility of the aroma is assumed to be 4 and the operation pressure taken at 150 mmHg absolute. The cost will be calculated for two cases. Case A: partial flashing in a preconcentrator. The flashed vapours are fed to a distillation column. The liquid is concentrated to 35% solids in a second (film) evaporator. Case B: the liquid is concentrated to 35% in a centrifugal evaporator. All vapour escaping from the evaporator is fed to a distillation column.

Case A: Costs of a two stage falling film evaporator including pumps, vacuum pumps, condenser, tanks etc. \$30,000. Cost of distillation column including reboiler, condenser, pumps, instrumentation etc. \$15,000. Total investment \$45,000. Capital costs 60 working days or 220 days amount to \$4·68 and \$1·27 per ton water removal respectively. Maintenance costs 5% or \$0·23 per ton water removal. Steam consumption 1·25 ton/hr or \$3·44/ton water removal. Water consumption 50 m^3/hr or \$1·50/ton water. Electricity 1 kwh/hr or \$0·017/ton water.

Case B: Costs of the one stage centrifugal evaporator inclusive of pumps, vacuum pumps, instrumentation etc. \$42,000. Cost of distillation column including reboiler, condenser, pumps, instrumentation, tanks etc. \$22,500. Total investment \$64,500. Capital costs 60 working days \$6·70 per ton water removal and for 220 working days \$1·83 per ton water. Maintenance costs \$0·33. Steam consumption 1·40 ton/hr or \$3·86. Water consumption \$1·50. Electricity 1·5 kwh or \$0·255.

Cost specification reverse osmosis

Case A: Water removal 4 gal/ft^2/day at 150 atmosphere. Membrane surface 1590 ft^2. After Merson *et al.* (1969) we assume the original area cost to be \$39,000. Costs of pumps \$5,000. Auxiliary equipment \$5,000. Capital costs for 60 working days \$5·20 per ton water removal. Capital costs for 220 working days \$1·42. Replacement of membranes once a year. Maintenance costs \$3·00/ft^2/60 days, and \$3·00/ft^2/220 days. Maintenance costs per ton water removal for 60 and 220 working days become \$3·30 and \$0·90 respectively. Energy costs \$0·109 per ton water removal.

Case B: Water removal 2 gal/ft^2/day. Capital costs for 60 and 220 days are \$10·40 and \$2·82 respectively. Maintenance costs per ton water removal for 60 and 220 days are \$6·60 and \$1·80 respectively.

Cost specification 'freeze concentration'

Cost of two stage ammonia refrigerator with a cooling capacity of 100,000 kcal/hr (evaporator temperature $-30\,^{\circ}C$, condenser temperature $+35\,^{\circ}C$) amounts to \$13,800. We assume a direct evaporation of the refrigerant in the double wall of the scraped heat exchanger. Heat exchanger \$28,000. Crystallizer \$16,000. Wash column \$8,000. Pumps, auxiliary equipment, instrumentation \$7,000. Total investment \$72,800. Total capital costs per ton of water for 60 and 220 working days \$7·69 and \$2·10 respectively. Maintenance costs \$0·39/ton water removal. Total energy consumption 75 kwh or \$1·28/ton water removal. Water consumption compressor 30 m^3/ton or \$0·90/ton. Steam consumption melter wash column 0·2 ton/ton or \$0·55/ton.

In Table 3 the concentration costs per 1000 kg water removal are summarized.

TABLE 3. Concentration costs in dollars per 1000 kg water removal for 60 and 220 operation days

Process	Specification	Costs/1000 kg water	
		60 days	220 days
Two stage long tube evaporator with rectification tower	Capital costs + maintenance	4·91	1·50
	Utilities	4·96	4·96
	Total	9·87	6·46
Centrifugal film evaporator with rectification tower	Capital costs + maintenance	7·03	2·16
	Utilities	5·61	5·61
	Total	11·64	7·77
Reverse osmosis (4 gal/ft²/day)	Capital costs + maintenance	8·50	2·32
	Utilities	0·11	0·11
	Total	8·61	2·43
Reverse osmosis (2 gal/ft²/day)	Capital costs + maintenance	17·00	4·62
	Utilities	0·11	0·11
	Total	17·11	4·73
Freeze concentration	Capital costs + maintenance	8·07	2·49
	Utilities	2·73	2·73
	Total	10·80	5·22

Conclusions

The quality preservation of liquid foods in freeze concentration is almost 100%; chemical and biochemical decomposition is negligible and volatile aromas are fully retained. Care has to be taken, however, that there is no loss of dissolved solids with the ice.

Less favourable is the vacuum evaporation process with aroma recovery by vacuum distillation. Thermal decomposition can never be fully avoided and moreover all components with a relative volatility smaller than about three are partially lost. An advantage for fruit juices is that the keeping qualities of the aroma as an isolated essence are better than of the aroma in the high brix concentrate. The reverse, however, holds for the aromas of coffee and tea.

Reverse osmosis is very promising for the dehydration of liquid foods like milk and maple syrup of which the quality is hardly determined by its volatile constituents. With the membranes commercially available today the aromas with low molecular weights are partially or sometimes fully lost. These low molecular weight aromas are especially important for the quality of coffee and tea.

Evaporators with aroma recovery and freeze concentrators are already commercially available. The evaporation process has achieved during the last decade full maturity, freeze concentration on the other hand is still subject to further improvements. Especially the fundamentals of nucleation, crystal growth and washing of the ice need still a lot of

attention. Reverse osmosis for liquid food concentration has not yet passed the pilot plant stage. It will take several years before this process may become a competitor for the other two. The costs of concentration are about the same for evaporation and freeze concentration. The higher investment costs for freeze concentration are partially offset by the low costs of energy. Based upon rough cost estimates reverse osmosis appears to be very attractive for installations with year round operation.

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Retention and release of volatile food flavour compounds

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Summary

The retention and release of volatile flavour compounds such as aldehydes, ketones, alcohols, amines and sulphides from various substrates have been studied. Activation energies of desorption were measured using a thermal balance and heats of preferential sorption were measured with a flow microcalorimeter. Activation energies were obtained for the release of ethylamine from pectin, but insufficient amine was adsorbed to obtain values for Schardinger β-dextrin, gelatin and sodium alginate.

All the flavour compounds studied gave detectable heats of preferential sorption with silica gel. Of the other systems studied only triethylamine and ethylamine gave detectable heats of preferential sorption both with pectin and Schardinger β-dextrin.

Introduction

Flavour is one of the main acceptability attributes of a food. Consequently an understanding of the mechanism of formation of food flavours from their precursors is important. However another equally important factor is the subsequent release or retention of flavour compounds in foods. For example, in many food processing operations some flavour retention is essential for the product to be acceptable.

Several studies have measured the loss of food volatiles during the concentration of some food products. Saravacos & Moyer (1968) measured the loss of aroma compounds during the vacuum drying of aqueous solutions of pectin and glucose. The retention of volatile compounds during spray drying (Menting & Hoogstad, 1967) and centrifugal film evaporation (Mälkki & Veldstra, 1967) have also been investigated.

The present study investigates factors controlling the adsorption and retention of volatile flavour compounds or their analogues, known to occur in foods, on substrates which are also found in foods. Parameters such as (1) activation energy of desorption, (2) the reaction order of the desorption process and (3) heats of preferential sorption were studied. Parameters (1) and (2) were measured using a thermal balance and (3) using a flow microcalorimeter.

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Materials and methods

Adsorbates

Ethylamine (99% pure, BDH Ltd), triethylamine (99% pure, BDH Ltd), butyl acetate (redistilled, 99% pure, BDH Ltd), isobutyl acetate (redistilled, 99% pure, BDH Ltd), ethyl butyrate (redistilled, 99% pure, Hopkin and Williams Ltd), hexanal (Ralph Emanuel Ltd), methyl butyl ketone (Koch-Light Ltd), 2-heptanone (99% pure, Emanuel Ltd) 4-trans-nonenal (Prepared by method of Brandon, Derfer and Boord (1950), 95% pure), dimethyl di-sulphide (BDH Ltd), propyl-di-sulphide (BDH Ltd), hexanol (redistilled, 99% pure, BDH Ltd), benzaldehyde (99% pure, BDH Ltd), acetic acid (99% pure, BDH Ltd).

Adsorbents

Pectin (apple grade, 6% esterified, BDH Ltd.), Schardinger β-dextrin (Koch-Light Labs. Ltd), gelatin (Davis Ltd), and sodium alginate (BDH Ltd), Crosfield High Surface Area Silica Gel heated for 20 hr at 400°C. With the exception of silica gel, all the adsorbents were dried in a vacuum drying pistol at 80°C.

Thermal balance

The rates of desorption were measured on a Stanton thermal balance (model number HT–D). This had a sensitivity of 0·1 mg and a chart range of 10 mg. A direct sample temperature measuring device was employed. This was a 0·001 inch platinum/13% rhodium-platinum thermo-couple connected via compensated leads through cold junctions (at 0°C) to a Honeywell-Brown recording potentiometer, which had a full scale deflection of 2 millivolts. An all glass flow system containing a flow meter was attached to the balance by a short length of polytetrafluoroethylene (PTFE) tubing which was inert to ethylamine.

A quartz glass bucket was used to carry the 0·2–0·5 g samples of adsorbent. Nitrogen (99·9% purity, British Oxygen Company) was used as carrier gas and passed through a drying column (50 × 3·0 cm) packed with alternate layers of calcium chloride and self-indicating silica gel, before reaching the saturation chamber.

Flow microcalorimetry

A Microscal Mark I flow microcalorimeter was used. This instrument was similar to that described by Groszek (1960). It consisted essentially of a metal block with a cylindrical cavity in which the PTFE calorimeter cell was placed. The bottom of the cell was closed by a fine mesh stainless steel gauze on which the adsorbents were placed. The whole apparatus was enclosed in a draught free cabinet to prevent temperature changes. The carrier liquid, n-heptane, flowed down the walls of the cell and percolated through the adsorbent at a rate of 0·14 ml/min. The temperature change of the adsorbent was measured by two thermistors, and the response recorded on a chart.

The instrument was calibrated by feeding known amounts of heat energy (millicalories) into the thermistors and measuring the area under the curve on the potentiometric recorder. While n-heptane flowed through the cell, measured amounts of the adsorbates, dissolved in n-heptane were injected on to the surface of the adsorbent, by means of a 10 μl Hamilton syringe. The heats of preferential sorption (millicalories) were measured by the area under the peak, and were expressed in kcalories/mole of adsorbate. Several different volumes of the solutions (1–10 μl) were injected and the average value taken.

Results

Thermal balance

Isothermal rates of desorption of ethylamine from pectin were measured at 80, 90 and 100 °C. The effect of carrier gas flow rate on the desorption pattern was examined using the method described by Boyle, Gaw & Ross (1965). At a flow rate of 90 ml/min, it was found that the rate of desorption was practically independent of the flow rate. The drying procedure removed most of the water, the last traces being removed in the thermobalance before the amine was introduced into the system. The amount of pectin used was approximately 350 mg. At the temperatures studied with the pectin/ethylamine system it was found that as the temperature increased the amine adsorption became quicker, i.e. at 80 °C adsorption was complete in 2 hr, at 90 °C in 1½ hr, at 100 °C in 8 min. Rates of desorption of the amine from pectin were measured at 80, 90° and 100 °C (Fig. 1) and were found to be greater at the higher temperatures.

The rate of desorption (mg of amine/g of adsorbent/min) was calculated by measuring the gradients of the curves in Fig. 1 at various points. Plots of $\log_{10}$ (rate of desorption of amine) against $\log_{10}$ (weight of amine retained by pectin) for temperatures of 80, 90 and 100 °C were linear. The slopes of the lines gave the following orders of reaction for the desorption process 0·81 (80 °C), 0·80 (90 °C) and 0·80 (100 °C). As the desorption process is first order the following equation applies;

$$\frac{-dc}{dt} = kc$$

where c = concentration of ethylamine on pectin after time t, k = rate constant,

$$\text{by integration} \qquad \ln\left(\frac{c_0}{c}\right) = kt$$

c_0 = concentration of ethylamine on pectin at time $t = 0$.

By plotting ln (initial ethylamine concentration (c_0)/ ethylamine concentration at time

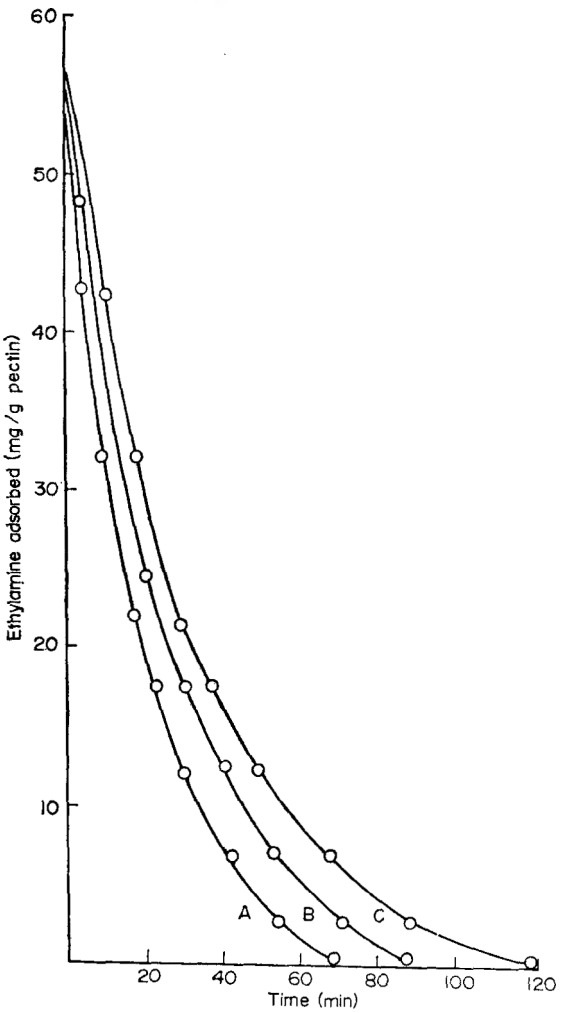


FIG. 1. Variation of the rate of desorption of ethylamine from pectin; A at 100°C, B at 90°C and C at 80°C.

t (c), against time, the rate constants of desorption at 80°, 90° and 100°C were obtained by measuring the slopes of the lines obtained (Fig. 2).

Using the Arrhenius equation:

$$\log_{10} k = \log_{10} A - \frac{Ea}{2{\cdot}303\ RT}$$

where k = rate constant, A = frequency factor which is a constant, Ea = activation

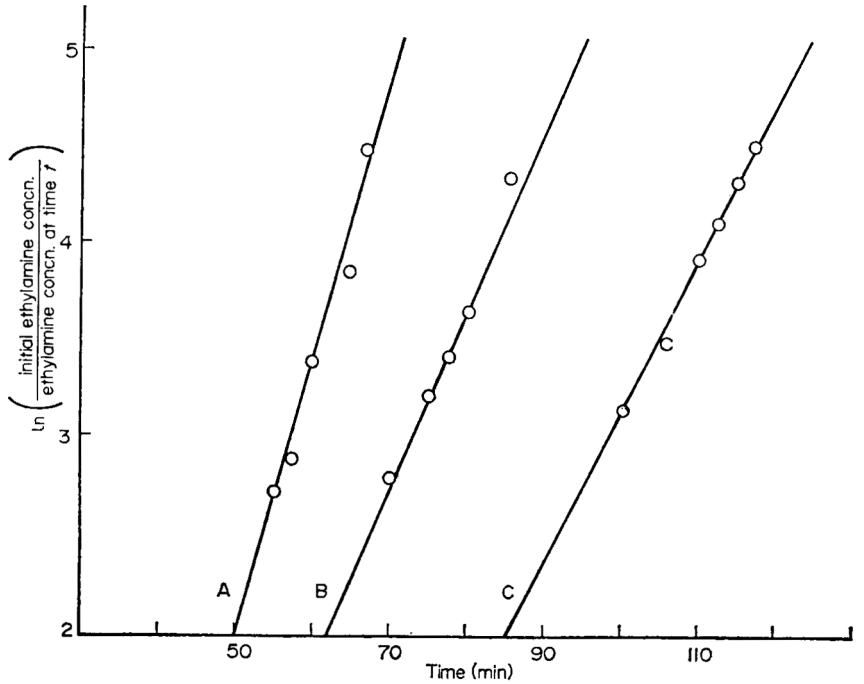


FIG. 2. A plot of $\ln\left(\frac{\text{initial ethylamine concentration}}{\text{ethylamine concentration at time } t}\right)$ against time; A at 100°C, B at 90°C and C at 80°C,

energy, T = temperature °K, R = gas constant, $\log_{10}k$ was plotted against $1/T$ and *Ea* calculated in the usual manner. The activation energy of desorption of ethylamine from pectin was calculated to be 5·8 kcalories/mole (Fig. 3)

Values of c (12·0 mg of ethylamine/g of pectin or lower) from the lower part of desorption curve (Fig. 1) were used in the above equation. This is because at the higher part the desorption is not first order.

With Schardinger β-dextrin only very small amounts of ethylamine were adsorbed, and no adsorption was detected, with gelatin or sodium alginate. The amounts adsorbed were too small for desorption studies.

Flow microcalorimeter

The heats of preferential sorption obtained by the replacement of n-heptane by more strongly adsorbed liquids on silica gel are given in Table 1.

When the same compounds were adsorbed on the food substrates only ethylamine and triethylamine gave detectable heats of sorption. The largest values were obtained with pectin and smaller values with Schardinger β dextrin (Table 2). Gelatin and sodium alginate gave no detectable response.

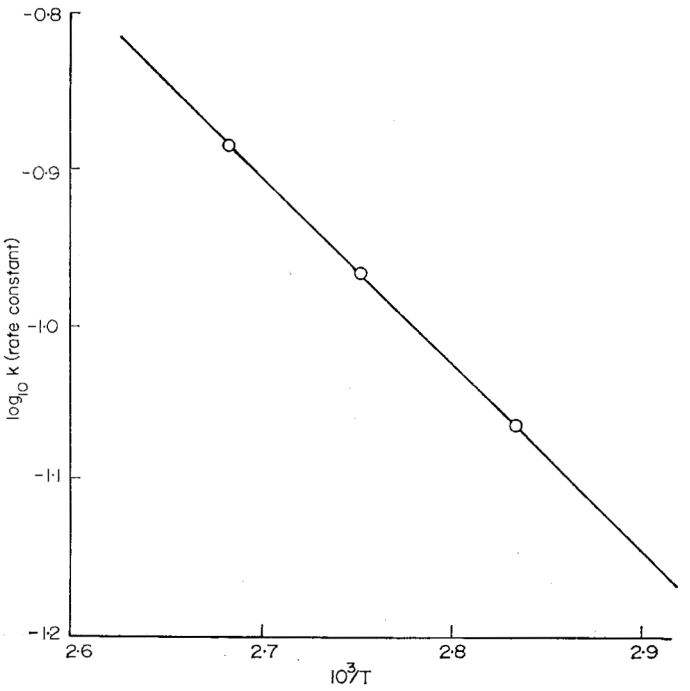


FIG. 3. Arrhenious plot of ethylamine desorption from pectin in the temperature range 80–100 °C.

TABLE 1. Adsorbent, high surface area silica gel

Injection, 5 μl of 0·1 M solution in n-heptane	
Adsorbates used	Heat of preferential sorption as kcals/mole adsorbate
Butyl acetate	5·6
Isobutyl acetate	4·5
Ethyl butyrate	4·7
Hexanal	4·3
Methyl butyl ketone	3·9
2-Heptanone	5·6
4-Trans–nonenal	6·7
Dimethyl disulphide	2·4
Di-propyldisulphide	3·5
Hexanol	5·8
Benzaldehyde	4·8
Acetic acid	2·7
Ethylamine	4·5
Triethylamine	16·0
Standard deviation	±0·1

TABLE 2. Heats of preferential sorption

Adsorbent	Adsorbate	Vol. and conc. of adsorbate in n-heptane		Heats of preferential sorption (k cals/molecule of adsorbate)
Pectin	Triethylamine	1–10 µl	0·1 M	2·60
Pectin	Ethylamine	1 µl	1 M	0·65
Schardinger β-dextrin	Triethylamine	5 µl	1 M	0·12 ± 0·01
Schardinger β-dextrin	Ethylamine	5 µl	1 M	0·23 ± 0·01

Discussion

The adsorbents studied were chosen because most of them are found in foods. Silica gel was included because amine desorption studies have been carried out on this substance (Ross & Taylor, 1967). Data from these studies would show whether our materials were more or less strongly adsorbed. Schardinger β-dextrin was chosen because it has been reported to occlude compounds (French, 1957).

The volatile compounds used, were chosen to give a cross section of the different types of flavour compounds occurring in foods, e.g. aldehydes, ketones, amines, sulphur containing compounds and esters.

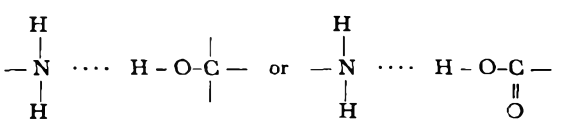
Activation energies of desorption

With the thermal balance system, only compounds with a boiling point below room temperature could be studied, since higher boiling point compounds condensed out in the apparatus.

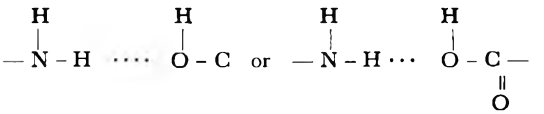
The desorption of ethylamine from pectin obeys first order reaction kinetics showing that the desorption process is dependent on the amine concentration alone.

The desorption activation energy (5·8 kcals/mole) of ethylamine from pectin, is much lower than the value obtained for silica gel (20 kcals/mole) (Ross & Taylor, 1967). This indicates that the forces involved in adsorption are weaker in the pectin/ethylamine system. This seems reasonable considering the extensive surface area and pore structure of silica gel.

The types of adsorption could be hydrogen-bonding between (1) amine nitrogen and hydrogen of the hydroxyl and carboxylic acid groups of pectin,



(2) amine hydrogen and oxygen of hydroxyl and carboxylic acid groups of pectin,



(3) formation of a salt between amine and carboxylic acid groups of galacturonic acid groups

Gelatin and sodium alginate should be capable of forming hydrogen-bonds with ethylamine. However no amine adsorption was detected with these adsorbents, indicating that pectin amine adsorption may be due to amine carboxylic acid group interaction. Recovery was greater than 100% showing that the pectin itself was losing weight. This indicates that the adsorption process is reversible. In adsorption experiments at 60 °C the pectin turned brown possibly due to a browning reaction between carbonyl groups and the amine in the presence of moisture. (Hannan & Lea, 1949). This did not occur at the other temperatures studied because last traces of moisture were removed at the higher temperature prior to amine adsorption.

Schardinger β-dextrin has been reported to occlude some molecules, e.g. acetylacetone (Cramer, 1953). A small adsorption (7 mg amine/g) was detected with our system.

Heats of preferential sorption

Adsorption of liquids on dry surfaces of solids is accompanied by the evolution of heat. These heat effects measure the changes in surface energy, produced in the process of adsorption. Similar heat effects were found to take place when one liquid displaced another as an adsorbed layer on a solid. If the displacing liquid is much more strongly sorbed than that displaced, the effect is considerable even when the displacing liquid is introduced as a dilute solution in the liquid being displaced (Groszek, 1960). Heats of preferential sorption give an idea of the surface area available for adsorption as well as the strength of adsorption.

All the volatile compounds studied gave detectable heats of preferential sorption on silica gel. The values obtained were between 2·4–6·7 kcals/molecule of adsorbate, with the exception of triethylamine which had a value of 16·0 kcals/molecule of adsorbate (Table 1). However, of the other systems studied only the sorption of ethylamine and triethylamine on the adsorbents, pectin and Schardinger β-dextrin, gave detectable heats of preferential sorption. None of the adsorbates gave detectable heats of preferential sorption with gelatin or sodium alginate.

Interactions similar to those described for the thermal balance systems are probably responsible for the sorption. When no sorption is detected possible explanations could be: (1) there are very few sites available on the surface of the adsorbent, (2) if sorption occurs the heat effect is too small to be detected and (3) the adsorbate does not replace n-heptane on the adsorbent.

A larger heat of preferential sorption was obtained with triethylamine than with ethylamine on pectin, showing that triethylamine is more strongly adsorbed. As both adsorptions take place on pectin the difference must be due to differences in structure between the two amines. The pKb values (negative logarithm of the equilibrium constant) in aqueous solution of ethylamine, diethylamine and triethylamine are 3·33, 3·07 and 3·12 respectively (Sykes, 1961). These differences are due to two effects, (1) the inductive effect of the ethyl group increases the dissociation constant and hence the basic strength; (2) the basic strength of an amine in water is determined by the extent to which the cation formed by the uptake of a proton can undergo solvation by water and become stabilized. It is the decrease of this effect which counteracts the inductive effect and gives triethylamine a pKb value of 3·12 (Sykes, 1961).

In our system, the amines are dissolved in n-heptane, so that the second effect should be absent. This would suggest that triethylamine would be more basic in n-heptane than in aqueous solution, and would explain the larger heats of preferential sorption obtained with triethylamine on pectin.

Groszek (1960) found in certain cases that negative heat effects occurred after the positive heat effect. The former effects are due to the material preferentially sorbed, being desorbed by the solvent. This can occur when the adsorbate's concentration in the solvent falls below the equilibrium value required for sorption. We did not find any negative heat effects showing that our adsorbents were probably not replaced by the solvent, n-heptane.

Comparison of the results obtained by the two methods show that the amine/pectin system in each case gives values which can be readily measured. This indicates that pectin-amine interactions are stronger than those of the other systems studied.

Acknowledgments

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The connective tissues of fish
III. The effect of pH on gaping in cod entering rigor mortis at different temperatures

R. M. LOVE AND M. A. HAQ*

Summary

When cod enter rigor mortis and are then filleted, the amount of gaping seen between the muscle segments depends on the previous body temperature, increasing progressively with warmth. In the present work it was noticed that in any batch of fish a few pairs of fillets showed little gaping even at relatively high temperatures (22–25 °C). The factor responsible was identified as the pH of the muscle, a low pH leading to much gaping and vice versa. At a given temperature, the gaping increased with time, and subsequent freezing increased it further. The practical implications of these findings are discussed.

Introduction

Previous papers (Love & Robertson, 1968; Love, Lavéty & Steel, 1969) have described the phenomenon of 'gaping' in the musculature of fish. Holes or slits appear between the myotomes (muscle segments) because of breakage of the minute tubes of connective tissue which issue from the myocommata (connective tissue sheets) and run between and around the muscle cells. Badly gaping fillets cannot be skinned or sold from open display, and have only a limited use in certain products such as fish-cakes. The present studies have been designed to identify the causes of gaping, with the object of increasing the production of first-class fillets.

Within a few hours of death, fish become stiff owing to the simultaneous slow contraction of opposing muscles ('rigor mortis'). It has already been observed (Jones, 1964, 1966, 1969) that gaping becomes appreciable if cod enter rigor mortis at 17°C, and becomes steadily worse at higher temperatures.

The work to be described in this report was originally intended as a straightforward confirmation of Jones' work, but preliminary experiments revealed an odd fact: although gaping increased as the temperature was raised, there were always a few fillets that remained virtually intact, even at relatively high temperatures. Moreover, the effect always applied to both the fillets of a fish, so evidently depended on some characteristic of the individual animal, rather than on haphazard variation. The most

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variable characteristic that springs to mind is the biological 'condition', which shows itself in the vigour of the newly-landed fish and depends on its state of nutrition, being poor during the spawning season. This seemed a possible parameter to study in relation to the new phenomenon. It can conveniently be estimated by measuring the water content of the muscle (Love, 1960), but such measurements would probably not be meaningful where the newly-killed fish had been incubated in tanks of water, as in the present work. However, there is often a good correlation between the water content and the ultimate pH of the muscle of cod treated similarly (Love, 1969), so it was decided to make further observations on 'thermal' gaping, this time in relation to pH. The water content was determined also, as an additional check.

Material and methods

Cod (*Gadus morhua* L.) of body lengths 46–70 cm, caught in the vicinity of Aberdeen (Scotland), were used throughout. Most of them were caught by seine net and placed in an aquarium ashore on the same day. The following morning they were stunned, immediately packed in crushed ice and gutted just before immersion in a tank of warm water, about 25 min after death.

A few batches warmed for 4 and 8 hr were caught by trawling, and here the fish were not held alive overnight, but packed in crushed ice as soon as possible after landing on the deck, then gutted and placed in a warm water tank on the ship. Any effects the different catching methods may have had on the gaping were not obvious, but it was noticed that the trawl-caught cod entered rigor mortis earlier.

Samples to be subsequently frozen were placed singly on trays in an air blast at −30 °C. They were thawed by leaving overnight, covered with a layer of paper, at room temperature (about 20 °C). Under these conditions, the larger fish were not completely thawed by the following morning, while small fish reached temperatures of up to 13 °C, usually less.

Gaping was estimated on the visual scale already described (Love, Lavéty & Steel, 1969), and pH measurements were made with a Beckman instrument on a homogenate of 10 g muscle in 20 ml water. Water contents were calculated from the loss in weight after keeping 10 g muscle in an open vessel for 7 days at 100 °C.

Results

Without freezing

In the first experiment, batches of whole gutted cod were placed in tanks of water maintained at 15 °, 17·5 °, 20 °, 22·5 ° and 25 °C for periods of 4, 8 or 11 hr. Following heat treatment, they were gently removed, taking care not to bend them, and packed in melting ice until the next day, when they were filleted and examined for gaping. Samples were then removed for water and pH determinations.

The gaping results after 11 hr are illustrated in Fig. 1 (a temperature of 15 °C was not employed in this batch). For fish of pH 7·1 or over, the gaping was not influenced

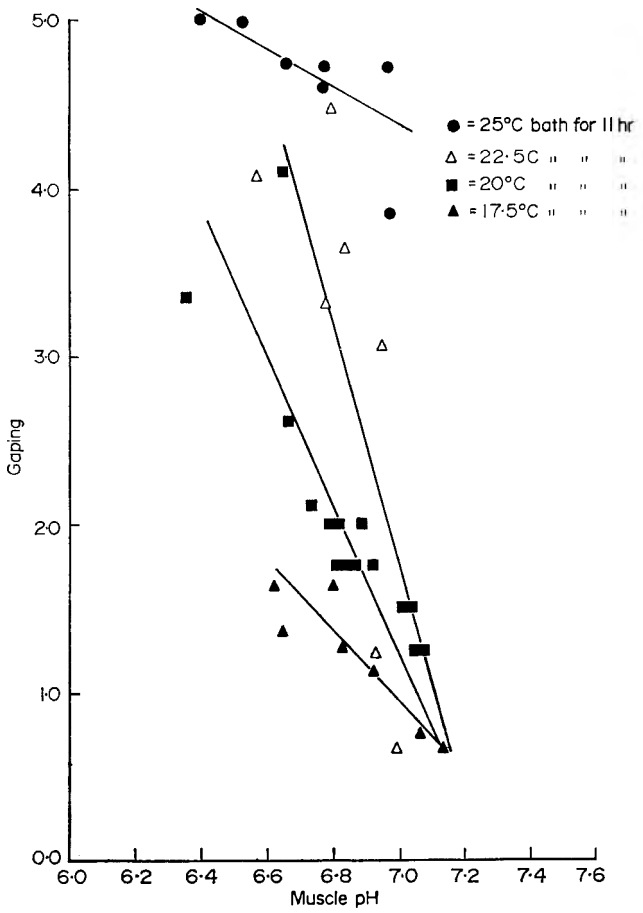

FIG. 1. Gaping scores of fish of different pH placed, pre-rigor, in baths at different temperatures for 11 hr, packed in ice until the following day and then filleted. Regression lines fitted by least squares method.

by any increase in temperature, except at 25 °C where the muscle blocks (myotomes) themselves gaped and presented a cooked appearance. Gaping is shown in the Figure to be strongly influenced by the pH, the coefficients of correlation between the two parameters being shown in Table 1.

TABLE 1. Correlation coefficients between gaping and pH in cod muscle incubated at different temperatures for different times

Incubation temperature	Time		
	4 hr	8 hr	11 hr
25°C	−0·31	−0·81*	−0·72
22·5°C	−0·77*	−0·53	−0·74
20°C	+0·16	−0·58*	−0·92*
17·5°C	−0·57	−0·50	−0·90*
15°C	+0·40	+0·19	—

Note: the nearer the figures approach 1 or −1, the better the correlation. The figure −0·58 in the 8 hr column is significant because this batch contained a larger number of samples. Asterisks show where the correlation is significant at the 5% level.

After 8 and 4 hr incubation, the correlation between gaping and pH was sometimes fairly good but usually poor. The reason is not far to seek. The pH of fish during life lies within a narrow range near the neutral point, but after death some of the residual carbohydrate is broken down to lactic acid and the pH falls, reaching its minimum about a day after death at 0°. In the present work, the two shorter periods were insufficient for the pH to reach the lowest possible value. After 4 or 8 hr the total range of pH obtained was only 6·65–7·1, compared with 6·36–7·1 after 11 hr—see Fig. 1. This smaller range resulted in clusters of experimental points having similar values, hence a poorer linearity. Further, the fish held at 15°C and 20°C for 4 hr and at 15°C for 8 hr had scarcely entered rigor mortis, so that the bodies had not fully stiffened. There was therefore little strain placed on the myocommata by the muscular contraction, and the maximum gaping encountered was less than 1·5 on the visual scale—a separation of the myotomes that is scarcely detectable by eye (Love, Lavéty & Steel, 1969).

Adjustment of the mean gaping scores for the effect of tissue water content gave slightly increased values (gaping decreases with increased water content—Love & Robertson, 1968), but the effect was of slight importance and in no way influenced the conclusions of this paper.

Fig. 1 (incubation for 11 hr) shows that several fish reached or closely approached the maximum value of five, where the fillets are falling to pieces all along their lengths, slits extending through to the skin. After 8 or 4 hr all but one of the gaping scores were below a value of three, where one or two slits extend through to the skin and numerous shallow slits are seen.

With freezing

The second experiment was like the first except that after incubation the whole fish were placed in an air-blast freezer at −30°C and left there overnight, air-thawed the following night and then filleted.

The general patterns obtained were similar to those of Fig. 1, and after 11 hr in the bath the curves of the gaping scores corresponding with temperature of 17·5°, 20° and 25°C intersected in the pH range 7·1 to 7·2, so that, as before, there was little effect of temperature during rigor mortis on gaping provided that the pH was high enough. Correlation coefficients of gaping with pH are shown in Table 2. Several high correlations were obtained at each period of time studied, illustrating the importance of pH in this work.

TABLE 2. Correlation coefficients between gaping and pH in cod muscle incubated at different temperatures for different times, then frozen, thawed and filleted

	Time		
Incubation temperature	4 hr	8 hr	11 hr
25°C	−0·93*	−0·92*	−0·83*
22·5°C	−0·78*	−0·53	−0·57
20°C	+0·35	−0·79*	−0·74*
17·5°C	−0·88*	−0·17	−0·27
15°C	−0·12	−0·35	−0·59

Asterisks show where the correlation is significant at the 5% level.

However, the most interesting result of freezing was the relatively large increase in the gaping compared with that in similar but unfrozen fish. The scores at the five temperatures and three times, averaging those of different pH, were from 26% to 93% higher after freezing (average 62%), while that of fish packed in melting ice immediately after death and frozen after 24 hr increased by 232%. The only exception was the batch incubated for 11 hr at 25° C, which showed a 9% decrease. It had already virtually reached the maximum value before freezing (Fig. 1), so presumably the 'decrease' was just experimental error.

It has already been pointed out (Love, Lavéty & Steel, 1969) that since gaping scores are 'adjectives' rather than exact mathematical relationships, they should not strictly speaking be averaged at all, so the 'percentage' increases are not to be regarded as absolute, but the figures do show strikingly that freezing greatly exacerbates the deterioration caused by warmth in rigor mortis.

The importance of the time for which the samples were incubated is illustrated in Fig. 2. The individual figures have been averaged, eliminating the pH effect. While

the values after 4 and 8 hr are not markedly different, there is a great increase after 11 hr, and the sharp rise in gaping between the temperatures of 15° and 17·5 °C confirms Jones' observation (Jones, 1964, 1966, 1969) that 17°C marks the beginning of 'thermal' gaping.

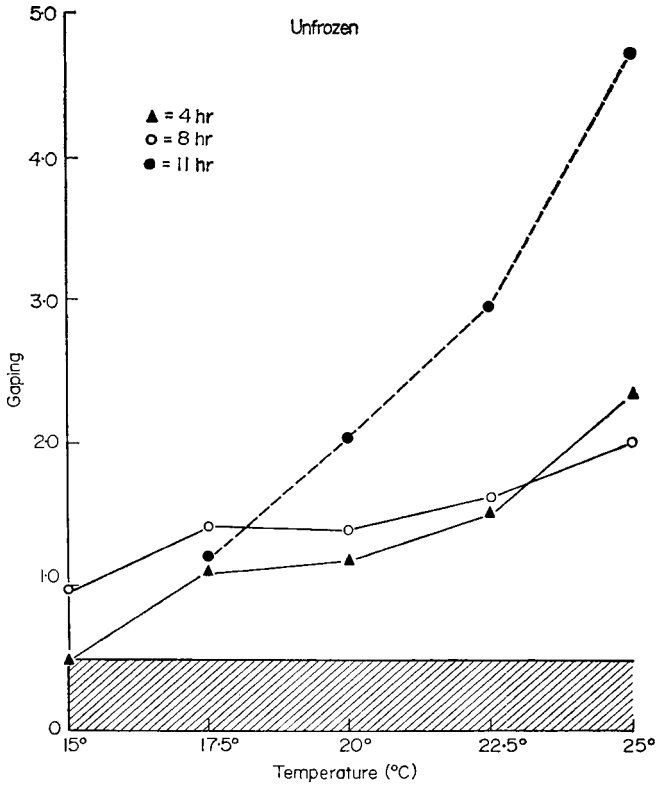

FIG. 2. The effect of time on the gaping of fish incubated, pre-rigor, at different temperatures. The hatched area shows the average gaping score of fish packed in melting ice for 11 hr after death, without freezing.

Discussion

In former times when fish for freezing were landed unfrozen (packed in melting ice) and then filleted and frozen ashore, gaping was rarely considered to be a problem in the fishing industry. Little or no gaping is also found after thawing if the musculature has been frozen as fillets after removal from the backbone, since the loose muscle has not been under tension. It is only since the advent of freezing the whole fish at sea that

the problem has become noticeable. Such fish are usually frozen whole after removal of the guts, and as we have seen there is a large increase in gaping due to the freezing, unless the gaping in the unfrozen material was maximal anyway.

Filleting some of the catch before the onset of rigor mortis and freezing the fillets in a horizontal plate freezer or air blast would certainly eliminate gaping, but can at times be detrimental to the texture of the cooked product. Freezing is not instantaneous, and some of the fillets would undoubtedly enter rigor mortis and, if they were above chill temperature, they would probably shorten before they froze. Such a shortening, impossible while the muscle was still attached to the backbone, causes denaturation of the proteins, exudation of fluid, and a rubbery consistency after cooking which is not considered desirable in this country (Love, 1962). Small fillets which had still not entered rigor when frozen would sometimes contract violently if thawed rapidly ('thaw rigor') and again be tough to eat. Thus it is still preferable to freeze the fish whole, expecially as fish fixed in a bent position in rigor cannot satisfactorily be filleted by machinery and gape if they are straightened by hand. Filleting and freezing after the resolution of rigor mortis would pose fewer problems in this direction, but lack of space and labour on board would preclude keeping the caught fish for 2 days in melting ice before freezing, especially during heavy fishing.

Whole gutted fish frozen before rigor mortis gape little and give a first-class product, but during heavy fishing the catch cannot all be put into the freezers immediately. Lying on the deck under warm conditions the fish can quickly reach most or all of the temperatures investigated in this paper, especially in the summer months, and it is obvious that such warming can quickly render much of the catch unsaleable after freezing and thawing. However, the work of the present paper has shown that another factor, pH, is of almost as great significance as rigor mortis temperature, and opens up a new possibility for controlling gaping in industrial practice, since pH varies seasonally and also according to the size of the fish (Love & Haq, in preparation). It therefore merits further study in this connection.

The present experiments do not show whether the 'thermal' gaping is caused by the partial hydrolysis of labile fish collagen in the myocommata or by an increase in the strength of the muscle contraction in rigor mortis or by both phenomena. A different procedure is required to answer this question, using isolated myocommata, and it is hoped to present the findings in a future publication (Love, Lavéty & Garcia, in preparation).

Acknowledgments

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The connective tissues of fish. IV. Gaping of cod muscle under various conditions of freezing, cold-storage and thawing

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Summary

The rate at which whole cod were frozen was shown to have little effect on the gaping of the fillets cut after thawing, though very slow freezing did cause a small increase. Cold storage at − 14°C to produce varying degrees of muscle protein denaturation did not affect gaping, neither did the manner of thawing (four methods used). However, the experiments, involving hundreds of fish amply confirmed that gaping increases when the fish are frozen after entering rigor mortis (compared with pre-rigor) and increases again if they are frozen after a longer time in melting ice.

Removing the skin before freezing the whole gutted fish was shown to reduce the gaping, presumably by reducing the tension on the myocommata. The greatest reduction was obtained with fish skinned *in* rigor mortis, where muscular tension is greatest.

Haddock always gaped more than whiting, although they are very similar related fish, and were selected to be of similar lengths. The present work showed that the ultimate pH of the two species was very different, that of haddock being lower. The difference in pH probably accounts for the difference in gaping, but the reason for the two species having such a disparity in pH is not known. It may relate to differences in intrinsic activity.

Introduction

Work described in the previous paper of this series (Love & Haq, 1970) demonstrated that any gaping induced in cod muscle was always enhanced by subsequent freezing, unless it had reached a maximum value already. The reason is probably to be found in Love & Robertson's observation (1968) that under a wide range of freezing conditions ice crystals form within the myocommata (connective tissue sheets), and so presumably weaken them.

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Gaping has already been observed to worsen if the fish are frozen unusually slowly. Reay (1939) found that the muscle of haddock (*Gadus aeglefinus* L.) gaped more as the temperature of the air in which they were frozen was raised from − 26°C to − 18·5°C and gaped more still when it was raised further to − 8·5°C, that is, as the rate of freezing decreased.

The purpose of the present work was to study the effect of various freezing and thawing conditions on gaping, and also to find out whether cold-storage, sufficient to denature the muscle proteins, exerts any influence.

Material and methods

Cod (*Gadus morhua* L.), whiting (*Gadus merlangus* L.) and haddock (*Gadus aeglefinus* L.) were all caught by trawling off the East coast of Scotland.

Water and pH determinations were as described by Love & Haq (1970), and gaping was assessed on the scale illustrated by Love, Lavéty & Steel (1969).

Results and discussion

Freezing rate

Cod from 39 to 70 cm long were used in this experiment. Conditions were chosen so that whole gutted fish were obtained frozen with (1) intracellular, (2) small extracellular and (3) large extracellular ice crystals (Love, 1966). The respective treatments were as follows. (1) Placing the fish in a bath of ethanol maintained at − 50°C by the addition of solid carbon dioxide. The freezing time (time for centres to cool from 0° to − 5°C) was about 8 min. The fish were left in the bath for 30 min, but the ethanol did not penetrate appreciably, as shown by the normal appearance of the muscle and the lack of smell of ethanol at the cut surface of the fillets after thawing. (2) Placing the fish in an air-blast freezer at − 30°C for 3 hr (freezing time at centre about 3 hr). (3) Placing singly in a room at − 14°C, the upper surfaces of the fish being covered by a single layer of 'cellosene' cellulose wadding. The freezing of the centres here took between 3 and 4 days.

The fish were thawed overnight as described by Love & Haq (1970).

Since one of the freezing rates was very slow, it was clearly pointless to attempt pre-rigor freezing. However, since Love, Lavéty & Steel (1969) showed that fish frozen 5 days after death gaped more than those frozen 1 day after death, it was considered worth while to submit fish of widely-spaced times after death to the same treatment. One batch in each experiment was frozen after being kept for 1–3 days after death, packed in melting ice, while the other was kept for 8 days under the same conditions. Ten fish of each degree of freshness (time after death) were frozen at each rate of freezing, and the whole experiment was performed five times, in the months of October and November 1968, making a total of 300 fish.

The mean gaping values at the two stages of freshness are shown in Table 1, values at all rates of freezing being grouped together.

TABLE 1. Mean gaping scores of fillets cut from fish kept for different times in melting ice, then frozen and thawed

Experiment	Date caught	Gaping score	
		1–3 days in ice	8 days in ice
1	6.10.68	2·62	2·71
2	15.10.68	2·47	3·28*
3	19.10.68	2·96	2·80
4	30.10.68	2·38	3·15*
5	4.11.68	1·67	2·60*

* Increase over 1–3 days in ice is significant at 0·1% level.

Although the differences in gaping in two of the experiments were not significant, the overall results support the previous findings, showing that stale fish gape more than fresh fish if they are subsequently frozen. Table 2 shows the effect of freezing rate, figures for fresh and stale fish being grouped together.

TABLE 2. Effect of rate of freezing on gaping in cod after thawing and filleting

Experiment	Gaping score		
	8 min	3 hr	3 days
1	2·89	2·53	2·56
2	2·86	2·70	3·05
3	2·92	2·89	2·81
4	2·81	2·42	3·06
5	1·80	2·29	2·32

There is no consistent difference between the gaping scores of rapidly- and medium-rapidly frozen fish, but in three experiments the slowest-frozen fish gaped more than the others. Statistically the differences are not significant, largely because of considerable batch-to-batch variation in the fish. When other factors were eliminated, it was found that there was significant correlation between gaping and the water contents of the muscle, and in some cases between gaping and length, these effects being sufficient to over-ride the effects of the freezing rate. Since there is no way of measuring the water content (and so of selecting one's batches) without cutting open the fish, it

was not considered worth-while to continue the experiments. However, we feel able to state as a working hypothesis that very slow freezing does sometimes lead to more gaping, but the effect is rather small.

This view is supported by further evidence reported in the next section: looking ahead for a moment to Fig. 1, we can again see that the gaping of the two most quickly-frozen groups is not distinguishable, but that that of each of the most slowly frozen batches is distinctly greater than the gaping of the other two. Statistically the difference was significant at the 1% level, and on this occasion the inherent batch variation did not entirely destroy the significance of the effect of freezing rate.

Cold storage

The storage of cod in the frozen state leads to extensive changes in the properties of the muscle proteins with the passage of time. The muscle becomes white in appearance, and after cooking it is found to be fibrous and tough to eat. When it is thawed out, the water resulting from the melting of the ice crystals is no longer reabsorbed by the changed muscle proteins, and exudes copiously from the cut surface of the fillet. There is no published information on the behaviour of connective tissue under these circumstances.

In the present work, it was decided to store whole gutted cod, caught 27 March 1969, for 0, 3, 6 and 9 weeks at − 14°C. After 9 weeks the change in the muscle proteins is more than half completed in this species, as measured by protein extractability (Love & Ironside, 1958) or cell fragility (Love, 1962).

Gaping is influenced by so many factors that it was thought desirable to consider the rate of freezing and the physiological state (pre-, in- or post-rigor) at the same time as the cold-storage period.

Fig. 1 shows the effect of cold-storage on fish frozen with intracellular, small extracellular and large extracellular ice crystals, as in the previous section, and, as already pointed out, it shows that slowly-frozen cod gape more than those medium- or quickly-frozen. There was no significant correlation between storage time and gaping.

For studying frozen storage time in relation to stage of rigor mortis, two experiments were done. Again ten fish were used under each condition, those of the first experiment being caught 7 April 1969, the second experiment 6 October 1969. These dates would usually give fish that were respectively in the worst and the best biological conditions according to the states of the spawning cycle, but the effect on these experiments was minimal because immature fish were used (less than 70 cm long).

Freezing was carried out on the research ship *Sir William Hardy* at Tod Head, near Dundee (N.E. Scotland). Fish to be frozen pre-rigor were gutted and placed singly in an air-blast freezer at − 35°C within 20 min of capture. In-rigor fish were packed in melting ice after gutting and frozen 9 hr after capture. Post rigor fish were kept in ice for 4 days before freezing in the same way. The results of the experiments are shown in Fig. 2. As observed by Love, Lavéty & Steel (1969), the pre-rigor fish all gaped less

than the other two batches, between which there was no significant difference in the present experiments. Adjustment of the gaping values for the effects of pH made virtually no difference to the results, and the correlations between gaping and storage time were again not significant.

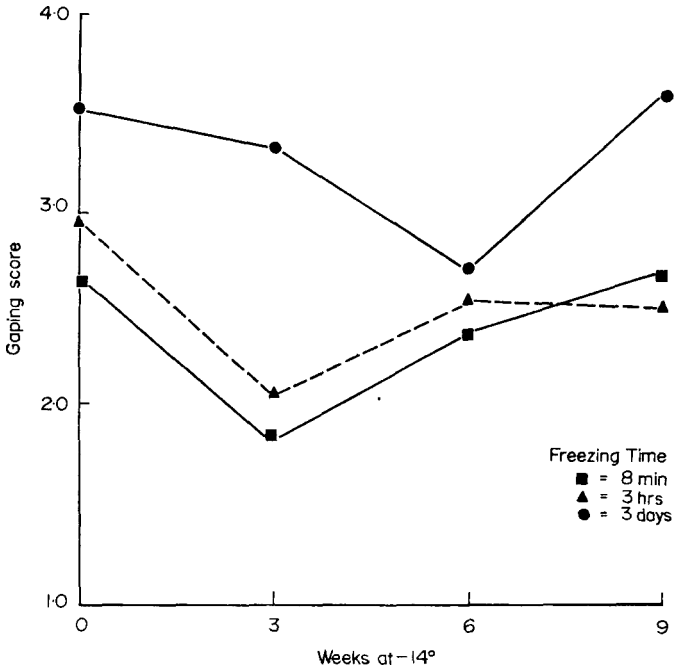

FIG. 1. Gaping of cod, frozen at different rates and stored for various times at −14°C.

It therefore seems unlikely that storage time can influence gaping, even when the musculature has toughened and changed extensively in other ways—at any rate in cod.

Thawing method

The way in which fish are thawed is known to affect the quality of the product—for example, thawing in water bleaches the skin slightly, and causes the fish to increase 1–2% in weight (Hewitt, 1969). If the thawing is such that the fish become warm after the ice has disappeared, gaping will increase. Hewitt (1969) found that cod thawed in water at 21°C gaped more than those thawed in water at 18°C. Different methods of air- and water-thawing have been described by Merritt & Banks (1964).

In the present work 120 cod from 33 to 77 cm long were caught (6 September 1969) at Tod Head. Forty fish were frozen in an air-blast freezer at − 35°C immediately after gutting (pre-rigor), forty were packed in melting ice and then frozen 9 hr after death

(in-rigor), and the remainder were frozen 4 days after death (post-rigor). All the fish were then stored until 20 September 1969 at − 30°C and thawed in one of four ways.

1. Ten fish at each stage of rigor were removed from the cold store, kept at room

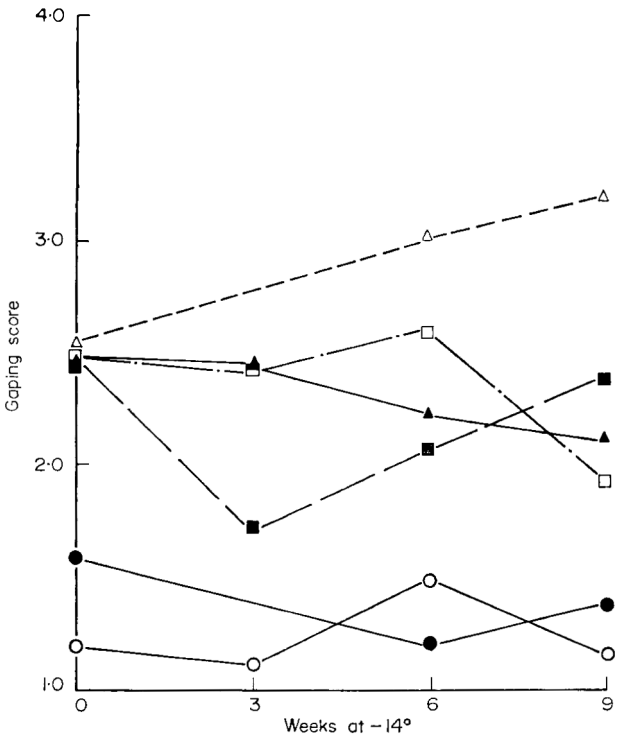

FIG. 2. Gaping of cod pre- in- and post-rigor, stored for various times at −14°C. Solid symbols: 1st experiment, open symbols: 2nd experiment. Circles = pre-rigor; squares = in-rigor; triangles = post-rigor.

temperature (18–20°C) for 5 hr and then overnight at 2·2°C. The following day it was found during filleting that four out of the thirty fish still contained a little ice.

2. Fish were removed from the cold store in the evening and left for 18 hr at room temperature, a single layer of paper being laid over them to reduce drying. The highest temperature in the middle of the thickest part of the body, measured with a probe thermometer just before filleting, was 14°C. All fish were completely thawed.

3. Fish were placed singly in an air-blast thawer which blew moisture-saturated air at 15–18°C for 2 hr. At the end of this time, the centres of some fish had reached 15°C, while ice was still present in a few larger fish.

4. Fish were placed in running water at 15–18°C for 2 hr. Most fish reached about 16°C and all were completely thawed.

The results are shown in Table 3.

TABLE 3. Effect of thawing by four methods on the gaping of cod
(each value is the mean of ten fish)

	Length	pH	Gaping score
Pre-rigor			
1. Warm air, overnight at 2·2°C	50·5	6·76	1·46
2. Overnight at room temperature	46·6	6·90	1·33
3. Air-blast at 15–18°C	48·5	6·84	1·11
4. Water at 15–18°C	44·6	6·90	1·11
In-rigor			
1.	50·0	6·81	1·86
2.	45·3	6·84	2·00
3.	48·4	6·86	1·78
4.	49·7	6·80	2·00
Post-rigor			
1.	45·4	6·83	2·25
2.	44·0	6·84	2·28
3.	54·4	6·74	2·64
4.	48·4	6·85	2·39

As usual, the gaping was influenced by the state of rigor mortis (significant at 0·1% level), and by pH (significant at 1% level). However, there are no significant differences in gaping according to the thawing method.

Analysis of covariance showed that the regression of gaping on body length exercised a negligible influence on the results.

The skin as a source of tension

If the muscle tissue is scraped away from an anterior myocomma in the fillet of a large cod, the distribution of collagen fibres can be seen to be non-uniform. At the end of the myocomma nearest to the skin they are small and evenly distributed, but at the 'bone' surface they are much larger and converge at a point, which, it has been suggested, is the place of attachment to a vertebra (Love, 1970). It is likely therefore that myocommata are the means whereby power from muscular contraction is transmitted to the skeleton. Since the other end merges with the skin, it is also likely that the skin, in anchoring it, is under considerable tension. The surface of a fish such as cod is curved, but it is an everyday observation, so often seen that one tends to ignore it, that the 'skin' surface of a *fillet* is flat, not curved: it is now the cut surface which has become cylindrical, suggesting that the skin contracted when the fillet was removed from the body. Presumably therefore in viewing a fillet, or one in which myocommata are exposed by scraping, we are not looking at tissues in the geometrical relationships they

held in the intact fish. Whole flat fish such as plaice (*Pleuronecte platessa* L.) have a body surface which is only slightly curved, i.e. not very different from that of the fillets, and flat fish gape less than round fish (Love, Lavéty & Steel, 1969). These authors also showed that the roundest of the flat fish, halibut (*Hippoglossus hippoglossus* L.) gaped most of the flat fish, and that the flattest of the deep-bodied fish, redfish (*Sebastes marinus* L.), gaped least of this group. Curvature may therefore be important, but there is a distinct possibility that skin tension is important also.

These suggestions must be very tentative, because at present so little research has been done on the directions of forces within the musculature of a fish: Ganguly & Nag (1964) have already said that 'The problem of the nature and arrangement of the myomeric musculature is a most vexatious one', with which remark we must agree.

However, the effect of removing the skin on the tensions exerted by the muscle on the myocommata seemed easy to check experimentally.

Three experiments were done with cod, haddock and whiting, caught at Tod Head on 21 January 1969, 7 April 1969 and 25 May 1969 respectively. The skin was removed after gutting by cutting through it at the posterior margin of the operculum and slitting round the head. It was eased free from the underlying muscle with a scalpel and then, when enough had been cut to give some purchase, the whole round skin was pulled off towards the tail in the manner of removing a stocking. Fish with skin removed and controls were frozen as before in an air-blast freezer within 20 min of death, after 9 hr and after 4 days, to include the stages of rigor when the myocommata are subjected to different amounts of tension.

In most cases, ten fish were used in each treatment. Where fewer (not less than seven) were used owing to inadequate catching, the analysis of variance was carried out as if each batch had consisted of ten fish; missing values were supplied by the least squares technique, and the degrees of freedom were correspondingly reduced.

Cod gave the most striking results, 169 fish being used (180 would have given 10 fish at each treatment). The numerous results are presented in small compass in Table 4.

Each of the mean values in Table 4 relates to at least fifty fish, so a difference may be taken to be significant at the 5% level if it is at least twice the standard error.

The removal of the skin significantly (at 0·1% level) reduces the gaping, the difference between the overall means being about seven times the standard error. There is a steady small increase in gaping as the season advances, probably due to a fall in pH resulting from recovery after spawning. However, it is not statistically significant and does not affect the results relating to removing skins.

As usual, the state of rigor markedly affects the gaping, scores showing a steady increase which is significant at the 0·1% level. However, the removal of the skin reduces gaping at each stage of rigor, giving an average (January, April and May) decrease of 0·265, 0·674 and 0·505 gaping units in pre- in- and post-rigor fish, respec-

TABLE 4. Effect of removing skin before freezing on the gaping of gutted whole cod frozen before, in and after rigor mortis. (Figures are overall mean gaping scores.)

(a) *Effect of skinning*

Skin on	Skin removed
2·11	1·63

Standard error of the difference between the two means = 0·0698

(b) *Seasonal difference*

January	April	May
1·78	1·90	1·94

Standard error of the difference between any two means = 0·0855

(c) *Rigor mortis changes*

Pre-rigor	In-rigor	Post-rigor
1·43	1·91	2·28

Standard error of the difference between any two means = 0·0855.

tively. The biggest effect of removing the skin is thus seen *in* rigor mortis, when the tension of the muscle is greatest.

The results for haddock and whiting were not so striking. Table 5 shows that in pre-rigor fish, where the muscular tension is least, removal of the skin did not reduce gaping. However, gaping was reduced in rigor and after rigor. Statistical evaluation of the degree of significance was not carried out with these two species.

TABLE 5. Effect of removing skin before freezing on the gaping of gutted haddock and whiting frozen before, in and after rigor mortis (mean of three experiments)

	Mean gaping scores	
	Skin on	Skin removed
Haddock: pre-rigor	2·17	2·22
in-rigor	2·47	2·25
post-rigor	2·52	2·32
Whiting: pre-rigor	1·61*	1·88*
in-rigor	1·99	1·60
post-rigor	2·13	1·99

* Two experiments only.

Species differences

Love, Lavéty & Steel (1969) showed that there were considerable variations in gaping according to species, haddock gaping by far the most. Since there have been indications that size plays an important part in gaping (Love & Haq, in preparation), it might have been supposed that the smaller size of haddock compared with cod could account for this phenomenon, but the whiting, not investigated by the above authors, is also a small gadoid and exhibits gaping comparable with that of cod, not haddock. Table 5 showed that gaping was always less than that of haddock, even pre-rigor.

While the behaviour of haddock might be explained by an anatomical peculiarity such as unusually thin myocommata, it seemed worth while to compare the ultimate pH values of the two species, since so much of the present work has shown the importance of this parameter, and in some work by Cutting (1953) a difference between the pH values of haddock and whiting muscle could be seen.

The fish were caught by the *Sir William Hardy* at Tod Head on 6 October 1969, twenty haddock and nineteen whiting being selected as of comparable mean body lengths from one haul. The haddock averaged 32·5 cm long (range 29–38 cm), the whiting 35 cm (range 27–52 cm). They were gutted and rapidly chilled in melting ice, kept in the fish room in ice for 9 hr and then singly air-blast frozen at − 35°C (in-rigor).

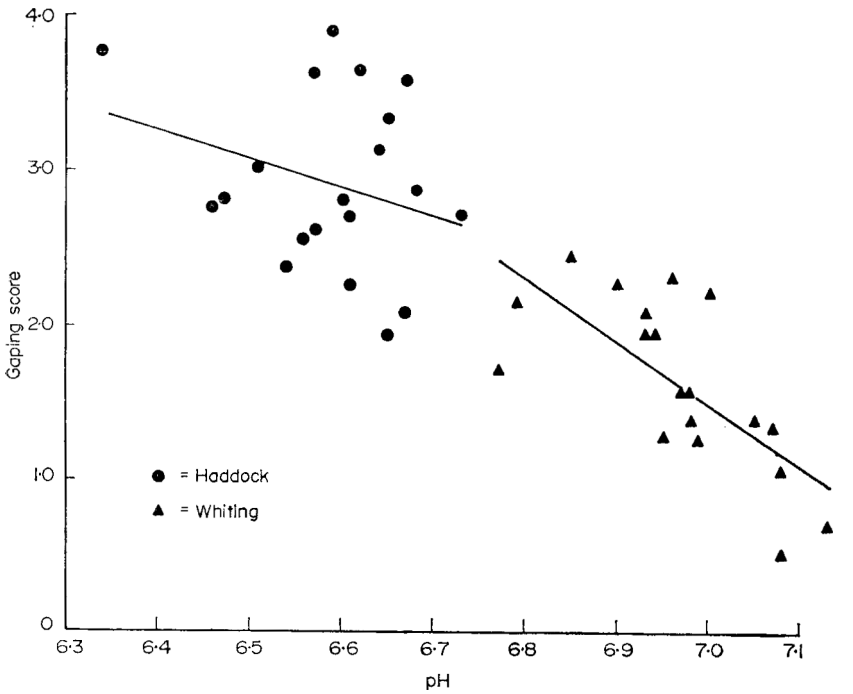

FIG. 3. Gaping of thawed haddock and whiting of comparable lengths, in relation to the pH of the muscle. The correlation between gaping and pH for haddock was −0·30, that for whiting −0·70.

The results (Fig. 3) are striking: the pH values of the haddocks were so much lower than those of the whitings that not even one value overlapped; the species difference in gaping is thus almost certainly a pH effect.

This in itself poses a problem of a different sort—why should such similar and closely-related fish be so biochemically different? The fact that the whiting chases food in a similar manner to cod, while the haddock 'grazes' the sea bottom in the manner of a cow (R. Jones, personal communication) may influence the carbohydrate reserves somewhat, as may the fact that haddock and cod have different diets (Kohler & Fitzgerald, 1969). The haddock seems to be a less active fish than either of the other gadoids, and therefore probably gives up struggling sooner when caught. Correspondingly larger reserves of carbohydrates may therefore remain after capture, hence more lactic acid will be produced after death.

These findings suggest that the halibut gapes more than other flat fish (Love, Lavéty & Steel, 1969) because of its well-known low ultimate pH, but this idea is difficult to prove because of the difference in the shape of the halibut compared with that of gadoids.

While the purpose of the present work was primarily to investigate the effect of variations in freezing practice on the incidence of gaping, the main substance of the results has in fact been a solid confirmation of the importance of the stage of rigor mortis when the fish are frozen and of pH, a fall in which greatly increases gaping. The gaping suffered by fish kept for 8 days in ice and then frozen has also been shown to be statistically greater than that in fish kept only 1–3 days in ice after death, at least in some experiments. This kind of gaping will be the subject of a future communication. Freezing rate was shown to be unimportant except when it was extremely slow, when it did give rise to a slight increase in the gaping. Such a small effect was unexpected, because slow freezing is well known in the early work of this research station as a cause of poor quality. A coarse or 'grainy' appearance is seen in the muscle of slowly-frozen fish after thawing, and Banks (1952) found that if thawed herrings (*Clupea harengus* L.) were 'split' mechanically, there were more rejects (fish damaged by the machine) among slowly-frozen fish than among those frozen in less than 2 hr. The cohesiveness of this species is evidently very sensitive to ice crystal size.

The reduction of gaping brought about by removing the skin before freezing cannot seriously be contemplated as a technique to be used commercially, but the tension in the skin of whole fish revealed by this work is obviously an important factor and goes a long way to explain why freezing the musculature as fillets, rather than intact fish, gives rise to little or no gaping. However, as already pointed out (Love & Haq, 1970), there are some disadvantages to freezing newly-caught fish as fillets on board the catching vessel.

Nothing has emphasized the importance of pH in governing gaping as much as the difference between haddock and whiting, two otherwise similar species with very

different gaping propensities. Haddock gape so much that if they are frozen whole then thawed and filleted, the fillets are unacceptable in appearance if sold as such, and are unsuitable for smoking. The present work suggests that the only way in which they could be made acceptable, assuming that gaping fish cannot be cemented together again, would be to arrange in some way for them to have a high pH.

If the pH were high, not only would the gaping be less severe, but also the texture would be more satisfactory when the cooked fish were eaten, so a double advantage would accrue. Cowie & Little (1966) showed that at low storage temperatures the pH was a more important determinant of texture than was the storage time. Love (1969) reported a relationship between texture and both pH and water content, samples with high pH and high water being softer. Such fish when frozen would accordingly keep for a longer time or at a higher temperature than low pH fish (Cowie & Little, 1967). However, at present there seems little likelihood of ensuring high pH fish to order during commercial catching, except during the spawning season, when they are unsuitable for processing anyway. Research on factors influencing the ultimate pH is continuing in this laboratory.

Acknowledgments

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Automatic application of polyphosphate solution to fish fillets

J. WIGNALL, D. P. POTTER AND M. L. WINDSOR

Summary

A pilot plant is described for the automatic polyphosphating of fish, the capacity being 570 kg per hour. The importance of volume control and maintenance of polyphosphate solution concentration is examined. Filtration and cooling systems fitted to the pilot plant are described. Data on changes in the solution, (concentration etc.), and changes in the fish, (weight changes, shelf-life changes), are presented; these data were obtained under commercial conditions with high throughput of fish.

Introduction

Polyphosphate dips are used to reduce drip loss in thawed, frozen fish. Drip is undesirable both because weight is lost and because drip is unsightly, particularly in prepackaged fish. It has also been demonstrated that treatment with polyphosphate can improve the quality of frozen fish, particularly sea-frozen fish, by restoring the glossy appearance or 'bloom' of the fillets.

The aim of this work was to develop a method for applying polyphosphate solution to fish on a commercial scale under controlled and reproducible conditions. Polyphosphates can cause skin irritation and this is an additional reason for mechanical handling.

Measurement of changes in phosphate concentration etc. in the fish and in the solution were made in large scale trials and are intended to describe the commercial operation of the plant rather than to give precise information on weight retention and chemical changes in solution. Precise information of this sort is, of course, best carried out under laboratory conditions (Sutton, 1967). Cod (*Gadus morhua* L.) were used throughout the trial and where quality changes and weight changes in the fish are reported they refer to first trial which was based on sea-frozen fish (Table 1).

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TABLE 1. Summary of operating conditions

Condition	First trial	Second trial
Solution in tank	10% PM 80*	7% 2 : 1 Tri/Hexa†
Make-up solution	10% PM 80	8% 2 : 1 Tri/Hexa
Dipping time	1 min	1 min
Volume in tank	64 litres	45 litres
Volume added during trial	47 litres	34 litres
Weight of fish dipped	1500 kg	1690 kg
Type of fish dipped	Fillets from sea frozen fish	Fillets from iced fish
Temperature of solution in tank	6°C	2°C
Filtering ratio	2·3 l/min continuously	Not filtered
Tank refrigeration	Off	On

* PM 80 is a proprietary polyphosphate mixture.

† 2 : 1 Tri/Hexa is a 2 : 1 mixture of sodium tripolyphosphate and sodium hexametaphosphate.

The pilot plant

The plant consists of an elongated tank fitted with a conveying system, a filtration system, a device for controlling the volume of liquid and a cooling system.

These will be described separately. Fig. 1 and Plate 1 show the complete plant.

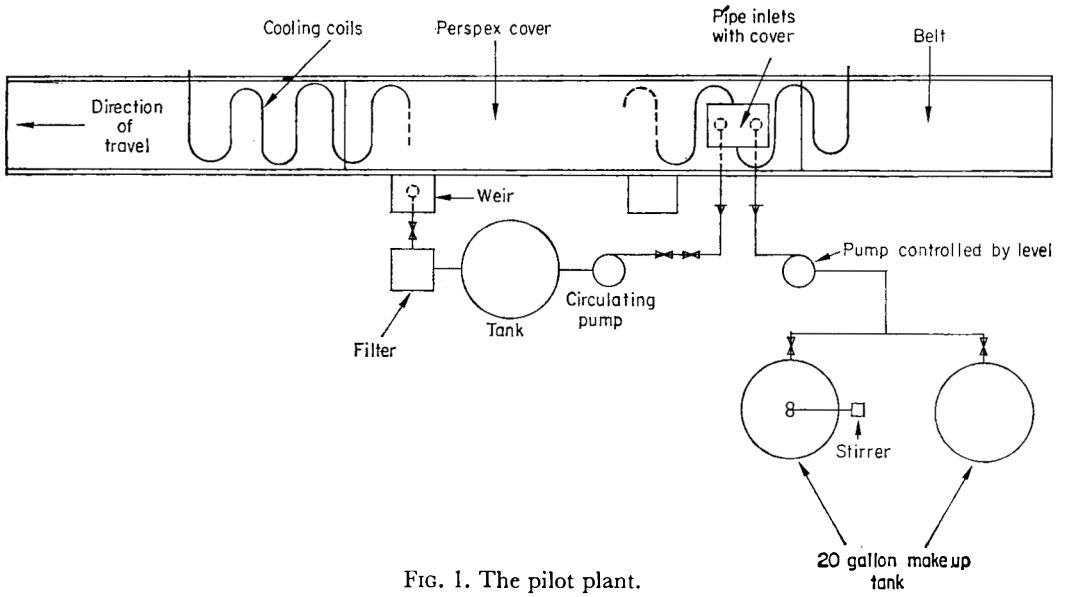
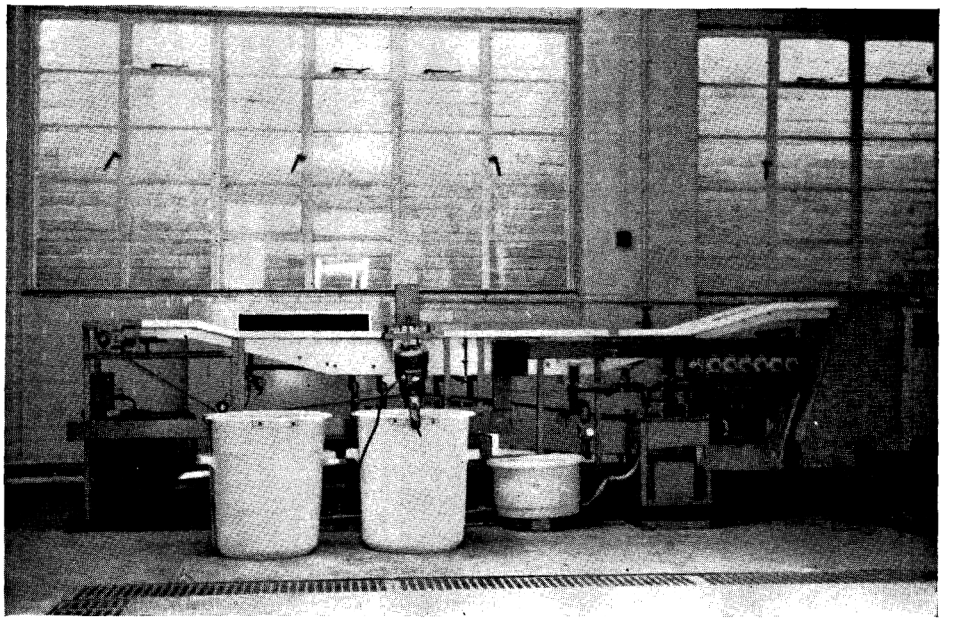
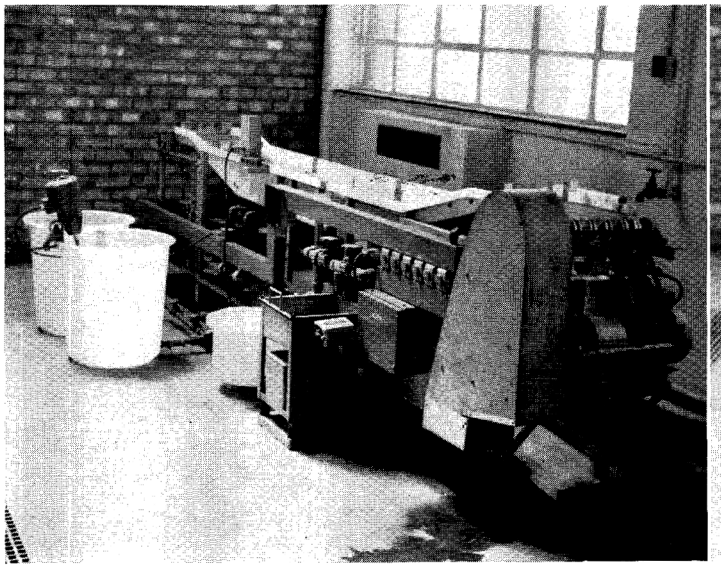


FIG. 1. The pilot plant.





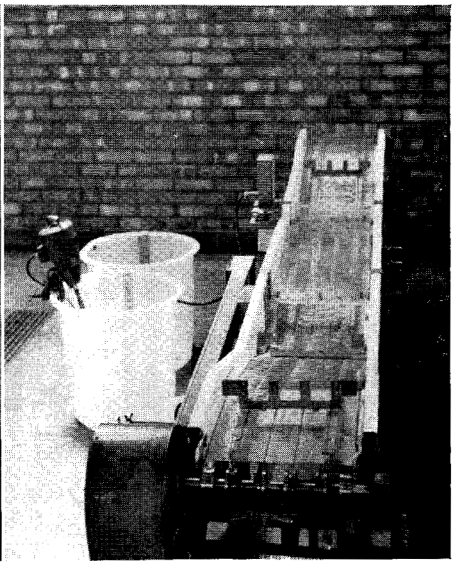


PLATE 1

(*Facing p.* 262)

The tank

The tank consists of three sections; feeding, dipping and draining. In the first section the fish are fed on to the conveyer and carried towards the liquid, in the next section they are submerged for the required period of time, and in the final section they are carried out of the liquid and drained. The length of the feed section is not critical but that of the drain section must provide for adequate drainage of surplus polyphosphate solution from the fish. The overall length of the tank is 3600 mm and the depth of the dipping section is 200 mm. However, the intended operating level of the liquid is only about 120 mm and it is important to keep this to a minimum if wastage of polyphosphate solution is to be avoided. Under normal conditions the tank will contain 64 litres of liquid. A number of outlets and weirs are provided to the tank and their functions are described below. The throughput of the plant is determined by the conveyer speed; this plant, which has a conveying system 300 mm in width, has a throughput capacity of 570 kg of fish per hour if the dipping time is 1 min.

Polyphosphate solutions can have a pH up to 9 and the material of construction is therefore rather important. Stainless steel or fibreglass coated mild steel would be ideal but rather expensive for experimental purposes. The tank described here was constructed from mild steel which was then shot blasted and painted with an epoxy resin protective coating to eliminate rusting and this was found to be satisfactory in use. All pipes, valves and other containers were constructed in plastic; pumps were in stainless steel.

The conveying system

Polyphosphate dip solutions are normally used at a concentration of between 5% and 10%. Fish float in 10% tripolyphosphate solution, but sink in 5% solution. Since it is desirable to be able to use the plant over the whole range of concentration the conveying system needs to cope with both sinking and floating fish fillets.

The conveyor belt is stainless steel of an open mesh type. It is fitted with flights and driven through a variable speed gear chosen so that the residence time of a sample in the tank could be varied from less than half a minute up to about 12 min. To ensure that even floating fish are completely submerged the dipping section of the tank is fitted with a clear plastic cover, so that the fish are forced under the surface of the polyphosphate solution. The conveyer belt is returned beneath the tank rather than within the tank. Although this requires a tray to collect surplus solution from the conveyer, it offers the advantage that the quantity of polyphosphate solution in use is kept to a minimum. A belt conveyer is more difficult to keep clean than, for example, a rotary drum, but causes less damage to the product.

Drainage of surplus polyphosphate solution takes place whilst the fillets travel on the conveyer over the final section of the tank. It was found impossible to provide the drainage time of 5 min recommended by Murray (1967) and a compromise between adequate drainage and length of conveyer was therefore made. Experimentally it was

found that after draining dipped fillets (weight approximately 680 g) for 36 sec, 80–90% of the drip collected after 5 min was obtained. Consequently the plant was arranged to provide a drainage period of 36 sec when belt speed gave a dipping time of 1 min. It would be convenient, in a large scale continuous operation, to allow subsequent drainage to take place on a separate conveying system.

The filtration system

A filtration system was included because it was anticipated that small particles of fish from the fillets would be deposited in the solution and could block the various pipe connections. It also seemed undesirable from a hygienic point of view to have particles from the first dipped fish coming into contact with the last dipped fish. Liquid in the tank is drained over a weir (Fig. 1) of controllable width so as to obtain an adjustable rate of flow, and is then passed to a 30 mesh stainless steel vibrating sieve, the filtered liquid being recycled to the tank via a non-return valve and stainless steel centrifugal pump. Polyphosphate solution is returned to the tank below the liquid level so as to reduce frothing; dissolved protein can cause the solution to froth badly if it is pumped or violently agitated.

Volume control

Polyphosphate solution is removed from the tank in two ways. Firstly, some of the polyphosphate combines with the fish by a mechanism which is imperfectly understood but which probably involves swelling of the protein with which it is in contact and the formation of a relatively impermeable film or coating. It is this surface effect which reduces drip loss. Secondly, excess polyphosphate solution is carried out of the tank.

Liquid level is controlled automatically by means of a two-level resistance operated controller which operates a pump connected to a reservoir containing stock solution used to restore the level of the tank, (the 'make-up' solution). The plant includes two such reservoirs; one is used for make-up whilst fresh solution is prepared in the other. Some polyphosphates are difficult to dissolve and a large stirrer is therefore included.

Cooling system

The dipping section of the tank is refrigerated; the cooling coils are plastic-coated and immersed directly in the polyphosphate solution. It is advisable to keep fish at a low temperature throughout the whole of the processing period, but low temperatures also help to limit bacterial growth in the solution. On the other hand, certain polyphosphate mixtures are precipitated at temperatures close to 0°C and the thermostat was therefore set at approximately 2°C.

Operation of the equipment

The pilot plant was operated under commercial conditions in a fish processing factory using skin-on cod fillets from the production line for normal wet fish distribution. For this outlet appearance and 'feel' are more important than maximum reduction in drip loss; too much polyphosphate gives an unduly glossy and slippery product. In pre-packaged fish, on the other hand, it is the reduction in drip loss that is more important and different dipping conditions would be used.

Observations made on the plant included consumption of polyphosphate solution, weight of fish put through the solution, feed rate, filtration rate and general observations relating to design e.g. frothing, draining, ease of working.

In the first trial, 1500 kg of fish were dipped in a volume of 64 litres of liquid; this gives a fish-to-liquid ratio on a weight-to-weight basis of 24 : 1 but if the make-up volume is included the ratio is 14 : 1. In the second trial the volume of liquid was reduced in an attempt to increase the fish-to-liquid ratio without substantially increasing the quantity of fish used. A fish-to-liquid ratio of 39 : 1 was obtained, 22 : 1 if make-up volume is included. It is important to establish a reasonable ratio since most factories would not be expected to follow changes in the solution by chemical analysis but would work to a pre-determined ratio.

The feed rate in both trials was spasmodic but was generally 320–380 kg/hr. However, it was found that the design capacity of 570 kg/hr could be achieved and maintained. The total volume of solution used in the first and second trials was 109 and 80 litres respectively; the cost of polyphosphate for treating the fish was therefore approximately 0·40d per kg in the first trial and 0·24d per kg in the second. In both trials the solutions were thrown away after each day's operation; this would be necessary in commercial practice. Cleaning the tank was not difficult since the refrigeration coils were set above the base.

The conveying system worked satisfactorily although there was some run-off of solution from the belt as it passed back beneath the tank. The design of the flight was satisfactory, but could be improved and might need to be different in shape for different products. The level control functioned satisfactorily throughout.

Filtration was not entirely necessary because the appearance of the fillets was not affected by dipping in unfiltered solution and the amount of 'debris' in the tank was quite small. In other conditions, however, filtration might be necessary but a simple static sieve fitted with an easily interchangeable filter surface might be adequate. The system of liquid take-off by means of a weir worked well and it was rarely necessary to vary the flow. Some frothing occurred towards the end of the day when dissolved protein in the liquid was high. In this plant the pump was deliberately oversized, and a smaller pump would probably cause less frothing.

In both trials the temperature of the fish fed to the pilot plant was approximately 5°C. In the first trial the refrigeration system was not used and, at an ambient tempera-

ture of 13°C, the liquid temperature dropped to about 6°C with passage of the fish. In the second trial the refrigeration system was used, and the temperature of the solution fell to about 2°C.

Changes in the solution

The extent of changes in solution concentration, bacterial count etc. was determined in order to establish a suitable procedure for use of the tank. The results obtained are summarized in Table 2. The concentration of the solution was determined as orthophosphate by the vanadomolybdate method of Kitson & Mellor (1944) prepared solutions of the two commercial polyphosphates being used as standards. Hydrolysis

TABLE 2. Changes in the solution

Trial	Hours after start of trial	Weight of dipped fish (kg)	Concentration of solution* (% w/w)		Specific gravity at 17·7°C	pH	Nitrogen content N_2/100 ml soln.	Total viable count (per ml $\times 10^{-4}$)
			hydrolysed	unhydrolysed				
First	0	0	9·1	0·4	1·081	7·55	0	0·4
	1	250	8·5	0·3	1·076	7·60	27·4	13
	3	800	7·5	0·4	1·071	7·55	112·8	64
	6	1270	6·8	0·2	1·063	7·60	163·0	106
	7	1500	6·7	0·2	1·064	7·60	171·2	95
Second	0	0	6·5	0·3	1·072	7·95	0	1·8
	1	335	6·5	0·4	1·059	7·85	1·1	46
	2	580	6·1	0·4	1·057	7·85	62·2	55
	4	—	—					37
	5	1270	5·7	0·4	1·055	7·70	88·8	38
	6	1690	5·1	0·4	1·053	7·65	176·0	103
Make-up solution	0	—	7·3	0·3	1·076	7·80	0	—

* Relative to prepared solutions of the two commercial polyphosphates which were used as standards and measured as orthophosphate.

The details are given in the text.

of the polyphosphates to orthophosphate was carried out by treatment with acid solution (1 ml phosphate solution + 10 ml N HCl boiled vigorously for 45 min). Determinations of orthophosphate in the unhydrolysed solution were made on used dips in order to estimate the extent of enzymic hydrolysis. Orthophosphate is not active in

preventing drip and if extensive hydrolysis were to occur in the tank due to the presence of enzymes from the fish, the activity of the solution would be considerably reduced. The results in Table 2 for unhydrolysed solutions indicate that the amount of orthophosphate present is very low and did not increase appreciably during dipping.

Some fall in total phosphate concentration occurred in the first trial which could have been compensated by using a more concentrated make-up solution. There is, however, an obvious danger in using a too highly concentrated solution in that dip concentration could closely approach make-up concentration if make-up rate was heavy.

The specific gravity of the solution (Table 2) also decreased during usage but because of the presence of increasing amounts of dissolved substances e.g. protein, measurement of specific gravity gives an inaccurate indication of changes in solution concentration. Dissolved protein probably does not affect the properties of the dip, but may lead to a higher bacterial count. (The total viable bacterial count increased with time.) The pH of the solution did not change much throughout either trial and could not be used as a guide to concentration.

At the end of each trial, samples of the solution in the tank were stored overnight at 0°C and at 21°C. The total viable count decreased in the samples stored at the lower temperature and increased in those at the higher temperature. However, although it would not be wholly undesirable from a bacteriological point of view alone to store solutions at a low temperature, they develop a sour smell overnight and darken in colour during use, and it is therefore preferable to discard them at the end of each day.

In the second trial concentrations of 7% and 8% polyphosphate were used in the tank and make-up tank respectively. The concentration of the dip solution dropped from 7% to 5·5% but only after the throughput of about 1700 kg; this throughput represents a fish-to-liquid ratio of 22 : 1.

Changes in the fish

Changes in fish after dipping in polyphosphate solution can be considered under weight changes and under quality changes.

Table 3 gives the results of weight measurements on the fish for the first trial each result being the mean of readings on five fish fillets. Both fresh and stale solutions were tested to determine whether the solution lost its effectiveness; Table 3 shows no such loss for a solution used for 7 hr. To examine the weight changes, three batches of fish samples were prepared and stored for 1, 2 and 5 days at 0°C.

After storage for 1 day there is clearly a loss in fluid retention, but this did not change subsequently during 2–5 days of storage. In each case dipped fish retained 1–2% more of its initial weight than undipped fish. However, the drip loss itself (1·4%–3·8%) was more or less the same for dipped and undipped fish; both produced about 3% drip loss

TABLE 3. Summary of weight changes in first trial

Storage period at 0°C	Condition of samples	% Initial uptake (u)	% Retention after storage period (r)	% Total drip loss (d)
1 day	Undipped	—	− 2·6%	2·6%
	Fresh solution	+ 1·7%	+ 0·3%	1·4%
	Solution after 3 hr	+ 1·6%	− 0·4%	2·0%
	Solution after 7 hr	+ 2·5%	− 0·2%	2·7%
2 days	Undipped	—	− 2·7%	2·7%
	Fresh solution	+ 1·4%	− 2·0%	3·4%
	Solution after 3 hr	+ 1·4%	− 1·0%	2·4%
	Solution after 7 hr	+ 2·1%	− 1·1%	3·2%
5 days	Undipped	—	− 3·0%	3·0%
	Fresh solution	+ 1·9%	− 1·3%	3·2%
	Solution after 3 hr	+ 2·0%	− 0·3%	2·3%
	Solution after 7 hr	+ 2·7%	− 1·1%	3·8%

If undipped weight = x, weight after dipping = y, weight after storage = z

% Initial uptake (u) = percentage weight increase immediately after dipping, relative to original undipped weight i.e. $\frac{y - x}{x} \times 100$

% Retention (r) = percentage weight increase after given storage period, relative to original undipped weight. i.e. $\frac{z - x}{x} \times 100$

% Total drip loss (d) = % initial uptake minus % retention i.e. $\frac{y - z}{x} \times 100$

after 2–5 days of storage. Although in this trial there was an increase in weight on dipping, the fish employed had been filleted in the factory some time previously and there is little doubt that a significant amount of drip loss had already occurred before dipping took place. It is important to dip fish immediately after filleting if the maximum benefit is to be obtained.

Quality changes in the fish from the first trial were also examined in order to determine whether there might be changes in the shelf-life of treated fish. The examinations carried out were; (a) bacterial counts after dipping and (b) taste panel determinations on the fish during storage. In each trial fillets taken from three blocks of sea-frozen fish were used. The storage periods cover the maximum expected shelf life of wet fish in distribution from the ports.

The total viable count of the polyphosphate solution increased during the day (Table 2) and this was reflected in the skin counts from the fish samples which increased from $3{\cdot}4 \times 10^3/cm^2$ on undipped fish to $10 \times 10^3/cm^2$ on fillets dipped towards the end of the day. In the second trial a larger quantity of fish was dipped in the same solution causing higher skin counts. The average skin count being $22{\cdot}5 \times 10^3/cm^2$ for the undipped fish, and $41{\cdot}5 \times 10^3/cm^2$ for dipped fish. However, it is very unlikely that such low and relatively small changes in bacterial count will have any effect on keeping quality.

TABLE 4. Taste panel scores for 'cooked flavour' on fish from the first trial

Sample	Average 'cooked flavour' score*				
	Storage temp. 0°C			Storage temp. 7·2°C	
	1 day	2 days	5 days	1 day	2 days
First trial					
Undipped	7·9	8·1	6·7	8·3	7·6
Fresh solution	8·1	7·4	6·7	7·9	7·6
Solution after 3 hr	8·0	7·5	6·9	7·9	7·7
Solution after 7 hr	7·8	7·7	6·5	7·6	7·2

* 10 = absolutely fresh, 1 = putrid, 4 = normally unacceptable. In each case the score is the mean panel score based on five samples.

The taste panel results are shown in Table 4. Samples from the first trial were stored for 1, 2 and 5 days at 0°C and 7°C. Again, fish which had been dipped in fresh solution as well as solution 3 and 7 hr old was sampled. The results given are the average obtained by the taste panel; five samples being tasted in each case. The Torry taste panel score for cod (Shewan *et al.*, 1955) is based on a scale from 1 to 10; fish scoring below 4 is normally unacceptable.

There is no evidence that dipped fish spoils more rapidly than undipped fish, or that the freshness of the dipping solution has a marked effect on spoilage rate. At high concentrations polyphosphate itself can be tasted in dipped fillets, at the levels used here however no member of the taste panel could consistently detect its presence.

Conclusions

Operation of the pilot plant proved to be satisfactory and few modifications were necessary. The trials indicate that in any plant of this type facilities for level control,

volume make-up, solution cooling and filtration are important, though a simpler filtration system would probably be satisfactory. Although it was thought that frothing of the polyphosphate solution might cause problems, frothing was virtually eliminated even in solutions containing relatively large amounts of dissolved protein by introducing solution to the tank below liquid level.

It is important that the processor determine the range of concentration which gives an acceptable product for the particular raw material and market concerned. This has to be determined by experiment. Polyphosphating can then be carried out within this range of concentration either by starting with tank and make-up solutions at the highest concentration and allowing the tank solution to fall in strength towards the lower limit during the days production, or by using an intermediate strength of solution and making up with one more concentrated. In the latter case the difference between tank and make-up solutions will depend on the condition of operation of the tank as well as on the nature of the product being dipped.

Used solutions should not be held overnight since a sour smell and dark colour develop, and the bacterial count rises considerably unless the holding temperature is low. There was no evidence from this investigation that dipped fish spoiled either more rapidly or more slowly than undipped fish, or that used solutions up to 7 hr old had a marked effect on the shelf life of the product.

Mechanical polyphosphate treatment of fish gives a product which has received a known and reproducible treatment, it avoids the danger with hand-dipping of over or under treatment.

CONVERSION TABLE

1 millimetre (mm)	=	0·0394 in
1 metre (m) = 1000 mm	=	3·28 ft
1 litre (l.)	=	0·220 gal
1 kilogramme (kg) = 1000 grammes (g)	=	2·205 lb

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The use of sulphur dioxide during the production of brined cauliflower

J. C. DAKIN AND J. SCHOLEY

Summary

The minimum level of sulphur dioxide necessary to maintain brined cauliflower in a good white condition and the stage in brining at which it is best added were determined. In a factorial experiment, samples of cauliflower were brined in 50° salinometer brine, with various sulphur dioxide contents (ranging from 50 to 1000 ppm overall) added at four different stages of brining. After 6 months storage the cauliflower was freshened and placed in acetic acid solution. The curds were ranked for whiteness at the completion of brining and after acidification. The texture of the stalk was measured with an Instron Universal Testing Rig, but no significant differences were found. Observed differences between samples were confined to the whiteness of the curd which progressively improved with increasing sulphite content to a constant level. It was concluded that, in relation to whiteness and residual sulphur dioxide, the optimum effect was produced when sulphur dioxide was added to the second brine and that 300 ppm overall was sufficient to retain the curd in a good white condition.

Introduction

Sulphur dioxide is normally added to brined cauliflower in order to keep the curd white. Anderson (1968) suggested that the addition of 50–100 ppm sulphur dioxide at the end of the fermentation period gives a satisfactory product. However, considerable variation in commercial practice occurs and the authors have found over 800 ppm in imported samples. It was thought that such high levels were unnecessary and were disadvantageous to the pickle manufacturer in that they necessitated unduly long freshening times to reduce the sulphur dioxide to a legally acceptable level in the finished pickle, i.e. 100 ppm (H.M.S.O., 1962). Furthermore such high concentrations would also tend to disguise faults in the product, such as iron contamination, which would later become apparent. The object of the present study was thus to determine the minimum level of sulphur dioxide necessary to maintain the curd in sound condition during processing through to the finished product, and also to ascertain the

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processing stage at which it is best added. There are four stages at which sulphur dioxide could be added, namely: to the first or shrinking brine; to the second brine; half way through fermentation; or fourthly, on the completion of fermentation.

Materials and methods

Good quality cauliflowers were obtained on each of 2 days (1 week apart) from a farm during October, 1967. On each occasion the heads of each batch were cut into individual florets of approximately 3–6 inches in size, the stumps being discarded. The florets were randomized and 1·5 kg samples placed individually in thirty-two 1-gallon jars (each group of thirty-two jars being one replicate). The jars were then filled with 50° salinometer brine (50% saturated) which was replaced after 24 hr with fresh 50° brine. Each jar was shaken once daily for 14 days to dispel stratification of the brine.

The thirty-two jars of each replicate were divided into four groups of eight and sulphur dioxide was added as follows:

(1) To the first brine immediately after its addition to the curd.
(2) To the second brine immediately after its addition to the curd.
(3) To the second brine 12 weeks after its addition to the curd.
(4) To the second brine 22 weeks after its addition to the curd.

Sufficient sulphur dioxide (as a 4% w/v solution of potassium metabisulphite) was added in order to give nominal overall concentrations of 0, 50, 100, 200, 300, 500, 750 and 1000 ppm respectively at the time of addition.

During brining the jars were stored at 10°C for 2 months followed by $3\frac{1}{2}$ months at 15°C and $1\frac{1}{2}$ months at 20°C. Each sample of brined cauliflower was then drained, allowed to freshen for 24 hr in each of two changes of water and then covered with 6% acetic acid. The acidified cauliflower was stored for $2\frac{1}{2}$ months at 20°C.

One week after the sulphiting of the second group of cauliflowers the sulphur dioxide concentrations of these brines were determined by titrating against standard iodine solution. The brines of all samples were similarly analysed at the end of the brining stage of the experiment. The sulphur dioxide contents of the samples of brined cauliflower curd to which 1000 ppm sulphur dioxide had been added were determined by the Monier-Williams method.

After the cauliflower had been in brine for 30 weeks, during which time, however, a normal lactic fermentation did not occur, the whiteness of the curd was assessed by four members of staff of the Research Association who ranked the curds in order of increasing whiteness. Four pieces of cauliflower were then randomly selected from each jar and five sections of 2 mm thickness were cut from the stem of each piece. A circular flat ended probe $\frac{1}{8}$ inch in diameter was used to punch a hole in the sections with an Instron materials testing rig, at a speed of 0·5 cm/min. The colour and texture of the acidified cauliflower were similarly determined at the end of acidification.

Results

The concentrations in which sulphur dioxide was actually added to the samples, and those found in the brines 7 days after its addition to the second group of treatments, are given in Table 1.

TABLE 1. The concentration of sulphur dioxide in the samples of treatment (2) one week after its addition (direct titration)

Overall concentration added (ppm)	Measured concentration (ppm)
0	0
50	46·1
100	91·5
200	182·8
300	274·5
500	459·0
750	687·0
1000	917·0

TABLE 2. Concentrations of sulphur dioxide (1000 ppm added) in the curds after 30 weeks in brine (Monier-Williams)

Treatment	Period of brining before the addition of sulphur dioxide	Sulphur dioxide concentration (ppm)
1	0 hr	135·7
2	24 hr	729·4
3	12 week	801·0
4	22 week	891·1

After 30 weeks in brine, the concentrations of sulphur dioxide, in those samples to which 1000 ppm had been added initially, are shown in Table 2.

The residual concentrations of sulphur dioxide in all brines, in relation to the corresponding amounts added are shown in Fig. 1.

The results of the measurements of texture showed no significant differences between any samples or groups of samples and hence are not shown.

The effect of sulphur dioxide on the whiteness of the cauliflowers at the end of brining and at the end of acidification are shown in Figs. 2 and 3 respectively.

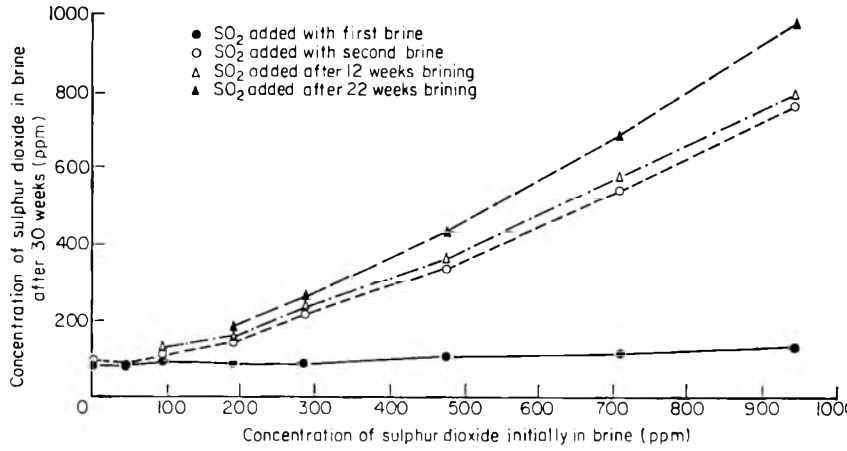

FIG. 1. Residual concentrations of sulphur dioxide in brines after 30 weeks.

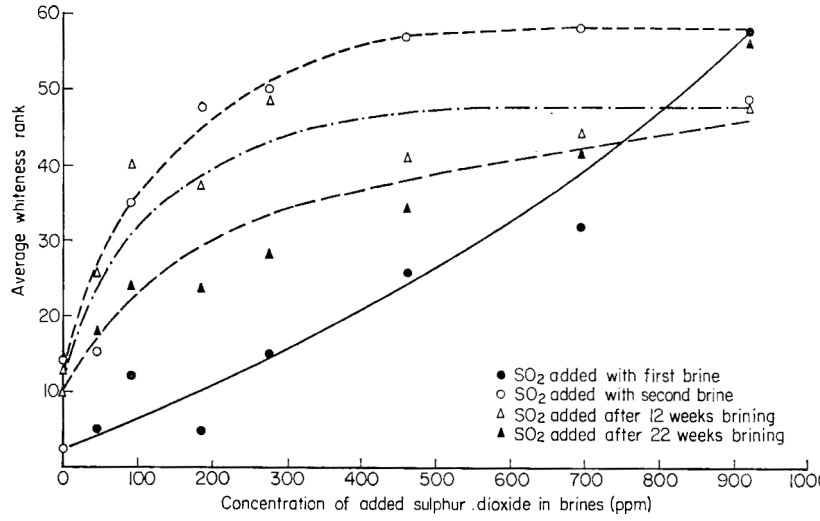

FIG. 2. The effect of sulphur dioxide concentrations on the whiteness of brined cauliflowers.

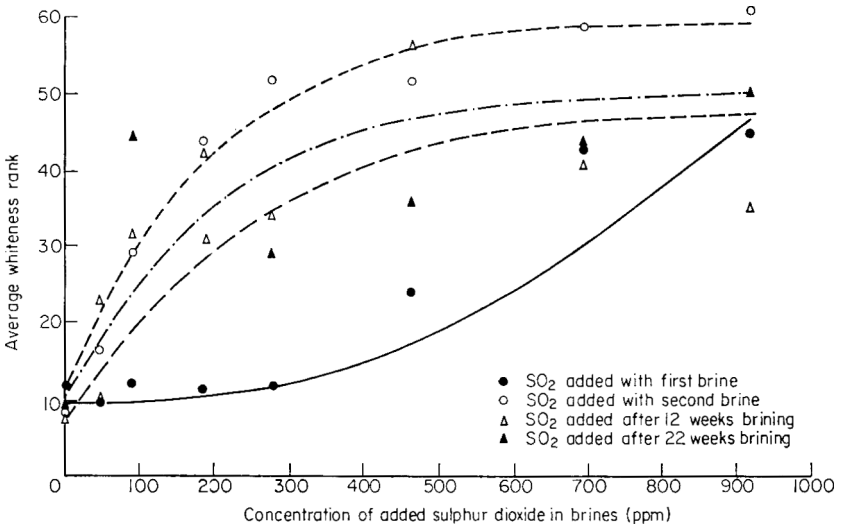

FIG. 3. The effect of sulphur dioxide concentrations on the whiteness of acidified cauliflowers.

Discussion

It is apparent from the results obtained that sulphur dioxide has a marked beneficial effect on the colour of cauliflower both before and after making into pickle. The degree to which discoloration of the curd was prevented was related to the quantity of sulphur dioxide added during brining but diminished with each succeeding increase, i.e. the law of diminishing returns was followed. Benefit was confined to the retention of whiteness of the curd and no other advantages were detected during this study.

The presence of sulphur dioxide in brined cauliflower is, apart from the advantage of colour protection, a hindrance to processing because it will either have to be removed or reduced to an acceptable level during freshening so that the finished pickle does not contain more than the amount permitted by the Preservative Regulations, i.e. 100 ppm. The level of sulphur dioxide to be added during the brining of cauliflower should thus be the minimum consistent with the maintenance of a good white colour.

From Figs. 2 and 3 it will be seen that the fulfilment of this condition is best achieved by the addition of sulphite to the second brine, and a level of 300 ppm overall produced an effect which was reasonably close to the optimum. Although adding sulphite to the first brine leaves a low level of sulphur dioxide in the final brined product (see Fig. 1), it was only at 1000 ppm that a good white colour was obtained. Surprisingly the higher level of additions at this stage produced only a marginally higher sulphur dioxide level in the brined product than the low level additions and from this it might be deduced that adding a high concentration of sulphite to the first brine might be the best practical

method. However, in practice, cauliflowers may be left in their first brines for considerably longer than 24 hr, despite the detrimental effects this may have, when proportionally higher pick-up of sulphite would occur. Consequently, the addition of sulphur dioxide to the first brine cannot be recommended, unless rigid procedures are followed, on the grounds that the level in the final product would be unpredictable.

It must be noted that little evidence of fermentation in the brines was observed during these experiments, and only half of the normal level of lactic acid developed. Sulphur dioxide would prevent fermentation but it was expected that the control samples would have fermented normally. No explanation for this can be offered.

The results of this study indicate that, under commercial conditions, in order to obtain optimum quality pickled cauliflower, sulphur dioxide should be added at an overall level of approximately 300 ppm to the second brine. This would involve using a covering brine with approximately 600 ppm. Slightly higher levels of sulphite could probably be used with advantage if the heads were of rather low quality. The quantities of the various sulphur dioxide containing chemicals which will give the required concentrations can be calculated from the tables given by Dakin (1963).

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A quantitative investigation of Shallenberger's sweetness hypothesis

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Summary

A method for assessing the validity of Shallenberger's sweetness hypothesis by measuring the sweetness of non-reducing sugars is described. The stable, conformationally analogous compounds, α,α-trehalose (mushroom sugar), and methyl α-D-glucopyranoside have the same sweetness on a molar basis. This indicates that only one of the glucose residues in the α,α-trehalose molecule is involved in binding to the taste bud protein, and hence a real chemical basis exists for the phenomenon of sweetness.

Introduction

Shallenberger's sweetness hypothesis (Shallenberger, Acree, Guild & Lee, 1963–9) is based on the assumption that the chemical criterion of sweetness is an AH,B system, where A and B are each electronegative atoms with an appropriate geometrical separation in the range 2·5–4 Å. In the sugars AH and B are two adjacent hydroxyl groups and the AH proton forms a hydrogen bond with a receptor site on the tongue, the strength of the resulting complex being directly proportional to the sweetness of the sugar. Hence it is clear that the geometrical arrangement of the AH,B system (dependent on the particular molecule involved) will govern the strength of the complex which can form, by hydrogen bonding, between the sugar molecules and the taste bud proteins. Some sugars are therefore sweeter than others.

Although Shallenberger's hypothesis is the most plausible description of the phenomenon of sweetness to date, some of the evidence on which it is based is questionable. In particular his experimental procedure for correlating sweetness with sugar structure relies on arbitrary scores being awarded by taste panels after a few milligrams of the reducing sugar crystals are placed on the tongue. Such a procedure, quite apart from lacking reproducibility due to crystal size and interval of dissolution problems, does not take account of the fact that rapid anomerization of reducing sugars following dissolution in the saliva will produce a complex mixture of isomers. Additionally, while a solution of a reducing sugar is too complex to be understood structurally, a crystal, too, is structurally complicated by hydrogen bonds in the lattice.

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In the work reported here, these difficulties have been avoided by measuring the sweetness of stable non-reducing sugars in solution by means of a selected panel. The sugars used in taste assessments were stable non-reducing glucosides: α,α-trehalose (Birch, 1963; Birch & Richardson, 1968) (mushroom sugar, i.e. *O*-α-D-glucopyranosyl-α-D-glucopyranoside) and its analogue methyl α-D-glucopyranoside (both reagent grade). They were selected for this work because their molecular conformations are each thoroughly understood. The configurations of all their hydroxyl groups in space are known, and would not be expected to change during the course of the experiment. The sweetness of each of these was organoleptically assessed by comparison with standard sucrose solutions.

Taste panel selection

Shutz & Pilgrim (1957) have found a linear relationship between a subjective score for sweetness and the logarithm of the concentration of sucrose (mass/100 ml solution) in aqueous solution (Fig. 1).

We have used the principle underlying their method for the quantitative assessment of sweetness. Volunteer panelists participated in six tasting sessions where they ranked three sucrose solutions in order of sweetness. The test solutions had concentrations in

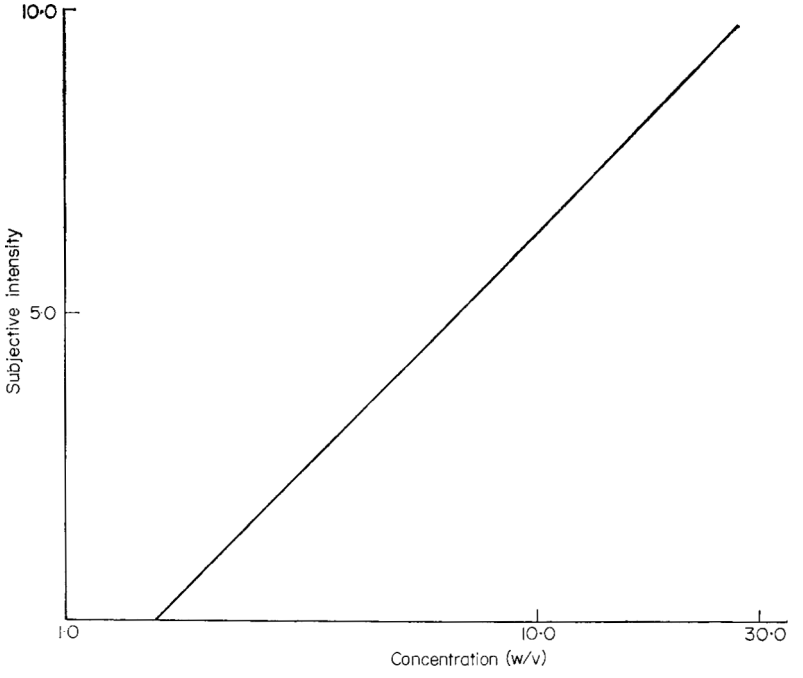

FIG. 1. Subjective intensity against concentration of sucrose solutions (Shutz & Pilgrim, 1957).

geometric progression so that they represented roughly equal steps in sweetness at intervals of 0·4 units on the Shutz and Pilgrim sweetness scale at a level of about 5 units. The solutions were tested in a different order at each of the six tasting sessions, so covering all possible orders of tasting. The rankings awarded by each panelist were transformed into scores and submitted to an analysis of variance (Larmond, 1967). Those panellists for whom the rank totals for the three samples, summed over the six sessions, fell in the correct order of sweetness and exhibited a variability significant at least at the 5% level were chosen for the panel assessment in the work that followed. It was noteworthy that no evidence was detected to suggest that the ranking of samples was affected by the order of tasting.

Estimation of relative sweetness

Small groups of panelists (between four and six) conducted a series of six experiments in which four samples were ranked in order of sweetness. One sample in each set was a solution of one or other of the two non-reducing sugars under test, the remaining three samples were sucrose solutions of graded concentration, similar to those used in the panel selection procedure. The test sugars were examined at three concentrations and the sucrose solutions were arranged, on the basis of preliminary trials, to have concentrations spanning the sweetness of the test sugar solution.

Each group of four solutions was presented to the same panel on four occasions, the order of tasting for the four sessions being determined by a Latin Square arrange-

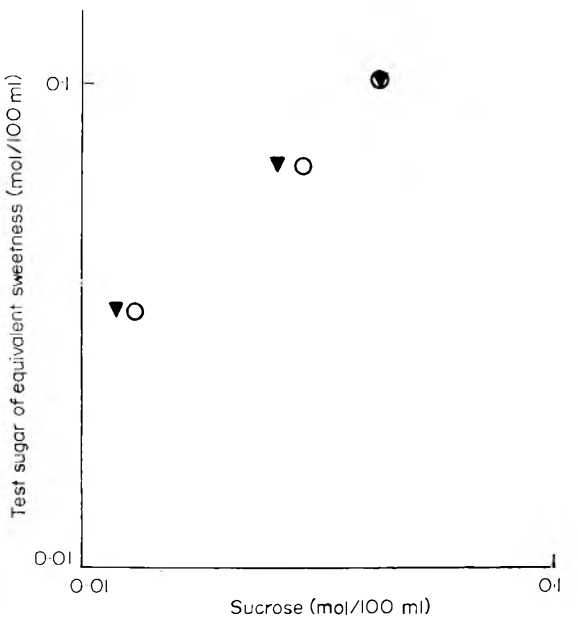

FIG. 2. Molar concentrations of α-α trehalose (O) and methyl α-D-glucopyranoside (▼) equivalent in sweetness to sucrose.

ment. Retasting of the solutions was not permitted. The rankings were again converted into scores and the sweetness of the test solution, on Shutz and Pilgrim's scale, evaluated by linear interpolation between the mean scores for the test and standard sucrose solutions.

The results of these six experiments are shown in Fig. 2, where the molar concentrations of the two test sugars are plotted against the molar concentration of sucrose solutions of equivalent sweetness.

Discussion

Panel members noted a slight bitter aftertaste in methyl α-D-glucopyranoside and some even claimed to detect a trace of bitterness in α,α-trehalose. Bitterness is a common property of rare sugars and their derivatives, though it is by no means certain if this is intrinsic or due to traces of impurities. Shutz & Pilgrim (1957) suggested that bitterness in some sugars might mask their sweetness, compared with sucrose. It is unlikely, however, that the slight trace of bitterness reported with methyl α-D-glucopyranoside could affect its sweetness to any extent.

Fig. 2 shows that equimolar solutions of methyl α-D-glucopyranoside and α,α-trehalose do not differ significantly in sweetness. This is of fundamental importance in assessing the validity of Shallenberger's sweetness hypothesis since it shows that a molar proportionality exists between two structurally related sugars, so pointing to the reality of a chemical basis for the phenomenon of sweetness. Further, since there are two glucose residues in the trehalose molecule and one in methyl α-D-glucopyranoside, it would appear that only one of the glucose residues in the trehalose molecule is involved in binding to the taste bud receptors, the other being excluded, presumably for steric reasons.

If this finding also applies to the disaccharide, sucrose, it is clearly the fructofuranose residue which is responsible for the greater sweetness.

Acknowledgment

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Preference tests to compare the acceptability of several processed foods

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Summary

Preference tests were carried out on seven products, each of which had been processed in different ways. Precooked frozen, canned, dehydrated and freshly cooked products were investigated.

In general, the dehydrated products were the least acceptable and the precooked frozen and fresh products were given the highest score, except in the case of carrots, where the canned product received the highest score.

There was no significant difference between any of the precooked frozen and fresh products tested.

Introduction

The use of processed foods is increasing rapidly in the catering industry. The provision of freshly cooked food for large numbers of people is always a problem because large quantities of food are needed for service at one time. The lengthy preparation and cooking times for freshly cooked foods are reduced by the use of processed foods. A saving of labour can also be made.

Although the advantages in using these products in mass catering are clear, it is important to be aware of consumer acceptability. Due to the processing technique, these foods differ in their organoleptic properties from the fresh product which until recently has been the sole raw material used by caterers.

This paper describes the acceptability of a number of products from a range of canned dehydrated and precooked frozen foods.

Materials and methods

Foods were selected that were available in fresh, canned, dehydrated or precooked frozen form. The following products were used: carrots, swede, peas, green beans, potatoes, apple sauce and white sauce. The products were purchased locally and those in processed form represented well-known brand names.

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Preparation of products

Precooked frozen products

The food was cooked to a standard recipe and was frozen in standard aluminium containers 240 mm × 240 mm × 40 mm (Hill & Glew, 1969). After freezing, the food was stored in polythene bags at −18°C. The containers of food were reheated immediately prior to taste panel assessment in a forced air convection oven at 180°C for a standard reheating period of 25 min.

Dehydrated and canned products

The products were prepared according to the manufacturers' instructions which were printed on the package.

Fresh products

The products were prepared as follows.

1. *Carrots*

385 g	prepared carrots
1135 ml	water
10 g	salt

The prepared carrots were sliced in circles, placed in the cold, salted water and brought to the boil. They were cooked for 20 min.

2. *Potatoes*

1000 g	raw potatoes
1135 ml	water
12 g	salt
100 ml	milk
30 g	margarine

The prepared potatoes were cooked in boiling salted water for 25 min. They were strained, dried and riced.

The milk and margarine were added and mixed with the potato to produce a smooth product.

3. *White sauce*

30 g	flour
30 g	margarine
2 g	salt
568 ml	milk

A roux was made with the flour and margarine. The cold milk was added slowly to make the sauce.

4. *Swede*

1000 g	prepared diced swede
12 g	salt
1135 ml	water
30 g	margarine

The prepared swede was cooked in boiling salted water. The margarine was added to the cooked swede.

5. *Apple sauce*

1050 g	prepared raw apple
40 g	sugar
12 g	margarine
5 ml	PLJ lemon juice

The raw apple was cooked in 150 ml of water and sieved when cooked. The sugar, margarine and lemon juice were then stirred into the apple.

Taste panel method

The method chosen was that described by Amerine, Pangborn & Roessler (1965). The taster was asked to taste the food and mark a preference scale which varied continuously from 'like extremely' to 'dislike extremely'. The score was then measured to give a numerical value. The taste panels were drawn from a total of twenty people. Six people attended at each tasting and six samples of food were presented singly to each taster at each tasting session. Each sample of food was presented for tasting four times during the period of the experiment thus giving a total of twenty-four tastings of each sample. Two forms of the same food (e.g. dehydrated carrots and canned carrots) were never served at the same session.

Statistical analysis

The analysis of variance and Duncan's multiple range test were used to assess the significance of the difference between the means of the samples (Duncan, 1955).

Results and discussion

Table 1 shows the mean palatability scores for the fresh and processed foods. Analysis of variance indicated significant differences between the type of process in each group of products with the exception of white sauce. Duncans' multiple range test (Duncan, 1955) was then used to test for significant differences between the mean scores for pairs of processes. This test allows a comparison of means derived from different total numbers of samples which occurred because taste panel members were occasionally absent. In the case of every food tested, with the exception of white sauce, the dehydrated product received the lowest score. The fresh or precooked frozen product in

every case received the highest score with the exception of carrots, where the canned product was preferred above the other three. (Fresh peas and fresh beans were not available when these tests were carried out and are therefore not included.)

The precooked frozen product had a significantly higher score than the dehydrated product in all cases except potatoes. In the case of carrots, the canned product was significantly better than the precooked frozen and dehydrated, but did not differ

TABLE 1. The significance of the difference between the mean scores for the fresh and processed foods

Product	Form	*F* value	Degrees of freedom of error	Mean score	Significance of difference between means
Apple Sauce	Fresh	5·57	87	7·27	NS, NS, NS, NS, NS, *, **
	Precooked frozen			6·69	
	Canned			6·49	
	Dehydrated			5·33	
White Sauce	Precooked frozen	0·54	70	5·84	NS, NS, NS
	Dehydrated			5·59	
	Fresh			4·85	
Green Beans	Precooked frozen	11·45	71	5·84	NS, NS, **, **
	Canned			5·50	
	Dehydrated			3·21	
Peas	Precooked frozen	4·38	71	6·90	NS, NS, *
	Canned			6·01	
	Dehydrated			5·60	
Carrots	Canned	15·64	93	6·40	NS, NS, **, *, *, **
	Fresh			5·56	
	Precooked frozen			5·37	
	Dehydrated			3·42	

TABLE 1. continued

Product	Form	F value	Degrees of freedom of error	Mean score	Significance of difference between means
Potatoes	Fresh	5·26	68	7·13	NS
	Precooked frozen			6·78	*
	Dehydrated			5·65	NS
Swede	Precooked frozen	8·93	70	5·58	NS
	Fresh			5·26	**
	Dehydrated			3·10	**

NS = Not significant; * = significant at the 5% level; ** = significant at the 1% level. A mean score of 5·00 indicated 'neither like nor dislike'. Scores below 5·00 indicated degrees of 'dislike', above 5·00, degrees of 'like'.

significantly from the fresh product. There was no significant difference between the scores of any of the precooked frozen or fresh products tested.

It is clear from Table 1 that generally the tasters considered the dehydrated products to be inferior in flavour and that the fresh or precooked frozen product received the highest palatability score. The effect on palatability of using some types of processed foods should be considered when caterers feel that a change towards the use of more convenience foods is necessary for economic reasons.

Acknowledgments

The authors would like to acknowledge the technical assistance of Miss S. Newsome, Miss S. Brock and Miss A. Crowther. They would also like to thank the members of the taste panel for their participation in this work and the Department of Health and Social Security for financial support.

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The keeping qualities of different grades of maize meal stored under different climatic conditions

P. VAN TWISK

Summary

The effects of prolonged storage on the quality of commercial maize meal were investigated. Maize meal was stored in atmospheres corresponding to climatic conditions prevailing in the more important 'consumer areas' in South Africa. The storage stability of the three main grades of maize meal, viz. unsifted granulated, sifted granulated and special sifted granulated, which differ in fat and fibre contents, was investigated. Furthermore, the relative merits of polyethylene and cotton as packaging material were studied. It was found that evaluation by means of acidity number and peroxidase activity values yielded results which provided the best basis for predicting the level of acceptance (by sensory evaluation) at that time and after further storage. Peroxide values, thiobarbituric-acid number and catalase activity could not be recommended as criteria for the evaluation of maize meal. It was found that all grades of maize meal, stored under relatively favourable climatic conditions, remained in edible condition for a longer period when packaged in cotton bags than when polyethylene was used. The reverse was found to be the case when ambient humidities were very high (75% or greater). The shelf life of maize meal decreased with increasing fat content, this effect being most significant at elevated temperatures and high humidities.

Introduction

Shelf life plays a very important role in the successful marketing of a food product. Several factors may influence the shelf life of a product; the more important being moisture content, storage temperature, relative humidity of the surrounding atmosphere and the nature of the packaging material. The original moisture contents of the experimental samples ranged from 11 to 13%. These levels are considered 'safe' for long-term storage.

In a literature survey, the author (1965) found that extensive research had already been carried out in respect of the storage of grain and grain products. Much information regarding the effects of various factors on the storage of maize meal, however, is not

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available although data on the relationship between shelf life and the colour of maize meal were published by Ballschmieter (1963, 1964), and the author (1969) had described the moisture adsorption and desorption characteristics of South African maize meal.

The legal requirements for the three grades of maize meal mainly consumed in South Africa, include the following: 'unsifted granulated' (minimum fat content 3·7%, fibre content 1·4–2·5%), 'sifted granulated' (minimum fat content 3·2%, maximum fibre content 1·4%) and 'special sifted granulated' (fat content 2·5–3·4%, maximum fibre content 1·4%).

As maize meal constitutes a major part of the diet of the majority of South Africans and as the relative shelf lives of the three grades referred to above had not been investigated, a study was made of the storage of maize meal in atmospheres corresponding to climatic conditions prevailing in the more important consumer areas in South Africa. Special attention was given to the effects of temperature, humidity and packaging material on palatability and in regard to chemical amd microbial changes. A further purpose of the investigation was to determine whether the acceptability of stored maize meal could be determined by chemical or biochemical evaluation and whether potential shelf life could be predicted.

Materials and methods

The maize meals used in the investigations reported below were commercial samples obtained from local mills. Samples were drawn directly after milling and were packed in the desired containers. The fat and fibre contents of samples were determined immediately after receipt to determine whether they complied with statutory requirements. The packaging materials used in the study were cotton and hermetically-sealed polyethylene (gauge 70μ) bags such as are normally used for packing smaller quantities of mealie meal.

Climatic cabinets, in which temperature and relative humidity were controlled electronically, were used for the storage of samples. The following conditions prevailed in the cabinets:

(a) 24°C and 45% relative humidity (RH), considered to represent dry, hot, conditions such as prevail in many parts of the interior of South Africa in summer;

(b) 21·5°C and 65% RH, considered to represent more moderate summer conditions;

(c) conditions of 18°C and 80% RH alternating with 25°C and 70% RH on an 8-hr cycle, considered to represent coastal conditions in summer; and

(d) alternations of conditions of 26°C and 85% RH and 17·5°C and 65% RH on a 12-hr cycle, considered to be an abnormally unfavourable climatic conditions.

In the case of the climatic cabinet used for conditions mentioned under (c) and (d), alternation of conditions was effected automatically.

Samples of maize meal were drawn periodically from the bags used for storage and

were examined for chemical, biochemical or microbial changes which might have taken place during storage, by the methods given below.

Sensory evaluation was done by a tasting panel consisting of seven to ten persons who evaluated a thick porridge made from the meal concerned (maize meal is usually consumed in the form of a thick virtually solid porridge). Moisture content was calculated from the weight loss found when the material was dried to constant weight at 130°C. Fat was extracted with petroleum ether (b.p. 40–60°C) while peroxides in the fat were determined according to the method of Lea (1946). Acidity number determination was based on the method of Schulerud (1932). The method of Schmidt (1959) was applied to the determination of the thiobarbituric acid number (TBA number). The tristimulus method of Croes (1960, 1961) was used for the determination of colour. Peroxidase activity was determined according to the colourimetric method of Pinsent (1962) and catalase activity was assessed by the method of Bergmeyer (1963). Microbial evaluation was based on methods described in the '*Laboratory Methods for the Examination of Dairy Products*' of the American Public Health Association (1953) and by Harrigan & McCane (1966).

Results

It was found that similar changes occurred in the samples under all the test conditions, although values differed numerically.

1. *Storage at* 24°C *and* 45% *relative humidity*

After storing maize meal for 44 weeks, the average moisture content of the different grades of maize meal stored in cotton bags was 10·5% as compared with that of 11·5% for maize meal stored in polyethylene bags.

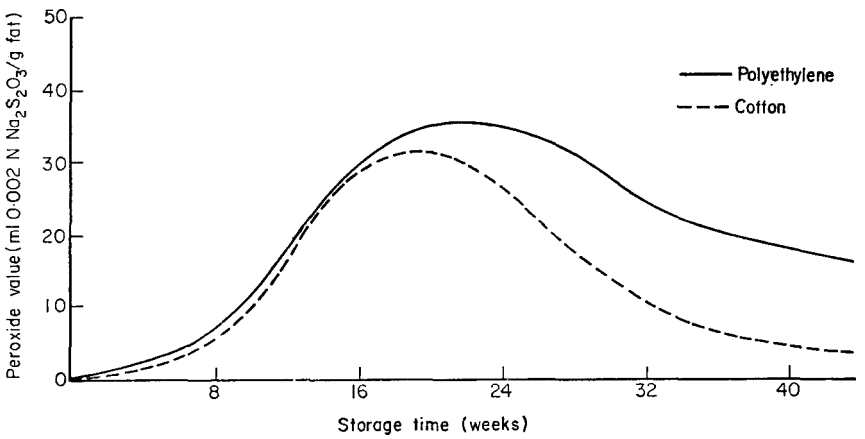

FIG. 1. Changes in peroxide values of unsifted granulated maize meal stored at 24°C and 45% RH.

The fat contents of 4·2%, 3·4% and 3·0% for unsifted, sifted and special sifted granulated maize meal respectively, remained constant throughout the investigation.

Peroxide values increased during storage, attaining a maximum at approximately 20 weeks storage after which values decreased. The results for the unsifted granulated grade are presented graphically in Fig. 1.

Acidity (expressed as mg NaOH per 100 g meal on dry weight basis) increased, with the rate of increase steadily diminishing during the entire storage period (40 weeks).

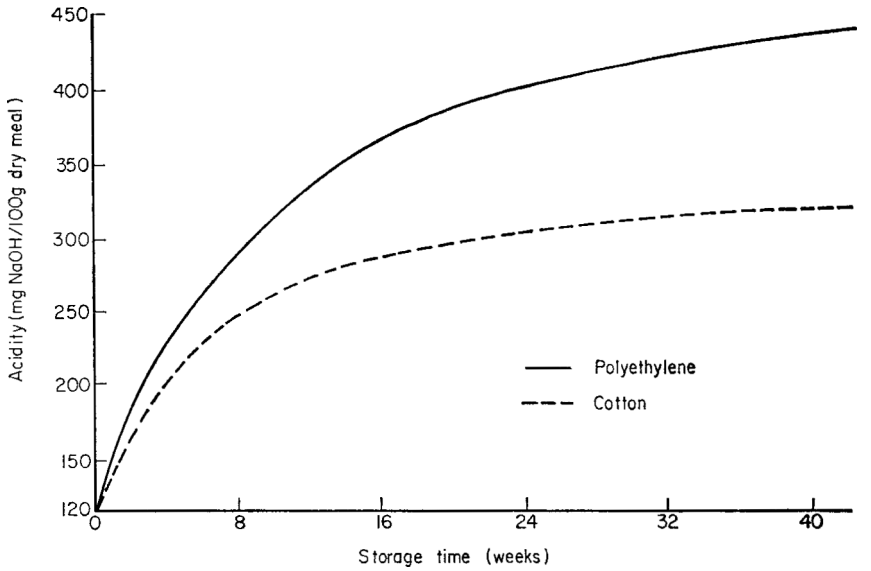

FIG. 2. Changes in acidity of unsifted granulated maize meal stored at 24°C and 45% RH.

The results for unsifted granulated maize meal are given in Fig. 2. The curves for sifted and special sifted maize meal had the same form (approx. log/log), although the numerical values differed—the values attained after 40 weeks being 250 and 220 mg NaOH/100g dry meal for sifted and special sifted granulated meals respectively. The rate of acid formation was much greater when polyethylene bags were used than when storage was effected in cotton bags.

Sensory evaluation tests showed that unsifted granulated maize meal was unacceptable (due to the development of rancidity) after 35 weeks storage while the other samples remained palatable throughout the investigation.

Small decreases in microbial counts were observed during storage and were attributed to the storage conditions. Microbial counts (MPN) ranged from 50 to 200×10^4 per gram.

Values for TBA number decreased to reach a minimum after about 20 weeks storage

and then increased although values fluctuated. The fact that the TBA number of unsifted meal stored in polyethylene (i.e. sample which became rancid) reached a minimum at an earlier stage than the other samples may be significant.

The peroxidase activity of unsifted meal (in both cotton and polyethylene bags) decreased to about one-fifth during storage while that of the other two meals decreased to about one-third. The levels of peroxidase activity for unsifted and sifted meal in cotton bags during the storage period are given in Fig. 3.

Catalase activity decreased during storage to approximately 25% of the original value. However the values obtained at intervals during the storage period revealed inconsistencies.

The changes in colour of all the meals during storage were considered to have been insignificant.

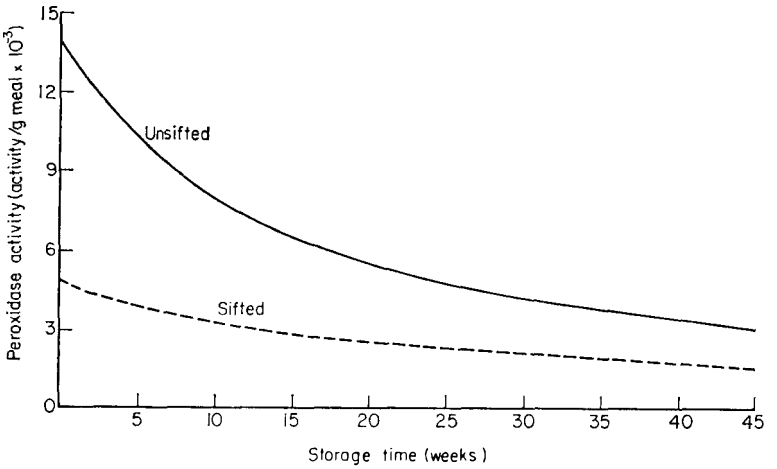

FIG. 3. Peroxidase activity of unsifted granulated maize meal stored in cotton bags at 24°C and 45% RH.

2. *Storage at* 21·5°*C and* 65% *RH*

The final moisture contents of samples stored in either cotton or polyethylene bags were almost identical (13·5%). Despite this fact the unsifted meal stored in polyethylene bags developed rancidity much more rapidly than the other samples—after 24 weeks storage the meal was unacceptable as human food. The unsifted meal in cotton bags and the sifted meal in polyethylene bags had a storage life of approximately 42 weeks while the other samples were acceptable up to 46 weeks.

Peroxide values for the stored meal attained two maxima—the first after 16 weeks and the other after 33 weeks of storage.

The curves representing acidity development in samples stored under these conditions were very similar to those described under paragraph 1, but all acid levels were about 25% higher. The highest acidity values were attained by unsifted meal stored in polyethylene bags.

Results of total microbial counts and for peroxidase activity, TBA number, colour and catalase activity followed the same pattern as for storage at 24°C and 45% RH.

Maize meals stored under these conditions became unacceptable in a shorter time than those stored at 21·5°C and 65% R.H.

3. *Storage under conditions alternating between* 18°C *and* 80% *RH and* 25°C *and* 70% *RH*

Maize meal was stored for a period of 10 weeks and at the conclusion of the test the samples in polyethylene bags had a moisture content of 13·5% while that of those packed in cotton bags was 15·5%.

Despite the relatively unfavourable storage conditions, there was no increase in total microbial count during storage.

Values for acidity number are given in Table 1. Samples stored in cotton bags were more acid than those stored in polyethylene bags.

Sensory evaluation showed that unsifted meal stored in cotton had the shortest shelf life (rancid after 5 weeks storage). The overall results indicated that samples stored in polyethylene were acceptable for longer periods than samples stored in cotton bags.

TABLE 1. Increase in acidity number of maize meal stored under relative unfavourable climatic conditions

Storage time (weeks)	Acidity (mg NaOH/100 g dry meal)					
	Cotton bags			Polyethylene bags		
	Unsifted	Sifted	Special sifted	Unsifted	Sifted	Special sifted
0	46·5	63·9	92·0	46·5	63·9	92·0
1	110·7	123·1	105·8	102·2	114·3	92·6
2	146·5	153·2	147·8	131·0	149·0	116·0
3	199·7	189·7	161·2	152·9	153·9	149·9
4	256·6	205·1	193·8	199·0	177·5	162·2
5	280·6	211·2	205·8	216·0	183·0	185·3
6	308·2	261·2	220·0	244·5	206·0	162·2
7	336·0	284·4	255·0	239·2	207·9	180·0
8	289·3	290·5	261·1	238·6	213·6	203·3
9	417·8	319·6	290·7	261·4	219·6	214·9
10	454·2	350·1	301·2	267·1	225·5	220·8

4. *Storage under abnormal unfavourable climatic conditions*

For the first time during the investigation mould growth was apparent. After 3 weeks storage maize meals stored in cotton bags were mouldy and unfit for human consump-

tion. Although the maize meals packed in polyethylene bags were not mouldy after 9 weeks storage, sensory evaluation by the tasting panel indicated that the samples were unacceptable after 7 weeks storage.

Discussion and conclusions

Peroxide, TBA and catalase-activity values, could not be used as criteria for assessing the condition of stored maize meals, owing to wide fluctuations of the values obtained. The maxima found in all the peroxide curves may be explained by the theory of Rothe, Feller & Tunger (1966). According to these authors, fat peroxides are formed as a result of the action of oxygen, lipoxydase and moisture but at a certain stage the peroxides decompose (temperature and moisture having a big influence) and are also split by peroxidases.

The increase in acidity can be attributed to the formation of free fatty acids by lipolytic enzyme activity as first described by Johnson & Green (1930).

Glutamic acid decarboxilase activity levels are used by many workers to evaluate the condition of cereals, and Linko (1960, 1961) successfully determined the quality of stored wheat in this manner. However, preliminary investigation by the author indicated that the activity level of this enzyme could not be successfully used as a criterion of maize meal quality.

Peroxidase activity levels correllated reasonably well with sensory evaluation of stored maize meals.

In summing up, the following conclusions, concerning the storage of maize meal, may be made:

(a) when maize meal is stored under relatively favourable climatic conditions, cotton is preferable to polythene as packaging material;

(b) for unfavourable climatic conditions (especially when relative humidity exceeds 75%), polyethylene is preferable to cotton;

(c) the shelf life of unsifted granulated maize meal was only slightly shorter than those of the more 'refined' grades when stored under conditions of relatively low humidity. However, the difference in shelf life is greatly accentuated by storage at high humidities and temperatures, and may be due to the higher fat content of the unsifted product;

(d) none of the chemical or biochemical criteria evaluated was entirely satisfactory for assessing the acceptability of maize meals;

(e) of these methods, acidity and peroxidase activity levels gave the best indications of the quality of stored maize meal; and

(f) peroxide values, TBA number and catalase activity were of little value as criteria for evaluating the condition of stored maize meal.

Acknowledgment

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Application of the statistical theory of rubber elasticity to the effect of heat on wheat gluten

R. BALE* AND H. G. MULLER

Summary

The statistical theory of rubber elasticity has been used to evaluate the effect of heat on crude and purified gluten. The number of rheologically effective cross links increase rapidly above 50°C. The significance of these results is discussed.

Introduction

Recently a method has been described which allows both M_c, the average molecular weight between cross links and $1/(2M_c)$, the number of cross links per unit volume of wet gluten to be determined (Mullen, 1969). The method is based on a formula developed by Flory & Rehner (1943) who applied the statistical theory of rubber elasticity, as described by Treloer (1958), to elastomers swollen in a liquid.

It was shown by Muller (1969) that when strong gluten was heated in water to 75°C, the number of cross links, in molecular weight units of 10^5, determined subsequently at 30°C increased from 5·9 to 15·7. In this paper the effect of heat on gluten is considered in more detail.

The topic is important for three reasons. Firstly, gluten is heated during the baking process and its changes determine to a large extent the characteristics of the baked product. Secondly, heat treatment of flour to improve its baking properties has been used intermittently since Weyl and Bischoff's experiments in 1872 (Kent-Jones & Amos, 1968). Thirdly, heat denaturation is often an important problem in the drying of vital gluten during its manufacture.

Hitherto the evaluation of heat treatment has been entirely empirical. It has been based on baking tests, empirical dough tests, or solubility studies (Alsberg & Griffiths, 1927; Geddes, 1929, 1930; Cook, 1931; Herd, 1931; Pence, Mohammed & Mecham, 1953; Knight, 1965). The only exception of which the writers are aware is the work of Ponomarev *et al.* (1962) who determined the heats of combustion of gliadin, glutenin and crude gluten. This work will be considered subsequently.

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In this paper an attempt is made to determine changes in molecular cross linkage due to heat by determining M_c and $1/(2\ M_c)$.

Materials and methods

The flour used was a strong bread flour, commercially milled and untreated. Throughout the study it was kept at + 5°C under nitrogen. The analytical data were as follows: ash 0·49%, protein 13·0%, moisture 14·1%, Farinograph absorption 66·1%, wet gluten 45·0%, dry gluten 13·7%.

All reagents used were of Analar grade. Two methods of isolating the gluten were employed. In the first 30 g of flour were weighed and mixed with 17 ml of tap water in a Simon Minorpin mixer for 3 min. The dough was rested in tap water for 30 min at room temperature and then washed under the tap in the usual way. The product will be referred to as 'crude gluten'.

In the second method the crude gluten obtained from 30 g of flour by the above method was dispersed in 200 ml of 0·01 N acetic acid with the aid of a Waring Blendor (3 min at slow speed). The dispersion was then centrifuged for 15 min at 2500 r.p.m. in an M.S.E. centrifuge with a 12″ head. Ten ml of 2 N ammonium hydroxide were then added to the supernatant to precipitate the gluten which was consolidated by further centrifugation for 15 min. The gluten was then washed in tap water for 1 hr and divided into two samples for testing. It will be referred to as 'purified gluten'.

The preparation of the test sample and the subsequent stretching was carried out as described previously (Muller, 1965). For the heat treatment the gluten was placed into a waterbath of the required temperature for 10 min. Every reading recorded in this paper represents the mean of at least six determinations.

Theoretical

The equation of Flory & Rehner (1943) for an elastometer swollen in a liquid under simple elongation states that:

$$f = \frac{RTe\,v_2^{\frac{1}{3}}}{M_c}\left(\alpha - \frac{1}{\alpha^2}\right)$$

where M_c is the average molecular weight of the chain between the cross links, α is the stretched length of the swollen polymer divided by the initial length, e is the density of the dry polymer, R the gas constant, T the absolute temperature, f the tensile stress and v_2 the volume fraction.

If f, R, T, e, and v_2 are kept constant, the Flory-Rehner equation reduces to

$$M_c = K\left(\alpha - \frac{1}{\alpha^2}\right)$$

where K is an experimental constant.

In these experiments both e and v_2 differed slightly for crude and purified gluten and thus two constants K_1 and K_2 were required, one for each set of experiments.

(a) Calculation of K_1 for crude gluten.

R was 8·314 × 10^7 ergs/mole/°C, T was 303°A, e was 1·34 g/cc, a figure taken from the literature (Knight, 1965; Ponomarev *et al.*, 1962), v_2 was 0·305 (mean of twelve tests), f equalled 5834 dynes/cm^2 and hence K_1 was 3·8954 × 10^6.

(b) Calculation of K_2 for purified gluten,

The values of R, T and f were the same as for crude gluten, e was found to be 1·28 g/cc (mean of twelve determinations carried out at 30°C in n-butanol), v_2 was 0·310 (mean of thirty determinations). Hence K_2 was 3·7507 × 10^6.

Results and discussion

In Fig. 1, M_c, the molecular weight between cross links and in Fig. 2, the number of cross links $1/(2M_c)$ in molecular weight units of 10^5 for both crude and purified gluten are plotted against the preheating temperature in °C. The results at 30°C and 75°C for crude gluten are in close agreement with those previously reported (Muller, 1969). Since several assumptions have been made in the Flory–Rehner equation, it is uncertain whether the absolute number of cross links is correct, but their relative values should be noted.

The number of cross links appear to increase rapidly at 50°C and this temperature has generally been accepted as the denaturation temperature of wheat gluten in the past (Kent-Jones & Amos, 1968) although one of the early workers, Maurizio (1924) cites a figure as high as 70°C. Alsberg & Griffing (1927) using gluten swelling methods concluded that there is no clear denaturation temperature but rather a range which

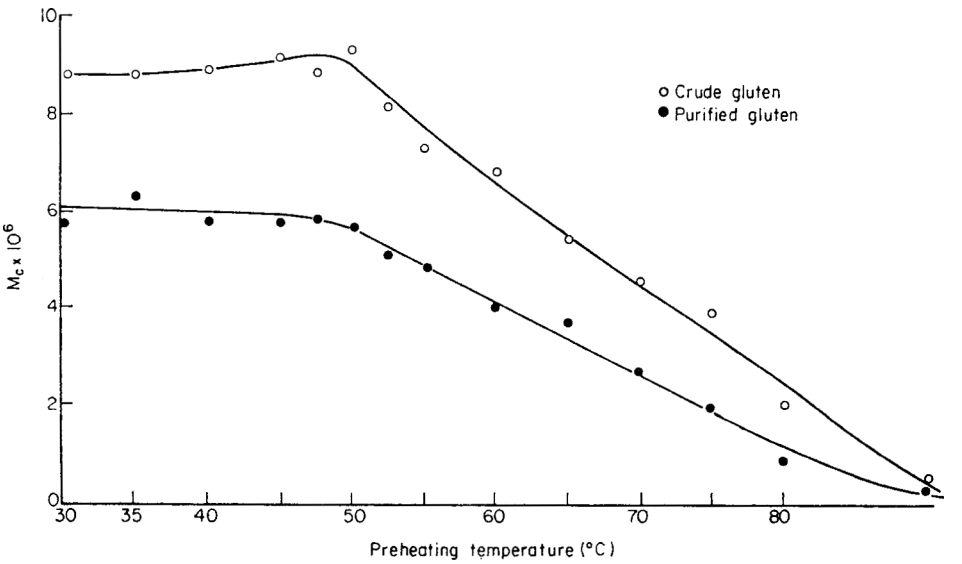

FIG. 1. The molecular weight between cross links, M_c, plotted against preheating temperatures in degree centigrade.

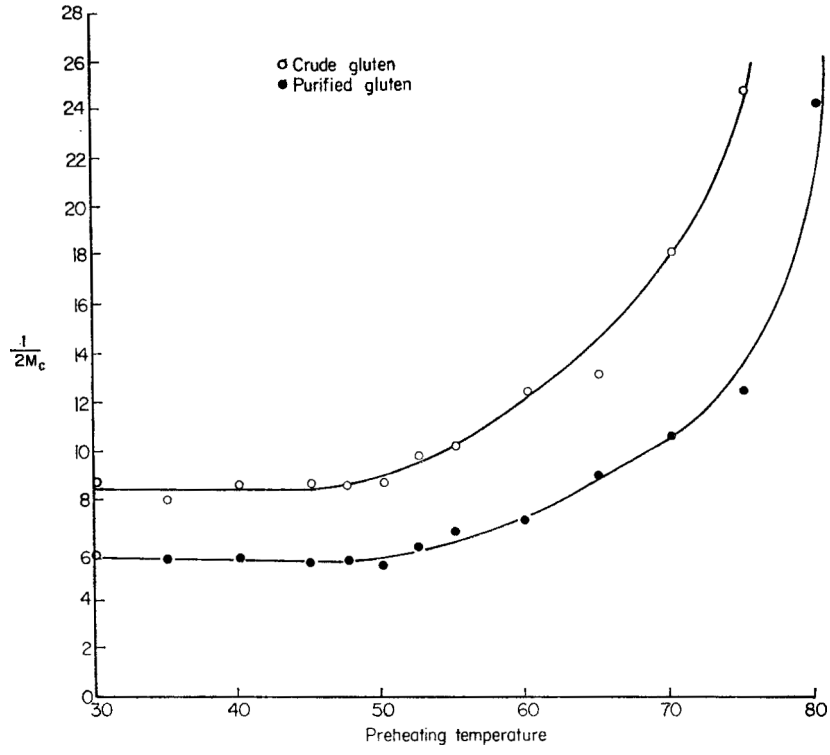

FIG. 2. The number of cross links $1/(2\ M_c)$ in molecular weight units of 10^5 plotted against preheating temperature in degree centigrade.

they gave as between 50°C and 65°C. The rheological evidence presented here also points to a denaturation range rather than a discrete denaturation temperature, but it appears to extend from 50° to 90°C. It is possible that this finding is of importance technologically, for instance in hot conditioning of wheat or in the drying of 'vital' gluten. Heat denaturation appears to be directly proportional to temperature. The curvature in Fig. 2 beyond 50°C is mathematically based. As M_c decreases the value of $1/(2\ M_c)$ increases proportionally more.

The M_c for purified gluten is lower than that for crude gluten. This is not unexpected since the latter contains both starch and lipids which would not presumably provide rheologically effective chains or cross links.

Table 1 gives the percentages of viscous and elastic deformation and it is apparent that under the conditions of the experiment the latter amounts to no less than 86% for crude and 91% for purified gluten. When heated to 90°C the viscous deformation disappears altogether. Hence it is likely that any error introduced through viscous flow is relatively small.

TABLE 1. Percentages of viscous and elastic deformation at various preheating temperatures

Temp (°C)	Crude gluten				Purified gluten			
	Elastic deformation (cm)	Viscous deformation (cm)	Elastic deformation (%)	Viscous deformation (%)	Elastic deformation (cm)	Viscous deformation (cm)	Elastic deformation (%)	Viscous deformation (%)
30	4·68	0·59	88·8	11·2	2·71	0·25	91·6	8·4
35	4·75	0·62	88·5	11·5	3·04	0·27	91·9	8·1
40	4·89	0·69	87·6	12·4	2·63	0·24	91·6	8·4
45	5·08	0·77	86·3	13·7	2·66	0·24	91·8	8·2
47·5	4·88	0·71	87·3	12·7	2·73	0·26	91·3	8·7
50	5·24	0·74	87·6	12·4	2·56	0·24	91·5	8·5
52·5	4·25	0·54	88·7	11·3	2·21	0·19	92·0	8·0
55	3·56	0·43	89·3	10·7	2·08	0·19	91·7	8·3
60	3·28	0·34	90·6	9·4	1·58	0·11	93·6	6·4
65	2·35	0·13	94·9	5·1	1·46	0·08	94·6	5·4
70	1·80	0·10	94·7	5·3	0·97	0·06	94·2	5·8
75	1·44	0·08	95·0	5·0	0·66	0·03	96·3	3·7
80	0·64	0·05	92·7	7·3	0·28	0·02	94·2	5·8
90	0·15	0	100	0	0·10	0	100	0

The fact that the viscous deformation in these experiments tends to zero with increasing preheating temperature is of importance in connection with a recent comment by Bloksma (1968). He stated that for a network to show viscous flow there must be a continuous opening and reformation of cross links under stress. He suggested that this was due to SS-SH interchange. If this assumption is correct then the mechanism is inhibited by sufficient increase in temperature.

Ponomarev *et al.* (1962) determined the heat combustion of gluten as a means of assessing structural changes of the molecules during thermal denaturation between 20 and 100°C. They found that the gluten denaturated by heating for 1 hr at 50°C was characterized by minimum heat of combustion and hence by increased bond stability. The subsequent rise in the heat of combustion was interpreted as a gradual weakening of these bonds in the breakdown of the gluten complex.

The present study also points to the importance of 50°C. Further similarities with the Russian work cannot perhaps be expected, since in this study only the rheologically effective bonds are considered while Ponomarev's work deals with all the bonds involved in the structure of gluten. Furthermore it is well known that the calorimetry of nitrogenous materials (e.g. proteins) is complicated by the possible formation of different nitrogenous products.

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A new model equation for predicting safe storage moisture levels for optimum stability of dehydrated foods

M. CAURIE

Summary

A new model equation for drawing up water sorption isotherms, applicable over a wide range of water activity, has been suggested from which safe moisture levels for dehydrated food storage may be easily calculated.

Introduction

The stability of dehydrated food substances depends on the control of enzyme activity and microbial growth. Both factors require water for their activity but in either case it is not the absolute moisture content that is decisive but its availability or water activity.

Until recently enzymes were not believed to be reactive in dry food materials and were ignored in most dehydrated food spoilage studies. Mossel & Ingram (1955) and other workers have hence suggested some equilibrium relative humidity (ERH) limits below which microbial growth did not occur as a means of preventing dehydrated foods from spoilage micro-organisms. Nonetheless dehydrated foods known to be fully protected against microbial growth by their low water content often suffer deterioration in storage.

More recent studies, however, indicate that these growth limiting humidities alone are not sufficient to stop deterioration in most storage problems because of the ability of enzymes to react in 'free' or mobile water present in the dehydrated foods (Duckworth & Smith, 1963).

Water present in food substances is believed to be absorbed in layers on some active ssites according to the B.E.T. (Brunaeur, Emmet & Teller, 1938) theory of adsorption. The monomolecular film of water predicted by this theory at the active sites is so firmly bound to the macromolecular constituents of the food that it is normally unavailable to micro-organisms. Acker (1963, 1969) has shown in addition that at this level of moisture content moisture-dependent enzyme reactions are also either non-existent or take place at a very low rate. Thus Salwin (1959, 1963) has indicated that this theoretical monomolecular layer of adsorbed water should in general accord with optimum stability of food substances.

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Several other models have been suggested to predict this moisture limit for optimum stability of dehydrated foods. This may be more precisely described in combination with its equivalent ERH (Rockland, 1969). It is the aim of this paper to describe a model to calculate safe moisture levels of food substances for optimum stability.

Existing models

The existing models for the prediction of the monolayer water content of foods have been reviewed recently by Labuza (1968). Of all the models the one that enjoys the greatest appeal is the B.E.T. isotherm after the work of Brunaeur, Emmet & Teller (1938). Nonetheless the assumptions on which the model rests are not entirely true for most materials (Labuza, 1968) and is only applicable over a limited range of humidity (10%–50% RH). It is for example, not valid for substances with high sugar contents (Salwin, 1963; Savaracos, 1967). Ayerst (1965) explains that due to the variability and complexity of the physical and chemical characteristics of stored food substances the free energy of sorbed water, one of the basic assumptions of the B.E.T. model, is reduced by different mechanisms which vary in relative importance with the product, with the water activity and with temperature.

Water in dehydrated foods and suggested transformation in water sorption isotherms

Water present in food substances behaves as if it is in solution and shows a lowered vapour pressure. The relative lowering of the water vapour pressure of a food substance, therefore indicates the intrinsic humidity or activity of the water present in the food.

This water activity, designated by the symbol Aw, is numerically equal to the equilibrium relative humidity (ERH) of the food expressed as a fraction (Scott, 1957) and its value measures the availability of moisture for biological and chemical actions.

Scott (1957) has stated that solutions permitting microbial growth are concentrated rather than dilute. Treating dehydrated foods, therefore, as highly concentrated solutions, concentration values (C) of data covering a wide variety of foods from various sources (Table 1) were calculated according to the method of Grover (1947). He expressed the concentration of syrups, which are also materials with low Aw, as grams of solid per gram of water, so that materials with a 50% solid content had a concentration of 1·00, an 80% solid concentration of 4·00 etc. Thus from the equilibrium moisture contents the concentration of the food substances were expressed as:

$$\frac{100 - \%H_2O}{\%\ H_2O} = \frac{\text{solid}}{\text{water}}$$

Suggested equation for drawing water sorption isotherms

It was found in this work that the natural logarithms of the calculated concentrations plotted against their corresponding equilibrium humidities gave negatively sloping straight lines from zero activity up to 0·85 Aw for most foods (Fig. 1). These straight

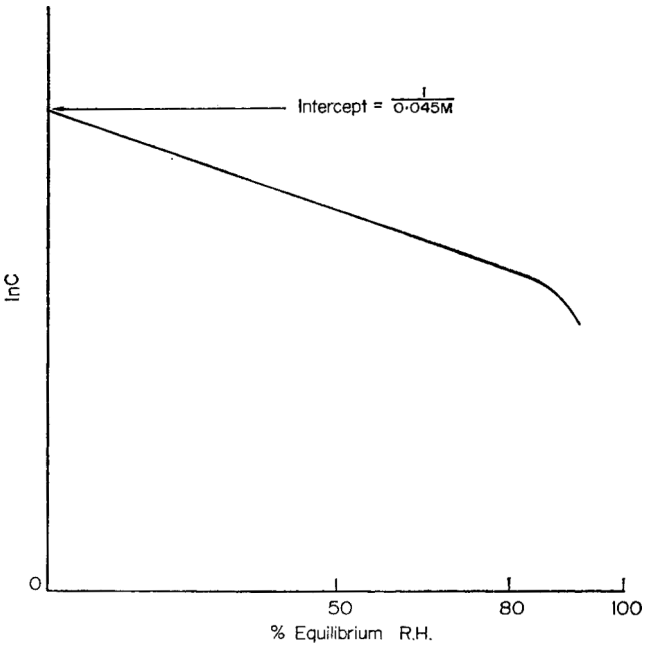

FIG. 1. Generalized water sorption isotherm of the new model.

line portions of what may be called 'natural' water sorption isotherms may be mathematically represented in the form:

$$\ln C = \ln Co - Aw \ln r \quad (1)$$

where C = Concentration at any Aw
Co = Concentration at zero Aw
r = Antilog of the magnitude of the gradient.

Derivation of the safe moisture level (M) *from the new model equation*

Values of ln r were rather uniform (Table 1) but ln Co varied widely and this was interpreted to reflect on the variability in the moisture content considered safe for the various foods. Labuza (1968), in his review, has stated that it is the last 10–20% of the moisture present in food materials which is of concern to their stability.

On the above evidence an empirical expression, $9\ e\ M^{-r}$, where e is the value given to the base of the natural logarithm, was derived and equated to the numerical value of

ln Co. This expression made ln Co a function of both M and r and it involved a constant numerically close to 20, the upper moisture limit which is of concern to the stability of foods. Therefore at zero activity equation (1) becomes:

$$\ln C = \ln Co = \frac{9e}{M^r} \tag{2}$$

When reciprocal values of M, calculated from equation (2), for the various foods were plotted against corresponding values of ln Co on the abscissa, a straight line was obtained through the origin showing that a good approximation of the relation between M and ln Co is given by a straight line equation of the form

$$\frac{1}{M} = K \ln Co \tag{3}$$

The slope of the straight line, K, was 0·045 and substituting this into equation (3) we have:

$$\frac{1}{M} = 0{\cdot}045 \ln Co \tag{4}$$

TABLE 1. Safe moisture levels and other parameters calculated from the suggested water sorption isotherm of food substances using data from the indicated sources

	Product	Intercept (ln Co)	Gradient (ln r)	Safe% H_2O (M)	Equivalent Aw
(a)	Cocoa (powder)	9·20	0·088	2·42	0·628
	Gari	3·48	0·026	6·39	0·300
	Kokonte	5·03	0·042	4·42	0·470
	Maize	3·80	0·025	5·85	0·415
	Cowpeas	4·88	0·040	4·55	0·470
	Bambara beans	3·07	0·023	7·24	0·350
(b)	Cereals	2·79	0·015	7·96	0·220
	Legumes	3·90	0·030	5·70	0·360
	Oil cakes	4·19	0·033	5·30	0·415
(c)	Manitoba wheat	3·17	0·020	7·01	0·300
	Capella wheat	2·89	0·017	7·69	0·240
	Bukuru Mahemba Sorghum	3·03	0·018	7·33	0·275
	Wiru sorghum	2·93	0·016	7·58	0·255

TABLE 1. continued

	Product	Intercept (ln Co)	Gradient (ln r]	Safe % H_2O (M)	Equivalent Aw
	Robusta / Arabica coffee	3·40	0·021	6·54	0·355
	Robusta coffee cherry	3·33	0·023	6·67	0·330
	Groundnut kernels	4·00	0·030	5·56	0·540
	Hazel nut kernels	5·13	0·031	4·33	0·670
	Groundnut extracted meal	4·73	0·040	4·70	0·435
	Pimento	3·47	0·023	6·40	0·350
	Black seed pepper	2·85	0·014	7·80	0·280
(d)	Orange crystals	5·42	0·090	4·01	0·255
(e)	Gelatin	2·83	0·022	7·85	0·180
(f)	Freeze dried salmon	3·30	0·022	6·73	0·316

Sources of data

(a) The author—following the method used in (b) on powdered samples (b) Snow, Crichton & Wright (1944, Table 1), (c) Ayerst (1965, Table 3), (d) Karel & Nickerson (1964), (e) Bull (1944), (f) Martinez & Labuza (1968).

Combining equation (1) and equation (4) into a new model water sorption Equation we have:

$$\ln C = \frac{1}{0{\cdot}045M} - Aw \ln r \qquad (5)$$

The safe moisture content for food stability (M) may, therefore, be easily calculated from the isotherm with equation (5).

Fresh values of M calculated with equation (5) (Table 1) were in close agreement with data obtained by Salwin (1959, 1963) and Gur-Arieh, Nelson & Steinberg (1967) for the monolayer water content of certain foods.

Illustrative comparisons

The application of the new model water sorption Equation (5) to the data of Bull (1944) and Karel & Nickerson (1964) is shown in Fig. 2. Gelatin was chosen because of its relative homogeneity compared with other natural products and because of the accuracy with which the hygroscopic properties of this protein has been determined by Bull (1944). The orange crystals data of Karel & Nickerson (1964) were used not only for their accuracy but also to show the applicability of the new model to materials of high sugar content which is a major limitation with the B.E.T. model.

It may be noticed that the sigmoid shape of the isotherms is transformed into straight lines by the use of the new model equation. At the same time the intersection, of the isotherms with the ordinate is spread along the ordinate instead of concentrating at the origin.

By these means the prediction value of the suggested isotherm at low moisture activity, which is of primary concern in storage, is greatly improved.

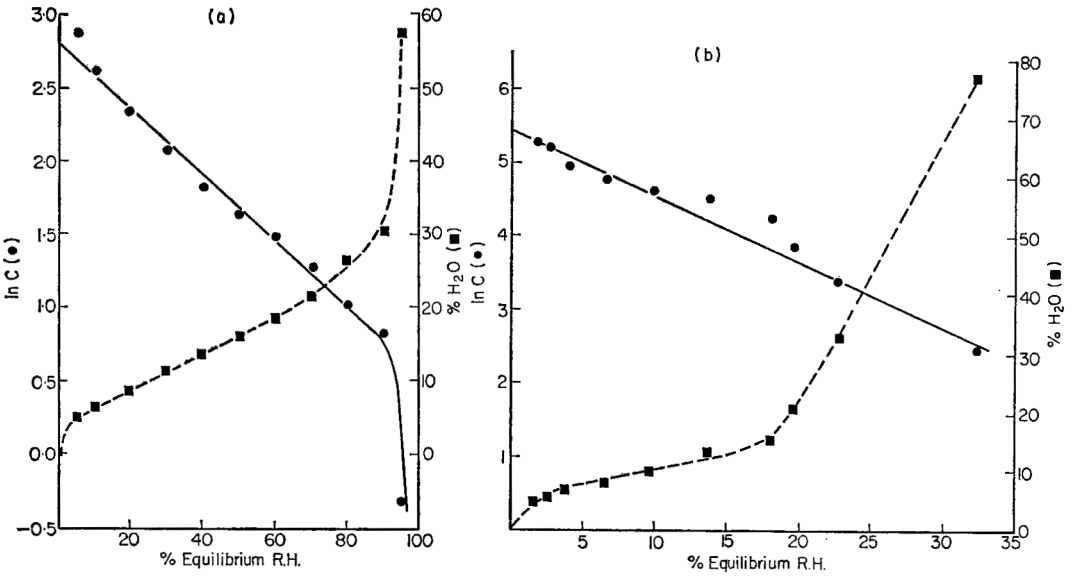

FIG. 2. Comparison of water sorption isotherms drawn with %H_2O (■) and with the new transformation (●) for (a) Gelatin data from Bull (1944); (b) Orange crystals data from Karel & Nickerson (1964).

The suggested model equation and product stability

Rockland (1969) has stated that optimum conditions for the stability of a product are generally satisfied when its M: ERH (moisture/equilibrium relative humidity) co-ordinates lie within his LI–II (Local isotherm II). The results of the present work agree with this (Table 1). It may be observed from Table 1 that all the M: ERH co-ordinates of the wide range of foods examined lay wholly within the LI–II.

Though the B.E.T. monolayer moisture is believed to correspond to optimum stability Martinez & Labuza (1968) reported that freeze-dried salmon was more stable at moisture levels considerably higher than the B.E.T. monolayer. A re-examination of the above data with the new model equation in this laboratory confirmed that the B.E.T. monolayer moisture indeed under-estimated the safe moisture for stability. The safe moisture content (Table 1) calculated with the suggested model was approximately 6·73% corresponding to a humidity of 32% as observed in practice instead of 19%

relative humidity and 5% moisture predicted with the B.E.T. model. These results lend support to the view of Rockland, Swarthout & Johnson (1961) that there is an optimum moisture level above and below which deterioration occurred at a more rapid rate.

It may appear from these results that this optimum moisture level may be more precisely predicted with the suggested new model equation than with the B.E.T. model.

Conclusion

A new model for drawing up water sorption isotherms has been suggested. The basic assumptions in this work, are that:

1. The maximum water content of concern to the stability of dehydrated foods is approximately 22%.

2. Dehydrated foods should be considered as highly concentrated solutions.

It is hoped that by this new model calculations and interpretation of water sorption data may be facilitated.

Acknowledgment

I am grateful to Dr S. K. Odoom of the Mathematics Department, Legon, for his advice.

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J. Fd Technol. (1970) **5**, 309–310

Book Reviews

Glossary of Sugar Technology. By C. A. MULLER.
Elsevier Publishing Co., Barking, Essex, 1970. Pp. 224. £5.

In his Preface, the author indicates the scope of this Glossary as an attempt to meet the needs of those concerned with the sugar industry in the sugar-producing countries of the world.

It is, therefore, unfortunate that so many technical terms of the cane sugar industry should have been omitted. No mention at all has been made of any terms concerned with the cane handling and cane milling sections of a cane factory: indeed, 'cane sugar' is not included. The sugar refining industry also deserves greater attention. No reference is made to the technology of granular adsorbent decolorization processes.

On a more general note, another surprising omission concerns the variety of forms in which sugar is manufactured and marketed around the world (e.g. refined, granulated, mill white, soft brown). From a purely technical stand-point, all important chemical species should have been included (e.g. ammonia, magnesium, chloride, sulphate).

This volume represents a Glossary of sugar *beet* technology and particularly Continental European beet technology. In this somewhat restricted field it achieves a high level of completeness and should prove to be a reference volume both useful and handy to European technologists.

M. C. BENNETT

The Destruction of Organic Matter. By T. T. GORSUCH
Pergamon Press, Oxford, 1970. Pp. viii + 151. 55s. ($7·50).

Applied analytical chemistry can be broadly divided into two parts, relating respectively to trace and to compositional analysis. Whilst the latter is important both in heavy industry and the biological sciences, trace analysis appears in recent years to have played something of a dominant role. This book is concerned with the preliminary process essential in most areas of trace analysis of biological substrates, that of preparing the measured sample for presentation to the eventual analytical technique on the laboratory bench; that is to say the controlled removal of most or all of the organic matter. Apart from carbon, hydrogen and oxygen, only nitrogen, sulphur, boron, phosphorus, the halogens and the rare gases are omitted from the scope. Methods not involving complete destruction of organic matter are dealt with briefly at the beginning: these include activation analysis, electron spin resonance techniques and ion-specific-

electrodes. It is perhaps curious, though arguably correct, to find emission spectrography included here. Another preliminary chapter deals with errors in sampling and in manipulation subsequent to the destruction of the organic matter. The latter survey covers contamination arising from and losses by adsorption on to apparatus and is a useful introduction to the main text on wet and dry oxidation methods which follow. In the chapters dealing with these, the hazards of perchloric acid are put into perspective (though the overall conclusion regarding this reagent is disappointingly inconclusive); low temperature combustion with excited oxygen is barely mentioned, in some reflection of the extent to which this technique is used in practice. As the holder of the first research fellowship of the Society for Analytical Chemistry the author made a study of the losses of trace elements under conditions of sample oxidation in the period 1956–58 so that he is uniquely qualified to discuss methods for investigating such losses in the following chapter. The largest chapter is devoted to the specific consideration of individual elements, some fifty of which are treated on eighty-one pages. This is a useful survey, though naturally some elements are dealt with in greater detail than are others. The losses of copper which can occur in dry ashing procedures, for example, are fully discussed; whereas the consideration of tellurium is largely by way of analogy with selenium.

The book, which concludes with full descriptions of a number of selected decomposition procedures, is of special interest to the food analyst. It deals with a somewhat neglected but important area of practical significance and where it is not able to answer questions or satisfy doubts directly it will serve as a valuable source book for further information in the published literature.

H. EGAN

Methods in Microbiology. Vol. I. Ed. by J. R. NORRIS and D. W. RIBBONS Academic Press, London and New York, 1969. Pp. xiv + 712. 170s.

This is the first of a series of volumes for which the editors have sought the co-operation of 150 international contributors and allowed personal presentation of their specialist material. The editors indicate a possible lack of structural homogeneity although this is not an obvious defect as cover to cover reading is not essential. Each chapter covers a specific topic in depth and the authors provide comprehensive theoretical backgrounds as well as the more practical aspects of equipment and methods.

The volume should be popular, for teachers there is a vast reservoir of information suitable for a wide range of students; Chapter I on Media and Equipment and Chapter III on Sterilization of Apparatus and Media being excellent for newcomers to the subject while later chapters, e.g. XV on Evaluation of Growth by Physical and Chemical

Means and XIX on Determination of Significance of Molar Growth Yields, provide more advanced material.

P. WIX

Methods in Microbiology. Vols. 3A and 3B. Ed. by J. R. NORRIS and D. W. RIBBONS
Academic Press, London and New York, 1969. Pp. 506 + xii. 140s; pp. 369. 100s.

The format of earlier volumes has been repeated with 3A covering media and formulations and 3B covering groups of organisms.

Many microbiologists will find value in chapters I to III of 3A where media for the maintenance and preservation of bacteria and formulation of culture media are dealt with. Storage life tables and details of the main culture collections are included. The rest of 3A consists of 'general' articles dealing with enrichment, nutrition and strain selection which probably have a more limited appeal.

Volume 3B covers selected groups of organisms in terms of isolation, growth and handling in the laboratory and the preservation of cultures. The groups covered are those where information in so called standard texts is often thin. Included are the autotrophs, phototrophs, strict anaerobes, psychrophiles and thermophiles, halophiles, myxobacteria and mycoplasmas, algae and bacteriophage. The authors include useful definitions of value to teachers. Most industrial microbiologists with involvement with special groups could profit from the improved handling techniques given.

P. WIX

Books Received

Olfaction and Taste. Proceedings of the Third International Symposium. Edited by CARL PFAFFMANN.
Rockefeller University Press, New York, 1970. Pp. xvi + 648.

Proceedings of the Conference on Tropical and Sub-Tropical Fruits, London, 1969. Edited by D. G. COURSEY.
Tropical Products Institute, London, 1970. Pp. 307. £1 17s. 6d.

Correction

The correct price of the book *The Value of Food*, by P. Fisher and A. E. Bender, which was reviewed in Vol. 5, No. 2 (June 1970) is 16s. and not 60s. as printed. The correct number of pages is 182 and not 174 as printed. We apologise to Oxford University Press for these errors.

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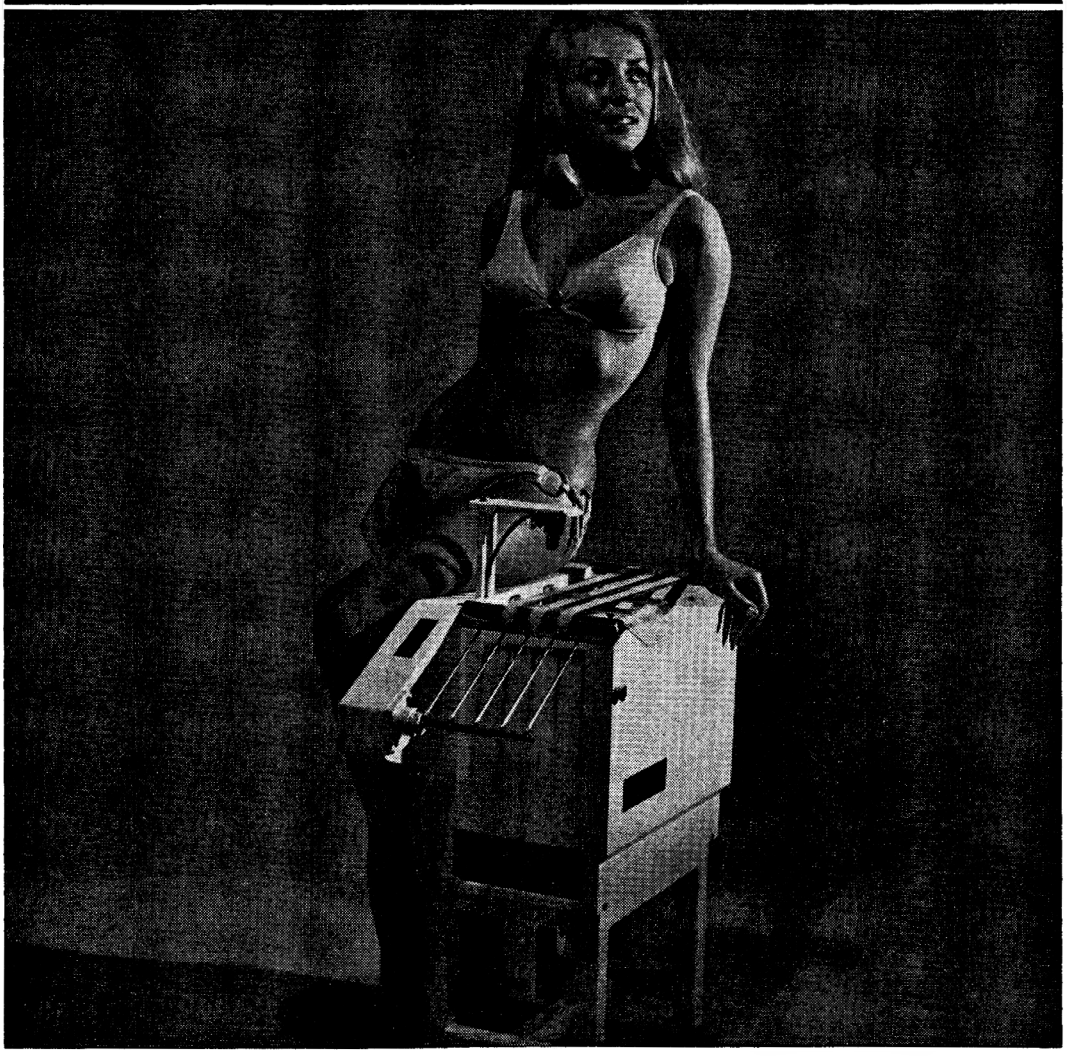

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References. Only papers closely related to the author's work should be included; exhaustive lists should be avoided. References should be made by giving the author's surname, with the year of publication in parentheses. When reference is made to a work by three authors all names should be given when cited for the first time, and thereafter only the first name, adding *et al.*, e.g. Smith *et al.* (1958). The '*et al.*' form should always be used for works by four or more authors. If several papers by the same author and from the same year are cited, a, b, c, etc., should be put after the year of publication, e.g. Smith *et al.* (1958a). All references should be brought together at the end of the paper in alphabetical order. References to articles and papers should mention (a) name(s) of the author(s); (b) year of publication in parentheses; (c) title of journal, underlined, abbreviated according to the *World List of Scientific Publications*, 4th edn and supplements; (d) volume number; number of first page of article. References to books and monographs should include (a) name(s) and initials of author(s) or editor(s); year of publication in parentheses; (b) title, underlined; (c) edition; (d) page referred to; (e) publisher; (f) place.

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

Figures. In the text these should be given Arabic numbers, e.g. Fig. 3. They should be marked on the backs with the name(s) of the author(s) and the title of the paper. Where there is any possible doubt as to the orientation of a figure the top should be marked with an arrow. Each figure must bear a reference number corresponding to a similar number in the text. Photographs and photomicrographs should be unmounted glossy prints and should not be retouched. Line diagrams should be on separate sheets; they should be drawn with black Indian ink on white paper and should be about four times the area of the final reproduction. Lines and lettering should be of sufficient thickness and size to stand reduction to one-half or one-third. Letters and numbers must be written lightly in pencil. Whenever possible, the originals of line diagrams, prepared as described above, should be submitted and not photographs. The legends of all the figures should be typed together on a single sheet of paper headed 'Legends to Figures'.

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JOURNAL OF FOOD TECHNOLOGY
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