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An experimentally simple method for measuring diffusion in food gels

P. S. BELTON* AND R. H. WILSON

Summary

A simple method for measuring the diffusion coefficients of small molecules in food gels is described. The method is based on diffusion in a gel column and requires only the availability of a tube of constant cross section for the experiment. Determination of the concentration gradient in the column is made by sectioning, followed by analysis using any suitable technique. Both mutual and self-diffusion measurements may be made. The method is used to study the diffusion of K_2CrO_4 in agar and agarose gels and amaranth dye in agar.

Introduction

The diffusion of small molecules in food gels is of considerable practical and theoretical interest. It is involved in such diverse phenomena as drying, flavour transport and storage changes. On the theoretical side, effects of the size of diffusion species may be used to test the theories of gel structure. However, most methods of measuring diffusion coefficients are experimentally complex or require specialised apparatus. In this paper, we describe a method based on the well-known capillary method (Tyrrell, 1961), which when applied to gels becomes very simple experimentally. The capillary method relies on the fact that it is possible to obtain an exact solution (Jacobs, 1967) to the diffusion equation for diffusion from a column of constant cross section in contact with a solution of constant composition. In liquids, convective processes can seriously interfere with diffusion so that a fine capillary must be used in order to minimize these effects. In gels, no such processes can take place thus columns of arbitrary dimensions may be used.

An obvious advantage of this is that the experiment is manipulatively much easier. A second advantage is that the column may be sectioned after the

Authors' address: Agricultural Research Council, Food Research Institute, Colney Lane, Norwich, Norfolk, NR4 7UA.

* To whom correspondence should be addressed.

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experiment so that the concentration profile within it may be determined by any convenient method. Thus reliance on a particular analytical method such as radiotracers or spectrophotometric concentration profile scanning are avoided, although such methods are not excluded. If radiotracers are used it is possible to use the method to determine self-diffusion coefficients, otherwise mutual diffusion coefficients are measured. In practical terms, the experiment consists of filling a column with gel, leaving it in contact with a solution for a suitable time and then analysing the sectioned column.

The method is used to study the effects of macromolecule concentration on diffusion of K_2CrO_4 in agar and agarose gels and amaranth dye in agar gel.

In principle, however, the method may be adapted to use with a uniform column of any food material which does not permit convection.

Materials and methods

The two pieces of apparatus required for the experiment are a tube of uniform cross section with a flat open end and a flask to act as a reservoir of solution.

The most available column of constant cross section is a plastic disposable syringe with the end cut off. This has the advantage of using the plunger as a means for sucking the gel into the syringe and extruding it at the end of the experiment. The syringe is held in contact with the solution by pushing it through a rubber bung in a round bottom flask of 100 ml capacity. Both 1 and 2 ml syringes have been successfully used.

The experimental procedure is as follows: Each gel is made up and held at sufficiently high temperature to keep it liquid: it is drawn into the syringe and allowed to set. (Care must be taken at this stage that there are no air bubbles trapped in the column.) Any gel adhering to the exterior of the syringe is removed and a small amount extruded and cut off square to form an end plane parallel to the end plane of the syringe.

The gels used were agar (Hopkins and Williams laboratory reagent) and agarose (BDH clinical reagent).

For amaranth diffusion experiments the gel was made up in 10^{-4} mol dm^{-3} HCl solution and then stored in contact with 10^{-4} mol dm^{-3} HCl at 20°C for at least 2 weeks before the diffusion experiment. This was to ensure that the gel would be in equilibrium with the acid solution to be used in the experiment. The gels for the chromate experiments were made up in water and used immediately after cooling or after ageing at 25°C for 4 days.

The syringe is then pushed through the rubber bung in a thermostatted, round bottom flask (containing about 50 ml of either 0.25 mol dm^{-3} potassium chromate solution or 0.016 mol dm^{-3} or 0.035 mol dm^{-3} amaranth dye solution) until the bottom surface is in contact with the solution.

Stirring was not found to be necessary; however, it may be necessary in more viscous solutions.

After a measured period (about 43 hr for chromate diffusion or 168 hr for

amaranth dye), the syringe is removed and the gel extruded and cut into sections of about 6 mm length (the total length of the column was about 6 cm).

The most effective method of sectioning was found to be to extrude a short length from the syringe and cut it off with a razor blade held against the end of the tube.

The segments are weighed and placed in a known volume of water. After an equilibration period, the concentration of diffusing species in the water is determined spectrophotometrically and the weight fraction of diffusant in the gel determined. The period of equilibration was chosen after some experimentation to determine the rate of efflux of diffusant from the gel. It was found that within the range of concentrations used here no further change in diffusant concentration in the solution was observed after 48 hr.

Weight fractions were chosen as the concentration units since it is not necessary to determine the volume of each segment. If molar concentration scales are chosen, the diameter of the tube must be accurately known since its squared value will be used in calculating concentration. The only dimension required when the weight fraction scale is used is the length of the gel column. The end of the column in contact with the plunger may be distorted because the plunger is not necessarily flat; the length to be determined is the effective length of the gel column. This is found as follows: The distance between two widely spaced marks on the syringe is determined (an accuracy of 1% is sufficient). Thus if the marks are greater than 50 mm apart, a ruler calibrated in millimetres may be used. The weight of gel extruded when the plunger is moved between these two marks is found and the weight of gel per unit length of tube calculated. The length of each segment can be calculated from its weight. The effective length of the segment in contact with the plunger is also calculated, this length represents the length of the segment if both ends are flat. The sum of all the lengths gives the total column length.

Theory

The solution of Fick's law for diffusion into a column of finite length is well known (2),

$$U_i = C_0\left(1 - \frac{4}{\pi}\sum_{P=0}^{P=\infty}\frac{(-1)^P}{(2P+1)}\cos\frac{(2P+1)\pi x_i}{2H}\exp\left[-\frac{2(P+1)^2\pi^2 Dt}{4H^2}\right]\right) \qquad (1)$$

The symbols have the significance shown in Fig. 1. U_i is the concentration at distance x_i from the closed end of the column, H is the length of column, t is the duration of the experiment in seconds, C_0 is the concentration of solution in the vessel. D is the diffusion coefficient, in the experiments described it is a time averaged integral mutual diffusion coefficient.

Since Equation (1) is derived for concentrations expressed in amounts of material per unit volume, the weight fractions obtained in the experiment should be converted to the appropriate scale using the gel density. In practice, in

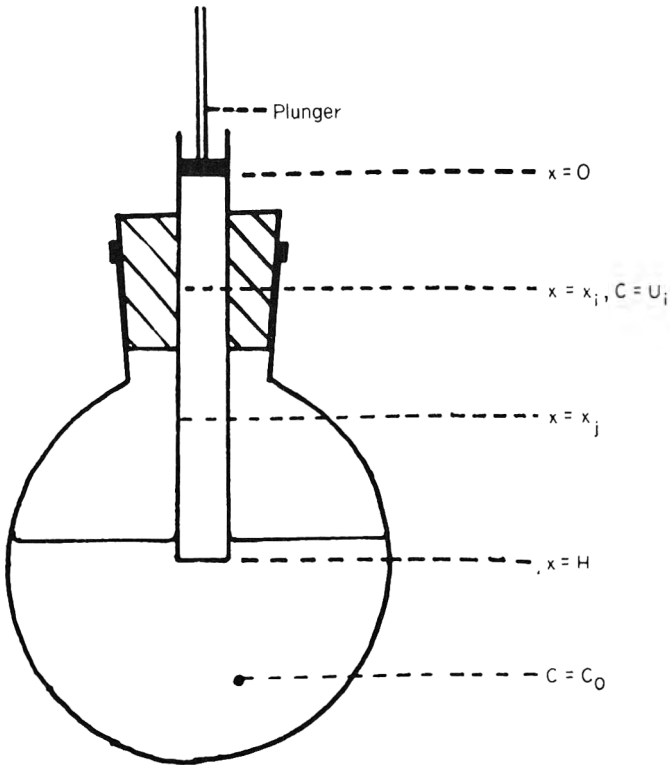

Figure 1. A diagram of the apparatus as used in the experiment. The symbols refer to the parameters used in Equation (1).

these gel systems, this correction is almost negligible making only about a 1% difference in a 5% gel.

In the experiments described, a slab of finite thickness is sampled, if the co-ordinates of the ends of the slab are x_i and x_j, the experimentally determined concentration (U_{ij}) is the mean value in the slab.

Thus,

$$U_{ij} = \int_{x_i}^{x_j} \frac{U\,dx}{(x_j - x_i)} = \frac{C_0}{(x_j - x_i)} \int_{x_i}^{x_j} \left(1 - \frac{4}{\pi} \sum_{P=0}^{P=\infty} A_P \cos(B_P x) \exp(-C_P)\right) dx, \qquad (2)$$

where

$$A_P = \frac{(-1)^P}{(2P+1)}, \quad B_P = \frac{(2P+1)\pi}{2H} \quad \text{and} \quad C_P = \frac{2(P+1)^2\pi^2 Dt}{4H^2}$$

$$\therefore \quad U_{ij} = C_0 \left[1 - \frac{4}{\pi} \sum_{P=0}^{P=\infty} \frac{A_P}{B_P(x_j - x_i)} (\sin B_P x_j - \sin B_P x_i) \exp -(C_P)\right] \qquad (3)$$

This is the general expression relating the concentration in a slab to its position and the diffusion coefficient. However, fitting the data to Equation (3)

presents some problems: the slab nearest to the solution has the highest concentration and is most prone to error since it may be affected by attempts to remove excess solution from the tube containing the gel when measurements of concentration are made. Thus fitting the data to Equation (3) can result in a value of D heavily weighted towards a possibly anomalous sample. In addition, U_{ij} is a function of two co-ordinates and cannot therefore be displayed on a normal two co-ordinate concentration *versus* distance profile.

Both these problems can be overcome by summing the concentrations. If there are n slabs then the sum of the mean concentrations is given by

$$\sum_{m=1}^{m=n} U_{m-1,m}(x_m - x_{m-1}) = \int_0^{x_1} U_{0,1}\,dx + \int_{x_1}^{x_2} U_{1,2}\,dx + \ldots \int_{x_{n-1}}^{x_n} U_{n-1,n}\,dx$$

$$= \int_0^{x_n} U dx\,, \tag{4}$$

where x_0 corresponds to $x = 0$.

Thus from Equation (3),

$$\sum_{m=1}^{m=n} U_{m-1,m}(x_m - x_{m-1}) = C_0\left[x_n - \frac{4}{\pi}\sum_{P=0}^{P=\infty}\frac{A_P}{B_P}\sin B_P x_n \exp -(C_P)\right] \tag{5}$$

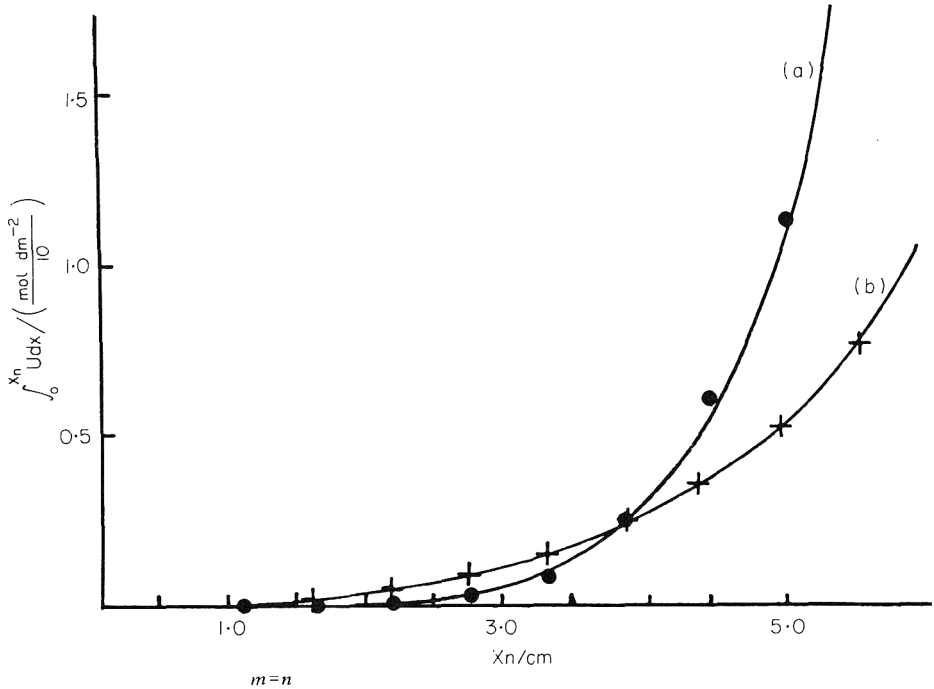

Figure 2. A plot of $\sum_{m=1}^{m=n} U_{m-1,m}(x_m - x_{m-1})$ versus x_n for two samples of gel. Curve (b) is chromate in 5% agar gel, Curve (a) is amaranth in 5% agar. The solid lines represent the fitted curve.

The right hand side of the equation contains terms only in one vertical co-ordinate. There are the same number of data points as slabs. These correspond to $U_{0,1}(x_1)$, $U_{0,1}(x_1) + U_{1,2}(x_2 - x_1)$, etc.

This has the effect of weighting the low concentration end more than the high concentration end, since low concentration regions appear more times than high concentration regions.

A computer program has been developed to fit experimental data to Equation (5) and a listing is available from the authors. Examples of fits to data are shown in Fig. 2.

Results and discussion

The values of the diffusion coefficients for K_2CrO_4 in agar gel are shown in Table 1 and in agarose gel in Table 2. Replicate determinations show that reproducibility is within about 10%. Results for amaranth diffusion in agar are given in Table 3. A potential source of error in the interpretation of both the chromate and amaranth results is that they may be affected by the binding of the diffusant to the polymer matrix or that there may be partition effects occurring between solution and gel. These phenomena could cause incomplete extraction of the diffusant from the gel in the analytical stage or an erroneous value of D to be calculated. Crank (1957) has analysed the effects of binding and distinguishes two cases: (a) The general case where binding does not have a linear dependence on diffusant concentration; and (b) the limit case where binding is linearly proportional to the concentration of substance free to diffuse.

In case (a) although not case (b) the apparent value of D would be expected to vary along the column length. Since the fit to Equation (5) is a single parameter fit this would be expected to cause a consistent deviation of the fitted curve from the data points. This is not observed. In both cases (a) and (b) the apparent values of D would be a function of C_0 and the concentration of the matrix to which binding was occurring. For chromate D is independent of C_0 in the range of 0.1–0.25 mol dm^3 and did not vary significantly within a gel concentration

Table 1. Diffusion of chromate in agar as a function of agar concentration. The value of D given is the mean of all the experimental values at that concentration

Agar (%)	$D/10^{-5}$ (cm^2 sec^{-1})	Standard deviation/10^{-5} (cm^2 sec^{-1})	Number of measurements
1	1.12	0.05	8
2	1.02	0.08	3
3	1.09	0.08	2
4	0.91	0.10	5
5	0.99	0.09	3

Table 2. Diffusion of chromate in agarose as a function of agarose concentration. The value of D given is the mean of all the experimental values at the concentration

Agarose (%)	$D/10^{-5}$ ($cm^2\ sec^{-1}$)	Standard deviation/10^{-5} ($cm^2\ sec^{-1}$)	Number of measurements
1	1.14	0.09	3
2	1.05	0.09	3
3	1.02	7.1×10^{-3}	2
4	1.00	0.03	2
5	0.97	0.06	3
6	0.96	0.03	2
7	0.88*	0.05*	4
7	0.87†	0.06†	4

*Measurements on an unaged gel.
†Measurements on an aged gel.

range of 1–5%. For amaranth, although D was a function of agar concentration, it was independent of C_0 Thus for both gels these effects can be eliminated.

The possibility of partition effects in the chromate case may be eliminated since such effects would be a function of matrix concentration. In the case of amaranth, independent experiments using gels made up with known amounts of the dye were carried out. In all cases the amounts of dye extracted, using the procedure described, were equal to the total amount of dye in the gel. Thus, here too, partition effects may be eliminated, and in both systems studied extraction is complete and the implicit assumption that C_0 is the concentration of diffusant on the gel side of the interface is validated.

In the chromate case the results at 1% show the smallest standard deviation (s.d.). This is in contradistinction to the results of Busk & Labuza (1979) who

Table 3. Diffusion of amaranth dye in agar as a function of agar concentration. Only two experiments were carried out at each concentration

Agar (%)	$D/10^{-6}$ ($cm^2\ sec^{-1}$)	Standard deviation/10^{-6} ($cm^2\ sec^{-1}$)
1	4.88	0.11
1	4.69*	0.15*
2	4.39	0.08
3	4.25	0.09
4	3.09	7.1×10^{-3}
5	2.65	0.14

*This experiment was carried out using 0.035 mol dm^{-3} amaranth.

observed large variations of D at low agar concentrations. These they attributed to different thermal histories of different samples. The samples used here came from a single batch of agar and agarose as did those of Busk & Labuza. In the case of CrO_4 diffusion gels were in general not aged, thus the lack of variation cannot be attributed to a longer ageing time than those reported by Busk & Labuza (1979). In one experiment, a 7% agarose gel was aged for 4 days at 25°C but no significant effect on diffusion coefficient was observed. Slade, Cremers & Thomas (1966) report a self-diffusion coefficient for 0.01 mol dm^{-3} NaCl in 1% agar as $1.246 \pm 0.004 \times 10^{-5}$ cm^2 sec^{-1} from ten separate determinations. This is consistent with our observations.

The change in D with concentration in our chromate experiments is small. This again is consistent with the results of Slade *et al.* (1966), who for self diffusion of 0.25 mol dm^{-3} NaCl in agar find for a 1% gel $D = 1.315 \pm 0.006 \times 10^{-5}$ cm^2 sec^{-1} and for 4% agar, $D = 1.234 \pm 0.004 \times 10^{-5}$ cm^2 sec^{-1}.

The results for amaranth dye (Table 3) show a marked effect of gel concentration in agreement with the results of Busk & Labuza (1979).

The absolute values of D reported here are about twice those of Busk & Labuza (1979). However, since the concentration ranges over which the diffusion coefficient is integrated are different some difference in absolute value may be expected. In addition, Busk & Labuza (1979) did not pre-equilibrate their gels with an acid medium, thus they were observing a flow of amaranth in a flow of acid. This process may also affect the value of D obtained. Finally, the temperature of the Busk & Labuza (1979) experiment is not accurately defined, thus it may simply be a temperature effect.

The results suggest that the amaranth molecule is sufficiently large (mol wt = 604.48 compared to K_2CrO_4 = 194.19) that its diffusion is affected by the pore size in the gel.

Acknowledgments

The authors would like to thank Mr R. Stansfield and Mrs S. Ring for their generous assistance with the preparation of the computer programs.

Appendix

List of Symbols

U_i is the concentration of diffusant at a distance x_i from the closed end of the column.

U_{ij} is the mean concentration of diffusant in a slab of gel the ends of which are x_i and x_j from the closed end of the gel column.

$U_{m-1,m}$ is the mean concentration of a slab of gel the ends of which are x_{m-1} and x_m from the closed end of the gel column, $x_m > x_{m-1}$.

x_n is the distance of the furthest end of the nth slab from the closed end of the gel column.
C_0 is the concentration of diffusant in the solution in contact with the gel.
D is a time averaged integral mutual diffusion coefficient.
t is the duration of the experiment.

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Chemical and sensory changes in iced *Nephrops norvegicus* as indices of spoilage

G. D. STROUD, J. C. EARLY AND G. L. SMITH

Summary

Changes in trimethylamine (TMA), total volatile bases (TVB), hypoxanthine and pH, and in cooked odour, flavour and texture have been followed during the iced storage of *Nephrops norvegicus* at approximately monthly intervals in order that seasonal variations could be investigated. None of the chemical methods investigated could give a prediction of age-in-ice to a standard error of less than 2 days. Initial TMA and TVB figures were significantly higher than other published figures.

Introduction

Nephrops norvegicus, the Norway lobster, commonly known as scampi, is currently the most important, in terms of value, of all shellfish landed in the U.K., accounting for 55% by value and 24.6% by weight in 1979. *Nephrops* is caught by a specially designed light trawl and landed either whole or as shell-on tails. Less frequently, they are caught in baited pots by inshore boats, when they are usually landed whole. Voyages are usually short, rarely lasting more than 24 hr, and so the *Nephrops* can be landed in a very fresh condition, if not alive, at the port. They may be processed at the port of landing, but are often transported long distances to the processing factories, sometimes with inadequate icing, which increases the rate of spoilage.

This investigation, which is part of a larger study on seasonal variations in the composition of *Nephrops*, was carried out to measure chemical and sensory changes which take place during spoilage, and to examine the former with a view to developing a chemical index of spoilage. Samples were taken at approximately monthly intervals to investigate the effect of seasonal variations. Furthermore, buyers are specifying maximum levels of total volatile bases

Authors' address: Torry Research Station, P.O. Box 31, 135 Abbey Road, Aberdeen AB9 8DG.

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(TVB) in samples imported into France and there is a shortage of information on how levels change during storage.

Materials and methods

The raw material was obtained from Pittenweem, Fife. Vessels from this port fish close inshore and so voyages are invariably less than 12 hr. The fish were usually live when landed and were transferred to boxes, iced and transported by road to Aberdeen. The cephalothorax was then parted from the abdomen, and the shell-on tails were boxed, iced and stored in a chill store at 2–4°C. At periodic intervals up to 12 days in ice, samples were shelled, trichloroacetic acid (TCA) extracts were prepared for trimethylamine (TMA) analyses, and neutralized perchloric acid extracts were prepared for hypoxanthine determinations. A shelled sample was minced for pH determinations. In addition, shelled meats were steamed for 12 min and examined for cooked odour, flavour and texture by an experienced panel of 5–6 tasters. It was not always possible to prepare the extracts at exactly the same intervals because of the irregular pattern of landings.

In a later, more limited series of experiments, TVB was assessed on trichloroacetic acid extracts of *Nephrops* flesh.

Trichloroacetic acid extracts were prepared by homogenizing 15 g of tail meat from two individual fish with 50 ml of TCA for 1 min in an MSE 'Nelco' homogenizer and filtering the homogenate. Perchloric acid (PCA) extracts were prepared by homogenizing 5 g of tail meat from one fish in 50 ml of 0.6 M PCA for 1 min and filtering the extract. A 5 ml aliquot of the filtrate was taken and neutralized by adding 5 ml of 0.577 M KOH in 0.02 M phosphate buffer (pH 7.6).

Trimethylamine was determined by the method of Dyer (1945), but modified by using 4% formaldehyde and 40% KOH to suppress interference by dimethylamine. Total volatile base nitrogen was determined by steam distilling 15 ml aliquots of the TCA extracts with 3 ml of 20% NaOH for a total of 12 min in a Hoskins distillation apparatus. The distillate was collected in 2% boric acid and titrated with 0.01 N HCl. Hypoxanthine was determined by the method of Jones *et al.* (1964). The pH values were obtained by direct readings with a probe electrode and a Beckman 'Expandmate' pH meter on a mince prepared from fifteen fish.

Six TCA and six PCA extracts were prepared at each sampling. Three individual pH readings were taken from the mince.

Results

Chemical

The results are given in Figs 1–4 for TMA, TVB, hypoxanthine and pH respectively. The values of the first three indices are plotted on a log scale, and

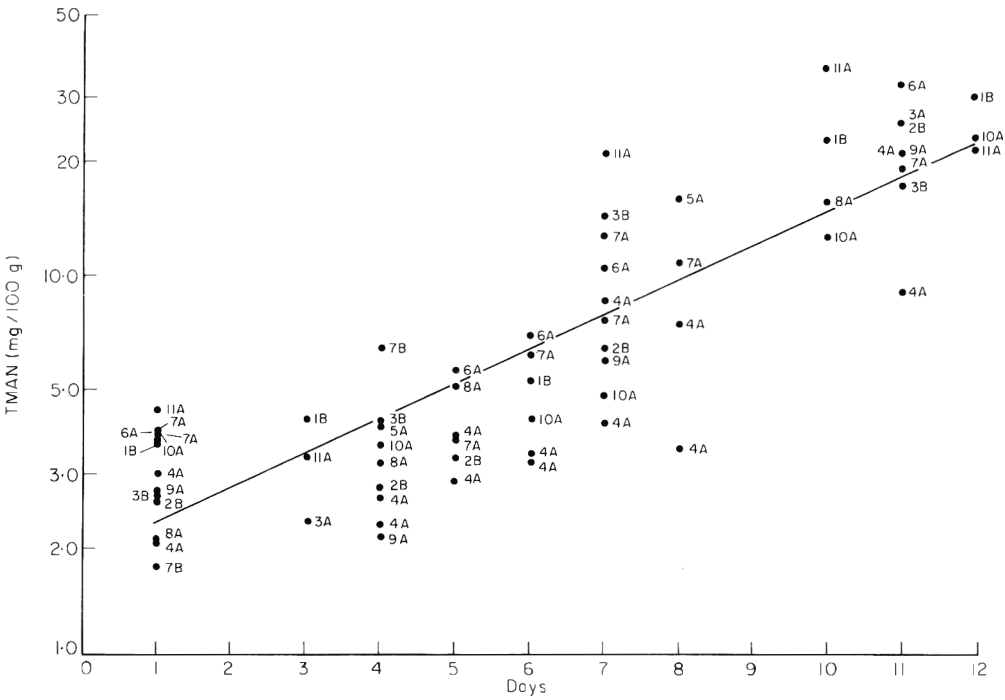

Figure 1. Changes in TMAN concentrations (mg/100 g) during iced storage; numerals represent months (1 = January, 12 = December), and letters represent years (A = 1976, F = 1981).

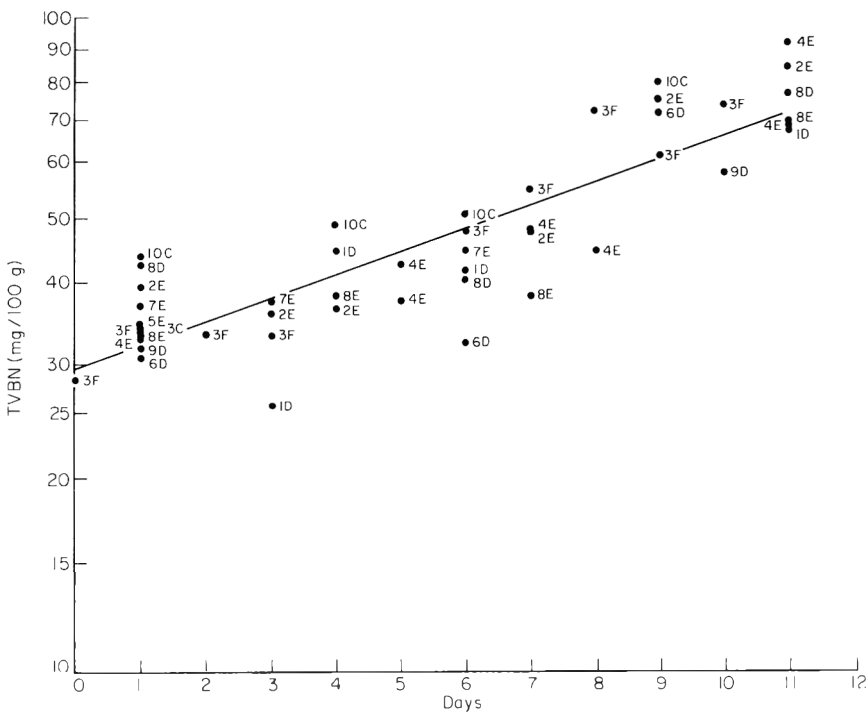

Figure 2. Changes in TVBN concentrations (mg/100 g) during iced storage; for Key see text and Fig. 1.

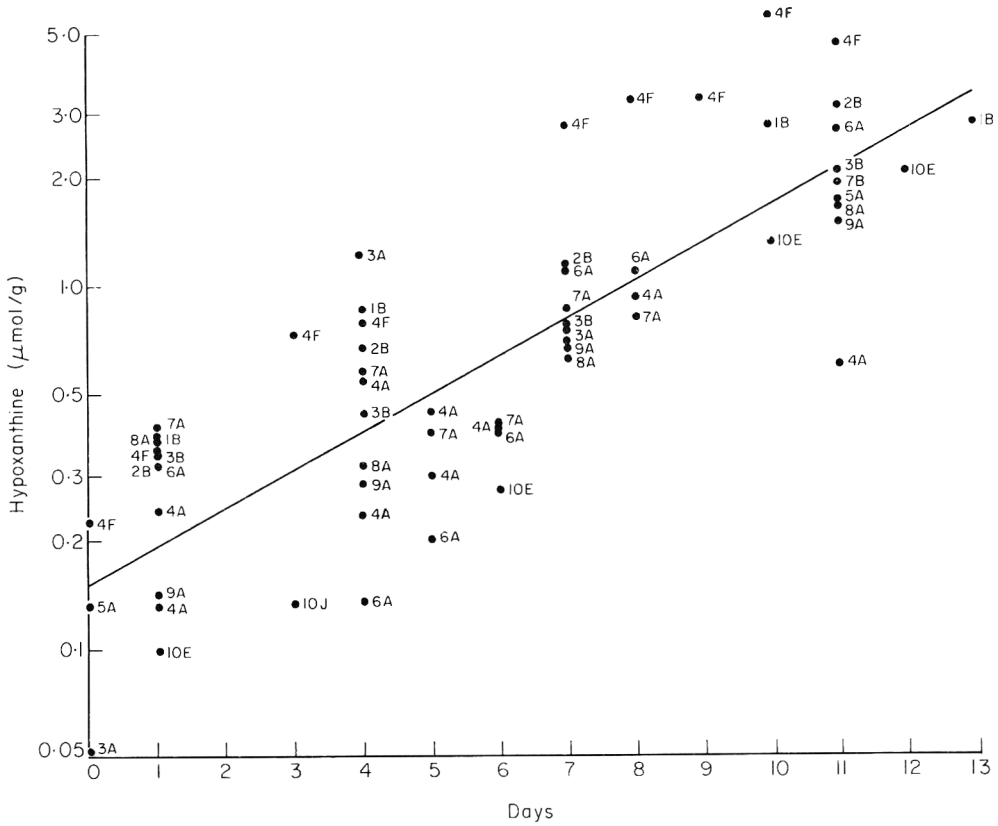

Figure 3. Changes in hypoxanthine concentrations (μmol/g) during iced storage; for Key see text and Fig. 1.

the straight line on the graph represents the least square line. The points on the graph show the mean result for each sampling time, and the figure beside each point identifies from which month and year the result was obtained. The numbers 1–12 represent the month (1 = January, 12 = December) and the latter the year (A = 1976, F = 1981). This method of presentation of the results was adopted in an attempt to distinguish any seasonal variations. Should seasonal variations be present, results for different seasons would tend to consistently lie either above or below the line, and this pattern would be repeated from year to year.

Pooled, within-batch standard deviation (s.d.) for each storage time for each of the parameters measured, the overall means and the number of degrees of freedom (d.f.) on which each pooled s.d. was based are given in Table 1. (In the case of a single batch of n determinations, there are $n - 1$ d.f.; for more than one batch it is the sum of the separate '$n - 1$'s. The pooled variance, from which the pooled s.d. were calculated, is a weighted average of the separate variances, each one being given a weight proportional to its d.f. The pooled s.d. is the square root of the pooled variance.)

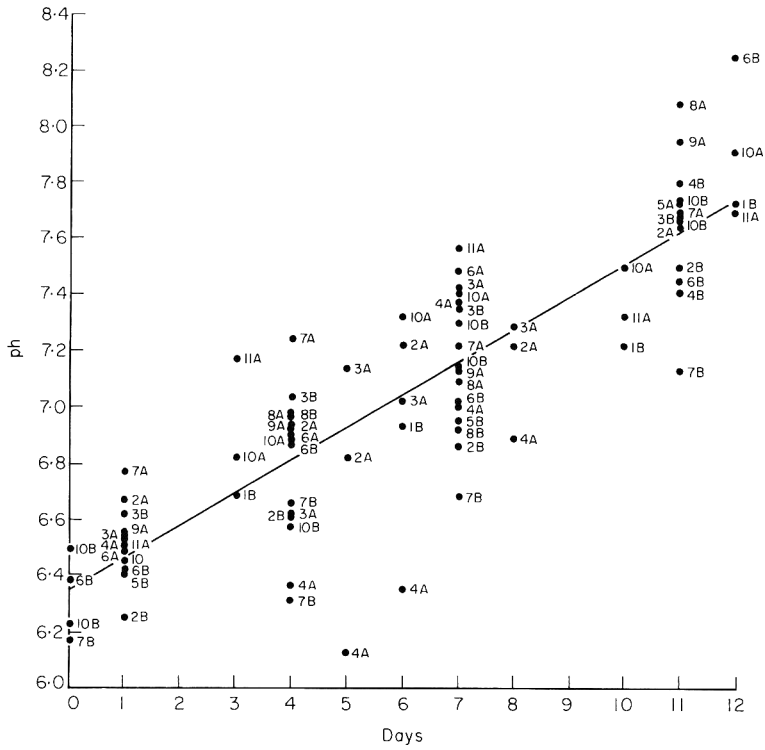

Figure 4. Changes in pH during iced storage; for Key see text and Fig. 1.

Table 1. Degrees of freedom (d.f.), mean values and overall standard deviations (s.d.) of TMAN (mg/100 g), TVBN (mg/100 g), hypoxanthine (μmol/g) and pH as a function of storage time

	TMA			TVB			Hypoxanthine			pH		
Days	d.f.	Mean	s.d.	d.f.	Mean	s.d.	d.f.	Mean	s.d.	d.f.	Mean	s.d.
0	—	—	—	5	27.9	3.08	12	0.15	0.09	8	6.32	0.07
1	59	3.2	0.93	52	35.6	3.61	52	0.31	0.18	22	6.51	0.04
2	—	—	—	5	33.0	2.43	—	—	—	—	—	—
3	13	3.4	0.60	20	32.6	2.56	10	0.50	0.34	6	6.90	0.07
4	50	3.7	1.53	20	41.5	4.72	51	0.49	0.27	30	6.80	0.16
5	29	4.4	1.88	10	39.4	2.03	16	0.36	0.14	4	6.85	0.14
6	30	5.0	1.51	27	43.5	3.96	19	0.38	0.11	8	7.06	0.09
7	47	10.5	4.87	22	47.3	8.44	37	1.16	0.48	32	7.15	0.08
8	20	9.9	3.88	10	58.4	6.61	19	1.50	0.61	6	7.13	0.14
9	—	—	—	16	72.1	12.70	5	3.24	0.46	—	—	—
10	15	18.3	3.40	10	65.9	6.65	15	3.36	1.52	4	7.30	0.06
11	41	22.3	6.16	30	76.6	10.24	45	2.28	0.75	22	7.65	0.08
12	13	25.9	7.11	—	—	—	5	2.23	1.15	8	7.90	0.08
13	—	—	—	—	—	—	5	2.74	0.48	—	—	—
Overall	317		3.62	227		6.63	291		0.56	150		0.10

Sensory

Cooked odour. A large number of different descriptions were used by the panel to describe the cooked odour, particularly during the early stages of spoilage, the initial odour being variously described as 'seaweed', 'shellfish', 'boiled vegetable' and 'milky–sweet'. After 4 days storage the 'milky–sweet' and characteristic odours were still apparent and ammoniacal odours were just detectable at this stage. The latter rapidly increased in intensity and became the predominant odour after 6 days storage in ice. Odours described as 'sour', 'off' and 'boiled clothes' were also detected.

Cooked flavour. The changes in cooked flavour followed a well-defined pattern. The initial flavour was described as intensely sweet, 'cloying' and 'metallic', and this flavour was retained for between 4 and 6 days in ice with only a slight loss of intensity. During this time 'milky' and 'slightly musty' flavours also developed. Between 6 and 8 days a bland, neutral flavour replaced the initial sweetness. After this time sour, off-flavours rapidly developed, with very strong, sour, off and bitter flavours being apparent after 12–13 days storage, when all samples were judged to be inedible.

Cooked texture. The texture of the cooked samples tended to be soft initially, but after 5 days storage in ice the texture was more frequently described as firm. The texture, however, appeared to be affected as much as by season as by the length of storage in ice, the samples with the firmest texture tending to occur during the period from May to August.

A sensory scoring system, developed from these results, is given in Table 2, with the approximate days in ice which correspond with the scores.

Table 2. Sensory assessment score sheet for cooked odour and flavour for *Nephrops norvegicus*

Days in ice	Score	Cooked odour	Cooked flavour
0–1	5	Milky-sweet, seaweed, slightly sulphurous, characteristic shellfish	Intensely sweet, metallic
1–3½	4	Milky, creamy, slight ammonia	Very sweet, creamy, milky
3½–6	3	Slight ammonia, loss of milkiness	Sweet
6–8½	2	Ammonia	Loss of sweetness, neutral
8½–11	1	Strong ammonia	Sour, off, creamy-sour
11–13	0	Strong ammonia, sour	Strong, off-flavour, bitter, very sour

Discussion

Earlier limited studies on the spoilage of *Nephrops* indicated that TMA and TVB determinations could be useful indices of spoilage during iced storage (Walker, Cann & Shewan, 1970; Vyncke, 1970). The present work confirms the earlier findings by Walker *et al.* (1970) that overall TMA and TVB concentrations increase during the useful storage time in ice and that the spoilage pattern for *Nephrops* is somewhat different from that of white fish. Typical

figures for TMA and TVB concentrations after different storage times in ice for gutted North Sea codling obtained from different grounds and different seasons (Burt *et al.*, 1976) and for *Nephrops* are compared in Table 3. These differences in the contents and rates of change of TVB and TMA are attributed to the differences in bacterial flora (Cann *et al.*, 1971; Walker *et al.*, 1970) and the higher levels of non-protein nitrogenous compounds present in *Nephrops* flesh compared with that of cod.

Table 3. Comparison of TMAN and TVBN values for cod and *Nephrops* after iced storage (mg N/100 g)

	0–6 days iced		11 days iced	
	Nephrops	Cod	*Nephrops*	Cod
TMA	2–8	0–1	10–30	2–8
TVB	30–50	19–21	60–90	25–35

The TMA and TVB values found in this work are higher than those reported previously (Vyncke, 1970; Walker *et al.*, 1970). Vyncke's work, however, was carried out on cooked material using the Antonacopoulos distillation method (Lücke & Geidel, 1935; Antonacopoulos, 1960), and the results obtained cannot be compared with those from the present work. The differences in initial levels of TMA and TVB between the present work and the more limited trials of Walker *et al.* (1970) could be explained to some extent by the different methods of chilling and icing employed. Further work on TMA and TVB levels may be required on *Nephrops* from other fishing grounds if TVB levels are to be written into product specifications, as the initial TVB levels found in this work are higher than the standard specification of < 30 mg TVBN/100 g, typically applied to raw tropical shellfish (Cann, 1973).

Examination of the shape of the curves for TVB and TMA raises points of interest. As TMA and TVB are essentially measurements of bacterial spoilage, the type of curves would be expected to be, and in fact are very similar. There is little overall change in either of the indices during the first 4 days of storage, with small rises and falls in concentrations being recorded, before concentrations start to increase significantly. The TMA content accounts for approximately 25% of the total volatile base, a ratio which does not alter significantly during the storage life of samples. Limited analyses of the extracts by enzymatic and gas–liquid chromatographic techniques showed the remainder of the TVB to be largely ammonia, with very small amounts of dimethylamine (DMA) present. The variation in TVB levels is therefore the sum total of the variations in TMA, DMA and ammonia levels. The pooled, within-set s.d. indicate that the TMA levels show less variation than those for TVB. This is not surprising when one considers the analytical methods used. The method for TMA probably determines all the TMA present but minor variations in the TVB method can give rise

to differing TVB values. The accuracy of prediction of days in ice of the two methods is, however, similar, ± 2.02 days and ± 2.04 days for TMA and TVB respectively.

Nephrops flesh contains high levels of non-protein nitrogen (Kent & Stroud, 1981), and these high concentrations could be responsible for the high initial levels of TVB found. Some breakdown of low molecular weight nitrogenous compounds occurs during the distillation procedure, releasing volatile base nitrogen. The non-protein nitrogen in the flesh also provides a readily utilizable food source for bacteria.

Values of pH also provide an index of bacterial spoilage, in that basic compounds produced as a result of bacterial spoilage cause the pH of the flesh to rise. From the results of the pH measurements it would appear that the production of acids by post-mortem glycolysis does not significantly affect the pH of the muscle, as is the case with white fish (Fraser *et al.*, 1967). The standard error (s.e.) of prediction of days-in-ice of the method was ± 2.13. Although this figure is slightly worse than that for TMA and TVB, the method as a predictor of quality has a number of attractions in that it is rapid and can be made non-destructive by using a direct reading combination electrode on the intact shelled flesh.

The results of the hypoxanthine analyses showed that the concentractions varied widely. As a predictor of days-in-ice, hypoxanthine was the least satisfactory of the four methods examined, with a s.e. of prediction of days-in-ice of

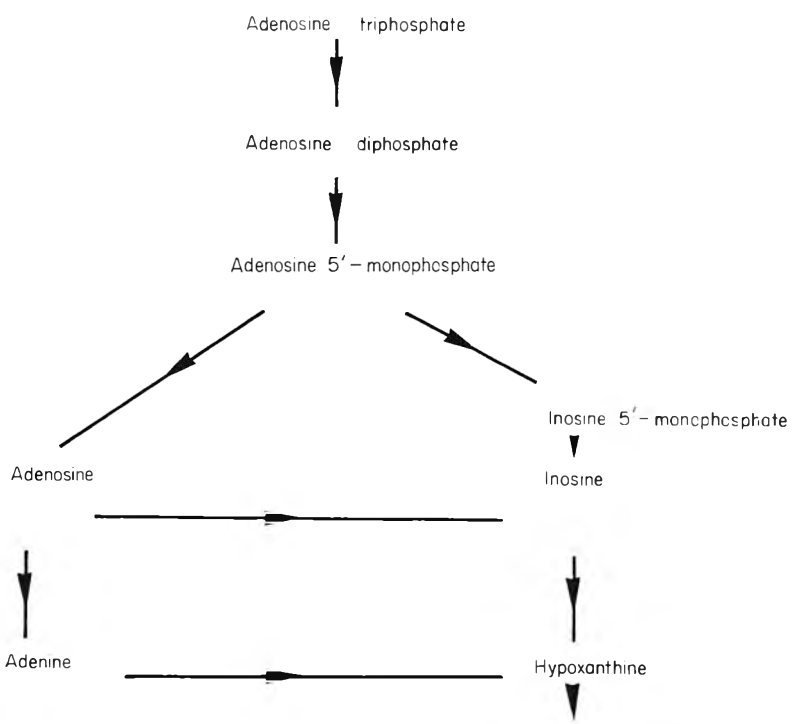

Figure 5. Possible pathways of production of hypoxanthine in *Nephrops* muscle.

± 2.68 days. The shape of the curves obtained show differences from run to run, on some occasions the shape approximating to a straight line when plotted on log paper. At other times there appears to be a lag phase when hypoxanthine values remain unchanged or even show slight falls between 0 and 4–6 days before the concentrations increase. This pattern is different from that found in the 120 of the approximately 150 species of freshwater and marine teleosts, elasmobranchs, crustacean and molluscs so far examined. In these species, hypoxanthine concentrations have been found to increase at a reasonably steady rate during the useful period of chill storage (Burt, 1976).

The wide variations in hypoxanthine concentration are noteworthy, particularly those between 0 and 4 days in ice. As hypoxanthine is the final autolytic degradation product of adenosine triphosphate (ATP), hypoxanthine concentrations would be expected to increase steadily during ice storage, assuming that each of the enzymes of the degradation pathway is present and that conditions in terms of substrate concentration and pH were favourable. The results of this present work suggest that the enzymes responsible for the breakdown of ATP and its catabolites to hypoxanthine do not operate at the same rate throughout the year. It is also possible that more than one pathway operates to produce hypoxanthine, and the importance of the different pathways could alter throughout the year, as has been shown to occur in scallop muscle (Hiltz & Dyer, 1970). Possible pathways are shown in Fig. 5 (Burt, 1976).

Further investigations into changes in the concentrations of the intermediate catabolites are required before a definitive explanation can be given for these variations.

In all of the four indices examined, no clear trend of seasonal variation was present. Examination of Figs 1–4 shows that although results for some months do fall above or below the line, the pattern is not reproducible.

As each method of determination could not give a prediction of age-in-ice to a standard of less than 2 days (e.g. 95% confidence limits of predicted days ± 4), a procedure was sought to combine all four predictors into a single measure.

A principal components analysis (e.g. Kendall, 1980) was performed using log TMA, log TVB, log hypoxanthine and pH and the first principal component (which accounted for 86% of the combined variance) was entered into the linear regression against time. Each of the indices had a similar weighting in the first principal component. As all four measures were highly inter-correlated and only a limited number of occasions had determinations of all four, there was little improvement, the s.e. of prediction being 1.8 days. This is demonstrated in Fig. 6, where the first principal component is plotted against time.

Of the four parameters measured, none were particularly useful as predictors of freshness. There are a number of reasons which could explain this relatively poor performance. Crustacean shellfish undergo profound physiological changes during ecdysis as the animal absorbs water to increase in size. This normally occurs once or twice a year for commercially sized individuals, and can take place at any time, although peak times occur betwen March and April and May to November (Howard, in press). The ratio of male to female specimens

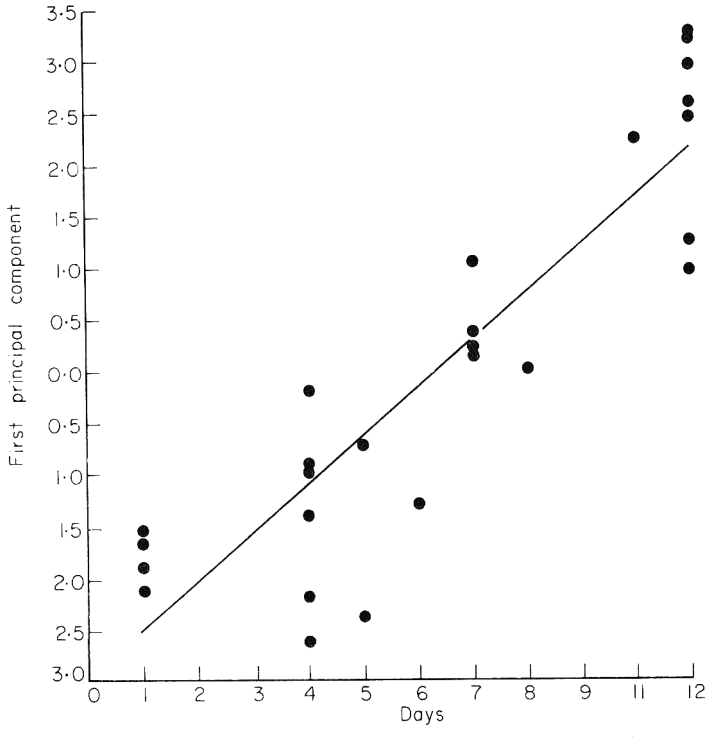

Figure 6. Regression of the first principal component on time.

also differs throughout the season, as the females tend to hide in the mud when they are carrying eggs, and there is much less likelihood of catching them when they are in this condition. The spoilage pattern is also affected by the fact that *Nephrops* are stored in ice with the gut still present, which then provides a focus for rapid bacterial spoilage. There is also a greater chance of the animals being contaminated during the catching operation by bacteria present in the mud in which the animals live, than with pelagic or demersal fish. The large surface : body ratio and comparatively small size of the animal also tends to accelerate post-mortem spoilage.

Examination of the taste panel data shows that for cooked odour the score sheet is an intensity score for ammonia and ammonia-like flavours, except for the very fresh samples when amines and ammonia content is low. Similarly, the predominant fresh flavour is an intense sweetness which is gradually lost. When the incipient point of spoilage is reached the flavour is neutral, sour and bitter spoilage flavours then being produced. It is interesting to note that the panel did not describe the samples as having a characteristic shellfish or shrimp-like flavour at any time during the storage period.

Conclusion

Although each of the four measured chemical indices changed during the useful storage time in ice, variations between samples and different sampling times

were too great for any of the parameters measured to provide a useful index of freshness. No consistent differences due to season were noted.

Further work on the measurement of individual pH readings and investigations into the intermediate catabolites of ATP degradation may provide more useful information.

Changes in sensory properties showed that during chill storage there was a gradual increase in the intensity of ammonia and ammonia-like odours in the cooked odour and a loss of sweetness in the cooked flavour. The samples became inedible between 8 and 11 days storage in ice.

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Biochemical and technological characteristics of hot chicken meat

J. KIJOWSKI, A. NIEWIAROWICZ AND B. KUJAWSKA-BIERNAT

Summary

In the hot breast and leg muscles of broiler chicken the level of ATP, the 'R' value, the lactic acid content, the pH value, the length of sarcomers, the water and fat retention capacity, the fat emulsion stability, thermal drip, and the extractability of protein fraction were investigated. It was found that in the breast muscles the onset of rigor mortis commenced within 30–60 min, and in the leg muscles as early as 15–30 min after killing of the birds. The deepest rigor mortis occurred between the first and fourth hour, and then gradually declined, sooner in the leg than in the breast muscles. The addition of sodium chloride (2.0–2.5%) to the minced pre-rigor meat not later than 40 min after slaughter, or better, an injection of NaCl brine into intact muscles 15 min after slaughter of birds, preserved their good technological properties.

The tenderness and the thermal drip of hot salted and chilled salted muscles showed no significant differences, but water retention and fat emulsifying capacity were better in the hot salted meat samples. The hot salted and cooked muscles were preferred by the sensory panel to corresponding samples of chilled muscles.

From the hot salted chicken meat more sarcoplasmic and myofibrillar proteins were extracted than from meat salted after chilling. However, after frozen storage the extractability of myofibrillar proteins were higher in the salted chilled meat.

Introduction

There is little information on the biochemical and technological characteristics of so-called hot poultry meat. De Fremery & Pool (1960) showed that rigor mortis in broiler breast muscles is developing between 2 and 4½ hr after slaughter of the birds. Just after slaughter the content of ATP was of about 4.8 mg/g tissue and at the moment of rigor decreased to about 30% of its initial level.

Author's address: Institute of Animal Products Technology, Agricultural University of Poznań, ul. Wojska Polskiego 31, 60-624 Poznań, Poland.

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Khan & Lentz (1965) and Ristič, Kijowski & Schön (1980) found lower shear values and lower thermal drip in frozen, pre-rigor broiler muscles 15 min after slaughter than in muscles frozen 24 hr post mortem.

Klose *et al.* (1972) and Wyche & Goodwin (1974) reported that cooked or roasted hot meat from broilers and hens demonstrated a higher shear value. However, Arafa & Chen (1978) did not find differences in tenderness between hot and chilled broiler meat.

Hamm (1973) found that the technological properties of beef required in meat processing can be retained for several days by salting the minced pre-rigor muscle, or for several months by freezing the pre-rigor minced muscle in the absence or presence of salt.

Khan & Frey (1971) and Davidek & Velisek (1973) suggested that the ratio of adenine nucleotides to inosine nucleotides characterize indirectly ATP level, and may be useful for the determination of the onset of rigor mortis in poultry meat.

Honikel & Fischer (1977) called the above-mentioned ratio the 'R' value and used it as a method for the differentiation of normal, PSE and DFD porcine muscles.

Smith, Judge & Stadelman (1969) observed the degree of shortening in isolated pectoralis major muscles of chickens and sarcomere length of isolated myofibrils and found shortening in muscles as early as 15 min post mortem. Shortening of muscles was essentially completed after 3 hr post mortem and it was directly related to the sarcomere length.

The objective of this study was as follows: to establish the time of the beginning and declining of rigor in the broiler breast and leg muscles; to evaluate the effect of salting on the technological properties of hot (pre-rigor) broiler meat; and to investigate the extractability of protein fractions from hot salted and frozen, chilled salted, and frozen meat, and to evaluate the quality of this meat after frozen storage.

Materials and methods

The experiments were performed on breast and leg muscles of 8-week-old broilers, slaughtered in a commercial processing plant. The birds were passed through the electrical water stunner (80 V for 3 sec) and bled for 180 sec. After bleeding the samples of muscle intended for analysis for 3 min post mortem were excised. The other birds were processed as usual, i.e. scalded (90 sec at 59°C), mechanically defeathered and manually eviscerated. After evisceration the experimental broiler carcasses were taken off from the overhead conveyor and kept in a temperature of about 18°C, whereas the control carcasses were chilled and stored at 3–4°C. The muscle samples after 15, 30 and 60 min, and after 2, 4, 8 and 24 hr post mortem were taken for analysis. For each analysis the meat samples were taken from the same muscles of the same carcass at a post-slaughter time mentioned above.

For tenderness determination and thermal drip measurement the muscles left on the carcass were manually injected with brine of 25% NaCl concentration, and 10% brine to the muscle weight. Meat mixture of breast and thigh muscles consisted of the muscles excised from six carcasses and ground using a 2 mm plate. This material was mixed with 2.5% salt (w/w), not later than 40 min after slaughter of the broilers.

The ATP content was determined by an enzymic method (Jaworek, 1970) and the 'R' value according to Honikel & Fischer's (1977) procedure. The ATP and lactic acid were extracted from meat with 1 M perchloric acid. The lactic acid was determined according to the Dische Laszlo method where, after oxidation, the colour reaction was developed with hydroquinone. The other samples of muscles were fixed in the EDTA, borate-KCl buffer solution of pH 9.0 and after mincing the length of the sarcomers was measured in the light microscope (1600× magnification).

The other analyses were performed according to well-recognized methods, i.e. water holding capacity (WHC) (Wierbicki, Tiede & Burell, 1962); free water (FW) (Hamm, 1972); water and fat retention capacity (WRC, FRC) (Klima & Kopalowa, 1960); fat emulsifying capacity (FEC) (Webb *et al.*, 1970); emulsion stability (ES) (Townsend *et al.*, 1968; Hag *et al.*, 1973); gel forming capacity (GFC) (Trautman, 1966).

The sarcoplasmic proteins were extracted with 0.03 M phosphate buffer solution of pH 7.4, and the myofibrillar proteins with the same 0.1 M buffer

Table 1. ATP, 'R' value and lactic acid content in broiler chicken muscles depending on the time after slaughter of birds

Muscles	Number of birds*	Time after slaughter of birds							
		3 min	15 min	30 min	1 hr	2 hr	4 hr	8 hr	24 hr
Breast									
ATP, (μmol/g tissue)	6	6.8^{a}	5.5^{b}	3.6^{c}	2.4^{cd}	1.6^{ce}	0.7^{e}	0.6^{e}	0.7^{e}
'R' value	15	0.88^{a}	0.97^{b}	1.09^{c}	1.18^{d}	1.28^{e}	1.32^{e}	1.37^{f}	1.38^{f}
Lactic acid (mg/100 g tissue)	18	106.5^{a}	152.3^{b}	164.8^{b}	173.9^{b}	178.5^{b}	175.3^{b}	200.0^{c}	220.0^{c}
Leg									
ATP (μmol/g tissue)	5	4.3^{a}	2.9^{b}	2.3^{b}	1.0^{c}	0.7^{c}	0.5^{c}	0.4^{c}	0.15^{c}
'R' value	5	0.96^{a}	1.10^{ab}	1.12^{b}	1.24^{bc}	1.37^{c}	1.33^{c}	1.50^{d}	1.31^{c}
Lactic acid (mg/100 g tissue)	5	63.4^{a}	72.9^{a}	82.2^{a}	81.9^{a}	81.9^{a}	95.4^{a}	87.2^{a}	78.0^{a}

* For the muscle of each bird, two or three parallel determinations were carried out.

[a–f] Figures in the *rows* marked with various letters demonstrate statistically significant differences at $P = 0.05$.

mixed with 1.1 M KJ, according to the procedure of Helander (1961). The myofibrillar and sarcoplasmic proteins in mixed breast and leg hot and chilled muscles were determined prior to freezing and then after 21 and 63 days of frozen storage at −18°C. Dynamic viscosity (DV) of homogenized muscles was tested on the Rheo-Viscometer of Höppler (PWM Freital, GDR).

The rheological evaluation was preformed using an Instron Food Tasting Instrument (Table model 1140). For the determination of tenderness the earlier excised whole breast muscles were wrapped in aluminium foil and heated in a grill device, type Turmix AG (Swiss), until the internal muscle temperature reached 90°C. The temperature was monitored with Thermistor thermometers connected to an 'Elab' temperature recorder. Three samples of 25 mm in diameter were punched out from the middle part of each muscle. The samples were weighed with regard to the differences in the muscles thickness. This made it possible to calculate the maximal cutting strength, expressed in Newtons (N), and the work used to cut 1 g meat. The energy used to shear 1 g sample (N × cm) was re-calculated from the surface of the curve registered by the Instron instrument.

The thermal drip was calculated from the differences between the weight of muscles before and after heating. The organoleptic scores for tenderness, juiciness and taste were evaluated by the sensory panel of nine judges using a 5-point scale.

Results and discussion

As shown in Table 1 the initial level of ATP in the breast and leg muscles was 6.8 and 4.3 μmol/g respectively. As early as after 1 hr post mortem, the ATP content decreased approximately three-fold, more evidently in the leg muscles. The 'R' value, i.e. the ratio of adenine to inosine nucleotides, increased to nearly 1, as early as after 30 min, and became stable between the second and fourth hour of rigor. According to the suggestion of Khan & Frey (1971) and

Table 2. Sarcomer's length and their shrinkage* depending on the time of slaughter of chicken

Muscles	Number of birds*	Time after slaughter of birds							
		15 min	30 min	1 hr	1½ hr	2 hr	4 hr	8 hr	24 hr
Breast									
Length (μm)	10	1.94[a]	1.88[ab]	1.81[b]	1.79[b]	1.77[bc]	1.77[bc]	1.82[b]	1.81[b]
Shrinkage (%)	10	—	3.1	6.7	7.7	8.8	8.8	6.2	6.7
Leg									
Length (μm)	8	2.17[a]	2.00[b]	1.90[bc]	—	1.77[c]	1.78[c]	1.92[bc]	2.15[a]
Shrinkage (%)	8	—	7.8	12.7	—	18.5	18.3	8.6	0.1

* Shrinkage in relation to sarcomer length at 15 min after slaughter.
† For the muscle of each bird fifteen measurements were performed.
[a–c] See Table 1.

Table 3. Technological properties of the fresh chicken breast muscles as influenced by the time after slaughter of birds

Technological properties	Number of birds*	Time after slaughter of birds						
		15 min	30 min	1 hr	2 hr	4 hr	8 hr	24 hr
pH value	12	6.14[a]	6.08[a]	5.97[b]	5.80[c]	5.73[c]	5.75[c]	5.75[c]
Water retention capacity (%)	8	159[a]	157[a]	146[a]	130[b]	126[b]	137[b]	135[b]
Fat emulsifying capacity (g oil/g meat)	5	211[a]	217[a]	198[a]	193[a]	188[a]	188[a]	181[a]
Emulsion stability (ml drip/100 g emulsion)	8	45[a]	44[a]	42[a]	47[a]	46[a]	51[a]	45[a]

* For the muscle of each carcass, two to three parallel determinations were made.
[a–c] See Table 1.

Davidek & Velisek (1973) an 'R' value higher than 1 indicates the beginning of rigor. The content of lactic acid increased steadily, more in the breast than in the leg muscles. However, the lactic acid content cannot be used as an indicator of the beginning of rigor mortis.

From Table 2 it can be seen that the sarcomers became a little shorter as early as 15–30 min after slaughter of broilers. However, the most pronounced decrease in sarcomer length was observed in the onset of rigor, between 2–4 hr post mortem, and amounted to 18% in leg and only 9% in breast muscles. From the biochemical and histological investigations one can conclude that the onset of rigor commenced after about 1 hr post mortem in the breast muscle and after 30 min in the leg muscles.

Of the technological properties, only WRC showed a noticeable decrease after 2 hr post mortem. However, FEC and ES did not change significantly during ageing of meat, though the FEC seemed to be best just after slaughter of broilers (Table 3).

Table 4. Technological properties of the mixed chicken breast and leg muscles* as influenced by the time of salting after bird's slaughter

Technological properties	Time of salting				
	40 min	1 hr	1½ hr	2 hr	24 hr
WHC (%)	134[a]	133[a]	123[b]	120[b]	195[c]
Free water (%)	5.7[a]	8.1[b]	9.5[c]	7.4[b]	5.2[a]
Water retention capacity (%)	169[a]	141[b]	140[b]	151[a]	144[b]
Fat emulsifying capacity (g oil/g meat)	200[a]	182[b]	178[b]	198[a]	188[b]
Gel-forming capacity, LCE (% protein)	1.08[a]	0.69[a]	0.65[b]	0.91[a]	0.99[a]
Dynamic viscosity (N.sec/m^2)	14.6[a]	14.4[a]	14.2[a]	12.9[b]	12.7[b]

* For the mixture of muscles from six birds, four parallel determinations were carried out.
[a–c] See Table 1.

The addition of 2.5% of sodium chloride to the minced pre-rigor meat not later than within 40 min after slaughter (earlier salting is impossible in practice) resulted in good technological properties (Table 4). Salting of minced meat later than 40 min after slaughter of the birds decreased some technological properties (WHC, FW, WRC, FEC and DV), so the usefulness of such meat for further processing is evidently lower.

As it can be seen in Table 5, the shear value and thermal drip in hot and chilled brine-injected muscles showed no significant differences. But the thermal drip in control samples—non-chilled, water-injected muscles—was much greater than in the muscles injected with brine. This is an agreement with the beneficial effect of salt on meat tenderness. Hot salted cooked muscles were scored higher in the organoleptic evaluation by a sensory panel than corresponding samples of chilled muscles.

Frozen storage of hot salted broiler meat (frozen at −25°C) had a significant influence on the solubility of meat proteins and its technological characteristics. It is evident from the figures shown in Table 6, that the extractability of myofibrillar and sarcoplasmic proteins by Helander buffer and 2% NaCl solution was significantly higher in the hot, than in chilled, aged meat. On the other hand, during the frozen storage, the content of extractable myofibrillar proteins significantly decreased up to 63 days in the hot salted meat, while in the chilled salted meat the level of extractable myofibrillar proteins increased significantly. It is assumed that this is due to the damage to the structure of muscle fibres in chilled salted meat. It is well known that the better extractability of muscle proteins, particularly their myofibrillar fraction, leads to better technological properties of meat and of meat products.

A higher content of myofibrillar proteins found in the hot meat in comparison

Table 5. Shear values (tenderness) of chicken breast muscles injected with brine* at 15 min after (hot), and at 24 hr after (chilled), and control injected with water within 15 min after slaughter of birds

Kind of sample	Number of birds*	Maximum strength, directly (N)	Maximum strength 1 g of sample (N)	Work (energy) (N × cm) 1 g of sample	Thermal drip (%)
Non-chilled (hot) injected with brine (2.5% NaCl in meat)	12	31.2[a]	4.6[a]	17.9[a]	20.3[a]
Chilled, injected with brine (2.5% NaCl in meat)	12	34.5[a]	5.2[a]	20.4[a]	19.2[a]
Non-chilled (hot) control, injected with water	12	31.5[a]	4.8[a]	19.6[a]	29.3[b]

* Brine concentration = 25% NaCl, 10% brine to the meat weight.

[a–b] Figures in the *columns* marked with various letters demonstrate statistically significant differences at $P = 0.05$.

Table 6. Effect of frozen storage on the solubility of sarcoplasmic and myofibrillar proteins of hot and chilled, mixed chicken breast and leg muscles,* per cent to total proteins

Time of storage at −18°C (days)	Kind of protein							
	Sarcoplasmic				Myofibrillar			
	Helander buffer†		2% NaCl in water†		Helander buffer		2% NaCl in water	
	40 min‡	24 hr‡	40 min	24 hr	40 min	24 hr	40 min	24 hr
0§	29.4[a]	21.3[a]	24.2[a]	17.8[a]	54.8[a]	27.7[a]	10.5[a]	7.2[a]
21	21.1[b]	18.5[a]	19.4[b]	14.7[a]	33.5[b]	42.2[b]	8.7[a]	14.7[b]
63	11.9[c]	8.4[b]	11.9[c]	4.7[b]	35.5[b]	45.7[b]	9.6[a]	21.8[c]

*For the mixture six birds, four parallel determinations were carried out.
†Methods of extraction.
‡Times after slaughter of birds that meat was taken for analysis—40 min (hot), 24 hr (chilled).
§Control, non-frozen.
[a–c]See Table 5.

with the chilled meat (Table 6) may be attributed to the presence of 'free' myosin and 'free' actin in hot meat, not complexed as actomyosin.

In Table 7, WHC, FW and FEC showed lower values during frozen storage of both hot and chilled salted meat. However, the WRC remained unchanged and GFC even demonstrated some increase after 50 days of frozen storage. This indicated that the technological properties of such meat after cooking could be preserved after cooling.

Table 7. Effect of frozen storage on the technological characteristics of hot and chilled salted, mixed chicken breast and leg muscles*

Technological characteristics	Time of salting after slaughter					
	40 min (hot meat)			24 hr (chilled meat)		
	0†‡	21†	49†	0‡	21	49
WHC (%)	134[a]	77[b]	66[c]	195[d]	70[bc]	68[c]
Free water (%)	5.7[a]	8.3[b]	10.1[c]	5.2[ad]	7.9[d]	8.7[bc]
Water retention capacity (%)	169[a]	170[a]	181[a]	144[b]	155[b]	145[b]
Fat emulsifying capacity (g oil/g meat)	200[a]	190[b]	183[c]	137[bcd]	139[e]	130[f]
Gel-forming capacity, LCE (% protein)	1.08[a]	0.98[b]	0.94[bc]	0.99[bd]	0.92[cde]	0.89[ef]
Dynamic viscosity (N s/m²)	14.6[a]	13.3[b]	11.2[c]	12.7[d]	13.7[be]	13.9[e]

*For the mixture of muscles from six birds, four parallel determinations were carried out.
†Times of frozen storage at −18°C (days).
‡Controls, non-frozen.
[a–f]See Table 1.

It was proved in some additional investigations that rapid freezing at −50°C of hot salted chicken meat resulted in an improvement of its technological properties.

It may be generally concluded that the minced, hot salted and frozen poultry meat is a good raw material for processing of various meat products. However, favourable technological properties of such meat will be limited by the time of frozen storage.

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The use of hot salted chicken meat for processing

J. KIJOWSKI, J. PIKUL AND A. NIEWIAROWICZ

Summary

Frankfurter-type sausages and meat rolls were prepared from chicken broiler breast and leg muscles, the former from comminuted breast and leg muscles salted pre-rigor within 40 min, the latter from breast and leg muscles separately injected with brine 15 min after slaughter. Their properties were compared with those of similar products made from chilled meat.

Introduction

Little information can be found concerning the use of hot poultry meat for further processing. Nixon & Miller (1967) and Kardouche & Stadelman (1978) proved at the yield of rolls manufactured from hot turkey meat was higher by about 1% than from chilled, aged meat. The rolls from hot meat showed higher shear values, but in the organoleptic evaluation the rolls from hot turkey meat were scored higher than those from chilled meat.

Froning & Neelakantan (1971) observed that pre-rigor poultry muscles produced extremely rubbery emulsions and the histological examination further indicated that such emulsions produced more uniform fat globules than those emulsions from post-rigor muscles. Hale & Mayfield (1976) reported that the yield of meat from hot, cooked, hen carcasses was about 1.26% higher than from those cooked after chilling. The shear value of hot cooked breast muscles was slightly higher, but in the leg muscles no differences in shear force between the hot and chilled process were found. The authors concluded that the elimination of chilling of hen carcasses used for further production of various ready-to-eat products, should bring about benefits for the producers.

In contrast, Wardlaw, McCaskill & Acton (1973) found higher yields of meat loafs manufactured from broiler meat, chilled and aged for 24 hr, than of those from hot meat, used 30 min after slaughter of the birds.

The aim of the investigations presented here was to verify the usefulness of

Author's address: Institute of Animal Products Technology, Agricultural University of Poznań, ul. Wojska Polskiego 31, 60-624 Poznań, Poland.

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hot chicken broiler meat for manufacturing of products such as frankfurter sausages and so-called chicken rolls.

Materials and methods

From the pre-rigor hot breast and leg muscles, comminuted and salted (2% NaCl + 0.015% $NaNO_2$) within 40 min post-mortem, and from the control chilled muscles, excised, comminuted and salted 24 hr post-slaughter, model frankfurter-type sausages were made. There are two types of model sausages: The meat mixture of the first type of sausage contained 36% chicken meat, 29% fat (pork jowl) and 28% added water. The formulation of second type of sausage was as follows: 46% chicken meat, 21% fat and 23% added water.

The components for sausage production were cuttered for 8 min. The synthetic protein casings of 35 mm diameter were filled with the meat mixture and were hot smoked for 70 min. The sausages were heated afterwards in a water bath at 70–72°C for 20 min to an internal temperature of 69–70°C which was monitored with Thermistor thermometers connected to an 'Elab' temperature recorder. After heating the sausages were chilled in tap water and stored at 5°C.

The meat rolls were manufactured from intact, pre-rigor excised chicken breast and/or leg muscles. The excised breast and leg muscles were injected within 15 min, and the chilled ones within 24 hr post-slaughter, with a 20% NaCl solution amounting to 10% of muscle weight. With the brine 150 mg $NaNO_2$/100 g meat were injected. Twenty per cent of the cured muscles were ground, using a 3 mm plate, cuttered with seasonings, had 20% water added, and finally 1% egg white was added. One half of the remaining cured muscles were cut into pieces of about 30–40 mm. All samples were 'massaged' in a mixer. Synthetic protein casings of 65 mm diameter were filled with this meat mixture, hot smoked for 90 min, and heated afterwards in a water bath at 75°C until the interior temperature reached 69–70°C. The temperature was monitored in the same manner as in sausage production. After chilling in tap water, the rolls were stored at 5°C.

In frankfurters and in rolls some of their technological, rheological and organoleptic properties were evaluated. The rheological measurements were performed on Instron food testing instruments, Table Model 1140, with accessories. The shear values were calculated as a maximal strength, expressed as a work (energy) for shearing 1 g meat sample (N × cm). Strain, Ls/Lp, expresses the ratio of energy needed to cause elastic deformation to the energy used to produce plastic deformation of sausage sample.

Results and discussion

The frankfurters from mixed breast and leg muscles showed a higher yield of about 2% than those made from control, chilled meat (Table 1).

Table 1. Percentage yield of chicken frankfurters and rolls calculated on the next day after production in relation to the weight of cured meat

Kind of sample	Hot meat (%)	Chilled meat (%)
Sausage I	122.1	119.6
Sausage II	117.9	116.5
Rolls from breast meat	100.3	99.3
Rolls from leg meat	98.1	97.5

Table 2. Shear values (tenderness) and resistance to deformation (strain) of model frankfurter-type sausage manufactured from hot and chilled, mixed, chicken breast and leg muscles

Types of sample meat	Maximal strength directly (N)		Work (energy) 1 g of sample (N × cm)		Strain (Ls/Lp)	
	Hot*	Chilled†	Hot	Chilled	Hot	Chilled
Sausage I	6.5^{a}	5.4^{b}	26.3^{a}	20.4^{b}	0.97^{a}	0.80^{a}
Sausage II	5.4^{a}	6.5^{a}	23.1^{a}	26.3^{a}	0.61^{a}	0.62^{a}

*Hot meat, ground and salted within 40 min after slaughter of birds.

†Chilled meat, ground and salted within 24 hr after slaughter of birds.

$^{a-b}$Figures in the *rows* marked with various letters demonstrate statistically significant differences at $P = 0.05$.

In Table 2 the summarized results of sausage consistency (texture) are presented.

The shear value significantly depended on the composition of the sausage mixture. The higher content of fat, and in particular of water, resulted in better binding ability of fat and water after cooking. In the first type of sausage from hot meat the maximal strength and the total energy used to shear the sample were significantly ($P = 0.05$) higher, than in the second type of sausage with the lower content of fat and water (Table 2). Moreover, in the case of the second type of sausage the maximal strength and the values of shear energy were slightly higher for the product manufactured from chilled aged meat, but the differences were not significant.

It was found also that the higher amount of water added to the meat mixture in a cutter-mixer increased the resistance to deformation in the ready-to-eat sausage. In the general sensory evaluation the frankfurters from hot meat were scored higher than those from chilled meat. This was probably due to the greater juiciness of that sausage.

In the rolls manufactured from hot breast or leg meat a higher yield, by about 1%, was noticed as compared with the controls made from chilled meat. The

Table 3. Shear values (tenderness) of model rolls from chicken meat injected with brine* within 15 min (hot) and 24 hr (chilled) post-slaughter

	Maximal strength directly (N)		Work (energy) (N × cm) 1 g of sample	
Types of sample meat	Hot	Chilled	Hot	Chilled
Rolls from breast meat	9.8[a]	7.8[b]	34.4[a]	26.2[b]
Rolls from leg meat	9.8[a]	9.2[a]	31.6[a]	28.3[a]

*Brine concentration = 20% NaCl, 10% of brine to the meat weight.
[a–b]See Table 2.

Table 4. Summary of triangle test of roll tenderness after one day of storage

Sample		Judges (n)	Correct (n)	Significance at $P = 0.05$
Rolls from breast meat	Hot-chilled	9	2	Not significant
Rolls from leg meat	Hot-chilled	9	3	Not significant

yield of rolls produced from both hot and chilled breast muscles was about 2% higher than that made from leg muscles (Table 1).

As shown in Table 3, the rolls from hot breast muscles had significantly higher shear values than those from chilled breast meat, but for rolls made from leg muscles the differences in the shear force was not significant. The organoleptic triangle test, performed on the day following the production of the rolls, demonstrated no significant ($P = 0.05$) difference in tenderness as affected by hot and/or chilled meat, as well as by the type of meat (Table 4). However, after 5 days of storage at 5°C the tenderness, colour, juiciness and binding capacity of slices were scored higher in rolls from hot meat, manufactured both from breast and leg muscles than in those made from chilled meat.

The authors consider that the use of hot meat from chicken broilers and hens should bring about considerable benefits in poultry products technology. They may be attributed mainly to the higher yield of ready-to-eat product without lowering its quality. Moreover, the energy and water used for chilling poultry can be conserved. However, the operations of rapid carcass de-boning and grinding, and salting of meat require good training of workers employed. In the case of brine injection method some investment will be required for the multi-needle brine pumping device.

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Indirect measurement of the fat content of beef mince using the Infra-Tester

J. C. CASEY AND A. R. CROSLAND

Summary

A technique for the indirect estimation of the fat content of beef mince by the direct measurement of moisture content was evaluated. Samples of commercially produced beef mince ranging from 7 to 25% fat were analysed for moisture content using infra-red heating, and for fat and moisture content by standard laboratory procedures. Moisture content measured by infra-red heating using the Infra-Tester was highly correlated with fat content measured by the standard method and could be used as a rapid and inexpensive method of predicting the fat content of beef mince.

Introduction

In recent years public analysts have expressed concern at the sale of minced meat with an excessive fat content (Anon, 1978). Prosecutions based on high fat content have shown that there is a need for a cheap, reliable method of determining the fat content of minced meat at the retail level which would meet the requirements of both small butchers and supermarkets. Standard laboratory methods are unsuitable because they require laboratory facilities and are slow and expensive.

In a review of methods for fat and moisture analysis of meat and meat products Pettinati, Swift & Cohen (1973) selected a number of rapid methods for quality control in the meat industry. Some of these involved standard laboratory procedures such as acid digestion and solvent extraction and hence are unsuitable for use in premises retailing foodstuffs. Other methods involved the use of instruments such as the Anyl-Ray, Foss-let and Neotec which are specially designed for rapid fat measurement and as a consequence tend to be rather expensive. The most promising of the methods available for the estimation of moisture in meat were those using infra-red heating which were both rapid and accurate. This suggested that the Infra-Tester, widely used to

Author's address: ARC Meat Research Institute, Langford, Bristol BS18 7DY.

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measure the moisture content of materials such as grain and flour, might be suitable for the rapid analysis of minced meat.

Previously Callow (1962) studying the moisture and fat content of meat from dissected carcasses, observed that the water content of fatty tissue was almost entirely dependent on the percentage of fat in the tissue and that the percentage of water in lean tissue decreased as the percentage of fat increased. Using published data from carcasses which had been handled commercially he showed that there was a simple relationship between fat and water in the total boneless meat from whole carcasses. From this relationship it appeared that it should be possible to predict the fat content of meat by measuring the moisture content, and that the Infra-Tester might be suitable for this purpose. Accordingly, the following experiments were carried out to evaluate its precision and accuracy when used in this way.

Materials and methods

The Infra-Tester consists of a sensitive chain balance and an infra-red heating lamp. The weighing pan has a large surface area, allowing the sample to be distributed in a thin layer to ensure rapid drying. Weighing is simplified by the adjustable scale which covers the range 0–10% moisture; the range can be extended to 100% by using the extra weights provided. The drying time depends on the moisture content of the material under test: for beef mince two drying times 30 and 40 min were investigated.

In a preliminary investigation eight samples of beef mince containing known amounts of added fat were prepared in the laboratory by the following procedure. Meat was passed twice through a mincer fitted with a plate with holes of diameter not exceeding 4 mm. The minced meat was thoroughly mixed and replicate samples taken for analysis. Samples were freeze dried and the fat content determined by extraction with 40–60° petroleum spirit. Moisture was determined by drying to constant weight in a vacuum oven at 70°. Replicate samples were also analysed using the Infra-Tester.

Commercially produced samples of beef mince were also analysed by both methods. By arrangement with a local supermarket, retail samples were taken on the day of manufacture and sub-sampled as quickly as possible. Additional samples were bought locally from butchers' shops. These samples were not pre-packed and may have suffered some evaporative loss before purchase. Samples were collected from seventeen retail outlets and only those products described as minced beef or beef mince were purchased.

Results and discussion

The precision and accuracy of the Infra-Tester for measuring the moisture content of beef mince was studied using two sub-samples from each of eighteen samples of beef mince and a drying time of 30 min. A typical drying curve is

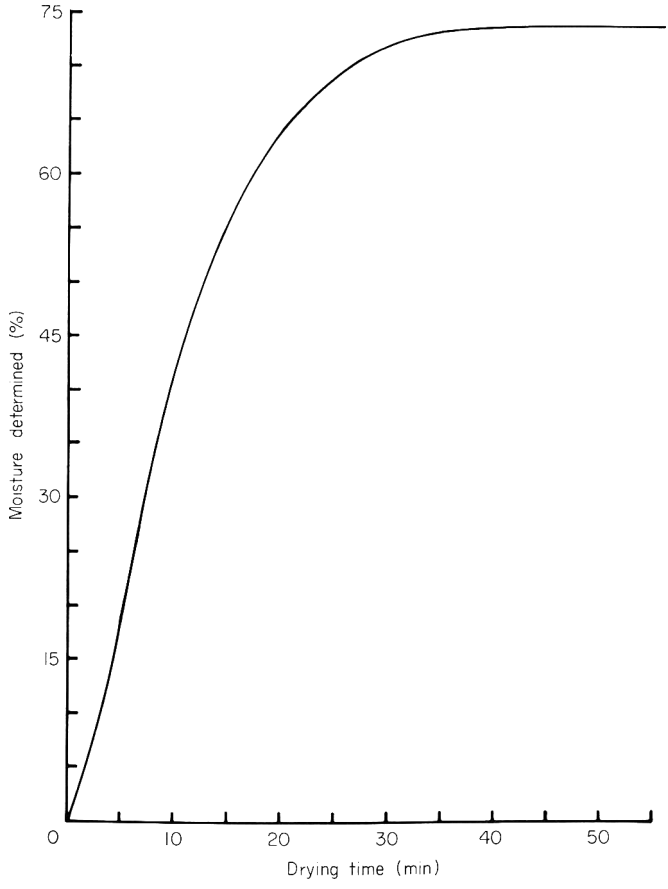

Figure 1. Drying curve for determination of percentage moisture in product as determined by the Infra-Tester.

shown in Fig. 1. Analysis of the variation between samples and within duplicate sub-samples showed that it was possible to estimate the mean of a sample from two sub-samples with a standard error of 0.45 giving 95% confidence limits about the mean of 0.96. There was no significant difference between the Infra-Tester and the standard method for the determination of moisture content (Table 1).

The predictive value of moisture content as measured by the Infra-Tester for the estimation of fat content was assessed. Analysis of forty-nine samples using at least two sub-samples from each batch of beef mince showed that percent moisture content measured by the Infra-Tester was highly correlated with percent fat measured by the standard method (Table 2) and that there was very little difference between results for 30 and 40 min drying times.

The theoretical 95% confidence limits for a predicted meat fat percentage of around 25% are approximately ± 3%. The line of best fit to the data (Fig. 2) for a drying time of 30 min is expressed by

$$\% \text{ Fat} = 87.39 - (1.127 \times \% \text{ moisture}) \quad (1)$$

Table 1. Moisture content of minced beef samples

Sample	Infra-Tester (30 min) (% moisture)			Standard method (% moisture)
	A	B	Mean	
1	69.3	69.3	69.3	70.1
2	65.5	67.1	66.3	65.0
3	70.2	71.3	70.8	70.4
4	70.2	69.6	69.9	70.3
5	60.3	59.7	60.0	60.0
6	60.4	59.3	59.9	59.5
7	59.8	60.0	59.9	60.8
8	59.2	59.1	59.2	59.9
9	57.9	58.7	58.3	59.6
10	57.7	59.9	58.8	59.9
11	59.7	60.3	60.0	60.3
12	63.7	63.8	63.8	63.9
13	68.7	68.0	68.4	69.0
14	69.2	68.8	69.0	68.4
15	69.0	69.4	69.2	67.9
16	66.1	65.6	65.9	65.6
17	64.7	65.0	64.9	65.7
18	63.7	62.5	63.1	64.1

Standard error of the mean = 0.45.

and could be used in this form for prediction of fat content. Callow (1962) established the relationship

$$\% \text{ Moisture} = 77.0 - (0.77 \times \% \text{ fat}) \quad (2)$$

based on data derived from dissected beef carcasses which covered a much wider range of fat levels than the present study. If applied to the values obtained in this study, Equation (2) would give a higher estimate of fat content than Equation (1), based on data mainly derived from commercially produced beef mince with a fat range of 7 to 25%.

In addition to Callow's observations, Lawrie (1974) stated that both the percentage water and the nitrogen content of lean muscle from mature animals

Table 2. Regression of percent fat on percent moisture

Methods	Residual standard deviation	Correlation
Infra-Tester (30 min)	1.21	− 0.97
Infra-Tester (40 min)	1.22	− 0.97
Standard	0.86	− 0.98

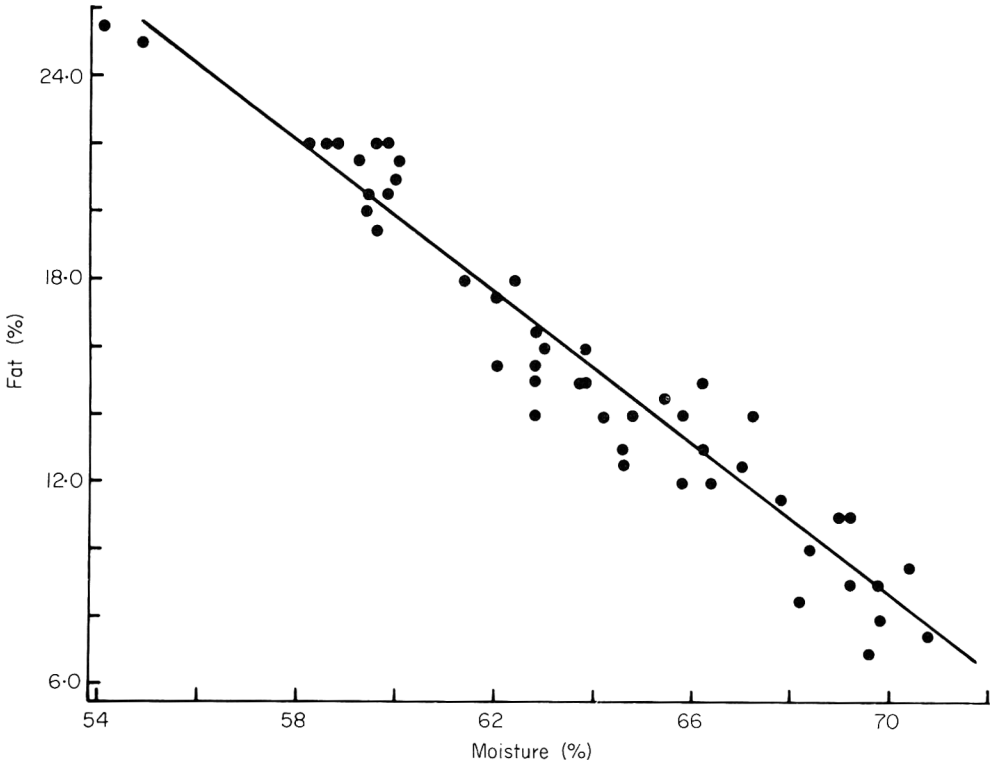

Figure 2. Percentage fat determined by standard method *versus* percentage moisture determined by the Infra-Tester.

is relatively constant for several species including sheep, pig and ox. Reid *et al*. (1967) concluded that for sheep, pigs and cattle, 97–98% of the variation in fat content is associated with the variation in water content, while Karmas, Thompson & Wistreich (1961) using fat/lean mixtures prepared in the laboratory established a correlation between pork leanness and moisture content.

The relationship between fat and moisture content of beef mince would be affected by the inclusion of poor quality meat or meat from very young animals whose carcasses have comparatively high moisture and low fat levels, or from animals suffering from any condition which might cause excessive fatness or excessive water retention. If substantial amounts of such meat were present in beef mince the application of Equation (1) would lead to erroneous results. The relationship would also be affected by the presence of added materials such as carbohydrate or meat extenders, and products containing such materials would be unsuitable for analysis by this method. The presence of any extraneous moisture would seriously affect the accuracy of the method. When using the Infra-Tester attention must be paid to the following points during use otherwise the accuracy is affected.

Drying time. If this is less than 30 min, the sample weight changes too quickly

to permit accurate weighing, whilst if more than 40 min further loss of weight may occur due to changes such as sample decomposition and oxidation.

Sampling. The material to be tested must be sampled as soon as possible after manufacture. The weight of sample must be between 4.5 and 5.0 g and must be spread evenly in a thin layer to ensure uniform drying. Spreading of the sample and initial weighing should take place within a period of 1 min to avoid changes in the moisture content.

Environment. The instrument should be situated on a flat, level surface, free from draughts and vibrations.

Apart from these restrictions the Infra-Tester appears to be suitable for the indirect measurement of fat in beef mince.

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The relationship between pH_{45} and drip in pig muscle

P. D. WARRISS

Summary

The relationship between pH_{45} and drip loss from the *M. longissimus dorsi* (LD) was examined using data collected from 433 pigs of various breeds. In pork with a pH_{45} <6.1 a high but relatively constant weight of drip was produced in storage; above 6.1 the water holding capacity improved and, with higher pH_{45}, correspondingly smaller weights of drip were lost. Assuming that the amount of drip from the LD is related to that from the whole carcass, and based on recent published survey data on pH_{45} in British cross-bred pigs, the cost of the incidence of PSE in the U.K. can be estimated as 2.2% of the value of the weight of lean in all pigs slaughtered.

Introduction

Weight loss through exudate or drip is economically the most important meat quality trait in pigs (Lundstrom, Nilsson & Malmfors, 1979). The amount of drip produced from muscles ranges from 1 to about 14% and the variation is generally attributed to different degrees of denaturation of the proteins caused by the rate and extent of pH fall after death (Penny, 1977). If a low pH is reached in the muscles while the carcass is still warm, a relatively large amount of exudate is lost from cut surfaces of the meat. However, there appears to be some disagreement about the relationship between the water holding capacity (WHC) of muscle and the rate of glycolysis immediately after slaughter as measured by the pH at 45 or 90 min post mortem (pH_{45} and pH_{90}).

Wismer-Pedersen (1959) found that at pH_{45} values between 6.2 and 6.8 there was good correlation between pH_{45} and WHC while below 6.2 the correlation was poor and non-significant. He concluded that below pH 6.2 the pH_{45} had only a slight effect on the WHC while above 6.2 it had considerable effect. In contrast, Penny (1969) from studies of the WHC of myofibrils, stated that at pH_{90} values above 6 the amount of exudate from muscles was likely to be small

Author's address: ARC Meat Research Institute, Langford, Bristol BS18 7DY.

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but, as the pH fell below 5.9, the exudation would become increasingly greater. In other words, although it is agreed that an initial pH of below about 6 leads to more exudate, it is not clear whether below this point lower pH values are associated with increasingly more exudate (Penny, 1969) or whether the WHC remains relatively constant and does not decrease further with decreasing pH (Wismer-Pedersen, 1959).

Therefore, the relationship between pH_{45} and drip loss from the *M. longissimus dorsi* (LD) has been examined using data collected from 433 pigs slaughtered in various experiments at the Meat Research Institute. Since the amount of variation in WHC or drip reported to be explained by variation in the ultimate pH (pH_u) in pig muscle has ranged from 0 to 37% (Wismer-Pedersen, 1959; Vetterlein & Kidney, 1965; Herring, Haggard & Hansen, 1971; Martin, Fredeen & L'Hirondelle, 1975; Walstra, Jansen & Mateman, 1976; Lundstrom *et al.*, 1979) the effect of the pH_u on drip loss was also investigated.

Materials and methods

The pigs came from several breeds. There were 171 Large White, 159 Landrace and forty-two Pietrain pigs represented in the sample, the remaining animals being crosses. The pH and drip were measured on samples of the LD taken in the loin region. The pH was measured on homogenates of muscles in 5 mM sodium iodoacetate, 150 mM potassium chloride, pH 7.0 at 45 min and 24 hr post mortem. Drip loss (percentage drip) was estimated on slices 1.0–1.5 cm thick cut across the long axis of the muscle 24 hr post-mortem and hung individually in netting bags inside inflated polythene bags for 72 hr at 1°C.

Results

Values of pH_{45} ranged from 5.34 to 7.16, pH_u from 5.10 to 5.90 and drip from 2.6 to 21.0%. The data were initially grouped into subsets corresponding to pH_{45} values lying within intervals of 0.19 units and pH_u values lying within intervals of 0.09 units. The frequency distributions of pH_{45} and pH_u values are shown in Fig. 1 and the relationships between percentage drip and pH_{45} and pH_u in Fig. 2.

The relationship between pH_{45} and percentage drip was biphasic. Below a value of 6.1, decreasing pH_{45} had no significant effect on the weight of drip lost. The regression equation calculated from the 106 samples with $pH_{45} < 6.1$ was

$$\text{Percentage drip} = 16.0 - 0.37\ pH_{45} (r = -0.04, \text{N.S.})$$

and the residual variance exceeded that of the y variate. Above a value of 6.1, increasing pH_{45} resulted in decreased drip. The regression equation calculated from 327 samples with $pH_{45} \geqslant 6.1$ was

$$\text{Percentage drip} = 66.5 - 8.61\ pH_{45} (r = -0.68, P < 0.001).$$

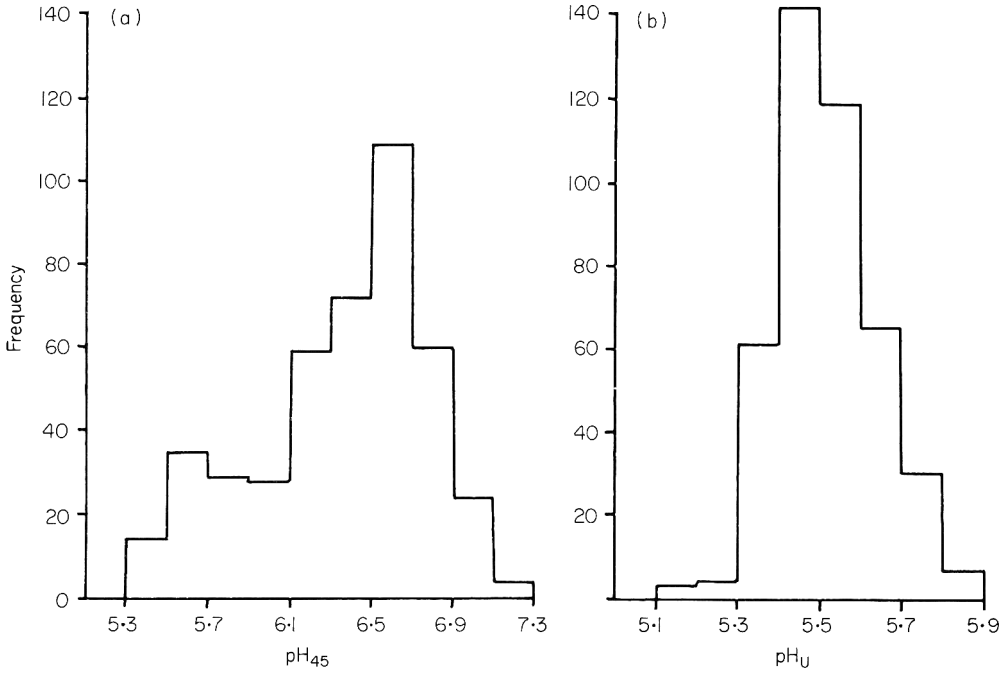

Figure 1. Frequency of (a) pH_{45} and (b) pH_u in 433 pigs sampled.

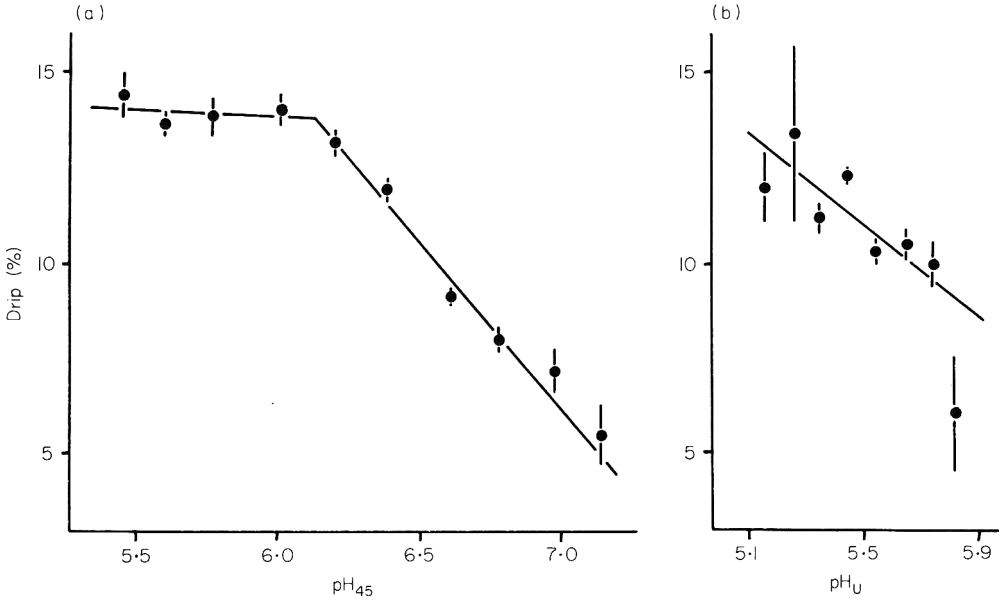

Figure 2. Relationship between percentage drip and (a) pH_{45} and (b) pH_u. The points are the means of the grouped data and the intervals are 0.19 units for pH_{45} and 0.09 units for pH_u. The regression lines were drawn from equations calculated from the ungrouped data. Vertical bars represent standard errors.

The regression accounted for 45.8% of the variation in percentage drip. The two regression lines are plotted in Fig. 2(a). They intersect at pH 6.14 corresponding to 13.7% drip.

Drip also significantly decreased with increasing pH_u. The overall regression equation was

Percentage drip = 45.1 − 6.19 pH ($r = -0.24$, $P < 0.01$).

Variation in pH_u only accounted for 5.5% of the variation in drip and including pH_u in a multiple regression with pH_{45} resulted in no significant improvement in the amount of variance in drip accounted for in samples with a pH_{45} either below or above 6.1. Samples with higher pH_{45} also tended to have higher pH_u, and pH_{45} and pH_u were significantly, though poorly, correlated ($r = 0.25$, $P < 0.01$). Thus, over the range of pH_u encountered, samples with high pH_u produced less drip because they also had higher pH_{45} rather than as a result of any direct effect of pH_u on WHC.

The data from 372 pure-bred pigs were used to examine the effect of breed on the relationship between pH_{45} and drip. There were differences between the breeds in the distribution of pH_{45} values (Table 1). Three Large White pigs had a $pH_{45} < 6.1$, 39% of Landrace pigs had $pH_{45} < 6.1$ and 71% of Pietrains had $pH_{45} < 6.1$. The small number of Large White pigs with $pH_{45} < 6.1$ and Pietrains with $pH_{45} \geq 6.1$ precluded separate analysis but individual regressions were calculated for Landrace and Pietrain pigs with $pH_{45} < 6.1$ and Large White and Landrace pigs with $pH_{45} \geq 6.1$.

For carcasses with $pH_{45} < 6.1$ the regression equations were

Percentage drip = 16.9 − 0.54 pH_{45}; $r = -0.05$ (N.S.) (Landrace)

and

Percentage drip = 16.4 − 0.44 pH_{45}; $r = -0.04$ (N.S.) (Pietrain).

For carcasses with $pH_{45} \geq 6.1$ the regression equations were

Percentage drip = 66.4 − 8.65 pH_{45}; $r = -0.65$ ($P < 0.001$) (Large White)

and

Percentage drip = 67.4 − 8.74 pH_{45}; $r = -0.64$ ($P < 0.001$) (Landrace).

Table 1. Numbers of pigs with $pH_{45} < 6.1$ or ≥ 6.1 in three breeds

	pH_{45}	
Breeds	< 6.1	≥ 6.1
Large White	3	168
Landrace	62	97
Pietrain	30	12

There were no significant differences in slope or position of the regression lines between the compared breeds for $pH_{45} < 6.1$ or ≥ 6.1.

Discussion

The results for the relationship between pH_{45} and drip agree exactly with those of Wismer-Pedersen (1959). In pork with a $pH_{45} < 6.1$ a high but relatively constant weight of drip is produced in storage; above 6.1 the WHC improves and, with higher pH_{45}, correspondingly smaller weights of drip are lost. The differences between the results presented here and the conclusions of Penny (1969) may be attributable to the latter author's use of extracted myofibrils, rather than whole muscle, since it is likely that factors in addition to denaturation of muscle proteins (both myofibrillar and sarcoplasmic) influence the amount of drip produced from muscle to a fairly large degree (Penny, 1977). From the limited data available there was no evidence of breed differences in the relationship between pH_{45} and drip.

Although a significant relationship between pH_u and drip was found this was most likely due to the observed correlation between pH_{45} and pH_u. None of the samples of meat in this study had a $pH_u \geq 6.0$ however, and a direct effect of pH_u on drip may occur above 6.0 resulting in the characteristic dry appearance of dark, firm, dry (DFD) pork.

In a recent survey of meat quality in British cross-bred pigs Evans, Kempster & Steane (1978) found that 7.8% of animals had a pH_{45} below 6.0 in the LD. The mean pH_{45} for all pigs in their sample was 6.41 and this agrees fairly well with results from other surveys of the British pig population (Kempster & Cuthbertson, 1975; Smith *et al.*, 1976). For those pigs with a $pH_{45} \geq 6$ the mean pH_{45} can be calculated from their data to be 6.47 and for those pigs with a $pH_{45} < 6$, 5.81. Assuming that the amount of drip from LD is related to that from the whole carcass (Taylor & Dant, 1971), then, from the regression equations relating pH_{45} and drip, it can be calculated that the extra drip lost from the pigs with a $pH_{45} < 6$ amounts to 28.3% of that lost from a 'normal' carcass with pH_{45} 6.47. For a population of pigs with 7.8% having $pH_{45} < 6$ then 2.2% more weight as drip will be lost than if all animals had $pH_{45} \geq 6$. Based on the survey of Evans *et al.* (1978) the cost of the incidence of PSE in the U.K. can therefore be estimated as 2.2% of the value of the weight of lean in all pigs slaughtered.

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Dried milk powder containing fluoride

C. G. BEDDOWS* AND V. N. WADE†

Summary

A milk powder was prepared from a skim milk containing 10 p.p.m. fluoride. The powder showed that the size of the powdered milk particles produced were not affected by the presence of the fluoride. The fluoride in the reconstituted milk existed in at least two reversible ionic equilibria and all of it could be recovered as 'free' fluoride after precipitation of the protein. The fluoride was evenly distributed throughout the range of milk particles, and thus mechanical handling and particle segregation would not produce unequal concentration of fluoride in a stored milk powder. The fluoride did not change its status even after 2 years storage.

Introduction

Fluoride in cows milk has been used as a prophylactic measure for dental caries (Ziegler, 1964; Konikoff *et al.* 1962).

In certain circumstances the use of a dried milk powder that contained fluoride would have advantages over liquid milk, this would particularly apply to areas where milk fluoridation could not be carried out without adequate supervision, or to areas that are geographically remote from a fresh milk supply.

The status of fluoride added to cold milk has been examined and it was shown that the fluoride was in a simple reversible ionic complex (Beddows & Blake, 1982). However, when milk containing fluoride was pasteurized by a number of different commercial processes, the heat treatment caused a change in that some of the fluoride became more firmly bound, but it remained in more than one reversible ionic complex mainly with the whey proteins (Beddows, 1982).

A level of 5 or 10 p.p.m. fluoride in milk was advocated as a prophylactic measure (Borrow, 1971), so that a 200 ml drink provided an adequate daily intake.

Authors' addresses: *School of Health & Applied Sciences, Leeds Polytechnic, Leeds LS2 3HE, and †Department of Dairy Technology, West of Scotland Agricultural College, Auchincruive, Ayr KA6 5HW.

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For the present work, 10 p.p.m. was taken as the standard level, which is likely to be the maximum to be used. Any effects found at 10 p.p.m. are likely to be reduced at lower concentrations.

It is important that if a fluoride-containing milk powder were to be used, then the fluoride should be readily available for absorption in an ionic form, and not in a covalent complex having unknown or little investigated physiological properties. It is also important with such milk powders, that the fluoride should be evenly distributed throughout the particle size range of the powder, otherwise the handling of large packages (e.g. 25 kg bags) could result in a size separation of the particles, with the production of an uneven distribution of the fluoride. The amount of the ion subsequently imbibed would then be affected by the position in the pack from which the powder was taken, thus giving rise to the possibility of reduced and perhaps larger doses of the fluoride on ingestion.

Materials and methods

Preparation of spray-dried milk containing fluoride

Preliminary experiments were carried out in which 1 l of raw skim milk was added to 20 ml sodium fluoride solution (0.22% w/v) containing approximately 5 m Ci of ^{18}F (MRC Cyclotron Unit, Hammersmith Hospital, London). The mixture was stirred and heated at 65°C for 30 min, followed by concentration under recycle conditions in a steam-heated Quickfit and Quartz laboratory climbing film evaporator at an average boiling temperature of 63.5°C and pressure of approximately 23.5 kN/m^2 absolute.

The concentrate was withdrawn from the evaporator at approximately 30% refractometric solids content and fed into an electrically heated Niro Mobile Minor spray drier using a peristaltic pump at a feed rate of 1 $l\,hr^{-1}$ and a temperature of 45°C. The spray drier had been previously brought to a steady operating condition using distilled water and the fluoridated milk was dried with a centrifugal wheel atomizer and average air inlet and outlet temperatures of 185 and 85°C respectively.

A control sample of skim milk powder was prepared in a similar manner but without the addition of fluoride to the raw milk. Both the reconstituted powders were subjected to the precipitation method of Beddows & Kirk (1981) and the recovery of ^{18}F was compared with an aqueous solution of sodium fluoride (with ^{18}F) at the same concentration. The fluoride-containing skim milk powder and the control sample were sieved (Endecott EFL 1 Mark 11) to obtain a range of particle size fractions for subsequent radiofluoride analysis.

Further experiments were carried out at a pilot-scale level using approximately 37 kg of raw skim milk prepared by separation in an Alfa laval 29 AE/63 disc-bowl centrifuge. After sampling, the skim milk was added to a stock solution of aqueous sodium fluoride (0.221% w/v) to give a mixture containing 10 p.p.m. of fluoride and a sample was taken. The fluoridated skim milk was pasteurized at 65°C for 30 min using hot water-operated in-can 'whirling tube'

heater, followed by immediate cooling to just above 30°C with a chilled water supply. The pasteurized milk was sampled for analysis.

The warm fluoridated skim milk was transferred to a Scott single effect, submerged tube evaporator heated by a steam supply in the pressure range 39.5–69.0 kN/m² gauge pressure (5–10 p.s.i.g.). The evaporation was carried out under vacuum with boiling temperatures in the range 27.8–31.1°C until a refractometric solids reading of 35% was obtained. After removing a sample portion, the concentrate was discharged from the evaporator and fed to a direct gas fired Spray Processor/Becker tall-form drier using a Rannie (1.80198) variable speed triple-acting homogenizing pump with recycle flow control. The average feed pressure to the Spray nozzle was 15 170 kN/m² gauge pressure (2200 p.s.i.g.) and the air inlet temperature was held in the range 182 to 185°C with a steady air outlet temperature of 85°C.

Very little powder was retained on the drying chamber wall. The cyclone and chamber powders were thoroughly mixed prior to sampling for chemical analysis. The 'free' fluoride was determined at each stage of the process by using an Orion fluoride ion-selective electrode model 94–09, with an Orion Model 09–01 reference electrode in conjunction with a Corning–EI1 Digital 110 expanded scale meter.

A control sample of fluoride-free skim milk powder was prepared in a similar manner.

Examination of the powder

The powder was dried to constant weight at 102 to 103°C (B.S. 1743: 1980) and the moisture content was determined.

The lipid content of the powder was determined by extraction with ether and petroleum ether according to B.S. 1743: 1980.

The total fluoride content was determined by the method of Beddows & Kirk (1981).

The particles size distribution was determined by sieving a 250 g protein for 30 min with an Endecott Test sieve shaker (EFL 1 Mark 11). Each fraction was analysed for free and for total fluoride, as above.

The tendency of the powder to settle into different particle sizes and possibly cause a change in the concentration of the fluoride was determined by subjecting 5 g portions of the dried powder in a stoppered test tube ($14 \times 2\frac{1}{2}$ cm) to a variety of weak mechanical shaking motions, including horizontal, vertical and circular, for periods up to 4 hr at room temperature and then removing 1 g from the top and 1 g from the bottom of the tube and analysing the samples for total fluoride according to the method of Beddows & Kirk (1981).

Examination of the reconstituted milk

A portion of the initial milk powder containing ^{18}F (2.405 g) was added to de-ionized water (25 cm³), with gentle stirring for a period of 30 min. The reconstituted milk was examined further.

Standing at 4°C. Two test tubes containing 10 ml portions were maintained at 20°C for 4 hr. The tubes were then analysed according to the method of Beddows & Blake (1982) when a sample (2 ml) was carefully removed from the top, and then two further 2 ml samples were removed from the surface of the milk, and finally a 2 ml sample from the bottom of the tube. Each sample removed was transferred to a standard glass vial, and the radioactivity of each was measured using a Panax scintillation counter type D657 (Panax Ltd, Redhill, Surrey).

Centrifugation at 6000 g for 20 min. Tubes containing 10 ml were centrifuged at room temperature and 2 ml samples were removed and analysed for radioactivity as before.

Centrifugation at 30000 g for 30 min. Tubes were centrifuged at 4°C and 2 ml samples were removed and analysed for radioactivity as before.

Dialysis. Reconstituted milk (100 ml) was dialysed using a beaker dialyser (Bio-Rad Laboratories, Bromley, Kent) against a flow of distilled water. Samples of the milk in the beaker (2 ml) were removed over a period of 5 hr and the radioactivity (the ^{18}F content) of each sample was determined at the end of the period. A portion (10 ml) of milk was removed after completion of dialysis, and subjected to total fluoride analysis. The water that had flowed through the fibres of the dialyser was collected, and evaporated to 100 ml at 38°C using a Büchi rotary evaporator. The 'free' fluoride content was determined using a fluoride ion-selective electrode and compared with a standard prepared by adding fresh sodium fluoride to a similar dialysate obtained from a reconstituted skim milk that did not have fluoride added to it initially.

Recovery of fluoride by precipitation. Portions (10 ml) of the reconstituted milk were analysed by the precipitation method of Beddows & Kirk (1981). The radioactivity (^{18}F) of the supernatant liquor from the analysis was also determined as above and compared with sodium fluoride solution containing the same initial amount of ^{18}F and subjected to the same procedure. The precipitate was resuspended in pH 6.5 buffer solution and its radioactivity was determined.

Results and discussion

In the initial preparation of the milk powder, it was noted that the fluoride-containing powder was somewhat finer than the control sample (Fig. 1). However, this was thought to be due to the lower solids content of the fluoride-containing skim milk concentrate used for spray drying, since variations in feed concentrations have been reported to influence the physical properties of spray-dried powders (Masters, 1972; Pisecky, 1978; Rothwell, 1980). Other factors which may have contributed to differences in particle size distribution may have been the relatively small product weights and minor differences in the atomiser wheel speed.

The fluoride-containing powder was reconstituted and examined. On standing at 4°C no uneven distribution of ^{18}F occurred, which showed that there was no

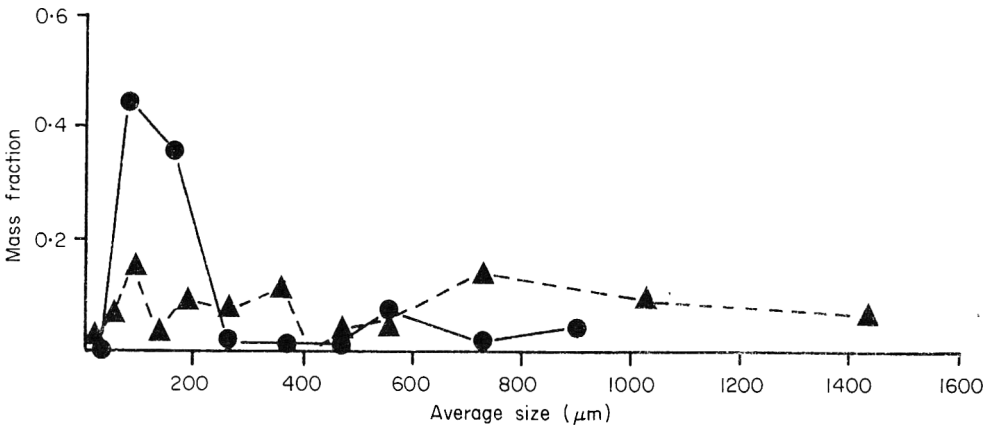

Figure 1. Fluoridated (●) and unfluoridated (▲) skim milk powder (Niro mobile minor).

settling out of the fluoride. Similarly centrifugation at 6000 *g* resulted in an even distribution of the fluoride throughout the tube. If calcium fluoride had been formed then precipitation could have occurred (Beddows, 1982). Centrifugation at 30000 *g* produced a clear centrifugate in the upper ~8 ml. The results (Table 1) confirm that, as with pasteurized milk (Beddows, 1982), the bulk of the fluoride remained in the supernatant. This shows that fluoride in milk is stable.

Precipitation of the milk protein using pH 3.2 citrate buffer according to the method of Beddows & Kirk (1981) gave a total recovery of the fluoride (23 949 cps compared to 23 405 cps with an aqueous standard). No radioactivity was present in the precipitate. The fluoride in the supernatant liquor was shown to be totally in the ionic form by readjusting to pH 5.5 and comparing with an aqueous standard in fluoride-free milk dialysate. Thus only ionic fluoride-containing complexes had been formed. However, more than one such complex must exist, as shown by the change in the 'free' fluoride concentration.

Table 1. Measurement of the ^{18}F content (in cps) of sample of reconstituted fluoride containing milk powder, subjected to standing or centrifugation

	Standing at 20°C	Centrifugation	
		6000 *g* for 30 min	30 000 *g* for 30 min
Top layer	22 507	32 764	10 682
Second layer	22 720	33 878	11 221
Third layer	22 671	32 931	10 781
Bottom layer	22 601	34 471	28 661
Blank (no milk)	22 695	33 486	—

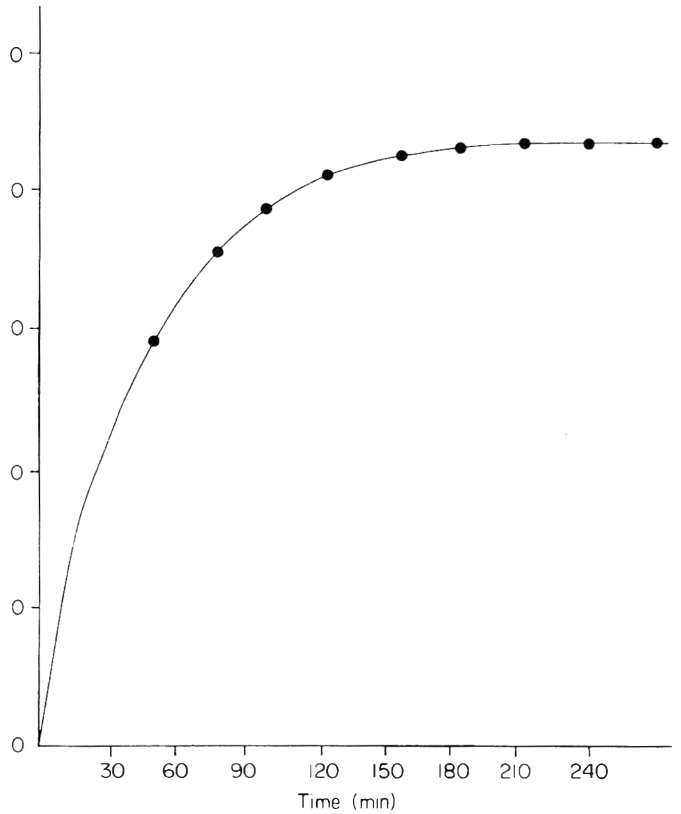

Figure 2. The rate of removal of fluoride from reconstituted fluoride milk powder on dialysis with a hollow fibre beaker dialyser.

This was demonstrated when a portion of the reconstituted milk was dialysed against water, using a hollow fibre beaker dialyser. The rate of removal of fluoride from the milk was measured by following the change in the radioactivity of the milk in solution. The results (Fig. 2) showed that although a large amount (some 84%) of the fluoride dialysed, not all was removed.

To confirm the ionic status of the dialysed fluoride the dialysis eluent was concentrated *in vacuo* to 100 ml, and the fluoride content was measured using the fluoride ion-specific electrode. This was compared with a standard prepared by adding fluoride to a dialysate from a non-fluoride treated skim milk. The sample showed that 8.3 mg/l of fluoride was present, thus all the dialysed fluoride was in the ionic form.

The 16% of the fluoride left in the milk after dialysis must be in more tightly bound complexes, which must also be ionic since all the fluoride could be reclaimed by the precipitation method. These results were similar to those obtained with a variety of heat treatment processes used to pasteurize milk (Beddows, 1982). Each of the sieved fractions were analysed for ^{18}F after precipitation. No difference was obtained with each of the fractions (17 251 ± 127 cps).

Table 2. Processing data for the production of fluoridated and unfluoridated skim milk powder using a Spray Processes/Becker tall-form dryer

Types of milk	Fluoridated	Unfluoridated
Raw		
Density (kg/l)	1.034	1.035
Fat (%)	≤0.1	≤0.1
Total solids (%)	9.34	9.37
	9.22 (fluoridated)	—
Pasteurized		
Total solids (%)	9.20	9.34
Concentrated		
Total solids (%)	32.3	34.4
Dried		
Moisture content (%)	4.0	3.6
Bulk density (g/ml)	0.69	0.68
Solubility (%)	≥99.9	≥99.9

The preparation of the milk powder was repeated on a pilot plant scale (Table 2).

A raw skim milk of solids content 9.22% with a concentration of 10 p.p.m. of fluoride ion contained 4.7 p.p.m. of the fluoride in the 'free' form, which is in close agreement with the results obtained by Smith, Beswick & Rosie (1978).

Pasteurization of the skim milk caused a reduction of the amount of free fluoride, as measured by the ion-selective electrode to 3.7 p.p.m. The milk was concentrated in a Scott submerged tube evaporator to a solids content of 32.25%. A fluoride-free milk concentrate was also prepared, from the same initial raw milk. This concentrate contained 34.4% solids and was evaported under similar conditions.

A portion of the fluoride-containing concentrate was rediluted to the initial solids content. Analysis showed the free fluoride content to be 2.9 p.p.m. Both the skim milk concentrates were spray dried in a Spray Processes/Becker gas-fired tall form drier to give powders which contained 4.0 and 3.6% moisture for the fluoride and non-fluoride containing milks respectively. The lipid content of the fluoride containing powder was 1.22% and that of the fluoride free control was 1.09%. Both the moisture and fat content conform to the Condensed and Dried Milk Regulation, 1977.

When the solids from the fluoride-containing milk were mixed with water to give the same solids content as the original, the free fluoride had decreased to 2.6 p.p.m., the total fluoride was found to be 10.0 p.p.m.

The milk powders produced were examined further. The fluoride containing milk powder was shaken in a variety of ways at a slow rate, to imitate what could happen with handling a large pack of the milk. After each operation the powder was sampled at the top and the bottom and analysed for total fluoride (Beddows

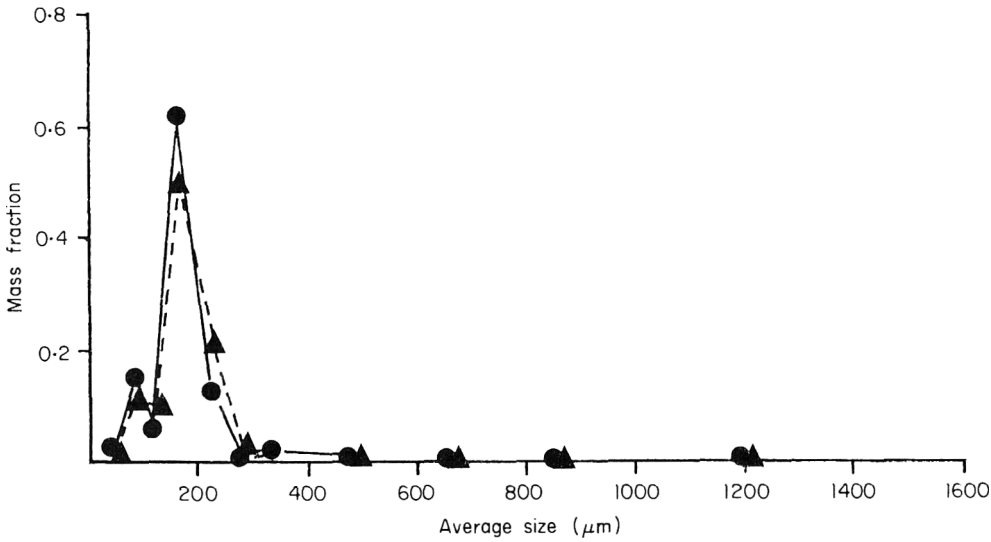

Figure 3. Fluoridated (●) and unfluoridated (▲) skim milk powder (Spray Processes/ Becker).

& Kirk, 1981). In none of the handling operations could any difference be found. All readings were the equivalent of 10.0 ± 0.1 p.p.m.

It was important that the milk powder produced from the fluoride-containing milk had the same physical characteristics. To determine this approximately 250 g of both the fluoride and fluoride-free skim milk powders were sieved for 30 min on an Endecott Test sieve shaker (EFL1 Mark 11) and the amount of each fraction was weighed and the mass fraction on each sieve determined.

The results (Fig. 3) clearly show that there was no significant difference in particle size distribution between either skim milk type. Furthermore the particle size distribution was compatible with that which would be expected from a commercial spray drier operating with a 'straight-through' drying principle without fluid bed agglomeration after drying and cooling.

Many commercial milk spray driers utilize the two-stage drying principle for the production of semi-instant and instant milk powders. However, the use of a fluid bed drier for the second stage of drying is unlikely to alter the fluoride distribution because the process will essentially consist of the agglomeration of particles in which the distribution of fluoride is regular, as shown by the present work.

The only circumstance in which redistribution might occur would be with the use of a re-wetting agglomeration process where some redistribution of fluoride might occur.

The solids which had been sieved were examined for free and total fluoride. Although very slight differences in the amount of free fluoride was obtained with different particle sizes, the amount was 2.6 ± 0.2 p.p.m. and the total fluoride was the same for each sieved portion when reconstituted and analysed

as before. Thus it would not be expected that handling of the milk powder would produce any change in the distribution of fluoride in a packet.

The stability of the fluoride-containing milk powder was determined by removing samples at intervals of time up to 2 years, reconstituting and analysing for total fluoride as before. Each sample reconstituted well. The fluoride concentration obtained was 10.0 ± 0.2 p.p.m. in terms of the original liquid; all of the fluoride was recovered thus it must be still in the ionic form.

Conclusion

Spray-dried skim milk powder has been produced from a milk containing 10 p.p.m. fluoride. The powder showed the same physical characteristics as a control fluoride-free powder produced under identical conditions.

Although the amount of free fluoride changed with each stage of processing, the final product contained fluoride in reversible ionic complexes, one of which could be easily dialysed. All of the fluoride could be recovered by precipitation (shown by using ^{18}F as a marker) and was in the ionic form, as shown by using the fluoride ion-selective electrode.

The fluoride was evenly distributed throughout the powdered milk particle size range, and so no uneven distribution would occur in handling. The status of the fluoride remained unchanged over a 2 year period.

It could be claimed that the fluoridated milk powder could be considered for use in the treatment of dental caries. Appropriate screening trials would be necessary to establish the efficacy of the fluoridated powder as a prophylactic measure.

The disadvantage, as with all milk powders, is to ensure that the correct concentration of powder is taken by the consumer and, therefore, both unambiguous labelling and calibrated dispensing aids should be provided.

Acknowledgments

One of us (V.N.W.) would like to thank Mr J. Abbot of the Hannah Research Institute for assistance in drying some of the powders. Thanks are also due to Mr G. Davies and Mr C. Kelly of the West of Scotland Agricultural College for the routine analyses of the milk during and after processing.

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Effect of pasteurization, vitamin C supplementation and ultraviolet irradiation on the nitrosamine content of palm wine

E. N. MADUAGWU

Summary

Palm wine contaminated with varying quantities of the carcinogen dimethylnitrosamine (DMN) was subjected to heat treatments and ultraviolet irradiation. Dimethylnitrosamine (DMN) recoveries and nitrite concentrations were investigated by gas–liquid chromatography (g.l.c.) and colorimetry respectively. Whereas up to 2–6% of the initial DMN concentration was detectable in samples of the alcoholic beverage after raising the temperature of the fermenting drink to 62.5°C and also to 70°C and maintaining these for 30 and 10 min respectively, no nitrosamine was found in any of the palm wine samples treated for 20 min with UV light. Incorporation of 20 mg and 50 mg ascorbic acid into the pasteurized wine containing 2 μmol sodium nitrite, as well as increasing its acidity, appeared to enhance the disappearance of nitrite ions from the beverage.

Introduction

Palm wine is an alcoholic beverage which is drunk mostly in the tropics and particularly along the west coast of Africa and in the central region of the continent. In these areas the wine is derived from both the raphia and oil palms of which two main species, namely *Raphia hookeri* and *Elaeis guineensis*, are tapped. In addition, in North Africa notably in Libya, Tunisia and Algeria, the date palm (*Phoenix dactylifera*) and a wild variety (*P. sylvestris*) are usually tapped for palm wine.

Palm wine is the fermented juice of palm trees. Juice is obtained by tapping the tree either at the base of an immature male influorescence or the base of the topmost frond. The latter site is rarely used because of the injurious effect on the life of the tree (Faparusi, 1973). Tapping methods have been described by Bassir (1962), Tuley (1965a, b) and Okafor (1972). The wine is a fast fermenting juice and the taste and composition change very rapidly. During the tapping of palm

Author's address: Department of Biochemistry, University of Ibadan, Ibadan, Nigeria.

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trees the sap that emanates from the tapping slit is known to be contaminated by yeasts and bacteria (Bassir, 1962), and fermentation of the resulting beverage usually lasts about 48 hr.

Apart from the presence of micro-organisms in palm wine, this beverage also contains sugars, amino acids, proteins, vitamins and minerals, depending on the palm species tapped (Faparusi, 1966). In Nigeria, palm wine is consumed quite frequently and in fairly large quantities by many people. The popularity of this drink has grown very fast over the years, so much so that the production and sale of fresh palm wine have become flourishing industries in virtually all parts of the country. In recent times however, the preservation of palm wine by pasteurization and bottling has been engaged upon by some government sponsored research institutes. The result is that bottled palm wine is now appearing on bar shelves and is being served and drunk with relish even in elite and governmental social gatherings.

Recently, however, palm wine has been shown to contain some carcinogens, namely; dimethyl- and diethylnitrosamine (Bassir & Maduagwu, 1978; Maduagwu, Joaquim & Bassir, 1979; Maduagwu, Spiegelhalder & Preussmann, 1981). The implication of this finding to the health of consumers of this drink certainly cannot be over emphasized. In this investigation, therefore, the effectiveness of some simple processing techniques in the elimination of dimethylnitrosamine from contaminated palm wine has been assessed.

Materials and methods

Fresh palm wine was purchased from a dealer and aliquots containing 0.0, 0.5, 1.0, 2.0 and 5.0 mg DMN/l respectively were prepared. Three 100 ml samples from each of the aliquots contained in separate 500 ml Erlenmeyer flasks plugged lightly with non-absorbent cotton wool were pasteurized for 30 min at 62.5°C using the Oxford pasteurizer, which has an automated rapid heating and cooling cycle. The process was repeated at 70°C for 10 min using a new set of palm wine samples.

A recovery test of DMN was carried out for each of the treated palm wine samples, whose concentrations (0.5–5.0 mg/ml) were much higher than 0.6 ppb reported by Bassir & Maduagwu (1978), using the g.l.c. procedure described by these workers. The limit of detection of the nitrosamine by the g.l.c. method was 2 ng DMN. The purchased palm wine sample contained no detectable dimethylnitrosamine prior to the investigations.

In the experiment to determine the effect of UV light on the nitrosamine content of palm wine two 50 ml samples of each of the standard solutions of DMN in palm wine, described above, contained in 100 ml beakers were placed for 20 min under a UV lamp (240 nm) at a distance of 10 cm from the light source. Nitrosamine recovery tests were repeated after UV treatment while the nitrite concentration in each of the irradiated samples was estimated by the colorimetric method of Montgomery & Dymock (1961) and after having

clarified an aliquot of each treated sample using activated animal charcoal and filtering the slurry.

In the next experiment, aliquots of 50 ml pasteurized palm wine were clarified as described above and then spiked with 2 μmol sodium nitrite. Each sample was adjusted to and maintained for 30 min at pH 3.0 and 5.5 respectively, using 6 N NaOH or HCl. To each of these media 20 and 50 mg ascorbic acid respectively, was added and nitrite concentration was measured with time. Analysis for nitrite was carried out in duplicates.

Results and discussion

Pasteurization of palm wine under the experimental conditions described in this investigation resulted in the 'disappearance' of up to 98% of the dimethylnitrosamine content of the beverage (Table 1). This loss is predictable since

Table 1. Recovery* of dimethylnitrosamine (DMN) in pasteurized and unpasteurized palm wine enriched with the nitrosamine

Nitrosamine added to palm wine (mg DMN/l)	DMN recovered from unpasteurized palm wine (%)	DMN recovered from palm wine pasteurized at two different temperatures (%)	
		70°C†	62.5°C‡
0.0	0	0	0
0.5	85	6	4
1.0	90	4	3
2.0	92	5	3
5.0	91	4	2

* Mean of three determinations per sample by g.l.c.
† Pasteurization for 10 min.
‡ Pasteurization for 30 min.

Table 2. Ultraviolet* (UV) degradation of dimethylnitrosamine (DMN) added to pasteurized palm wine

Nitrosamine concentration in pasteurized palm wine (mg DMN/l)	Nitrite concentration of pasteurized palm wine (μg/ml)	Nitrosamine concentration of pasteurized palm after UV irradiation	Nitrite concentration of pasteurized palm wine after UV irradiation (mg/l)
0.0	0.0	n.d.	0.0
0.5	0.0	n.d.	0.35
1.0	0.0	n.d.	0.59
2.0	0.0	n.d.	1.03
5.0	0.0	n.d.	2.60

* 240 nm for 20 min at a distance of 10 cm from light source.
n.d. No detection by g.l.c. of 2 ng detection limit.

DMN is very volatile at atmospheric pressure. However, commercial pasteurizations, which are likely to be carried out in a closed system (the bottle), will record minimal loss of DMN, if any. More nitrosamine was recovered after pasteurization of the beverage at the higher temperature condition over shorter time than at the lower temperature condition through longer period of time (Table 1). These differences were insignificant. It seems probable that processing of the contaminated wine at much higher temperatures and for longer periods of time is bound to eliminate virtually all the nitrosamine in the beverage. Nevertheless, the presence of DMN in the pasteurized palm wine, apart from being due to residual contamination, can occur as a result of *in situ* formation of the nitrosamine from its precursors, nitrite and dimethylamine or derivatives of these, which are known to occur in the drink (Bassir & Maduagwu, 1978). This synthesis can be enhanced by heat treatment (Lijinsky & Epstein, 1970).

At the levels of DMN contamination of the test beverage subjected to UV treatment, no residual nitrosamine was detected (Table 2). UV treatment appears to result in denitrosation of nitrosamine, converting it into the corre-

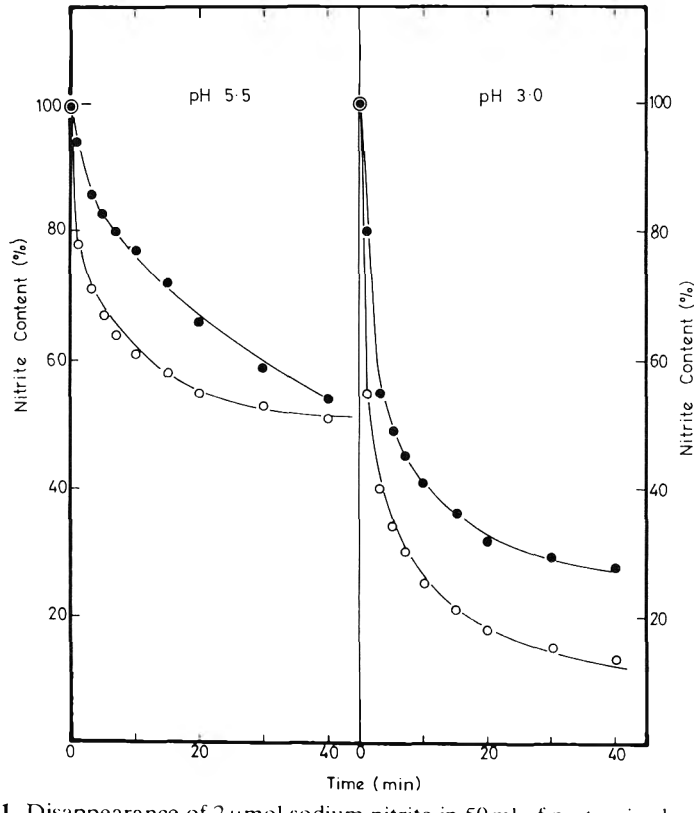

Figure 1. Disappearance of 2 μmol sodium nitrite in 50 ml of pasteurized palm wine enriched with different levels of vitamin C and incubated at 30°C and pH 3.0 and 5.5 respectively. ●, 20 mg vitamin C; ○, 50 mg vitamin C.

sponding secondary amine and producing nitrite in corresponding amounts. Under this condition, in which these nitrosamine precursors are produced, there is the obvious likelihood that nitrosation will occur. Incorporation of ascorbic acid into the drink prior to UV treatment, which has been shown (Fig. 1) to reduce the amount of nitrite present in the test drink and in other beverages (Ziebarth & Scheunig, 1976), particularly at higher acid pH and vitamin C levels, therefore, appears beneficial in the de-toxification of the palm wine of secondary contamination due to *in situ* nitrosamine chemical synthesis.

Most nitrosamines are toxic and carcinogenic. Therefore, their presence in food material intended for human consumption must be considered a potential health hazard. The values of 0.6 and 0.5 ppb DMN found respectively in fermenting palm wine (Bassir & Maduagwu, 1978) and in two samples of pasteurized and bottled palm wine (Oguro) analysed by g.l.c. and chemiluminescence detection (Maduagwu *et al.*, 1981) are not high when compared with the concentrations of the same compound and other volatile nitrosamines that have been reported in some European and American foodstuffs. For example, Gough, Webb & Coleman (1978) showed that some normal dietary constituents in the U.K., such as fried bacon, could contain up to 5 ppb DMN and 1–20 ppb nitrosopyrrolidine (NPY). In two cases 200 ppb NPY was detected.

To date, there are no universal threshold limit values for carcinogenic nitrosamines, although some 'no-effect level' in rats, 1–2 ppm DMN (Terracini, Magee & Barnes, 1967), < 1 ppm diethylnitrosamine (Druckrey *et al.*, 1963) and ~ 5 ppm NPY (Preussmann *et al.*, 1977) in food, have been estimated. Most indigenous food materials being hawked for sale in the tropics are contaminated with harmful micro-organisms and chemicals, some of which are amenable to simple processing. However, it is very important to emphasize that no amount of a carcinogen in food or drink or in any other human environment should be regarded as safe. Such a comparatively minimal concentration of a carcinogen as that detected in palm wine can only represent a low risk level of contamination.

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Apparent shear viscosity of native egg white

ELIZABETH ROBINSON LANG AND CHOKYUN RHA*

Summary

Temperature and shear dependency of the apparent viscosity of the thick and thin portions of egg white from fresh hen eggs, in their native state was investigated. The viscosity of the egg white was determined in the temperature range of 5–30°C and the shear rate range 34–600 sec^{-1}. The viscosity of both the thick and thin portions of the egg white decreased with increase in temperature. The thin portion showed no decrease in viscosity with shearing time at constant shear rates while the viscosity of the thick portion decreased within the first 6 min of shearing and then remained constant. The rate of decrease in viscosity with shearing time was more at higher temperatures. At 20°C and a shear rate of 34.2 sec^{-1}, the equilibrium-apparent viscosity of the thick portion was 160 cp, approximately forty times greater than that of the thin portion (4 cp). This difference in viscometric properties may be due to the presence, in the thick portion, of high molecular weight complexes which are disrupted under shearing.

Introduction

Currently, approximately 240 eggs are consumed per capita in the U.S.A. each year (Wilson *et al.*, 1977). Of these, approximately 35% are processed commercially (Berquist, 1979). During processes such as pasteurization, pumping, filtration or spray drying, egg white is subjected to varying shear rates. For example, in continuous pasteurization egg white is sheared at 1–100 sec^{-1} for 3.5 min at 60°C whereas in spray drying at 38°C, the egg white is sheared for less than half a second at approximately 10^5 sec^{-1} (adapted from Gordon, 1971).

Egg white is a food ingredient valued for its unique functional properties. The characteristic quality of egg white changes with handling and processing and the

Authors' addresses: Biomaterials Science and Engineering Laboratory, Department of Nutrition and Food Science, and *Room 56-137, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

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functional properties vary in response to external stresses such as temperature and shearing. The combination of shear rate and duration of shear, along with the thermal stresses and handling history associated with processing may cause changes in the egg white which decrease quality and impair subsequent functional performance in end use. The rheological behaviour of egg white is an important quality indicator. In order to evaluate the effects of processing conditions on quality, the behaviour characteristic of native, unprocessed egg white needs to be established as the basis for comparison.

Background

There are three major fractions in egg white; an inner thin portion which lies close to the yolk; a thick portion which surrounds the inner thin; and an outer thin portion which lies close to the shell (Romanoff & Romanoff, 1949). The observed difference between the thick and thin fractions is, in fact, a reflection of the difference in rheological properties. The thick portion clings to the yolk and its gel-like character prevents it from spreading. This phenomenon is the basis for the primary method of egg quality evaluation, the Haugh score (Romanoff & Romanoff, 1949; Tung *et al.*, 1970; Tung, Watson & Richards, 1971; Hill & Hall, 1980; Kamel, Bond & Diab, 1980). In the Haugh score, the height and weight of the thick egg white are combined to give a quality index. The Haugh score, although often used, is a point value measurement which does not describe the flow characteristics of the egg white. Furthermore, such a test cannot be used for bulk lots, or processed egg white. It is therefore, necessary to consider a more fundamental method for characterization which can describe or detect quality changes which occur as a result of processing conditions. Rheological measurement is a candidate for such a purpose because it reflects the overall composition and organization in a material.

Several studies on the rheology of egg albumin have been reported in the literature (Forsythe & Berquist, 1951; Brooks & Hale, 1959; Scalzo *et al.*, 1970; Tung *et al.*, 1970: Tung *et al.*, 1971; Pitsilis, Walton & Cotterill, 1975). Much of the early data is reported in a manner which cannot be reduced to fundamental units. Often egg white samples which had been subjected to various chemical and physical treatments were employed. Most studies were made on large lots of homogenized egg and consequently the information obtained was related to a pooled sample. The pooling eliminated the problem of scatter in the data due to the variability between individual eggs and provided a convenient sample for experimentation. On the other hand, the characteristics inherent to the native egg white in each individual egg were lost. Furthermore, the pooled sample may not represent the average of the individual eggs because of the mixing process or other treatments which accompanied the pooling process. Since the shear treatment varied from study to study and in some cases was quite severe, as when homogenized in a blender (Pitsilis *et al.*, 1975) (which represents a shear rate of 6000 sec^{-1} according to Lee & Rha, 1978), the apparent viscosity of native egg white cannot be estimated from the current literature information.

The viscosity of egg white differs significantly with origin and conditions of storage and measurement (Romanoff & Romanoff, 1949). Generally it has been shown that egg white can be pseudoplastic, has apparent viscosity decreasing at higher temperatures, and may exhibit shear hysteresis, in one study, shear stress decay at a constant shear rate has been observed for whole albumin and was independent of temperature (Tung *et al.*, 1970).

The objective of this study is to examine some of the rheological properties of untreated, unmixed, native thick and thin fractions of egg white from individual eggs. This study of native egg white provides a reference point for the estimation of the effects of shear, time and temperature on egg white quality as reflected in the rheological behaviour.

Materials and methods

Sample preparation

Grade A large brown eggs used in this study were produced by Dekalb-Warren 6L layers of up to 68 weeks in age at a local commercial poultry hatchery. The eggs were collected 2 days before use and held unopened at 5°C for a period of between 48 and 60 hr until the experiments were performed. The results reported in this study represent seventy-five individual eggs collected over a period of 10 weeks. The samples were treated with the objective of minimizing shear and avoiding mixing of the thick and thin portions of the egg white, while providing a reproducible sample.

The albumin preparation method used by Heath (1978) was modified for use in this study. Each egg was opened and the egg white transferred to a mesh screen (with square openings of 0.1 in). The yolk and chalazae were removed and discarded. The thin portion of the egg white was allowed to drain into a pre-chilled glass Petri dish. This thin portion was then transferred to a finer mesh (square openings of 0.05 in) and allowed to drain into another pre-chilled dish and stored covered, at 5°C until use. The thick portion remaining on the 0.1 in mesh screen was lifted with a spatula and transferred to a clean, pre-chilled dish and stored covered at 5°C until use.

A whole egg white portion was prepared by opening each egg into a pre-chilled Petri dish and discarding the yolk and chalazae. The thick portion was then carefully pulled apart using two tweezers until a well-dispersed sample was obtained.

All egg samples were analysed within 2½ hr of opening. Preliminary tests indicated that no significant change in viscosity occurred during this time.

Viscosity measurement

The shear stress *versus* shear rate relationship of the thick and thin portions of egg white samples were determined using a Ferranti-Shirley cone and plate viscometer (Ferranti Electric, Commack, U.S.A.) equipped with a 100 g spring.

The thin portion exhibited time-independent behaviour; thus further examination of the thin portion was carried out using capillary viscometers. For direct comparison with the thin portion, the behaviour of the whole egg white portion was also studied using the capillary viscometers.

Cone and plate viscometer. One millilitre aliquots of the prepared thick portion of the egg white were placed on the plate of the viscometer using slow suction with a 5 ml disposable syringe (Becton-Dickson, Rutherford, U.S.A.) having a 2 mm opening. Each sample was allowed to rest 10 min after placing it on the plate of the viscometer in order to achieve shear recovery and to reach temperature equilibrium. Temperature was maintained within 0.05°C using a circulating water heater-cooler (Haake, Saddle Brook, U.S.A.). The shear stress as a function of time at the lowest constant shear rate experimentally attainable (32.4 sec^{-1}) was measured for each sample at a constant temperature in the range 5–30°C. Measurements were taken for a period of 15 to 20 min.

The volume of the thick portion of each egg was sufficient to make six samples. With each individual egg, shear stress was measured at two different temperatures in triplicate or at three different temperatures in duplicate. Temperatures were measured alternately in increasing and decreasing increments.

During the first minutes of shearing, the shear stress decreased and then remained constant. This constant shear stress value was used to calculate the apparent shear viscosity of thick egg white at any given temperature.

A decay time was defined as the time for the shear stress to decay to 1/e of the initial value. The shear stress after 15 sec was designated the initial value in order to avoid any inertial or equipment response effects present at shorter times.

The shear stress as a function of shearing time of 1 ml aliquots of the thin portion were measured in triplicate at 32.4 sec^{-1} at 20°C only, in the manner described above.

Capillary viscometer. The thin portions of the egg white from two eggs of the same daily lot were prepared as described above and combined in a clean, pre-chilled dish to provide sufficient quantity for testing. Five millilitre aliquots of this thin egg white were removed using the 5 ml syringe as described above and transferred to Cannon-Fenske type capillary viscometers (Nos. 100 and 200, Induchem Lab Glass Co., Roselle, U.S.A.) for viscosity measurement. The capillaries were immersed in a circulating water heater-cooler (Haake, Saddlebrook) and allowed to stand for 20 min in order to reach temperature equilibrium. Each sample was measured at three temperatures in duplicate with the temperature measured alternately in increasing and decreasing increments in order to ensure that temperature did not impose a systematic error. The maximum shear rates in the capillaries were estimated at approximately 400 and 600 sec^{-1} for the Nos. 100 and 200 viscometers respectively (Van Wazer *et al.*, 1963).

The viscosity of the whole egg white was determined using the No. 200 capillary in a manner similar to that described for the thin portion. The shear rate was estimated as approximately 400 sec^{-1} (Van Wazer *et al.*, 1963).

Data analysis

The values of apparent viscosity, decay time and temperature of the thick egg white samples from various individual eggs were treated by analysis of variance for a random block design experiment with replicate measurements (Brown & Hollander, 1977). Linear regression was used to determine the temperature dependence of the shear decay and the equilibrium apparent viscosity (Ryan, Joiner & Ryan, 1976).

The temperature dependence of the apparent viscosity of the thin and whole portions of egg white for each sample tested was determined by linear regression. In addition, the regression lines thus obtained for the thin albumin samples at the two shear rates were compared using a Student's *t*-test for unpaired samples (Brown & Hollander, 1977). A significance level of $P \leq 0.05$ was used unless otherwise stated.

Results

Variation between eggs

Table 1 shows the average apparent viscosity values at 34.2 sec^{-1} for the thick egg white at temperatures from 5 to 30°C. Analysis of variance showed significant difference between the apparent viscosity of individual eggs at the same temperature and shear rate. However, there was no difference in behaviour among different aliquot samples drawn from one egg. In all cases, the experimental and statistical analyses were designed to account for these differences and to detect trends in rheological behaviour characteristic of all eggs studied.

The experimental design allowed the evaluation of native, untreated egg white in the absence of a shear history. However, it did lead to high standard deviation values which ranged from 7 to 16% (Table 1) of the average reported apparent viscosity values. These deviations reflect the normal variation between individual eggs. The trends in behaviour shown in the Fig. 2 and Tables 1 and 2 represent the averages of all eggs tested and in each case any reported differences were tested and found to be significant at the $P \leq 0.05$ level.

Table 1. Average equilibrium viscosity of the thick portion of egg white

Temperature (C°)	Viscosity (cp)
5	297 ± 18
10	233 ± 14
20	164 ± 10
30	113 ± 7

Shear rate, 34.2 sec^{-1}.

Table 2. Apparent viscosity of whole egg white (cp)

Shear rate (sec^{-1})	Temperature 2°C	10°C	20°C	Reference
400	7.5 (± 0.3)	6.2 (± 0.2)	5.0 (±0.2)	Figure 2
400		9.1		Tung *et al.*, 1971
400	13.9			Tung *et al.*, 1970
36	12.8	10.9	8.7	Pitsilis *et al.*, 1975
36	39.7			Tung *et al.*, 1970

Time dependence

Figure 1 shows typical data for the decay in the shear stress of the thick egg white to an equilibrium value at the constant shear rate of 34.2 sec^{-1}. The decay occurred during the first 2–6 min, after which the apparent viscosity remained constant for up to 20 min of shearing.

Physically, the decay time represents the time for structural re-arrangements or breakdown to occur in egg white under the shearing forces corresponding to

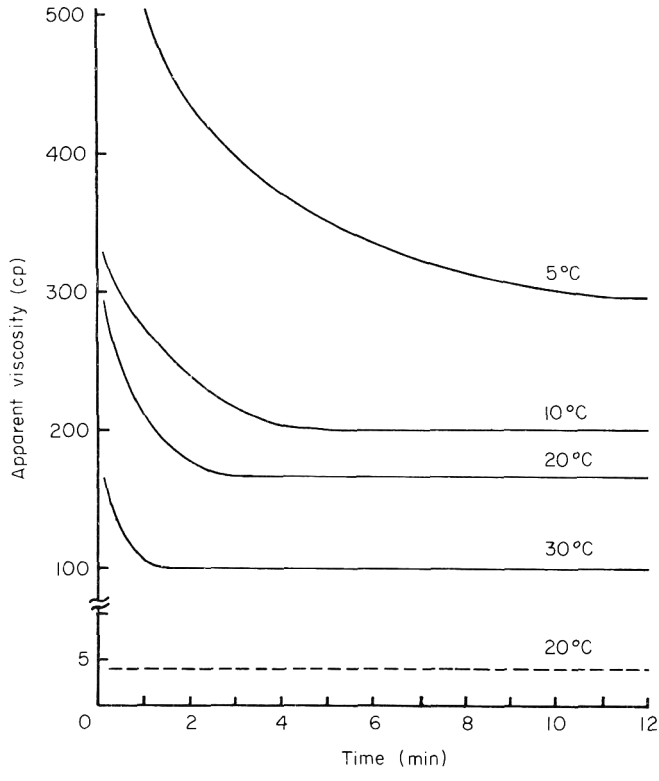

Figure 1. Apparent viscosity of the egg white at shear rate of 34.2 sec^{-1} showing the shear decay in the thick portion. Data from a typical sample are shown. ———, thick; – – – –, thin.

the constant shear rate used. The decay time is dependent on both intrinsic factors such as the shape, size and strength of interactions between structural components in egg white and certain extrinsic factors such as the temperature and the shear rate. Physically, this type of time-dependent rheological behaviour is characteristic of a dispersion containing high molecular weight aggregates (Rha, 1979).

At a shear rate of 34 sec^{-1}, the apparent viscosity of the thin portion of the egg white measured with the cone and plate viscometer was approximately one-thirtieth that of the thick portion of the egg white (Fig. 1). No shear decay was observed for the thin portion indicating that the thin portion responds very quickly to the applied shearing stress and that no structural re-arrangements or breakdown occur within the observed time frame at the shear rate of 34 sec^{-1}. This type of time-independent response is characteristic of a molecular solution (Rha, 1978, 1979).

These results suggest that the native thin portion of egg white does not contain any components which could impart time-dependent behaviour to native whole egg white at shear rates above 34.2 sec^{-1}. Thus, most likely it is the structural form of incompletely mixed thick portion of the egg white which has caused the shear decay in the whole egg white observed occasionally by others (Tung *et al.*, 1970).

Temperature dependence

Typical temperature dependence of the equilibrium apparent viscosity of the thick portion of the egg white at a shear rate of 34.2 sec^{-1} is shown in Fig. 1. Table 1 summarizes the results averaged over all eggs tested. The temperature dependence followed Arrhenius type of behaviour, with

$$\eta_{app} = (4.0 \times 10^{-3}) \exp (3.10 \times 10^{3}/T)$$

where η_{app} is the apparent viscosity in cp, and T is the temperature in °K. The decrease in viscosity with increasing temperature reflects the decreased resistance to structural breakdown in the egg white as a result of the weakening of secondary bonds and associations at higher temperatures (Rha, 1975).

The apparent viscosity of the thin portion, measured using a capillary viscometer, is shown in Fig. 2. The apparent viscometer *versus* temperature dependence followed a typical Arrhenius type behaviour, with

$$\eta_{app} = (1.8 \times 10^{-3}) \exp (2.25 \times 10^{3}/T)$$

at a shear rate of approximately 400 sec^{-1}, and

$$\eta_{app} = (2.2 \times 10^{-4}) \exp (2.86 \times 10^{3}/T)$$

at a shear rate of approximately 600 sec^{-1}. The apparent viscosity of the thin portion is slightly less temperature-dependent than the equilibrium-apparent viscosity of the thick portion at 34.2 sec^{-1}.

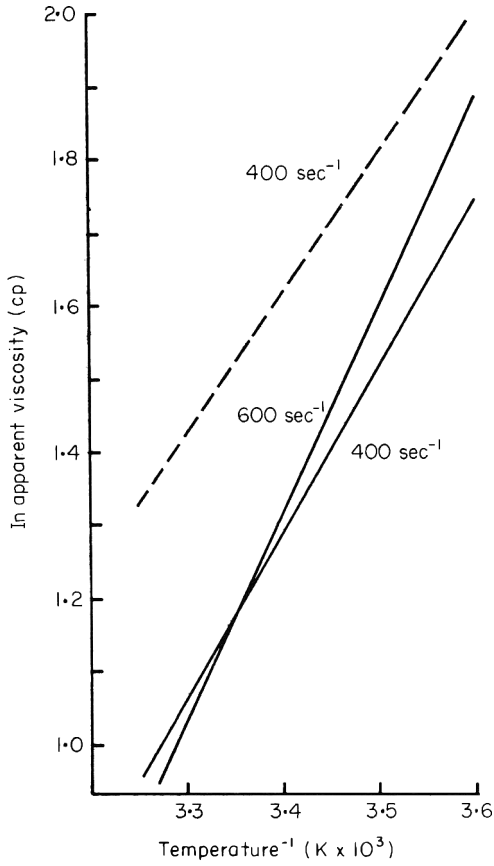

Figure 2. Apparent viscosity *versus* temperature for the thin portion and whole egg white determined with capillary viscometers. Data represent the average of ninety samples. ————, thin; – – – –, whole.

The apparent viscosity of the whole egg white was evaluated using the No. 200 capillary viscometer with a corresponding shear rate of approximately 400 sec^{-1}. The results in Fig. 2 show that the apparent viscosity of the whole egg white is of the same order of magnitude as that for the thin portion alone. Although the thick portion represents approximately 60% of the whole egg white (Heath, 1978), the process of mixing the thick and thin fractions apparently breaks down the characteristic structure of the thick portion sufficiently to result in a viscosity of the whole egg white portion similar to that for the thin portion.

The temperature dependence of the apparent viscosity of whole egg white exhibited typical Arrhenius type of behaviour, with

$$\eta_{app} = (7.4 \times 10^{-3}) \exp (1.90 \times 10^{3}/T)$$

as shown in Fig. 2. The magnitude of the Arrhenius constant is smaller ($P \leq 0.05$) than that for the thin portion at a comparable shear rate.

The values of the equilibrium apparent viscosity (Table 1) of the thick portion are approximately ten times higher than those reported in the literature for

whole egg white (Table 2) (Tung *et al.*, 1970, 1971; Pitsilis *et al.*, 1975). The difference may primarily reflect the high molecular weight complexes present in the native thick portion of the egg white which are destroyed in the preparation of the whole egg white sample. However, difference may also be due to the shear rates used or the source, species or history of the egg samples used.

Combined effect of temperature and shear dependence

The temperature dependence of the rate of the shear decay in the thick portion of egg white was examined. At any temperature, the decay time varied from 2 to 6 min between eggs. In order to allow better comparison, the decay times for each egg were normalized so that at 10°C the decay time was 0 sec. The relationship between decay time and temperature of 160 egg white samples was averaged and showed that the decay time decreased ($P \leq 0.01$) with increasing temperature. The relationship could be expressed as,

$$(\tau_2 - \tau_1) = 9.6(t_1 - t_2)$$

over the range of temperature from 5 to 30°C, where τ is the decay time in sec and t is the temperature in °C.

The decay time decreased by about 3 min with a temperature increase of 20 °C, indicating that the thick egg white becomes more sensitive to shearing as temperature is increased. For the native thin portion of egg white the magnitude of the Arrhenius constant at a shear rate of 600 sec^{-1} is larger than it is at the shear rate of 400 sec^{-1} ($P \leq 0.02$), suggesting that temperature and shearing may act together to disrupt the thin egg white in a manner similar to that of the thick egg white.

Stress decay has been observed previously in whole egg white (Tung *et al.*, 1970) and in the thick portion (Brooks & Hale, 1959). Tung *et al.* (1970) fitted the decay behaviour with two exponential functions and concluded that the decay did not depend upon temperature. That the combined effect of shearing and temperature has not been demonstrated previously may be due to the fact that the egg white samples used previously had been already exposed to shear before the viscometric measurement. The shearing encountered during the sample preparation may have been sufficient to disrupt those structural elements which are sensitive to temperature. For samples of egg white with particularly severe shear viscosity history (Pitsilis *et al.*, 1975), no shear decay was observed. In such a case, the original structure was disrupted to such an extent during sample preparation that no structural elements remained which could be further broken down during the rheological measurement.

Discussion

Both the thick and thin portions of egg white contain approximately 85% water, 10% protein and 5% carbohydrate. Table 3 (Osuga & Feeny, 1977) shows the percentages of the major proteins which have been identified in egg white. it is

Table 3. Composition of whole egg white (adapted from Osuga & Feeny, 1977)

Protein	Amount in egg albumin (%)	Molecular weight (g)
Ficin inhibitor	0.05	12 700
Lysozyme	3.4	14 307
Ovoglygoprotein	1.0	24 400
Ovomucoid	11	28 000
Ovoflavoprotein	0.8	32 000
Ovalbumin	54	45 000
Ovoinhibitor	1.5	49 000
Avidin	0.5	68 300
Ovotransferin	12	76 600
Ovomucin	3.5	110 000
Ovomacroglobulin	0.5	800 000

generally accepted that the only significant difference, in terms of chemical composition, between the two portions of egg white is the percentage of the protein ovomucin (Forsythe & Berquist, 1951; Donovan, Davis & White, 1970; Osuga & Feeny, 1977). The thick portion contains approximately four times as much ovomucin as the thin portion.

The structure of the ovomucin in the thick portion has been studied in detail (Donovan *et al.*, 1970; Robinson & Monsey, 1971, 1975). It has been demonstrated that ovomucin consists of two fractions, α-ovomucin, which has a mol. wt of approximately 140000 and β-ovomucin, which has a subunit mol. wt of 103000 but exists as aggregates of mol. wt of approximately 720000. This β-ovomucin aggregate is probably the macroglobulin identified in Table 3. Furthermore, approximately 10% of the β-ovomucin aggregates into filamentous super aggregates with an axial ratio of greater than 130:1 and a mol. wt of 10^7 (Robinson & Monsey, 1975). The super aggregates are held together by a combination of secondary bonds such as hydrogen bonds, hydrophobic bonding and electrostatic interactions.

It is the filamentous super aggregates which impart the gel-like character to the thick portion of the egg white. The presence of such a very large, asymmetric molecular entity could increase the time for structural re-arrangements within the material to the order of minutes according to the Kirkwood-Auer model for rod-like macromolecules (Bird, Armstrong & Hassagar, 1977) in which case, time dependency under steady shear could indeed occur within an observable time frame (Rha, 1979). During shearing, these aggregates may be broken down causing the viscosity of the thick portion to approach that of the thin portion. The results (Fig. 1) show that the structure can be disrupted at shear rates as low as 34.2 sec^{-1}. It is interesting that the thin portion contains proteins in their

globular form, not as complex association products, and exhibits time-independent behaviour characteristic of a molecular solution.

The super aggregates in the thick portion of the egg white should also affect the rheological response as a result of introducing additional association sites in the material. This is supported by the temperature dependence of the native thick portion which is greater than that for the thin or mixed whole portion. The increased temperature sensitivity results from the additional associations in the super aggregates present in the thick portion.

Conclusions

This study showed significant difference in the apparent viscosities of the thick and thin portions of native egg white. The viscosity of the thick portion exhibited time dependency and had an equilibrium apparent viscosity approximately forty times greater than that of the thin portion. The behaviour of the thick portion is attributed to the presence of filamentous super aggregates with mol. wt on the order of 10^7. At shear rates as low as 34.2 sec^{-1} these structures were partly disrupted within approximately 5 min of shearing.

The rheological behaviour of whole egg white observed in this study, and reported by others (Table 2), is most similar to the behaviour of the thin portion of the egg white. The degree of mixing necessary to completely homogenize the two fractions in fact breaks down the super aggregate structure characteristic of the native thick portion.

The apparent viscosity of all portions of the egg white decreased with increasing temperature. In addition, the rate of shear decay of the thick portion increased with temperature suggesting that shearing and temperature act together to cause the structure disruption in the thick portion. Similarly, although the apparent viscosity of the thin portion was time-independent, at higher shear rates the temperature dependency increased.

The temperature sensitivity of the apparent viscosity is dependent on the number of intermolecular associations in the material. The thick portion of egg white has the higher temperature dependency as a result of the increased associations due to the aggregation. The whole egg white showed the weakest temperature dependency because the shear pre-treatment had destroyed a significant number of associations.

These results indicate that the shear and temperature of processes such as pasteurization and ultrafiltration are sufficient to alter egg white and effect the characteristic rheological behaviour. Therefore, the processes should be optimized for egg white quality in terms of time, shear rate and temperature of processing. The results in this study show that mild conditions or careful handling may cause some structural breakdown of the thick portion. Future studies should be devoted to correlation of the changes in rheological behaviour, with time and temperature of shearing, and with specific functional qualities such as gelation, foaming or water-holding capacity.

Acknowledgments

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Effect of pressurized gas freezing pre-treatment of carrot dehydration in air flow

C. SUAREZ AND P. E. VIOLLAZ

Summary

The effect of pressure freezing on the rate of drying of carrots was studied. It was found that the diffusion of water in the carrots were strongly affected by pressure freezing, and that the pre-treatment maintained its effect on the rate of drying in samples which were stored (previous to drying) for various times in a freezer at $-10°C$.

Introduction

It is well known that air dehydration of solid foods causes changes in chemical, physical and other characteristics of the foodstuffs. Changes in the structure of the tissue by cell collapse was observed by Pendlington & Ward (1962), during air drying of carrots and turnips, resulting in a less porous structure with poor rehydration.

Haas (1971) and Haas, Prescott & D'Intino (1972) have found that it is possible to improve the quality of the dehydrated products by means of a pressurized gas freezing pre-treatment before air drying. In short, samples of fruits and vegetables were pressurized in the range of 3–100 kg/cm^2, followed by freezing at $-20°C$. After this operation, the pressure was released and the products were dried in a conventional air drier. A substantial improvement in the rehydration rate and, to a lesser extent, in shrinkage were observed.

Lately, Viollaz, Vaccarezza & Chirife (1975) determined quantitatively the effect of pressure freezing on the shrinkage of potato slabs and found that shrinkage decreases with increasing pressure. They found that the relation between pressure and shrinkage is linear, in the range of 9–40 kg/cm^2.

It is the purpose of this work to evaluate the effect of pressurized freezing prior to air dehydration of carrot slabs. Although Haas *et al.* (1972) observed that this pre-treatment improved the rate of drying of some vegetables and fruits, they did not report quantitative results.

Authors' address: Departmento de Industrias, Facultad de Ciencias Exactas y Naturales, Ciudad Universitaria, 1428 Buenos Aires, Argentina

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In our work we have measured the drying rate of carrot slabs, which were pre-treated in the way described by Haas *et al.* (1972), and the results were compared with the drying rates obtained with control samples (without pre-treatment).

Materials and methods

Materials

Carrot samples were sliced mechanically in square pieces; the dimensions of the slabs were $5 \times 5 \times 0.4$ cm approximately.

Thickness was measured at different points of the slab using a dial micrometer. In all cases, the maximum deviation from the average values was 6%. Initial thickness (corresponding to the initial moisture content) and the thickness of the fully dried samples were measured to account for the different degree of shrinkage occurring in the pre-treated and control samples.

Gas pressurization freezing procedure

Carrot slabs were pressurized with nitrogen at room temperature in a Parr bomb for 2 hr; after this operation the system was frozen by immersion in a bath at -20°C, for 1 hr. A thermocouple inserted into the slab has shown that this time was enough to attain a total freezing of the sample.

Once the sample was frozen, the pressure was released and the sample was let to thaw at room temperature for half-an-hour, previous to drying. During this time approximately 10% of the initial water content was lost by dripping.

Three different pressures 20, 30 and 40 kg/cm^2 were used in our experiments. The time of pressurization (2 hr) was considered sufficient to achieve gas saturation on the sample, Viollaz *et al.* (1975).

Drying procedure

The laboratory drier consists of a centrifugal fan which blows air over twelve 0.75 kW electric bar elements inside a chamber and then upwards through a vertical duct. A high constant air velocity, between 12–14 m/sec was used in all the experiments. The inlet air dry bulb temperature was regulated ($\pm$ 0.1°C) by means of an electronic proportional controller.

Carrot slabs were placed on a tray inside the drying duct, with the air blowing in the direction of the principal faces. Two temperatures, 51 and 60°C, were used for the drying experiments.

Drying progress in each run was followed by weighing the sample periodically on a precision balance ($\pm$ 0.0001 g). The moisture content of the samples was determined gravimetrically, using a vacuum oven at 70°C, with magnesium perchlorate as a desiccant.

Results and discussion

Drying runs were conducted with pressurized samples and control. The results, in terms of log m/m_0 *versus* θ/L_0^2 are shown in Fig. 1, where $\bar{m}$ is the average moisture content (dry basis), m_0 is the initial moisture content, L_0 is the initial thickness of the slab and θ is the drying time. The factor L_0^2 was introduced to account for small thickness differences among different samples. Reproducibility can also be observed in Fig. 1, which shows a satisfactory agreement between different runs performed under identical conditions.

In the analysis of the experimental results, Fick's law for diffusion in an infinite slab was used. This equation, for constant boundary conditions is (Luikov, 1968).

$$m^* = \frac{\bar{m} - m_e}{m_0 - m_e} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp\left\{-(2n+1)^2 \pi^2 \frac{D_{\text{eff}}\,\theta}{L^2}\right\} \tag{1}$$

where m_e is the equilibrium moisture content, L is the thickness of the slab, and D_{eff} is the moisture diffusion coefficient.

Since the Biot number for mass transfer, calculated from the experimental conditions existing during drying, is greater than 100, it seems reasonable to

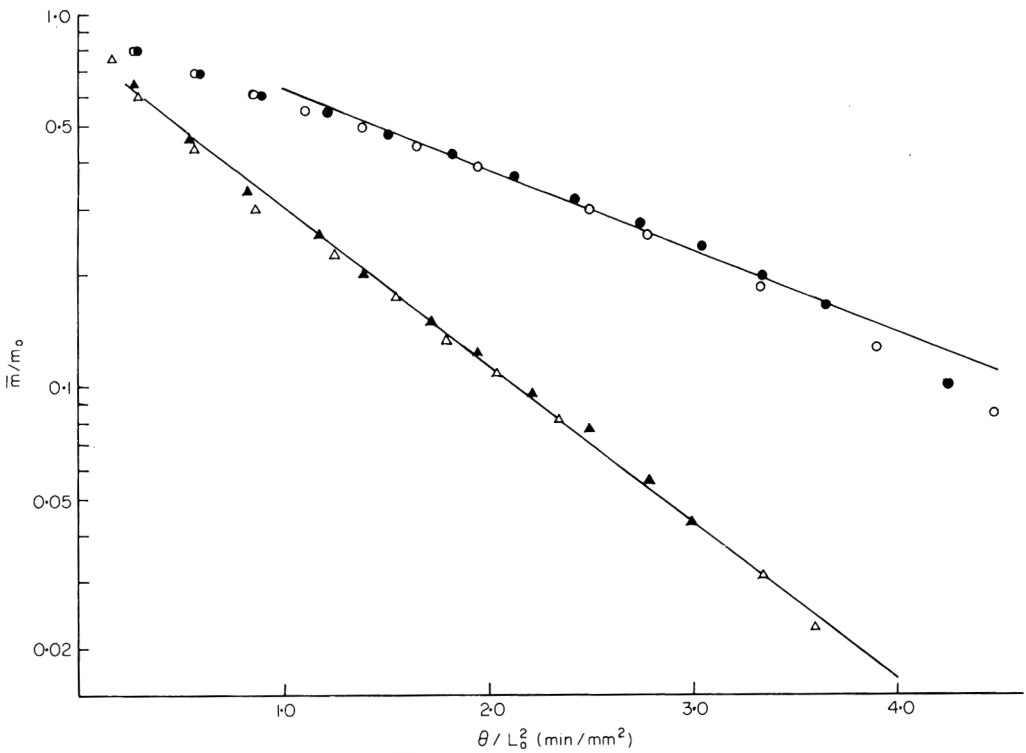

Figure 1. Effect of pressure freezing on the rate of drying of carrot slabs. Reproducibility of drying experiments. T_{db} = 51°C; ○, ●, control; △, ▲, pressurized frozen (40 kg/cm²)

neglect the external mass transfer resistance and consequently to assume a constant value for the equilibrium moisture content during drying time. In addition, if the equilibrium moisture content is very low (Iglesias, 1973) compared with the average moisture content of the samples, as is the case in this work, it seems reasonable to analyse the drying results in terms of $\bar{m}/m_0$. Similar analyses were conducted by Vaccareza, Lombardi & Chirife (1974) and Alzamora & Chirife (1980) in their works on dehydration of sugar beet root and avocado respectively, with satisfactory results.

It can be observed that Equation (1) reduces to only one term, for high values of Fourier number, $D_{\text{eff}}\,\theta/L_0^2$. In terms of dimensionless moisture content, it occurs when $m^* \leq 0.6$. So the asymptotic solution will be a straight line in terms of log $\bar{m}/m_0$ *versus* θ; therefore, moisture diffusion coefficients can be calculated from the slopes of the experimental straight lines shown in Fig. 1. The values of D_{eff} calculated by this method at different experimental conditions are given in Table 1.

It follows from this data that water diffusivity of pressurized frozen samples is in average 96% higher than the control.

This difference in the rate of drying, may be explained in terms of the cellular damage produced as a consequence of the pre-treatment of the samples. This change of the structure would be the cause of the water loss which was observed during and after thawing of the samples.

Haas *et al.* (1972) have reported a similar effect in celery and peppers, concluding that drip losses increase at high pressures.

Although the moisture content measured after thawing in carrots that were pre-treated, was approximately 10% less than the controls, no effect of higher pressures on the quantity of water loss was observed.

It is worth mentioning that during the drying process differences were noted between the control and pre-treated slabs. In the control, the surface was completely dried in a very short time, while in the pressurized samples, the surface remained wetted during the first 5–10 min of drying, depending on the drying conditions in each case. It is likely, therefore, that during this time, an external control to mass transfer existed.

Another parameter which is very much affected as a consequence of the pressure freezing effect, is the degree of shrinkage of the samples. Values of

Table 1. Calculated values of diffusion coefficients

Pressurized frozen (kg/cm^2)	Drying temperature (°C)	Diffusion coefficient (cm^2/sec)
20	51	1.49×10^{-5}
30	51	1.61×10^{-5}
40	51	1.73×10^{-5}
Control	51	8.2×10^{-6}

L/L_0, where L and L_0 are the initial and final thickness of the slab, measured at the beginning and at the end of each run, are $0.1 \sim 0.2$ for the control and $0.8 \sim 0.9$ for the pressurized sample. This different behaviour in the degree of shrinkage, was also observed by Haas *et al.* (1972). Viollaz *et al.* (1975) studied quantitatively this effect on potato slices and found that the volumetric shrinkage decreases with the increase of pressure.

From the point of view of the influence of the thickness on the rate of drying, it would be expected that the treated samples would have a reduced rate of dehydration when compared with the control. However, this effect was not observed; it seems reasonable to think that the cellular damage and the change of the structure prevail over the shrinkage effect.

Storage of the samples after pressurization

Carrot slabs pressurized and frozen at 40 kg/cm² and −20°C respectively, were stored during various days at −10°C, previous to drying. At different intervals of time they were removed from the freezer, thawed at room temperature for half-an-hour and then dried.

The drying curves of three samples, conducted at the same temperature and air velocity, are shown in Fig. 2. It can be seen that no significant effect on drying

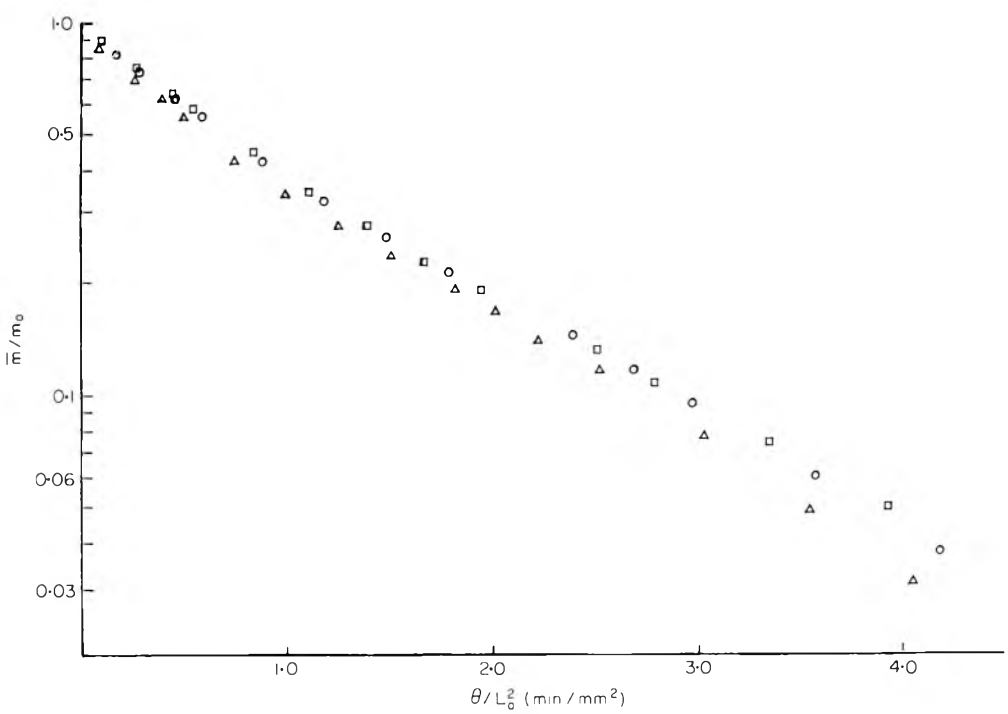

Figure 2. Effect of storage time on drying curves of pressurized frozen (40 kg/cm²) carrot slabs. T_{db} = 51°C; △, 0 hr; ○, 72 hr; □, 144 hr

rate of the samples appears; it was also found that the shrinkage of the samples after drying was practically the same in all cases.

From these results it can be concluded that the pre-treatment effect was not diminished by storage of the samples.

Pre-treatment of the samples at different pressures

Various samples of carrot slabs pressurized at 20, 30 and 40 kg/cm^2 and frozen at -20°C were dried, in order to investigate how different conditions of pressurization can modify water diffusivity of carrot samples.

The drying curves, conducted at two different temperatures, are given in Fig. 3. It is observed that the rate of drying is slightly increased in samples which were pressurized at higher pressures.

Conclusions

We have found that pressure freezing of carrot increases considerably the rate of drying in air flow. The diffusion coefficients calculated with samples which were

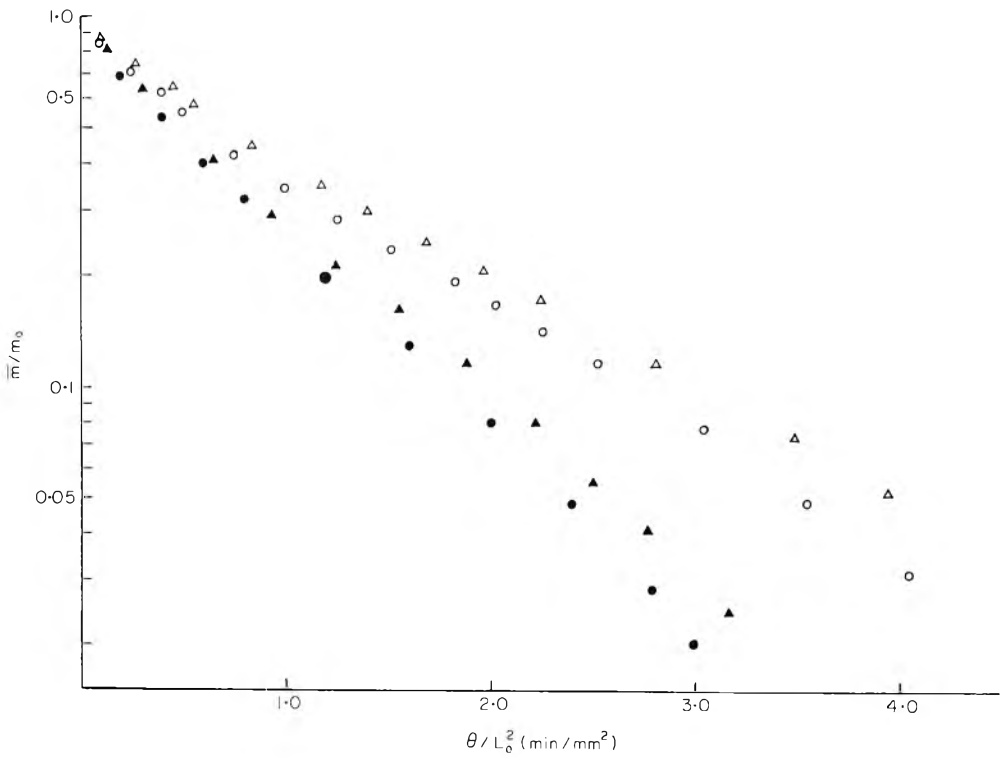

Figure 3. Effect of pressure on the rate of dehydration of pressurized frozen carrot. △, T_{db} = 51°C, 20 kg/cm^2; ▲, T_{db} = 60°C, 20 kg/cm^2; ○, T_{db} = 51°C, 40 kg/cm^2; ●, T_{db} = 60°C, 30 kg/cm^2

pre-treated were 96% (on average) higher than the control for similar air drying conditions.

It was also observed that at higher pressures this effect is slightly increased.

On the other hand, drying experiments conducted with pre-treated samples, which were stored at $-10°C$ during various days, shown that the pre-treatment maintained its effect on the rate of drying.

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Heat and mass transport in the freezing of apple tissue

J. L. BOMBEN* AND C. J. KING†

Summary

A newly developed cold-stage scanning electron microscope was used to examine ice morphology in frozen apple tissue as a function of freezing rate. The morphological structure of the ice was analysed using theories of cellular water transport and solution solidification. The transition from intracellular to extracellular ice occurred in apple tissue at a cooling rate of approximately 1 K/min. The dendritic spacing of the ice was proportional to the inverse square root of the cooling rate. This behaviour can be rationalized through an analysis of the dependence of the formation of dendrites upon solute mass transfer.

Introduction

Many micrographs of ice formation in various food tissues are available, and the conclusion of much of that work is that rapid freezing produces small intracellular ice, while slow freezing produces large extracellular ice crystals with a noticeable change in texture and an increase in loss of intracellular fluid. Microscopic observation of the freezing of tissue has led to a qualitative understanding of how cellular tissue behaves during freezing. The qualitative data may be better integrated and interpreted by examining the heat and mass transport processes associated with ice formation in cellular materials. Such a mechanistic view of ice formation in food materials may make it possible to define precisely conditions that reduce textural damage.

The literature on ice formation in cellular biological material may generally be divided into two categories: The first category consists of reports of ice forming in food materials where conditions and consequences of mechanical

Authors' addresses: *Western Regional Research Center, U.S. Department of Agriculture, 800 Buchanan Street, Berkeley, CA94710, U.S.A., and †University of California, Berkeley, California, U.S.A.

*To whom correspondence should be addressed.

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damage to the cells and cell walls are being evaluated. The other category of literature concerns studies that examine conditions for the freezing preservation of cell viability. The literature in the first category covers a long span of time, but the conclusions on ice formation and textural changes are generally consistent amongst these authors (Woodruff, 1938; Koonz & Ramsbottom, 1939; Luyet, 1968a; Reeve & Brown, 1966; Brown, 1967; Sterling, 1968; Love, 1966; Mohr & Stein, 1969; Manzini *et al.* 1975; Bevilacqua, Zaritsky & Calvelo, 1979). The literature in the second category is extensive and steadily growing, and only a few comprehensive papers and reviews will be mentioned here (Asahina, 1956 Luyet, 1957; Luyet & Raptz, 1958; Luyet, 1968b; Mazur, 1963; Meryman, 1966; Levitt, 1978).

Most of the work relating ice structure and freezing conditions in foods was done by viewing microscopic sections of frozen tissue. When freezing was slow, these reports demonstrate the existence of large ice structures, shrunken cells and ruptured cell walls in fruits and vegetables. A drawback of most of this work is that no quantitative measure of the freezing rate was used to correlate with the dimensions of the ice in the micrographs. Descriptive terms, such as 'sharp', 'slow' 'fast' or 'ultra-rapid' are often used. The recent work of Bevilacqua *et al.* (1979) is an exception since they quantitatively defined the freezing rate of their beef samples.

Most of the fundamental understanding of freezing in cellular material has come from work directed at an elucidation of the mechanisms of cellular death during freezing. Much of this work has been based upon observations of tissue as it is freezing in a cold-stage microscope (Asahina, 1956; Luyet, 1968a). The distinction between extracellular and intracellular freezing is clearly evident from these studies. In addition, this technique has documented the shrinkage of cells in response to the presence of extracellular ice, as well as the phenomenon of super-cooling of cells before freezing, evidenced by sudden freezing or 'flashing'. The cold-stage microscope reveals the details of ice-solute structures, and it has been used to observe ice forming in solutions as well as in actual cells.

An application of heat and mass transport theory to extracellular and intracellular freezing is best done by viewing the essential characteristics of a plant cell in the form of a simplified model. Fig. 1a is an idealized schematic drawing of a mature plant cell, such as one that would be in the parenchyma tissue of a ripe fruit or vegetable. These types of cells characteristically have a large central vacuole, and the cytoplasm is distributed in a thin layer between the tonoplast and the plasmalemma (Jensen, 1964). A plant cell with its metabolic activity is very complex, but for the purposes of a heat and mass transport analysis, it is reasonably accurate to think of a cell in the simplified manner shown in Fig. 1b. The cytoplasm, plasmalemma and tonoplast can be thought of as a single composite membrane, which is selectively permeable to water and may be characterized by a membrane permeability parameter. The individual cells are surrounded by semi-rigid walls, composed of cellulosic, hemicellulosic and pectic compounds. The walls are generally considered freely permeable to water and solutes. When the idealized individual cells of Fig. 1b are combined to form

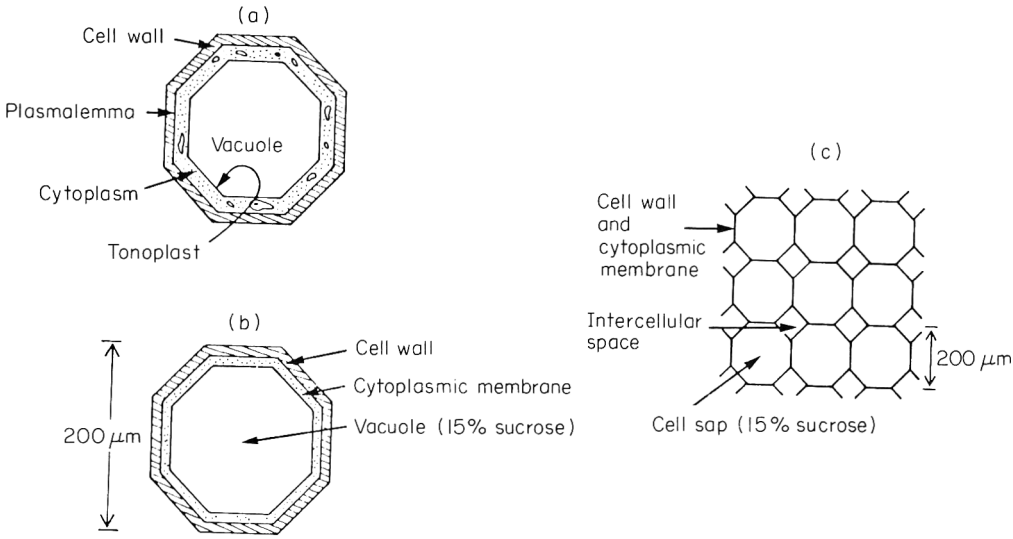


Figure 1. Model of cells in the parenchyma tissue of a plant. (a) Schematic diagram of a cell; (b) simplified model of a cell; (c) model of apple tissue.

a tissue, they may be represented two-dimensionally as shown in Fig. 1c. Reeve (1953) reported that the polyhedral cells of Pippin apples had an equivalent diameter of approximately 200 μm, and the intercellular gas spaces occupied 20–25% of the total volume.

When plant tissue freezes, two types of freezing are observed (Asahina, 1956). When the freezing rate is slow enough that the cell can undergo plasmolysis, ice forms extracellularly between the cytoplasmic membrane and the cell wall. Extracellular freezing is represented in an idealized fashion in Fig. 2a. The other type of freezing, intracellular freezing, is depicted in an idealized fashion in Fig. 2b. In intracellular freezing the freezing rate is rapid enough that plasmolysis does not occur, and ice forms within the cell.

Observing the ice morphology in frozen foods in more detail has suffered because of the necessity of processing the tissue before observation in optical or electron microscopes. The usual technique of preparation is either freeze substitution or freeze drying. In freeze substitution the ice is replaced by a solvent, such as methanol, and then the tissue is observed directly or after embedding (Jensen, 1962; Brown, 1967). The problem with this technique is that the cell solutes, as well as the ice, will dissolve in the solvent. Thus the structure of the solidified solutes will disappear, and the morphology of the ice dendrites will be lost. When freeze drying is used as a preparation technique, the loss of solutes is avoided, but the solutes, especially the soluble carbohydrates in plant material, are susceptible to collapse during freeze drying (Bellows & King, 1973). This collapse obliterates the detailed ice structures. Viewing a replica of the fractured surface of a frozen sample on the transmission electron microscope avoids the artifacts of the above two methods (Mohr & Stein, 1969); however, replication techniques are difficult, and the area viewed is only a very small fraction of the

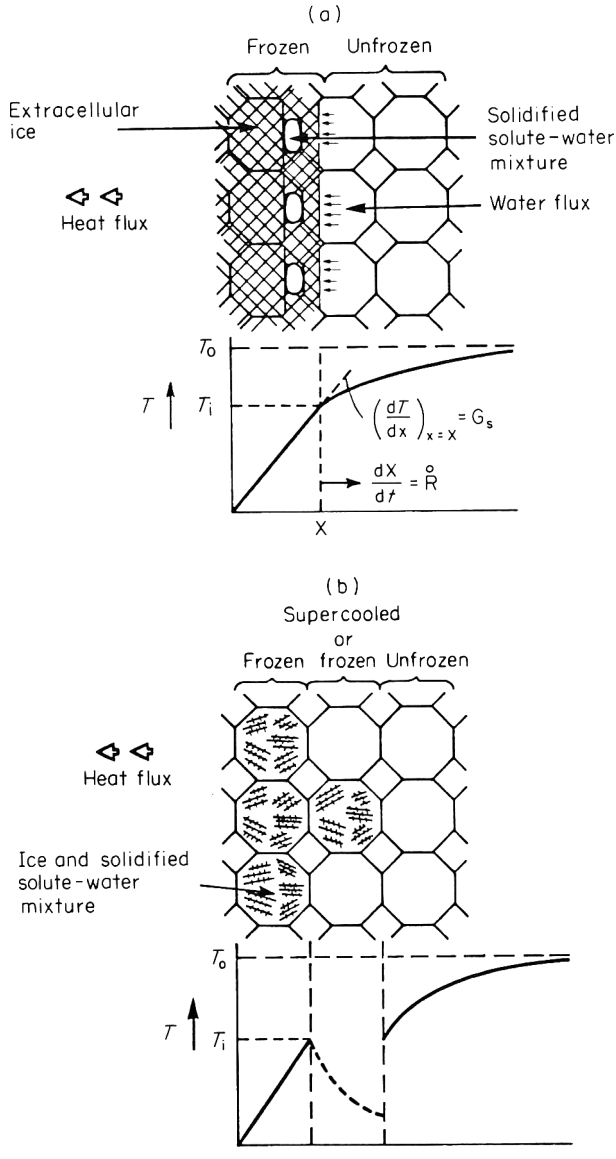


Figure 2. Schematic representation of tissue freezing. (a) Extracellular freezing—cross-hatched area represents extracellular ice and unmarked area represents a shrunken cell containing the solidified solution of solute and water; (b) intracellular freezing—the crossed lines represent the dendritic structure of ice and solute.

entire sample. The cold-stage scanning electron microscope (SEM) used in the present work is a newly developed instrument, which is ideally suited for observing ice morphology since the frozen sample is viewed directly. By means of heat and mass transport analyses this paper uses existing theories for cellular freezing and solution solidification to examine data obtained by a cold-stage SEM of frozen apple tissue.

Materials and methods

Cold-stage SEM

Discs 3 mm thick were sliced from 2·0 cm diameter cylinders that were cut axially from the outer flesh of Newton Pippin apples. The discs were blotted, and thermocouples (copper–constantan, 76 μm) were attached to the two faces of a disc using cyanoacrylate ester glue. Each disc was then frozen under different conditions to give various freezing rates as measured by the temperature recording (Bomben, 1981; Bomben, King & Hayes, 1982). Freezing rates were altered by using different cooling media and different depths of insulation around the discs (Bomben, 1981). For most conditions heat was removed from one face of the disc with the other face kept well insulated. Only in the case of freezing with boiling liquid nitrogen (450 K/min) and very slow freezing of a heavily insulated disc (0·031 K/min) was heat transferred from both faces of the disc.

The frozen apple discs were stored in liquid nitrogen until they were ready for microscopic viewing. No changes in ice structure from storage were apparent. The samples were fractured, etched, gold coated and viewed in the cold-stage SEM described by Pawley & Norton (1978) and Pawley *et al.* (1978). With this instrument the fractured surface of the frozen specimen was viewed directly while it was always maintained at 123 K or lower during fracturing, etching, coating and viewing. Polyethylene breakers containing 15% (w/w) sucrose solutions and having approximately the same dimensions as the apple discs were also frozen at three different rates and viewed on the SEM. The details of the experimental technique are described elsewhere (Bomben, 1981; Bomben, *et al.* 1982).

The dendritic spacing was measured on the micrographs by counting intersections on a circular test line located at random positions (Underwood, 1969). No attempt was made to correct for a non-planar viewing surface, but Howell (1978) showed that the error in using such a parallel projection for measuring distances was on the order of 5% for the working distance of 12 mm and magnification of 100 × that was used in most of the measurements in the present work.

Freezing rates

Freezing rates used experimentally were chosen to cover the range commonly encountered in food freezing operations. For this purpose it is desirable to adopt a definition of freezing rate and to calculate values of this rate for various conditions.

The most precise way to calculate freezing rates for different, well-defined conditions would be to use the numerical techniques that have been developed for solving the Stefan problem (see e.g., Bonacina & Comini, 1973; Heldman, 1975; Cleland & Earle, 1977, 1979). However, the lengthy computations required with finite difference techniques are more elaborate than are needed for

the present work. Of the two analytical solutions to the Stefan problem, the Neumann solution and the Plank equation, the Plank equation is the more useful since it includes an external heat transfer coefficient. Cleland & Earle (1977, 1979) have shown that the Plank equation with empirical corrections, which account for the effects of heat capacity in the frozen layer and an initial temperature higher than the freezing point of the food material, can give accurate results when compared to experimentally determined freezing times.

The Plank equation expressed as a freezing rate rather than the usual freezing time, is the following for an infinite slab (see Appendix):

$$\mathring{R} = \frac{T_i - T_a}{\rho_I \Delta H_{fs}} \frac{1}{\frac{P_p}{h} + \frac{R_p X}{k_I}}, \tag{1}$$

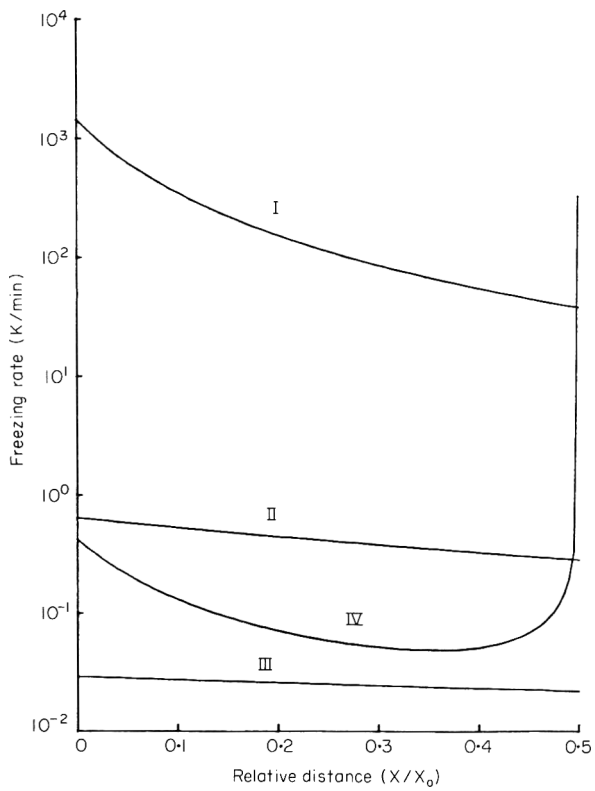


Figure 3. Freezing rates of apple typical for commercial freezing. I, slab in liquid nitrogen, h = 581 W/m²·K, T_a = 77 K, X_0 = 2 cm; II, slab in air blast freezer, h = 58.1 W/m²·K, T_a = 233 K, X_0 = 2 cm; III, slab in naturally circulating air, h = 17.4 W/m²·K, T_a = 244 K, X_0 = 2 cm; IV, cylindrical can in air-blast freezer, h = 58.1 W/m²·K, T_a = 233 K, X_0 = 24 cm. For all cases: T_i = 271 K, T_0 = 293 K, ΔH_{fs} = 374 kJ/kg, C_p = 3.6 kJ/kg K, C_{pI} = 1.9 kJ/kg K

where

$$P_p = 1{\cdot}014 + 0{\cdot}4036\ Pk + Ste\,(0{\cdot}644\ Pk + \frac{0{\cdot}0210}{Bi} + 0{\cdot}1362)$$

$$R_p = 1{\cdot}347 + Ste\,(2{\cdot}129 - 0{\cdot}108)$$

$$Ste = C_{pI}(T_i - T_a/\Delta H_{fs})$$

$$Pk = C_p\,(T_o - T_i/H_{fs})$$

$$Bi = h\,X_o/k_I.$$

The temperature gradient through the frozen layer can be expressed as

$$G_s = \frac{\rho_I\,\Delta H_{fs}\,\mathring{R}}{k_I} \tag{2}$$

Thus the cooling rate at the solidification front will be

$$\mathring{T}_s = \mathring{R} G_s \tag{3}$$

$\mathring{T}_s$ is used here to characterize freezing rates.

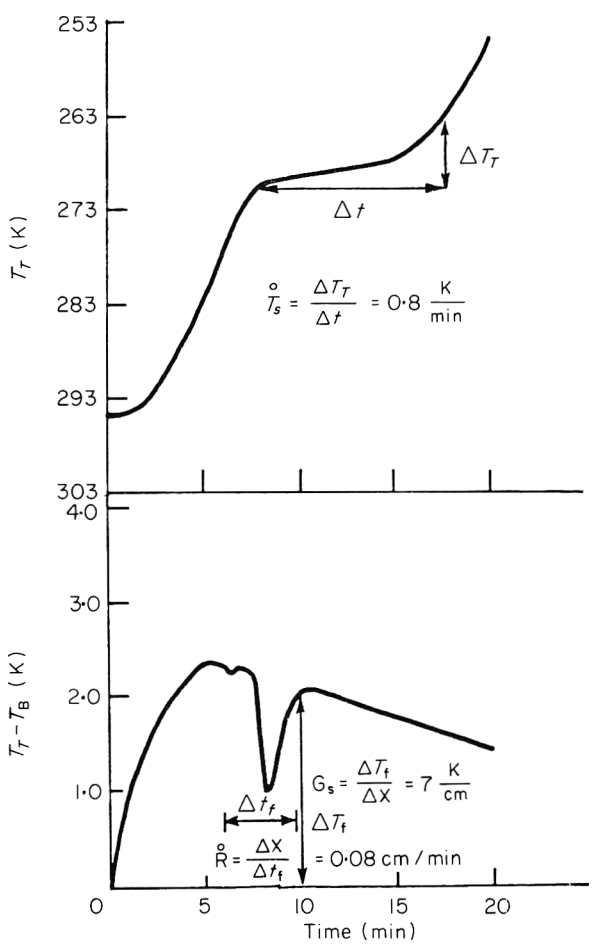
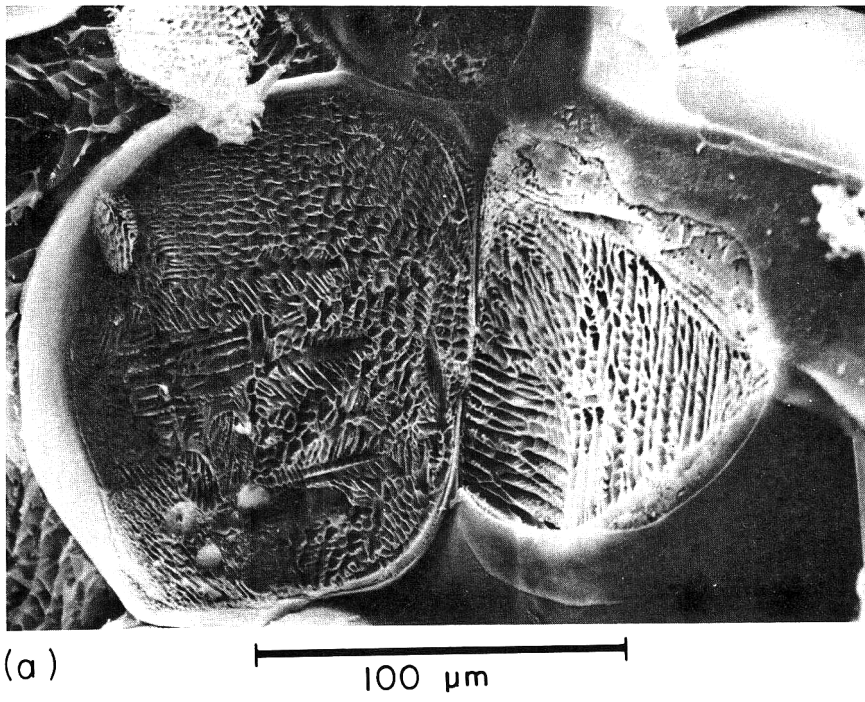


Figure 4. Temperature and temperature-difference history of apple disc frozen at 0.8 K/min.



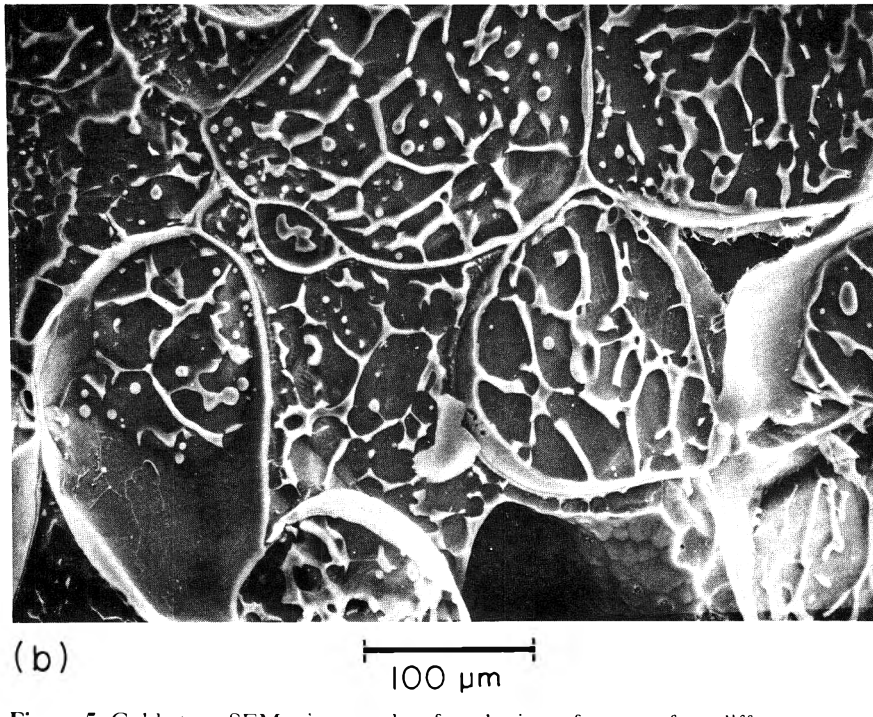
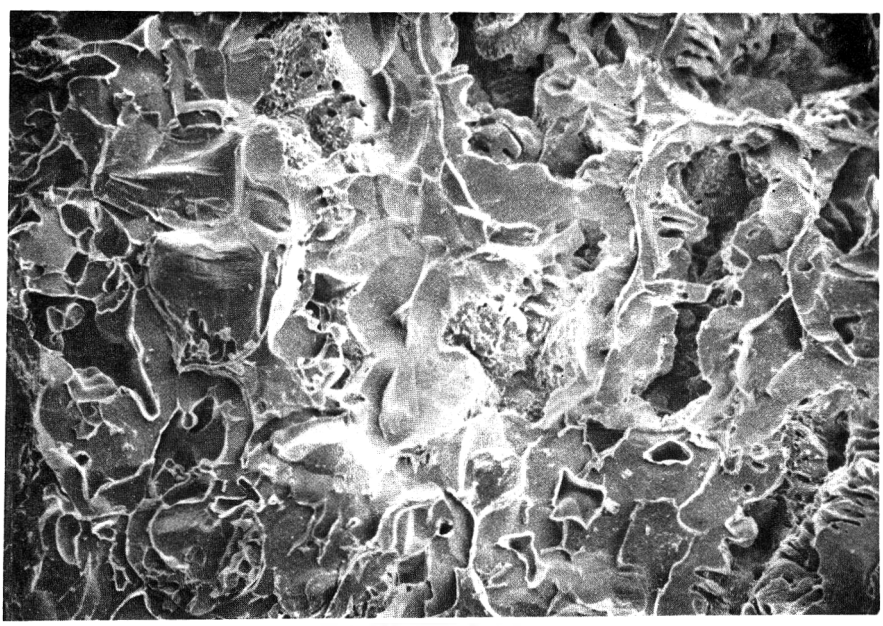


Figure 5. Cold-stage SEM micrographs of apple tissue frozen at four different rates. (a) 450 K/min; (b) 9 K/min; (c) 1 K/min; (d) 0.4 K/min.

(c) 100 μm



(d) 100 μm

The calculations of freezing rate in apple tissue using Equations (1), (2) and (3) are shown in Fig. 3. Cases I, II and III depict the variation in freezing rate across individual pieces of apple, while Case IV depicts the variation in freezing rate within a can of apple and syrup, assuming that the thermal properties of the

combination of apple syrup mixture are the same as that of the individual apple piece and that natural convection does not occur. The Plank equation for the freezing of an infinite cylinder in Case IV is different from that for a slab; it is derived by London & Seban (1943), and its use with the Cleland & Earle (1979) correction is shown by Bomben (1981). Figure 3 shows the wide range of freezing rates that are possible for typical conditions of food freezing. It should also be noted that for some conditions the freezing rate may vary considerably within a specimen (e.g. Cases I, IV in Fig. 3).

Interpretation of freezing rates from experimental data for temperature and temperature-difference histories during freezing is depicted in Fig. 4. $\mathring{T}_s$ was taken as the linearized slope for T versus time over the temperature range from 272 to 263 K. For this purpose the temperature measured at the face of the disc away from the cooled surface was used. Values of $\mathring{T}_s$ can also be obtained through Equation (3) from values of G_s and $\mathring{R}$ derived from the temperature-difference history. A comparison and an analysis of values of $\mathring{T}_s$ obtained in these two ways are presented elsewhere (Bomben, 1981).

Results

Figure 5 shows SEM micrographs of apple tissue frozen at different rates. The bright regions in the micrographs are the solidified solutes of the cell sap, the cytoplasmic membrane, and the cell walls. The darker regions in the micrographs are ice. The difference in intensity is because of the difference in height between the ice, which sublimed during etching, and the solute-water glass and insoluble structures of the tissue, which did not sublime during etching. In addition, the edges of the solidified solute-water glass, the cytoplasmic membranes and the cell walls cause an enhancement of the emission of secondary electrons, thereby giving a brighter image.

At rapid freezing rates (450 K/min) the dendritic structure of the intracellular ice is clearly evident. At lower freezing rates (9 K/min) the dendritic spacing in the cell becomes larger. At freezing rates of 1.0 K/min intracellular (lower left hand corner) and extracellular ice are both evident. At very slow freezing rates (0.4 K/min), only extracellular ice is evident.

Figure 6 shows the results of measurements of dendritic spacing as a function of the freezing rate. When the ice formation is extracellular, it no longer has the dendritic appearance of a frozen solution. The sugars remain within a shrunken cell in the form of a glassy structure of sugars and water. Since the ice formation disrupts the cell wall structure as well, the micrographs of extracellular ice formation no longer have the regular appearance of the ones showing intracellular ice, and the distinction between ice and solute-water glass becomes uncertain. When a least square analysis is performed with dendritic spacings, the slope of the line is -0.5 with a correlation coefficient of 0.89 as shown in Fig. 6. The dendritic spacings obtained in a 15% sucrose solution frozen at different rates are also plotted in Fig. 4, but they are not included in the correlation.

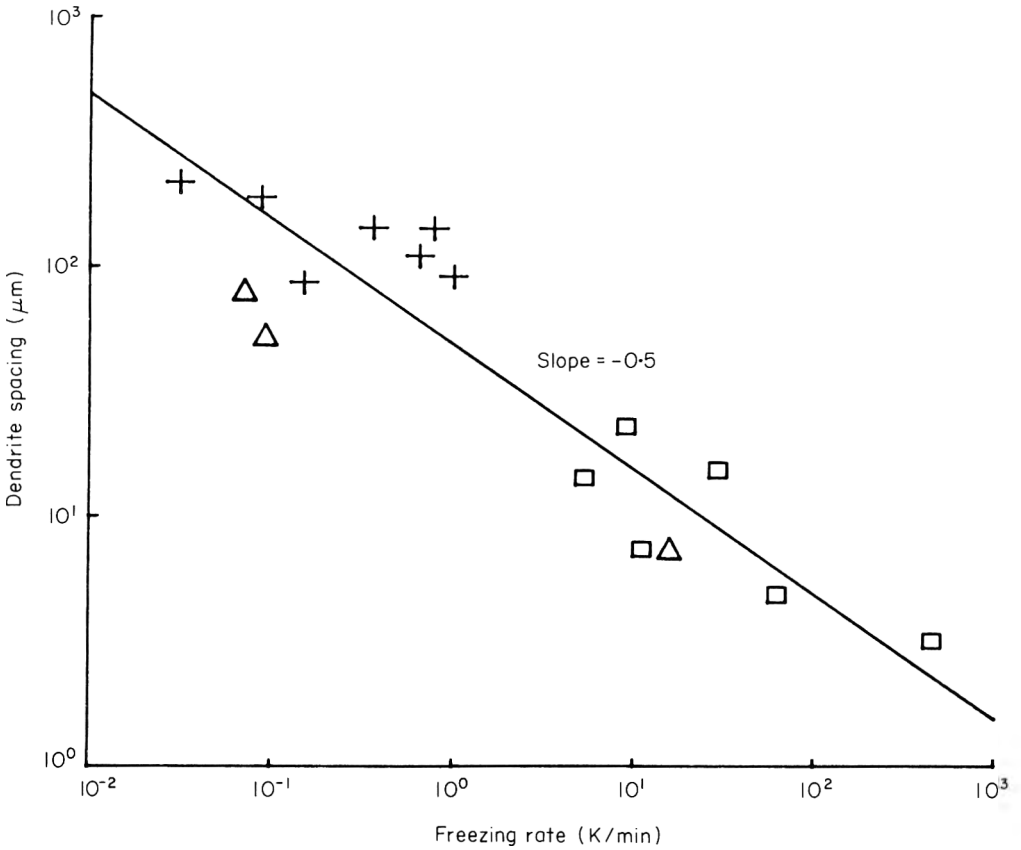


Figure 6. Dendritic spacing as a function of freezing rate △, 15% sucrose; □, intracellular; +, extracellular.

Discussion

Intracellular versus extracellular freezing

Mazur (1963) is generally given credit for being the first to examine quantitatively the water transport involved in cellular freezing. He applied basic thermodynamic and mass-transport concepts to the freezing around an individual cell surrounded by an infinite medium of an aqueous solution. Mazur's calculations showed that slow cooling of a cell allows time for water to leave a cell by permeation through the plasmolemma and thereby keep the intracellular solution near the solute concentration that has an equilibrium freezing point at the prevailing temperature. If the cell is cooled rapidly, water cannot permeate rapidly enough; thus, the intracellular solution departs markedly from the equilibrium concentration, and the probability of intracellular ice nucleation is increased.

Mazur derived the following equation, put into a dimensionless form, to show the relationship between the volume of a cell and the prevailing temperature

after extracellular ice formation (see Appendix):

$$\frac{d^2\psi}{d\theta^2} - \left[\frac{\alpha\beta}{(1-\theta)^2} + \frac{\epsilon\eta \exp\left(\beta - \frac{\alpha\beta}{1-\theta}\right)}{\psi(\psi+\eta)}\right]\frac{d\psi}{d\theta} - \frac{\epsilon\gamma \exp\left(\beta - \frac{\alpha\beta}{1-\theta}\right)}{(1-\theta)^2} = 0, \tag{4}$$

where

$$\psi = \frac{V}{V_0}, \quad \theta = \frac{T_i - T}{T_i}, \quad \alpha = \frac{T_g}{T_i}, \quad \gamma = \frac{\Delta H_f}{RT_i}$$

$$\eta = \frac{n_s^c V_w^0}{V_0}, \quad \epsilon = \frac{A_c P_g T_i}{B V_0}, \quad \text{and } \beta = \frac{\Delta E_m}{RT_g}.$$

The initial conditions are

$$\text{at } \theta = 0, \psi = 1 \quad \text{and} \quad \frac{d\psi}{d\theta} = 0.$$

Equilibrium would exist in the case of an infinitely slow cooling rate, ($B = 0$); thus

$$\ln\left[\frac{\psi(1+\eta)}{\psi+\eta}\right] = \gamma\left(\frac{\theta}{\theta-1}\right) \tag{5}$$

Mazur (1963) thoroughly discusses the assumptions made in deriving Equation (4). The more important assumptions are the following: (1) The membrane remains intact and is permeable only to water; (2) the cellular solution is ideal; (3) concentration polarization is insignificant; and (4) the extracellular solution is in equilibrium with ice, and the intracellular solution is at that equilibrium temperature. Mansoori (1975), Silvares *et al.* (1975), and Levin, Cravalho & Huggins (1976, 1977) made the cellular water transport calculation without assumptions of ideal solution, constant cellular area and constant heat of fusion, and they found that their results did not differ markedly from those of Mazur. Levin *et al.* (1976) showed that in red blood cells concentration polarization could become important at high freezing rates (>5000 K/min). At freezing rates typically used in food processing (10^{-2}–10^3 K/min), concentration polarization should be negligible in apple tissue (Bomben, 1981). Uncertainty in the data on the permeability of plant cells far overshadows any assumptions made in deriving Equation (4). The permeabilities used in the above-mentioned calculations were extrapolated from values obtained near room temperature. Levin *et al.* (1976) point out that such an extrapolation can lead to substantial errors.

Equation (4) was used to calculate the relationship for cellular volume and temperature at various cooling rates using the properties of apple cells and the quantities listed in Table 1. The diameter and volume of apple cells were reported by Reeve (1953). Although the freezing point of apple tissue is generally reported as 271 K (ASHRAE, 1977), in this calculation it was taken as

Table 1. Properties for an apple cell (15% w/w sucrose) used in Equation (4)

V_0 (μm^3)	4.2×10^6
d (μm)	200
T_i (K)	272
x_s	9.20×10^{-3}
n_s^c (mol/cell)	2.16×10^{-9}
ΔE_m (kJ/mol)	16.3 (Levin *et al.*, 1976)
T_g (K)	293
P_g (cm/s)	4.0×10^{-4} (Rotstein & Cornish, 1978)
R (kJ/mol K)	8.319×10^{-3}
V_w^n (μm^3/mol)	18×10^{12}
ΔH_f (kJ/mol)	6.0

272 K to make it consistent with the molality of a 15% sucrose solution. The permeability of the cytoplasmic membrane was taken from Rotstein & Cornish (1978), who review the data available for permeabilities of plant and animal cells. The activation energy for the permeability was that used by Levin *et al.* (1976) for red blood cells because permeabilities near the freezing point of water are not available. The other quantities in Table 1 are the ideal gas constant and properties of water.

When a cell freezes intracellularly, the cell sap has become a supercooled solution in which, having been nucleated in some fashion, ice grows throughout. The mechanism of nucleation is unclear. Mazur (1966) has postulated a theory based on the hypothesis that at rapid freezing rates the ice formed extracellularly has a sufficiently small radius of curvature to nucleate the intracellular solution through the pores that exist in cell membranes. Toscano *et al.* (1975) have proposed that there are naturally occurring catalysts in the cell which can trigger heterogeneous nucleation. The calculation of the degree of supercooling for nucleation is complicated, and the pertinent parameters are not readily available. What can be said is that experimentally plant cells have been observed to supercool readily 5–10 K before intracellular ice appears (Asahina, 1956; Marcellos & Single, 1979).

Figure 7 shows the results of the calculations using the properties shown in Table 1. At low cooling rates (< 0.1 K/min) the solution inside the cell does not depart far from equilibrium. Under these conditions most of the water should leave the cell and appear as extracellular ice. Even at 1 K/min the cells never supercool more than 10 K ($\theta = 0.037$) before reaching the equilibrium curve. If we assume that intracellular ice nucleates at a supercooling of 10 K ($\theta = 0.037$) and rapidly equilibrates within the cell, then at a cooling rate of 10 K/min, the volume of water in the apple cell would have been reduced to 88% of that originally present when intracellular ice forms. Similarly at 100 K/min, the volume shrinkage would be essentially imperceptible before intracellular ice was formed.

With this analysis one can make a quantitative interpretation of the observations made with the SEM. Rapid freezing rates (> 10 K/min) lead entirely to

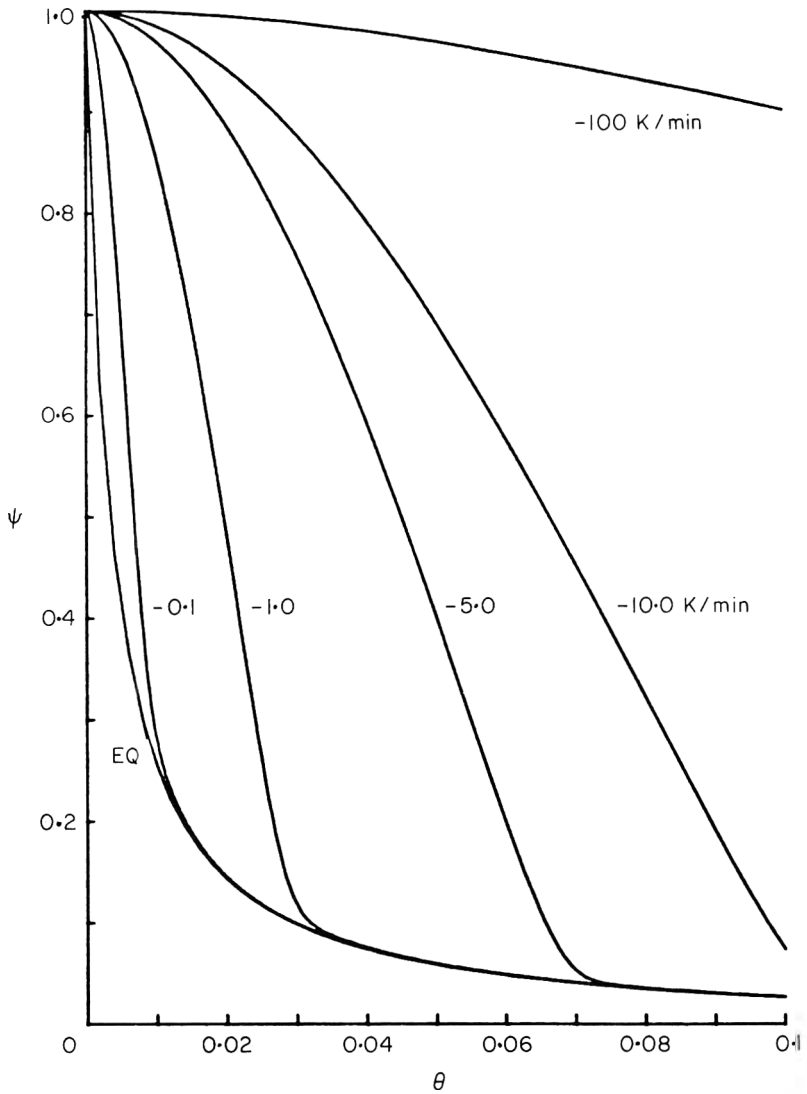


Figure 7. Relative volume of cellular water as a function of temperature and cooling rate

intracellular ice in apple tissue and no appreciable shrinkage in cell volume. Figures 4a and 4b show intracellular ice in unshrunken cells. At slower freezing rates (<1 K/min) the calculations show that cells plasmolyse, thereby leading to extracellular ice and drastically shrunken cells. Experimentally these effects are shown in Fig. 4d. Intermediate freezing rates ($1<10$ K/min) would show evidence of extracellular ice, partially shrunken cells and intracellular ice. The co-existence of extracellular and intracellular ice is shown in Fig. 4c.

Intracellular solution solidification

If we confine our consideration to what happens after intracellular nucleation, then we are basically investigating how ice grows in a solution. Ice, like

many other materials, usually does not solidify in a planar front. In a solution from which ice is being formed, there is a solute-rich layer ahead of the solidifying front. Under these conditions it is possible for a planar ice surface to be unstable, in which case any protuberance formed will grow into the region ahead of the planar surface. This condition is called constitutional supercooling, and the specific circumstances leading to it are described by Flemings (1974).

An approximate calculation for the dendritic spacing under constitutional supercooling was derived by Rohatgi & Adams (1967a, b). Their basic assumption is that the spacing between growing dendrites adjusts to make the constitutional supercooling a small constant value. The equation describing the supercooling between the dendrites is as follows:

$$\Delta T_L = \frac{\mathring{T}_s L_d^2}{2D_{ws}} \tag{6}$$

Thus, if during the freezing of a solution the dendritic spacing adjusts to keep a small and constant degree of supercooling between the dendrites as the theory proposes, a graph of log L_d *versus* log $\mathring{T}_s$ gives a straight line with a slope of -0.5. The result of this analysis is probably more general than the simplifying assumptions suggest since a dimensional analysis, assuming that the variables that enter Equation (6) are the only significant ones, leads to the same conclusion. Although this theory is a simplified picture of a complex phenomenon, it does appear to account for the few experimental observations available for dendritic spacing in alloys and solutions (Rohatgi & Adams, 1967a, b; Flemings, 1974). The dendritic spacings for the freezing of apple tissue and sucrose solutions shown in Fig. 4 agrees remarkably well with this dependence upon $\mathring{T}_s$.

Bevilacqua *et al.* (1979) correlated their data for ice crystal size in frozen beef versus log t_c rather than $(\mathring{T}_s)^{-0.5}$. The critical freezing time, t_c, was defined as the time for a point in the sample to go from the initial freezing point (272 K) to the temperature (266 K) where 80% of the water was frozen in beef. Their freeze-substitution method measured holes left by the intracellular ice formations between the myofibrils in the muscle fibres and the holes left by extracellular ice between the fibres. The behaviour of the protein solutions in muscle tissue could be considerably different than that of the dilute sugar solutions in apple tissue. Their data on ice size, when correlated as in Fig. 6, give a slope of -0.17. It is not clear whether this difference is the result of the morphological and compositional differences between muscle and plant tissue or the difference in the experimental methods used for observing the ice formations.

Appendix

A_c	Cellular surface area (m^2)
B	Cooling rate (K/min)
C_p	Heat capacity of solution (J/kg·K)
C_{pl}	Heat capacity of ice (J/kg·K)
d	Diameter of cell (m)
D_{ws}	Diffusion coefficient for solute and water (m^2/sec)

ΔE_m	Activation energy for cellular permeability (J/kg mol)
G_s	Temperature gradient in frozen phase (K/m)
h	Heat transfer coefficient (W/m^2·K)
ΔH_{fs}	Enthalpy change of solidification (J/kg)
ΔH_f	Heat of fusion of ice (J/kg)
k_l	Thermal conductivity of frozen phase (W/m·K)
L_d	Dendritic spacing (m)
n_s^c	Moles of solute per cell
P_g	Cellular permeability at 293 K (m/sec)
P_p	Defined in Equation (1)
R	Gas constant (J/kg-mol·K)
$\mathring{R}$	Velocity of freezing front (m/sec)
R_p	Defined in Equation (1)
t_c	Critical freezing time (sec)
T	Temperature (K)
T_a	Temperature of refrigerating medium (K)
T_B	Temperature of apple disc surface at refrigerating medium (K)
T_g	Reference temperature for cellular permeability (293 K)
T_i	Temperature of initial freezing point (K)
T_0	Initial temperature (K)
T_T	Temperature of apple disc surface farthest away from refrigerating medium (K)
$\dot{T}_s$	Cooling rate at freezing front (K/sec)
ΔT_L	Supercooling in interdendritic solution (K)
V	Volume of intracellular water (m^3)
V_0	Initial volume of intracellular water (m^3)
V_w^0	Molar volume of water (m^3/mol)
X	Position of freezing front (m)
X_0	Slab thickness or cylinder diameter (m)
x_s	Mole fraction of solute
α	Defined in Equation (4)
β	Defined in Equation (4)
γ	Defined in Equation (4)
ϵ	Defined in Equation (4)
η	Defined in Equation (4)
ρ_l	Density of frozen phase (kg/m^3)
θ	Defined in Equation (4)
ψ	Defined in Equation (4)
Bi	Biot number defined in Equation (1)
Pk	Plank number defined in Equation (1)
Ste	Stefan number defined in Equation (1)

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The development of a vocabulary and sensory profile for the assessment of watercress quality

ROSE-MARIE M. SPENCE

Summary

The development of a vocabulary and sensory profile for evaluating quality attributes is described. Simple profiles for colour, sheen, aroma, flavour, texture and the overall acceptability and appearance of watercress are established. The use of odour reference samples is discussed and an attribute ranking test carried out to establish the order of importance of the quality attributes.

Introduction

With the increasing number of specifications for the quality and packaging of produce, the grower must be aware of the quality of his product in order to comply with the standards required. However, it must be taken into consideration that fruit and vegetables are living materials and that the uniformity of the product is affected by environmental conditions which are often outside the growers' control.

Foodstuffs are submitted to sensory examination to obtain information which, associated with chemical analysis, can lead to product improvement, quality maintenance, development of new products, or analysis of the market. Sensory profiles have been developed for use in the canning and freezing of fruits and vegetables to accept or reject produce for processing (Arthey, 1973). The beverages industry has also developed profiles to assess different products (Clapperton, 1973; Shortreed, Rickards & Burtles, 1979; Williams, 1975). No such profile nor quality specification has been developed for watercress, and during a study of post-harvest processing, storage and distribution of watercress (Spence, 1980) it was thought that sensory evaluation of changes in quality after harvesting might prove of value.

This study was undertaken to establish simple sensory profiles describing colour, sheen, aroma, flavour, texture and the overall acceptability and appearance of watercress, all of which contribute to its quality.

Author's address: Food and Beverages Division, Long Ashton Research Station, Long Ashton, Bristol BS18 9AF.

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Materials and methods

Material

The watercress (*Rorippa nasturtium-aquaticum* [L.] Hayek) was obtained from local shops, grown in watercress bed simulation tanks (Spence, 1980), and supplied by two growers in Hampshire and Dorset.

Composition of panel

The panel used during the development of the vocabulary and assessment procedure consisted of ten members; four female and six male (age range 22–50 years). Six people from the group were selected for each assessment.

Procedure

The assessments were carried out in a quiet, well-lit room with a matt white background to the assessment area. The panelists were given written instructions and asked to carry out the assessment on their own, and in their own time. When each member of the panel had completed the assessment, results were collected and discussed by the group.

Development of the profile

The following sequence of sensory assessments was undertaken by the panel:

Collection of terms to describe watercress properties. In two initial assessments panelists were asked to describe five bunches of watercress of different quality, using their own adjectives, with only the following headings as guidelines: colour, sheen, aroma, size of leaves, flavour, texture, overall appearance.

Rationalization and reduction of descriptive terms. Discussion amongst panel members, directed by the group leader, resulted in a reduction in the number of adjectives used to describe each characteristic, but still covering a range from good to bad quality. By testing the use of these reduced numbers of terms on seven different watercress samples in two assessments, adjectives were added or deleted as thought necessary during discussion. The adjectives were selected to cover all possibilities of quality without duplication of terms.

Use of terms on different formats of record sheets; profile modification and scoring. Different assessment sheet lay-outs were tested and simple scoring was introduced for some of the characteristics. Alterations were made to the profile as thought necessary by the panelists during four assessments of ten different bunches until the final version was developed.

Odour reference samples

Reference samples were made for the five aroma categories developed in the sensory profile. The compounds were added to molten paraffin wax (BDH

paraffin wax with ceresin for embedding) in small 15 ml glass stoppered bottles. The concentrations of compounds used were decided by smelling for the correct odour.

Dimethyl disulphide	(Fluka A.G.)	25 p.p.m. (v/w)
Phenethyl isothiocyanate	(Fluka A.G.)	325 p.p.m. (v/w)
β-ionone	(Aldrich Chemical Co. Ltd.)	12.5 p.p.m. (v/w)
Cis-3-hexen-1-ol	(Aldrich Chemical Co. Ltd.)	25 p.p.m. (v/w)

One bottle contained only wax as the blank sample.

The bottles were numbered and presented to the sensory panel for identification from the following list of adjectives, with the last four being classified according to intensity, i.e. weak, medium or strong: wet vegetation, cut grass, primrose/flowery, watercress, seaweed, rotting cress.

Attribute ranking test

A ranking test was carried out to determine the order of importance of different attributes on the profile assessment sheet for use by the consumer. Thirty-six people were presented with the sheet shown in Appendix 1 (p. 640). The list of attributes was initially randomized, then divided into four groups, and the order of these groups randomized. Sheets with the attributes listed in twenty-four different orders were used to avoid the possibility of bias due to the order of attribute presentation.

Members of the sensory panel also carried out the ranking test. These results were separated from the untrained consumers' results for comparison. Statistical analysis of the results was carried out using rank total tables (Kahan *et al.*, 1973) and Fisher distribution tables (Kendall, 1970).

Vocabulary development

Appendix 3 (p. 643) presents the results during the development of the sensory profile for watercress. Results of the two initial assessments are given on the left, with intermediate changes in the centre, and the final version on the right. The results of each attribute in Appendix 3 are discussed in the following sections:

Colour

Descriptions of colour were found to be unsuitable and colour standards were used. Munsell colour standards were used in preference to those of the Royal Horticultural Society since Munsell standards are universally recognized (Munsell, 1905). Ten green standards were selected, covering an adequate range of shades for assessing watercress, without confusing the assessor.

Sheen

A 5-point scale from GLOSSY to MATT was altered to VERY SHINY to DRY MATT and scores added for assessing sheen.

Size of leaves

Measurements of leaves defined the size categories on a 6-point scale from VERY LARGE to SHRIVELLED. Standard cardboard discs with diameters of the means of each size category were made and used for comparison so that actual measurement of individual leaves before selecting a size category was no longer necessary.

Aroma

Aroma was found to be an accurate indicator of freshness in watercress. Similar adjectives used during initial descriptions were grouped together and one adjective selected for each characteristic aroma. The aroma of leaves and stalks was assessed separately, using the same categories with 2-point intensity scales expanded to 5 in the final version (1 = weak to 5 = strong, with 2 being twice the strength of 1 and 3 being three times the strength of 1, etc.). When fresh, watercress has either no smell or a wet vegetation aroma. It then develops a distinct floral odour, and as the plant deteriorates and cell damage occurs, a typical watercress smell due to the liberation of phenethyl isothiocyanate from its glucosinolate is detected. Further deterioration results in the production of sulphur compounds which produce a seaweed-like and rotting cress odour. The range and sensitivity of these aroma changes was unexpected.

Texture to fingers

Adjectives used in initial descriptions were grouped together if similar and a 4-point scale from VERY CRISP to WILTED was developed for leaves and stalks assessed separately. The associated 'snapping' test proved to be too destructive and a 5-point scale with scores was used. The FRESH BUT SOFT category was added to cater for watercress grown in the summer which is more delicate than the winter cress because it grows more quickly, and although fresh, is not VERY CRISP or CRISP. The texture of stalks was deleted because the crispness of the leaves was considered more important.

Texture to tongue

From initial descriptions a 5-point scale from CRISP AND EASY TO CHEW to INEDIBLE was tried unsuccessfully. After discussion, panelists decided on a 2-point scale of either FRESH AND CRISP (acceptable) or WILTED (unacceptable) because texture in the mouth was not considered a major contributing factor to quality.

Flavour

Panelists decided that the characteristic watercress flavour was most important; any other flavours being irrelevant. The 'hotness' of the flavour was

also considered a valuable attribute; the intensity preferred varying between members. Even in the initial descriptions, the time effect on flavour and hotness development was mentioned, and three time stages (initially, while chewing and after chewing) with 4-point scales for flavour and hotness were decided upon in the final assessment sheet. The time effect while eating has also been found with apples (Williams & Lewis, 1978) where, once the fruit cells are broken in the mouth, different volatile components are emitted due to the release of enzymes and possible pH alteration as a result of interaction with the saliva.

Overall appearance

After assessing individual attributes of the watercress, panel members decided that any other factors contributing to the overall quality of the bunch should be mentioned, and their importance assessed over several tests with modifications to descriptions as necessary, until a final version was developed. Factors contributing to the overall appearance of the whole bunch were its size and tightness. The colour of stalks, the colour and dryness of their cut ends and the number of yellow leaves, were included in the profile as affecting the quality of the stalks. The quality of the bunch head was affected by the number of yellow leaves and its physical condition. Since these characteristics were noted after the other attributes had been described, and because the development of terms for them was more difficult, they were placed at the end of the assessment sheet. Previous completion of other sections was thought to aid in the modification and clarification of these attributes. To assess the importance of these latter attributes with the former ones, the ranking test was carried out. Appendix 2 (p. 640) is the final version of the assessment sheet used in this work.

Odour reference samples

The identification of the samples by seven panel members is given in Appendix 4 (p. 647). The perception of aroma varies from person to person, and a threshold test was not carried out on panelists before selection for watercress assessment. However, five of the seven members identified dimethyl disulphide as a rotting cress smell and one as seaweed, with the intensity as either medium or weak, but not strong. Five of the seven members identified phenethyl isothiocyanate as strong watercress, and the other as medium watercress. The β-ionone was identified as the primrose aroma by six of the seven members, but all three degrees of intensity were used. The member of the assessment panel who could not identify β-ionone, could not detect the aroma of a sample double the concentration. It was also noticed that several other people could not detect this aroma, and possibly they have a particularly high concentration threshold value for this compound or are truly anosmic to it. The aroma of cis-3-hexen-1-ol, the classic 'green cut-grass' and 'green leaf' odour compound, was not identified by three panel members, and of the other four,

two described it as wet vegetation, and two as cut grass. A fairly low concentration was used in the hope that it would be identified as the wet vegetation aroma, but further work is needed to develop this reference sample because the wet vegetation odour is not very strong and cis-3-hexen-1-ol in low concentrations appears to be below the threshold values of many people. For the seaweed odour reference sample, a compound similar to dimethyl disulphide, or a mixture of dimethyl disulphide and another compound will have to be found.

Attribute ranking test

Using Fisher distribution tables, both results of sensory panel members and untrained consumers showed no difference in individual assessor's rankings of the attributes, i.e. all assessors agreed with respect to the ranking order.

The probability of any observed rank sum of an attribute being outside the range in the rank total tables was tested at the 5% level. The attributes not significantly different were re-ranked and the rank totals tested again until no more attributes were significantly different from the others. The results are given in Appendix 5 (p. 648).

Members of the assessment panel separated four attributes as the most important, with shape of leaves ranked 13, and the other eight attributes ranked equally as 5. The top three attributes chosen by the panel were ranked equal 1 by the untrained consumers, along with texture when in the mouth (crispness) and flavour and hotness. Sheen of leaves, ranked 4 by the panel, was ranked 6 by the consumers and they also separated firmness and appearance of stalk ends, colour of stalks and aroma of leaves, which were ranked 7, 8 and 9. The remaining four attributes were ranked equally 10 by the consumers, and they were also in the lower rankings of the panel members.

Panelists picked out the most important attributes and left the rest as equally unimportant, except for shape of leaves which was significantly less important, suggesting that experience in assessing causes the person to concentrate on the few major attributes contributing to good quality watercress, with the rest of secondary importance. Consumers were also able to recognize the most important attributes chosen by the panel, but they were not able to separate them into order of importance.

Further questioning of the consumers why texture in the mouth (crispness) and flavour and hotness were ranked in the first five attributes might reveal, as with the panel members, that texture in the mouth is not so important because watercress is rarely eaten on its own, and as long as the flavour of watercress is present, the intensity preferred, which varies considerably between individuals, is of secondary importance. Colour is probably more important than flavour and texture, although they were ranked equally; with other vegetables and fruits it is colour which is one of the major factors in attracting the consumer's initial attention in the shop.

Further ranking tests including the order of magnitude of importance of attributes would determine the size of the sensory difference between attri-

butes, and not only their order of importance. Tests to determine the major attributes when assessing watercress in the shop would provide useful information for the presentation of the product to the consumer, especially since there is an increase in demand for pre-packs.

Discussion and conclusions

The use of sensory assessments and consumer preference information, related to physico-chemical data, is an important tool in the definition of product quality.

The development of vocabulary for a sensory profile is a complex procedure with problems of determing the quality attributes and of selecting precise descriptive terms. This study has succeeded in producing a profile for the assessment of watercress which needs to be used in a wide variety of situations to determine whether further modifications are required. The scoring system needs to be completed, improved and tested for weighting certain attributes before it can be used for statistical analyses. The results of further ranking tests will provide information for appropriate weighting of attributes. Since aroma of watercress is important in indicating its firmness, the use of odour reference samples will aid assessment by panelists, and increase the precision of the results.

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Appendix 1

Sheet used for attribute ranking test.

Please rank the following attributes in order of importance when assessing watercress. If two or more attributes are of equal importance, bracket together.

Physical damage to leaves (bruising, torn edges)	
Aroma of stalks	
Tightness of bunch	
Texture when in the mouth (crispness)	
Flavour and hotness	
Colour of leaves	
Shape of leaves	
Sheen of leaves	
Texture when handled (firmness)	
Colour of stalks	
Aroma of leaves	
Firmness and appearance of stalk ends	
Size of leaves	
	1
	2
	3
	4
	5
	6
	7
	8
	9
	10
	11
	12
	13

If you consider any of the lower ranked attributes to be of no or little importance, please underline them.

If there are any attributes which you consider to be important, but which are not included, please list below:

Please complete the following details:

Male/Female .....
Age .....
Occupation .....

Frequency of eating watercress
Once a week or more .....
Two or three times a month .....
Once every 3 months or more .....
Less frequently .....

Do you eat watercress in a salad .....
or use it as a garnish .....
or use it in a cooked dish .....

Appendix 2

Final version of watercress assessment sheet.

COLOUR. Select the colour nearest to the overall colour of the bunch and write down the number:

SHEEN. Score the overall bunch according to the scale below and write down the appropriate number:

VERY SHINY	5
SHINY	4
DULL SHINE	3
MATT	2
DRY MATT	1

Appendix 2 *(continued)*

AROMA. Tick the category below for leaves and stalks—where there is a range within a category, 2 is twice the strength of 1, 3 is three times the strength of 1, etc. Insert an adjective if needed.

		Leaves	Stalks
No smell			
Wet vegetation smell			
Primrose/flowery smell	1—weak	.....	.....
	2	.....	.....
	3	.....	.....
	4	.....	.....
	5—strong	.....	.....
Watercress smell	1—weak	.....	.....
	2	.....	.....
	3	.....	.....
	4	.....	.....
	5—strong	.....	.....
Seaweed smell	1—weak	.....	.....
	2	.....	.....
	3	.....	.....
	4	.....	.....
	5—strong	.....	.....
Rotting cress smell	1—weak	.....	.....
	2	.....	.....
	3	.....	.....
	4	.....	.....
	5—strong	.....	.....

TEXTURE TO FINGERS. Score the *leaves* according to the scale below and write down the appropriate number:

VERY CRISP	5
CRISP	4
FRESH BUT SOFT	3
WILTING	2
WILTED	1

SIZE OF LEAVES. Using the size discs, decide which category most of the leaves in the bunch fall into and put a ring round it:

VERY LARGE (> 4 cm)
LARGE (3–4 cm)
MEDIUM (2–3 cm)
SMALL (1–2 cm)
VERY SMALL (< 1 cm)
SHRIVELLED

FLAVOUR AND HOTNESS. Eat a whole sprig and write down the appropriate number for each of the 3 stages according to the scale below:

Initially	No flavour or hotness	0
	Slight flavour and hotness	1
	Medium flavour and hotness	2
	Strong flavour and hotness	3
While chewing	No flavour or hotness	0
	Slight flavour and hotness	1
	Medium flavour and hotness	2
	Strong flavour and hotness	3
After chewing (persistence)	No flavour or hotness	0
	Slight flavour and hotness	1
	Medium flavour and hotness	2
	Strong flavour and hotness	3

Appendix 2 *(continued)*

TEXTURE TO TONGUE. Tick the appropriate word:

FRESH AND CRISP—acceptable . . . . . .
WILTED —not acceptable . . . . . .

OVERALL APPEARANCE

State of bunch—loose . . . . . .
—fairly tight . . . . . .
—tight . . . . . .

Colour of stalks—green . . . . . .
—green/yellow . . . . . .
—green/red . . . . . .
—yellow/brown . . . . . .
—brown . . . . . .

Colour and state of stalk ends—look at the cut ends of the stalks and write down the percentage of the total stalks which fall into that category, e.g. if half the stalks look green and half green/yellow, write 50% by 'green' and 50% by 'green/yellow'.

green . . . . . .
green/yellow . . . . . .
green/brown . . . . . .
yellow/brown . . . . . .
brown . . . . . .

Are the stalk ends—wet or dry? . . . . . .
—acceptable (not off-putting to buy) or not acceptable? . . . . . .

Yellow leaves—attached to stalks	none	*in head of bunch*	none . . . . .
	1–2		1–2 . . . . .
	3–5		3–5 . . . . .
	>5		>5 . . . . .

Damage to bunch head—score the bunch according to the scale below and write down the number.

no damage— 0
1
2
3
4
5
6
7
8
9
100% damage—10

Cause of damage—tick the appropriate word(s) for the *major* type(s) of damage in the bunch.

cut/torn . . . . . .
discoloured . . . . . .
wilting . . . . . .
disfigured . . . . . .

Percentage salvageable to eat—estimate the percentage and tick the appropriate category:

0% . . . . . .
0–10% . . . . . .
11–25% . . . . . .
26–50% . . . . . .
51–75% . . . . . .
76–100% . . . . . .

Bunch saleable at recommended price of . . . . . .? (Yes or No)
If 'No', would you pay half price? (Yes or No)

Appendix 3

Development of sensory profile for watercress—results of initial assessments on the left, intermediate changes in the centre, and final version on the right.

COLOUR

yellow	dirty green	*Intensity:*	→ Royal Horticultural Society colour fan for green shades →	Munsell colour standards	
yellow/green	dark green				
khaki	browny green	fairly		5 GY 4/4	7.5 GY 4/4
yellow/creamy green	not uniform	slightly		4/6	4/6
bright green	red veins			4/8	4/8
cooking-apple green	reddish-brown veins			5/4	
olive green				5/6	
				5/8	
				5/10	

SHEEN

dull	*Intensity:* →	5-point scale: →	Categories altered and scores added:	
dull shine	slight	GLOSSY	VERY SHINY	
velvet sheen		VERY SHINY	SHINY	
		SHINY	DULL SHINE	
		DULL SHINE	MATT	
		MATT	DRY MATT	

SIZE OF LEAVES

uniform	*Intensity:*	Measurements (diameter cm) →	6-point scale: →	Mesurement added: →	Cardboard discs used (diameter cm):	
variable						
large	very	3–4	VERY LARGE	≥ 4.0	4.5	
medium	mostly	2–2.5	LARGE	< 4.0 ≥ 3.0	3.5	
small	fairly	1.5	MEDIUM	< 3.0 ≥ 2.0	2.5	
shrivelled		< 1.0	SMALL	< 2.0 ≥ 1.0	1.5	
			VERY SMALL	< 1.0	0.5	
			SHRIVELLED			

Appendix 3 (*continued*)
Development of sensory profile for watercress—results of initial assessments on the left, intermediate changes in the centre, and final version on the right.

AROMA

fresh	brine	*Intensity:*	→ Divided into leaf and stalk aroma with same categories and 2-point intensity scale: → Intensity scale expanded to 5-points:
foliage smell	chlorine		
wet vegetation	fishy	strong	
apple smell	seaweedy	very	
beer smell	sea water smell	mild	No smell → No smell
primrose smell	river water smell	slight	Wet vegetation smell → Wet vegetation smell
perfume smell	brackish	little	Faint primrose/flowery smell → Primrose/flowery smell 1—weak
mashed rose leaves smell	dirty water smell	faint	Strong primrose/flowery smell → 5—strong
watercress smell	stale river or		Faint watercress smell → Watercres smell 1—weak
peppery	pond smell		Strong watercress smell → 5—strong
sour	decaying		Faint seaweed smell → Seaweed smell 1—weak
aromatic	rotting		Strong seaweed smell → 5—strong
acrid	stale		Faint rotting cress smell → Rotting cress smell 1—weak
			Strong rotting cress smell → 5—strong

TEXTURE TO FINGERS

turgid	smooth	limp	*Intensity:*	Divided into leaves and stalks with a 4-point scale and associated 'snapping test'. → 5-point sale for leaves only adopted and scores added
crisp	rough	lifeless		
springy	flexible	floppy	slightly	
waxy	bendy	flaccid	fairly	VERY CRISP—snaps 3 out of 3 times → CRISP 5
silky	rubbery	greasy	moderately	CRISP—snaps 2 out of 3 times → CRISP 4
cold	soft	slimy	very	WILTING—snaps 1 out of 3 times → FRESH BUT SOFT 3
wet	dry	clammy		WILTED—rubbery and will not snap → WILTING 2
				→ WILTED 1

TEXTURE TO TONGUE

crisp	bendy	smooth	*Intensity:*	5-point scale used:	Reduced to 2-point scale:
firm	rubbery	lumpy			
brittle	slimy	soft	slightly	CRISP AND EASY TO CHEW—TENDER	FRESH AND CRISP—acceptable
edible	limp	fibrous	quite	BIT CHEWY →	WILTED—unacceptable
waxy	flaccid	leatherv	fairly	SLIGHTLY THICK AND TOUGH	
silky	floppy	tough	little	TOUGH AND HARD TO CHEW	
	plastic-like	chewy	rather	INEDIBLE	
			very		

FLAVOUR

pleasant
sweet
apple-like
insipid
dry
sour
acidic
burning
hot
peppery
watercress
mustardy
'bite'
iron-like
metallic

Time of tasting:
no taste at first
initial taste
immediate
persistent
after taste
after effect
slow to develop
after swallowing
when leaf or stem is broken

Place of tasting:
on tongue
at back of mouth

Intensity:
strong
quite strong
slightly
little
rather
quite
medium
mild
very mild
very little
weak

→ Divided into FLAVOUR and HOTNESS with a 4-point intensity scale and 2 stage time aspect.

No initial flavour
Slight, immediate
Slight, after chewing
Medium, immediate
Medium, after chewing
Strong, immediate
Strong, after chewing
} watercress flavour

No initial hotness
Slight, immediate
Slight, after chewing
Medium, immediate
Medium, after chewing
Strong, immediate
Strong, after chewing
} hotness

→ FLAVOUR and HOTNESS combined and three stages of flavour development used with a 4-point intensity scale for each stage with scoring

Initially
Flavour and hotness—no 0
—slight 1
—medium 2
—strong 3

While chewing
Flavour and hotness—no 0
—slight 1
—medium 2
—strong 3

After chewing
(persistence)
Flavour and hotness—no 0
—slight 1
—medium 2
—strong 3

OVERALL APPEARANCE OF WHOLE BUNCH

too tightly packed
small
tight
stunted
ragged

loose
uniform colour
uniform size of leaves
fresh
high proportion of stalks

→ size of bunch
state of bunch—tight
—fairly tight
—loose

Appendix 3 *(continued)*

Development of sensory profile for watercress—results of initial assessments on the left, intermediate changes in the centre, and final version on the right.

OVERALL APPEARANCE OF STALKS

rooty
short
long
thick
slim
straight
green
yellow leaves attached
mushy
rotting
unappetising
untidy

→ Length of stalks
→ Rootiness
→ Colour → Colour of stalk ends → GREEN / GREEN/YELLOW / GREEN/BROWN / YELLOW/BROWN / BROWN
→ Attachment of yellow leaves
→ Presence of rotting ends
→ State of stalk ends → WET / DRY / ACCEPTABLE (not off-putting to buy) / NOT ACCEPTABLE
→ yellow leaves attached to stalks → none / 1–2 / 3–5 / >5

OVERALL APPEARANCE OF HEAD OF BUNCH

tatty
ragged
torn
wilted
limp
tired-looking
lifeless
floppy
shabby
crumpled
shrivelled

bruised
dry
withered
dull
fresh
unacceptable
undesirable
yellowing leaves
chlorotic leaves
dead leaves

→ Damage to head of bunch → no damage—0 ... 100% damage—10
→ Damage to leaves
→ Presence of yellow leaves
→ Veins prominent on leaves
→ Cause of damage → cut/torn / discoloured / wilting / disfigured
→ Yellow leaves in head of bunch → None / 1–2 / 3–5 / >5

→ Percentage salvageable to eat → 0
1–10
11–25
26–50
51–75
76–100

→ Bunch saleable at recommended price? Yes or No
or at half price? Yes or No

Appendix 4. Identification of reference compounds by seven members of the sensory assessment panel.

	Panelist						
Compound	1	2	3	4	5	6	7
Dimethyl disulphide	weak rotting	weak rotting	medium seaweed	—	medium rotting	weak rotting	weak rotting
Phenethyl isothiocyanate	strong watercress	medium watercress	strong watercress	strong watercress	strong watercress	strong watercress	medium watercress
β -ionone	strong primrose	medium primrose	strong primrose	medium primrose	weak primrose	medium primrose	—
Cis-3-hexen-1-ol	wet vegetation	—	cut grass	—	wet vegetation	—	cut grass

Appendix 5
Orders of ranking by panelists and non-panelists.

Order of Ranking by 7 Assessment Panelists

1 Physical damage to leaves (bruising, torn edges)
2 Colour of leaves
3 Texture when handled (firmness)
4 Sheen of leaves
5 Aroma of stalks
Tightness of bunch
Texture when in the mouth (crispness)
Flavour and hotness
Firmness and appearance of stalk ends
Colour of stalks
Aroma of leaves
Size of leaves
13 Shape of leaves

Order of Ranking by 36 Non-panelists

1 Physical damage to leaves (bruising, torn edges)
Colour of leaves
Texture when handled (firmness)
Texture when in the mouth (crispness)
Flavour and hotness
6 Sheen of leaves
7 Firmness and appearance of stalk ends
8 Colour of stalks
9 Aroma of leaves
10 Aroma of stalks
Tightness of bunch
Size of leaves
Shape of leaves

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Technical note: The significance of the presence of ß-hydroxybutyric acid in hen eggs

N. L. THOMAS AND S. W. STOCK

Introduction

Salwin, Staruszkiewicz & Bond (1972) showed that β-hydroxybutyric acid (βHBA) formed in fertile eggs during incubation. They further suggested that the presence of βHBA in liquid egg could be used to indicate that the product contained 'incubator rejects'. Incubator rejects are eggs from mated flocks which have been incubated to produce a chick, but when examined visually by 'candling' show no signs of embryonic development. Under commercial conditions incubation is normally carried out at 37.8°C. Candling is usually carried out after 6 to 8 days or on the eighteenth day of the 21-day incubation period.

In a later study Robinson, Barnes & Taylor (1975) suggested that the presence of 15.95 (± 8.45) mg βHBA/100 g liquid whole egg would indicate that the sample had been prepared from incubator rejects. Heaney & Curtis (1976), using an improved method for the assay of βHBA, showed that unfertilized eggs, whether incubated or not, had concentrations of βHBA below 0.2 mg/100 g egg contents. They also showed that the βHBA content of 18 day incubator rejects varied widely with a mean value of 13.8 mg/100 g egg contents. They suggested that limiting the concentration of βHBA to not more than 0.2 mg/100 g in any sample of liquid whole egg would effectively preclude the addition of incubator rejects.

Jones & Ellingworth (1979) demonstrated that there was no significant change in the concentration of βHBA as a result of either commercial pasteurization or of spray drying. They also showed that βHBA concentrations did not change significantly during 12 months frozen storage at −20°C. However, it is known that physiological processes occur in a fertile hen's egg at temperatures below that used for incubation (Romanoff, 1960). Philips (1941) demonstrated that fertile eggs show a linear increase in oxygen consumption between 22 and 38°C supporting the view that 'physiological zero' for the fertile hen's egg is well below the normal incubation temperature. It was therefore of interest to examine the possibility that βHBA might be produced in fertilized hens' eggs at temperatures below that used for incubation.

Authors' address: Imperial Foods Ltd, Worstead, North Walsham NR28 9RY.

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Materials and methods

Materials

Fertilized eggs were obtained from a commercial mated flock of Ross I birds which were in full production and known to be showing consistently high hatchability. Unfertilized eggs came from a commercial cage unit stocked with Ross Tint females. The eggs were collected on the day on which they were laid, brought immediately to the laboratory and each batch subdivided randomly into groups of thirty in plastic Keyes trays.

Preparation of samples

One group of thirty fertilized eggs and one group of thirty unfertilized eggs were immediately broken open, the contents homogenized and the resultant liquid whole egg frozen and stored at −20°C.

The remaining groups of fertilized and unfertilized eggs were divided into three sets and stored with the air cell uppermost at 20, 25 and 30°C respectively. After 10, 20 and 30 days storage one group of fertilized and one group of unfertilized eggs were broken open, the contents homogenized, frozen and stored at −20°C.

Analysis

The samples were thawed overnight at 5°C and analysed by the method of Heaney & Curtis (1976) with minor modifications to the technique used to purify the celite and the use of ether containing 2% of methanol as an eluent (Hobson-Frohock, 1981).

Results and discussion

The unfertilized eggs showed no visual change when opened apart from thinning of the albumen which normally occurs during storage. The fertilized eggs stored at 20°C showed no evidence of embryonic development even after 30 days. In those stored at 25°C the blastoderm appeared, in some cases, to be somewhat enlarged particularly on prolonged storage. In the groups stored at 30°C there was slow development of a 'blood ring' reminiscent of that associated with formaldehyde toxicity. However, in most cases the blood ring was attached to the inner membrane in the vicinity of an air space and usually remained with the shell when the egg was broken open. It would not, therefore, be obvious during the individual inspection of egg contents which is carried out at a commercial egg breaking plant.

The concentrations of βHBA in the unfertilized and fertilized groups, expressed as mg βHBA/100 g homogenized liquid egg, are shown in Tables 1 and 2.

Table 1. Unfertilized groups

Storage temperature (°C)	Storage time (days)			
	0	10	20	30
Fresh	0.14	—	—	—
20	—	0.12	0.08	0.07
25	—	0.06	0.06	0.06
30	—	0.04	0.15	0.18

Table 2. Fertilized eggs.

Storage temperature (°C)	Storage time (days)			
	0	10	20	30
Fresh	0.15	—	—	—
20	—	0.19	0.19	0.26
25	—	0.10	0.27	0.23
30	—	1.18	4.20	12.72

Concentrations of βHBA found in all the groups of unfertilized eggs are consistent with those reported elsewhere for both fresh and incubated infertile eggs (Heaney & Curtis, 1976; Jones & Ellingworth, 1979). However, under commercial conditions both infertile and fertile eggs may be marketed direct or used in the production of egg products. The fertile eggs normally come from flocks early in the production cycle before they are considered suitable for commercial incubation. Additional supplies result from the grading of eggs at the hatchery which lead to the rejection of undersized and oversized eggs together with those showing shell defects which might reduce hatchability or chick quality.

The present study has shown that the concentration of βHBA in liquid egg consisting wholly or in part of the contents of fertile eggs is a function of the time/temperature storage history of the fertile eggs and does not necessarily indicate the presence of incubator rejects. However, the results confirm that liquid egg containing less than 0.2 mg βHBA/100 g is unlikely to have been prepared from incubator rejects or from fertile eggs which have been subjected to gross thermal abuse.

Acknowledgments

The authors wish to express their gratitude to the Director of the ARC Food Research Institute for the loan of equipment and in particular to Mr A. Hobson-Frohock for invaluable advice and assistance in the analysis.

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Book reviews

Criteria of Food Acceptance: How Man Chooses What He Eats. Ed. by J. Solms and R. L. Hall. (Proceedings of Symposium on 'The Role of Food Components in Food Acceptance' Einsiedeln, Switzerland, 1979). Zurich: Forster Verlag, 1981. Pp. xvi + 461. Sw. Fr. 62.

The purpose of the symposium was to bring together nutritionists, psychologists, food technologists and all those interested in the many factors that contribute to the general acceptance of food. In order to cater for the immense variety of topics discussed, the editors of the book have found it necessary to widen its title, with the inevitable result that it lacks both cohesion and balance as an exposition of how man chooses what he eats. Though economic and cultural influences are mentioned, they are grossly under-represented when compared with science and technology. The food technologist will find a number of excellent reviews of some aspects of food acceptance, each written by a master of his own field. Other papers give accounts of the nitty gritty detail of food research which, though interesting in themselves, are of doubtful relevance to the title of the book.

The papers and poster presentations are assembled under seven headings—Nutritional aspects, Psychological criteria, Food patterns, Attitudes and legislation, Sensory aspects, Topics in physiology and chemistry, Aspects of technology and statistics, and Annexed abstracts. In addition, there is a final paper by one of the editors written as a commentary on the proceedings.

The book includes an astonishing variety of topics—from the Codex Alimentarius to individual differences in sensory ability, from minced Baltic herring to canned whale, from aniseed-flavoured gin to Swedish vodka, from re-heated potatoes supplied for institutions to the most exotic sounding Japanese dishes (including one made from Welsh onions), from the significance of colour in Hebrew temples to multi-dimensional scaling. It is hardly designed to be read consecutively from cover to cover, but the index is of very little help in finding items of interest because it is based almost entirely on words and phrases in the titles and sub-titles of the contributions.

With sixty-two contributors from twelve countries, the book illustrates well the multi-national, multi-disciplinary, multi-dimensional nature of its subject. The reader will find that, with few exceptions big is better, when looking for the most rewarding papers, but is also left with the impression that more contributions of the same wide-sweeping nature of the final paper would have made the book more digestible as a whole. Certainly it provides a varied diet, and

since it contains so many cordon bleu dishes perhaps one should not object at also having some roughage. Though it is still true that we cannot understand some of the vagaries of consumer behaviour, this book will help to reduce the credibility gap between scientists and trader, and between trader and customer.

J. M. Harries

Good Health—Is There a Choice? Ed. by P. H. Fentem. (Proceedings of the Fifth Kellogg Nutrition Symposium).
London: Macmillan, 1981. Pp. viii + 79 ISBN 0 333 31139 6. £8.95.

This small hardback book of seventy-nine pages brings together the eight papers which were presented at the Fifth Kellogg Nutrition Symposium held in London in 1980. The opening chapter of the book entitled 'The Choice is Yours' by Sir George Young, Parliamentary Under-Secretary of State at the Department of Health and Social Security, sets the scene by emphasizing the need for government to help the consumer to make informed choices about food, but that the ultimate responsibility for the maintenance of good health depends on the individual's lifestyle, and what and how much he chooses to eat or drink.

The following chapters record the contributions from eight distinguished scientists and educators, and examine the two major areas of 'exercise' and 'eating'.

Professor Fentem, Professor of Physiology at the University of Nottingham Medical School, discusses 'Diet and Exercise: Some of the Issues'. This second chapter underlines the point that if an intervention in national behaviour can be identified which could result in a real benefit to the health of a nation, then three sets of conditions should be met. Firstly, there must be agreement among the experts in the country that the message is worthwhile and necessary. Secondly, the advice which is to be offered is intelligible, practicable and safe; and thirdly, that the changes induced should be monitored and their effectiveness assessed. Professor Fentem concludes that an active lifestyle appears to be important for the enhancement of normal health and in the amelioration of the effects of old age and of cardiac and other chronic diseases. This theme is further explored in a later chapter (Chaper 5) by Dr A. Young, Clinical Lecturer in Rehabilitation Science, Nuffield Department of Orthopaedic Surgery at the University of Oxford, entitled 'But of course Exercise Wouldn't Help Me!—Physical conditioning for patients and normal subjects' (the title alone leaves one breathless!). This chapter is perhaps the most scientific and well referenced contribution in the book. The important messages put across are that exercise affects the body's oxygen transport system, muscle strength and metabolism, that there is a great need for all health professionals to ensure that the exercise 'habit' is perpetuated throughout life, and that government should consider a much greater commitment to the provision of convenient and adequate facilities for recreation and sport.

In Chapter 2, Dr R. G. Whitehead, Director of the Dunn Nutritional Laboratory discusses the topic of 'What is Good Food?' Attention is drawn to the existing dietary recommendations and the task of nutrition educators to advise on food choice. Professor A. E. Bender, Professor of Nutrition and Dietetics at Queen Elizabeth College, then summarizes the 'Mythology of Food' in an enjoyable and interesting way. The reader is provided with an array of facts, which include the potential benefits and hazards associated with the consumption of powdered rhinoceros horn and hedgehogs respectively! More seriously, the chapter suggests that once misconceptions and false claims about foods are firmly believed it is very difficult to change the minds of consumers. Reference is made to the wealth of mythology surrounding fruits and vegetables, nutrients and athletic performance and health foods.

Further contributions in the book are from Mrs L. Bailey of the Community Education Section of the Open University about 'Helping People Make Health Choices': a chapter on 'What Should We Tell People?' by Dr T. W. Mead, Director, MRC Epidemiology and Medical Care Unit, Northwick Park Hospital, which relates specifically to the scientific background linking diet and heart disease; and finally a chapter by Dr A. Maryon-Davis, Assistant Medical Officer, The Health Education Council which poses the question 'Are We Succeeding?' This chapter is derived from the paper which was probably the highlight of the actual symposium and which included films and posters used in mass-media education campaigns. The book is rounded off with a transcript of the question and answer session which took place at the end of the symposium.

In conclusion, this rather expensive book serves as a useful record of the proceedings of the day's events, drawing together many issues of importance to health education.

D. P. Richardson

Post-Harvest: An Introduction to the Physiology and Handling of Fruit and Vegetables. By R. H. H. Wills, T. H. Lee, D. Graham, W. B. McGlasson and E. G. Hall.
London: Granada, 1981. Pp. viii + 163. ISBN 0 246 11556 4. £12.00.

This book arose from a short international training course on the principles and practice of post-harvest work with fresh fruits and vegetables. In order to understand and explain the many different changes which this disparate group of plant material undergoes, the book is comprehensive in its layout. Starting with a botanical and then a consumer's definition of fruits and vegetables, the structure and chemical composition is then described. Following a brief description of biochemistry and physiology, there are three chapters devoted to how changes in the physical environment, temperature, water loss and gas composition affect fruit and vegetable post-harvest. Sections on physiological disorders

and pathological properties are interspersed with a chapter on quality evaluation. The last three chapters describe individual commodity treatments, packaging and technology of storage. There are five appendices giving information on practical points described earlier.

Whilst intended as an introduction to the subject for higher level students of agriculture, horticulture, food science and retailing in both Third World and developed countries, it is hoped that the book will be of direct use to industrial technologists in the area as well as concerned consumers.

Although obviously a multi-authored book, the chapters are laid out in a logical manner proceeding from a general description of the common metabolic processes to examples of how these have been controlled during post-harvest handling. The book achieves its aim of being a comprehensive introduction to this area of food handling, although it is perhaps expecting a higher level of science education in its concerned consumers and professional food handlers than will be attained in practice. As an example of this, the book briefly mentions glycolysis on p. 7 with a note to follow this up in Chapter 3. However, Chapter 3 never mentions glycolysis by name but refers to the Embden–Meyerhof–Parnas pathway alone. Neither are mentioned in the index and only people with a reasonable remembrance of school biology will understand that the glycolysis and the Embden–Meyerhof–Parnas are the same thing under different guises. It would, therefore, be possible to lose the interest of a non-technical reader early on in the book if they could not connect the cross-references. This is, of course, only a minor criticism of a much needed volume which certainly achieves most of its aims but does not extend to perhaps all the readership intended.

In its general approach to the subject, there seems to be a little repetition in some of the chapters, particularly with the chapter on technology of storage which could have been added to one or two of the other chapters, but otherwise there is a clear logical arrangement of subjects and the book is a much needed collection of information for post-harvest biologists. It is perhaps unfortunate that the references contain a large number of books and articles which are not readily obtainable in Europe. In particular the American Society of Heating, Refrigerating and Air-Conditioning Engineers have done a lot of work in this area but their publications are only held in one or two places in Britain. However, in many cases they are worth the effort in obtaining them.

When commenting on the layout and design of the book, one is bound to be impressed by the clear presentation and legibility of the typeface. A few proof reading errors have crept in, mixing of Table 5 for Fig. 5 in the text and omitting some of the information from Fig. 13 that is indicated in the legend, but generally the illustrations are very good, although Fig. 12 is probably an over-simplification of the facts. The index is rather short but the appendices are very useful in an introductory text. The book is a very useful addition to any course including some post-harvest content and is very well produced but here and there needs a little tidying up in subsequent editions.

P. W. Goodenough

A Settlement Amply Supplied—Food Technology in Nineteenth-Century Australia. By K. T. H. Farrer.
Melbourne University Press, 1980. Pp. xiii + 332 ISBN 0 522 84197 X. Aust. $26.00.

Food Technology and the food processing industry do not always get a good press, and those that practice in this area are frequently viewed with suspicion by members of the general public. The benefit conferred on mankind by the application of science to food manufacture and preservation can, it would appear, be easily overlooked and the standard, quantity and variety of the foods enjoyed in this country today taken to be a natural birthright. The crucial role of food technology can be seen more clearly in an historical setting and, perhaps, nowhere more so than in the development of Australia, New Zealand and the Americas as the provisioners of the densely populated and industrialized countries of Europe during the nineteenth century.

Dr Farrer's book is a substantial and well-researched contribution to this historical perspective. He first reviews the situation of the earliest European settlers and then charts the development of the canning industry in a series of chapters that comprise almost half the main text. Further chapters cover other preservation methods, e.g. chemical preservation and refrigeration, and food conversion operations such as milling, baking, brewing and the manufacture of dairy products. Another chapter is devoted to food legislation and control.

Dr Farrer's pages are dense with fact and nearly one-third of his book's modest length is given up to appendices, notes and bibliography. He concentrates his attention on the development of the Australian food industry and the rise and fall of many an ephemeral enterprise is charted. He gives many insights into the commercial problems of the time—problems not unrelated to those encountered today—the problems of obtaining and keeping skilled personnel (such as tinsmiths—though industries today rarely have their staff denuded by a gold rush!); the problems of promoting a new product (preserved and canned meats) to a market in the U.K. accustomed only to butcher's meat; the influence of can size on the acceptability, respectively, of Australian and American canned products and so on. This is one of the strengths of the book.

On the other hand, technological aspects are less well handled. On p. 78 a satisfactory heat process for a can is said to be one 'which raises the whole contents of the can above a certain temperature', while on p. 80, confusingly, it is said that 'the same effect could be produced at different temperatures by varying the time of heating'. On p. 142 the obsolete term 'Thermal Death Point' is introduced (and incorrectly defined in a note) while on the same page F_o values are referred to and a note explains that an F_o value is the numerical expression of a quantity of heat! Again, in the account of meat freezing, the terms 'drip' and 'freezer burn' are used without definition. The reviewer would have been happy to have sacrificed the accounts of the short and undistinguished lives of the Australia Felix, the Warrnambool Meat Preserving Company and their ilk to allow for more substantial accounts of the crucial technological

issues, presented in a form which would both inform the general reader and satisfy the professional.

While the author is rightly proud of the contributions made by pioneering Australians to the shipping of frozen meat, his concentration on this results in his paying little attention to the parallel development of the cold chain. As a contemporary writer noted, 'when these shipments first began, very serious losses had to be encountered by the colonial exporters having to place so much dead-meat in the market on one day' (*Chamber's Journal*, 4th series, **20**, 438, 1883). The same writer goes on to speak glowingly of a refrigerated store for meat, then operating in Sydney, though Dr Farrer (p. 198) notes no installation before 1895.

These criticisms aside, there is much of interest in this book and Dr Farrer is to be congratulated on bringing it together.

N. D. Cowell

Water Activity: Influences on Food Quality. Ed. by L. B. Rockland and G. F. Stewart.
New York: Academic Press, 1981. Pp. xv + 921. ISBN 0 12 591350 8. US$60.00.

This book is intended for scientists in the food industry concerned with the processing, packaging and storage of both raw and processed food. The book is divided into seven sections, each of which, the editors claim, is designed to supplement information available in 'Water Relations in Foods' (edited by R. B. Duckworth, Academic Press, London, 1975). Over fifty food scientists have contributed to this work, each of whom is a specialist in a chosen field; these authors were chosen from among those attending the Second International Symposium on Properties of Water, Osaka, Japan, 1978.

Section 1 is concerned with the characterization of moisture adsorption isotherms and the problem of hysteresis. In Section 2, the measurement of bound water is discussed and its relationship to the properties of food. The influence of solutes on water activity is dealt with in Section 3. Section 4 contains a critical evaluation of the influence of water activity on the functional characteristics of carbohydrates and proteins. In Sections 5 and 6 the connection between water activity and the preservation of foods is discussed. Section 7 is concerned with the influence of water activity on microbial growth.

The final result is very much a hotch-potch of contributions. In Section 1, the first chapter takes the novice slowly and laboriously through the elementary thermodynamic definitions of water activity to advanced statistical mechanical models: next follows a chapter on how to measure water activity, followed by chapters which are research papers. No such luck for the novice in Section 2, though; the reader is plunged straight into NMR relaxation times as all the

chapters of this section are research papers. Again in Section 3, the introductions to ESR is very brief and difficult for the non-specialist to grasp. It is difficult to see what reader level the editors had in mind when compiling this imbalance of material. Nevertheless, with its extensive bibliographies, this book is a must for the food scientist keeping abreast of his field. The editors are to be congratulated on the high standard of presentation they have achieved. The text is clear and easy to read and the editors have compiled a useful general index.

T. M. Hardman

Quality in Stored and Processed Vegetables and Fruit. Ed. by P. W. Goodenough and R. K. Atkin. (Proceedings of the 7th Long Ashton Symposium, 1979)
London: Academic Press, 1981. Pp. xi + 348. ISBN 0 12 289740 4. £25.80.

Examining imported apples in a cold storage complex one of my colleagues bit into an attractive fruit in the highest E.E.C. grade. She looked disgusted and the store manager explained that they were 'not for eating', but were excellent quality 'for buying and selling'. The word 'quality' means different things to different people and the qualities demanded of produce differ according to the demands of the various handlers and users. This book is the result of a multidisciplinary symposium covering a broad cross-section of workers in widely differing fields, and it clearly illustrates some of the complexity of the mixture covered by the word 'quality'. In fact the symposium, and this volume, covers some scientific and technical aspects of the development, measurement, change and control of a number of elements in the quality complex.

The contents of the volume are divided into five sections. The first defines some aspects of quality related to sensory perceptions, aroma and texture. The second covers breeding and cultural techniques. The third and fourth deal with quality at harvest and some post-harvest physiological changes, microbial and other causes of spoilage, taint caused by crop chemicals and effects of storage conditions on out-turn. The final section deals with some of the changes which may occur during processing of fruits, vegetables and juices. The book is aimed at a scientific and technical readership, used to the symposium proceedings format, who will appreciate the impossibility of covering all aspects of a subject embracing such a wide diversity of interests. To this extent the title on the cover may be slightly misleading as it is not, and was not intended to be, a text book on 'Quality in stored and processd fruits and vegetables'. Selected topics are covered in depth by a series of contributors (in addition to the Inaugural Lecture there are thirty papers). It achieves its objective as an extremely useful contribution to the literature. It will prove of value to professional workers, to final-year undergraduates, and to research students in this field. The papers are well presented and the references generally include the more significant recent

publications. The overall high standard of presentation reflects credit on the skill and sensitivity of the editors.

As a physical object the volume is pleasant to handle and to read. The quality of paper, binding, typeface, layout and proof-reading is up to the usual high standards expected of the Academic Press. There is, however, one important aspect where the publishers have not reached an adequate standard. The index, of only six pages following a total of 392 pages of often concentrated scientific writing, is too brief and quite disgracefully bad. A number of tests were made and the index failed all of them dismally. For instance, only two micro-organisms are mentioned by name in the index, one of them in brackets following the name of the disease it causes. Instances were found where, although a subject appears in the index, not all of the relevant pages are included. Other problems include such matters as 'auxins in brassicas' being indexed under 'auxins' but not under a whole list of references indexed under 'brassicas'. Even 'senescence' does not appear in the index although one paper is partly based on the subject.

There are few more irritating and potentially misleading faults than inadequate indexing. Where a book by a single author is involved one can look up the relevant chapter. Where a volume is made up of a series of diverse papers by people in different disciplines but looking at aspects of the same overall subject good indexing is vital. It is distressing to find such a fault in a volume of otherwise very high quality which will undoubtedly be needed as a reference source. It might have been better to have eliminated the index completely; at present it is misleading to say the least.

This is the record of a brave and successful stab at a multidisciplinary approach to a massive and not easily definable subject. The organisers, editors and contributors are to be congratulated. A series of similar symposia aimed at identifying and investigating the quality requirements in produce destined for different markets might form a valuable follow-up. Discussion of quality as understood by storage managers, carriers, manufacturers and retailers might also add further illuminating contributions to the available literature.

P. H. Lowings

Journal of the Science of Food and Agriculture

Published on behalf of the Society of Chemical Industry, the *Journal of the Science of Food and Agriculture* is an international journal concerned with the publication of research papers, notes and review articles in the fields of agriculture, the food sciences and other associated sciences. It is of interest to scientists and technologists in agriculture, the food industry and horticulture and deals with vegetable, fruit, meat, egg and milk technology together with all branches of agriculture.

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Typescripts (two complete copies) should be sent to the Editor, Dr H. Liebmann, c/o Institute of Food Science and Technology (U.K.), 105–111 Euston Street, London NW1 2ED. Papers should be typewritten on one side of the paper only, with a 1½ inch margin, and the lines should be doubled-spaced. In addition to the title of the paper there should be a 'running title' (for page headings) of not more than 45 letters (including spaces). The paper should bear the name of the author(s) and of the laboratory or research institute where the work has been carried out. The full postal address of the principal author should be given as a footnote. (The proofs will be sent to this author and address unless otherwise indicated.) The Editor reserves the right to make literary corrections.

Arrangement. Papers should normally be divided into: (a) Summary, brief, self-contained and embodying the main conclusions; (b) Introduction; (c) Materials and methods; (d) Results, as concise as possible (both tables and figures illustrating the same data will rarely be permitted); (e) Discussion and conclusions; (f) Acknowledgments; (g) References.

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 numbers; 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. 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 one hundred or greater.

Abbreviations. Abbreviations for some commoner units are given below. The abbreviation for the plural of a unit is the same as that for the singular. Wherever possible the metric SI units should be used unless they conflict with generally accepted current practice. Conversion factors to SI units are shown where appropriate.

SI UNITS

gram	g	Joule	J
kilogram	kg = 10^3 g	Newton	N
milligram	mg = 10^{-3} g	Watt	W
metre	m	Centigrade	°C
millimetre	mm = 10^{-3} m	hour	hr
micrometre	$\mu = 10^{-6}$ m	minute	min
nanometre	nm = 10^{-9} m	second	sec
litre	l = 10^{-3} m^3		

NON SI UNITS

inch	in	= 25·4 mm
foot	ft	= 0·3048 m
square inch	in^2	= 645·16 mm^2
square foot	ft^2	= 0·092903 m^2
cubic inch	in^3	= 1·63871 × 10^4 mm^3
cubic foot	ft^3	= 0·028317 m^3
gallon	gal	= 4·54611
pound	lb	= 0·453592 kg
pound/cubic inch	lb in^{-3}	= 2·76799 × 10^4 kg m^{-3}
dyne		= 10^{-5} N
calorie (15°C)	cal	= 4·1855 J
British Thermal Unit	BTU	= 1055·06 J
Horsepower	HP	= 745·700 W
Fahrenheit	°F	= 9/5 T°C + 32

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. 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'.

Tables. There should be as few tables as possible and these should include only essential data; the data should not be crowded together. The main heading should be in bold with an Arabic number, e.g. **Table 2.** Each table must have a caption in small letters. Vertical lines should not be used.

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