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Pigment changes in capsicum cultivars during maturation and ripening

F. M. M. RAHMAN AND K. A. BUCKLE

Summary

The quantitative distribution of chlorophylls and carotenoids in five capsicum cultivars at four stages of maturation and ripening has been established using chromatographic, spectroscopic and chemical methods. From immature, mature, half-ripened and fully-ripened capsicum fruits, up to twelve, twelve, twenty-nine and twenty-six individual pigments respectively were isolated and most identified. The pigment composition results were consistent with a proposed pathway of synthesis of the red keto-carotenoids, capsanthin and capsorubin. Significant differences were found in pigment concentrations among the cultivars at all stages of maturation and ripening, even though the cultivars showed the same visual colour. Lycopene and chlorophyll pigments other than chlorophylls *a* and *b* were not found in any cultivar at any stage of maturation or ripening.

Introduction

Studies of the pigment compositon of capsicum cultivars reported in the literature have been limited primarily to analyses of carotenoid levels in fruits at the mature stage and at the fully-ripened stage (Cholnoky *et al.*, 1955, 1956, 1958; Curl, 1962, 1964; Davies, Mathews & Kirk, 1970). Only in one study of maturing capsicum fruits did Schanderl & Lynn (1966) find at least five fluorescent chlorophyll-like compounds in fruits at various stages of maturation and ripening. The pigment composition of capsicum cultivars grown in Australia has not been studied previously. The present study involved a detailed quantitative analysis of both chlorophyll and carotenoid pigments of five capsicum cultivars at four stages of maturation.

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Materials and methods

Growing and harvesting of capsicums

Five capsicum cultivars, namely Long Red Cayenne, Pacific Bell, Ram Horn, College Gold and Golden Californian Wonder were grown at Hawkesbury Agricultural College, Richmond, N.S.W. during the summer season. Fruits of each cultivar were hand-picked at the immature, mature, half-ripened and fully-ripened stages and transported to the Kensington laboratories. Immature and mature fruits of a particular cultivar of the same colour and similar size were differentiated by touch. Soft fruits were graded as immature and tough fruits as mature. Half-ripened and fully-ripened stages were assessed by colour.

Immature and mature fruits of the Long Red Cayenne, Pacific Bell and Golden Californian Wonder cultivars were all deep green in colour whereas fruits of the Ram Horn and College Gold cultivars were greenish yellow and sulphury yellow respectively. At the half-ripened stage fruits of Long Red Cayenne and Pacific Bell cultivars turned pink, and fruits of Ram Horn and College Gold cultivars turned reddish yellow. Fruits of the Golden Californian Wonder cultivar changed to greenish yellow. At the fully-ripened stage fruits of the Red Cayenne, Pacific Bell, Ram Horn and College Gold cultivars turned a deep red colour, while fruits of the Golden Californian Wonder cultivar changed to a deep yellow colour.

Preparation and extraction of pigments from capsicum tissue

Three large fruits or ten small fruits of each cultivar at one maturity level were de-stemmed, de-seeded, cored and cut into approximately 1 × 1 cm pieces and thoroughly mixed. The resulting sample is referred to as the stock capsicum sample. The extraction of pigments from the stock sample in cold acetone was carried out by the method of Buckle & Rahman (1979).

Separation and estimation of individual pigments

The gross pigment extracts from the stock capsicum sample were applied as 16 cm streaks on cellulose thin layers using the method of Bacon (1964). Four solvent systems were developed for the separation on thin layers of pigments from all the five cultivars at four stages of maturation and ripening (Buckle & Rahman, 1979). The separated streaks of the individual pigments were eluted from the thin layers following the method of Jeffrey (1968). Mixed streaks of pigments were further separated on columns of magnesium oxide-Hyflo Super-Cel (1:1 w/w) and aluminium oxide and subsequently identified (Buckle & Rahman, 1979). The concentration of separated, characterized pigments was calculated (Davies, 1965) using extinction values recorded in the literature (Foppen, 1971). For unknown pigments, $E^{1\%}_{1cm} = 2500$ was used.

Results and discussion

Pigment levels in five capsicum cultivars

The results of pigment analyses of Long Red Cayenne, Pacific Bell, Ram Horn, College Gold and Golden Californian Wonder cultivars at the immature, mature, half-ripened and fully-ripened stages are presented in Tables 1 to 4 respectively. Chlorophylls *a* and *b* were the major pigments at the immature stages in green cultivars and represented 80, 72, 63 and 60% of the total pigment contents of Golden Californian Wonder, Pacific Bell, Long Red Cayenne and Ram Horn cultivars respectively. The yellow cultivar, College Gold, contained 17% chlorophyll at the immature stage (Table 1). At the mature stage, chlorophyll concentrations decreased in all cultivars except in the Long Red Cayenne in which there was a 39% increase in chlorophyll content because of the higher total solids content of this cultivar compared to the others (Rahman, Buckle & Edwards, 1978). The concentration of both chlorophylls *a* and *b* decreased significantly at the half-ripened stage, and at the fully-ripened stage chlorophylls disappeared completely from all cultivars.

At the mature stage the carotenoid pigment lutein (Straub, 1971) was present in the highest concentration followed in decreasing order by β-carotene, violaxanthin, neoxanthin and zeaxanthin in the cultivars Long Red Cayenne, Pacific Bell and Golden Californian Wonder (Table 2). These results are in agreement with those of Cholnoky *et al.* (1956), Curl (1964) and Davies *et al.* (1970). However, the College Gold and Ram Horn cultivars, which are yellowish in colour at the immature and mature stages, contained 24 and 11% respectively diepoxy-β-carotene and small amounts of monoepoxy-β-carotene (Tables 1 and 2). No pigments of this type were present in the green cultivars with the exception of Golden Californian Wonder which contained 1% diepoxy-β-carotene. Davies *et al.* (1970) found only 1.7% monoepoxy-β-carotene in green pepper, but such a high concentration of diepoxy-β-carotene as found in both the College Gold and Ram Horn cultivars has not been reported previously in capsicums. In addition, the College Gold and Ram Horn cultivars contained ζ-carotene and phytofluene which are not found in the green cultivars at the immature or mature stages.

Lutein, the dominant xanthophyll in the immature and mature stages, disappeared completely at the fully-ripened stage except for the Golden Californian Wonder cultivar in which lutein increased from 4 to 9 μg/g during ripening. This result is in agreement with the observation of Davies *et al.* (1970), who found 28% lutein in one ornamental pepper cultivar which changed colour from green to yellow at the fully-ripened stage. They also found no lutein in three other cultivars which changed in colour from green to either red or orange.

Although the role of lutein in the biosynthesis of the red pigments is not clear, the appearance of antheraxanthin and cryptoxanthin and the significant increase in levels of zeaxanthin and violaxanthin at the half-ripened stage in the cultivars Long Red Cayenne, Pacific Bell, Ram Horn and College Gold pro-

Table 1. Pigment composition of capsicum cultivars at the immature stage

Pigment	Pigment content (μg/g)				
	Long Red Cayenne (green)	Pacific Bell (green)	Ram Horn (greenish yellow)	College Gold (sulphury yellow)	Golden Californian Wonder (green)
Carotenoids					
Phytofluene	—	—	Tr	0.1	—
α-carotene	1	—	0.1	—	—
β-carotene	8	2	0.8	0.4	2
ζ-carotene	—	—	Tr	0.1	—
5,6-diepoxy-β-carotene	—	—	1	1	Tr
5,6-monoepoxy-β-carotene	—	—	0.1	0.1	Tr
Lutein	8	2	2	0.5	3
Zeaxanthin	Tr	Tr	0.1	0.1	0.2
Violaxanthin	5	2	1	0.4	0.6
Neoxanthin	2	1	0.2	0.2	0.4
Chlorophylls					
Chlorophyll *a*	27	12	5	0.4	16
Chlorophyll *b*	14	6	3	0.2	8

Tr = trace

vides further evidence in favour of the pathway for the formation of the characteristic red pigments, capsanthin and capsorubin suggested by Cholnoky and his collaborators (Cholnoky *et al.*, 1956, 1958) and later confirmed by Davies *et al.* (1970).

Violaxanthin, the major diepoxy carotenoid, increased significantly in all cultivars as the fruit changed from the immature to the fully-ripened stage. Only in the Golden Californian Wonder cultivar were luteoxanthin and auroxanthin, two other diepoxy carotenoids observed in the half and fully-ripened stages, and they were probably formed *in vivo* from violaxanthin by the action of plant acids. The monoepoxy carotenoids antheraxanthin and mutatoxanthin, appeared in all cultivars at both half and fully-ripened stages, and a small amount of neoxanthin was present at the immature stage but no significant change in concentration was observed in the latter pigment during ripening of any of the five cultivars studied.

The unripe College Gold and the fully ripe yellow-coloured Golden Californian Wonder cultivars contained virtually identical carotene pigments, phytofluene, ζ-carotene, and the mono- and diepoxides of β-carotene, although there were quantitative differences in the carotenes among the cultivars. Mature fruits of the College Gold cultivar contained about 24% diepoxy-β-carotene,

Table 2. Pigment composition of capsicum cultivars at the mature stage

Pigment	Pigment content (μg/g)				
	Long red Cayenne (green)	Pacific Bell (green)	Ram Horn (greenish yellow)	College Gold (sulphury yellow)	Golden Californian Wonder (green)
Carotenoids					
Phytofluene	—	—	0.1	0.1	0.1
α-carotene	3	—	0.2	—	—
β-carotene	12	2	2	0.4	3
ζ-carotene	—	—	0.1	0.1	—
5,6-monoepoxy-β-carotene	—	—	0.2	0.1	0.1
5,6-diepoxy-β-carotene	—	—	2	1	0.4
Lutein	12	2	2	0.6	4
Zeaxanthin	0.4	0.1	0.2	0.2	0.4
Violaxanthin	11	2	1	0.4	1
Neoxanthin	4	2	0.4	0.2	0.8
Chlorophylls					
Chlorophyll *a*	39	11	4	0.6	14
Chlorophyll *b*	18	6	2	0.4	8

yet at the fully-ripened stage there was no trace of this pigment; in the mature Golden Californian Wonder cultivar there was a trace amount of an epoxide of β-carotene, while at the fully-ripened stage the level was 3%. Thus the yellow coloured fruits contained epoxides of β-carotene but this may not occur in all situations as Davies *et al.* (1970) reported no epoxides of β-carotene in yellow ornamental peppers, but rather found a small amount of monoepoxide in green peppers.

Qualitative differences in pigment composition were found in fruits of the Golden Californian Wonder cultivar, which are yellow at the fully-ripened stage, compared to the other cultivars which are red when fully ripe, confirming the report of Davies *et al.* (1970) that fully ripened yellow capsicum fruits lack the enzyme(s) necessary for the formation of the red keto-carotenoids capsanthin and capsorubin.

From the results discussed above it is suggested that fruits of capsicum cultivars do not follow the general pattern of pigment composition and may indeed be an exception. The results confirm the conclusion of Valadon & Mummery (1972a,b) that in biological materials, especially in many plants and fungi, it is not always possible to generalize because even though one might expect to have the same mechanism and the same biosynthetic pathway in every organism, there are a number of individuals that have their own metabolic pathways and mechanisms.

Table 3. Pigment composition of capsicum cultivars at the half ripened stage

Pigment	Pigment content (μg/g)				
	Long Red Cayenne (pink)	Pacific Bell (pink)	Ram Horn (yellowish red)	College Gold (yellowish red)	Golden Californian Wonder (greenish yellow)
Carotenoids					
Phytoene	—	—	—	—	0.4
Phytofluene	0.6	Tr	0.8	2	1
α-carotene	5	0.4	0.4	—	0.4
β-carotene	40	3	7	3	9
ζ-carotene	—	—	1	1	0.8
5,6-monoepoxy-β-carotene	—	—	0.2	0.2	0.2
5,6-diepoxy-β-carotene	—	—	2	3	1
Mutatochrome	2	1	1	0.6	—
Hydroxy-α-carotene	—	—	0.4	—	0.2
Cryptoxanthin	4	1	4	4	0.4
Cryptoxanthin 5,6-epoxide	—	—	—	—	1
Cryptoxanthin 5,6-diepoxide	—	—	—	—	0.2
Cryptocapsin	—	2	0.4	—	—
Lutein	0.6	0.2	0.4	0.1	9
Capsolutein	—	—	0.5	2	—
Zeaxanthin	24	2	4	5	3
Antheraxanthin	3	0.6	0.4	0.8	0.4
Mutatoxanthin	0.8	0.4	0.2	0.6	0.2
Violaxanthin	16	3	6	6	7
Luteoxanthin	—	—	—	—	1
Auroxanthin	—	—	—	—	1
Neoxanthin	4	1	0.8	0.8	0.7
Capsanthin	43	29	18	21	—
Capsorubin	10	12	7	4	—
Capsanthin isomer	13	14	8	6	—
Capsorubin isomer	2	3	0.8	1	—
Unidentified	5	3	2	2	4
Chlorophylls					
Chlorophyll *a*	19	7	2	0.2	7
Chlorophyll *b*	10	2	1	Tr	4

Tr = trace

Table 4. Pigment composition of capsicum cultivars at the fully ripened stage

Pigment	Pigment content (μg/g)				
	Long Red Cayenne (red)	Pacific Bell (red)	Ram Horn (red)	College Gold (red)	Golden Californian Wonder (yellow)
Phytoene	—	—	0.1	0.4	1
Phytofluene	3	—	6	8	7
α-carotene	9	1	1	—	2
β-carotene	108	16	28	36	16
ζ-carotene	—	—	3	6	3
5,6-monoepoxy-β-carotene	—	—	—	—	0.4
5,6-diepoxy-β-carotene	—	—	—	—	3
Mutatochrome	9	4	3	2	—
Hydroxy-α-carotene	—	—	2	—	2
Cryptoxanthin	37	5	15	18	7
Cryptoxanthin 5,6-epoxide	—	—	—	—	3
Cryptoxanthin 5,6-diepoxide	—	—	—	—	2
Lutein	—	—	—	—	9
Cryptocapsin	—	3	1	—	—
Capsolutein	—	—	4	6	—
Zeaxanthin	82	18	16	16	5
Antheraxanthin	21	7	3	3	5
Mutatoxanthin	5	3	2	2	4
Violaxanthin	41	15	17	19	10
Luteoxanthin	—	—	—	—	4
Auroxanthin	—	—	—	—	6
Neoxanthin	4	2	0.8	2	1
Capsanthin	228	65	52	59	—
Capsorubin	68	27	15	19	—
Capsanthin isomer	97	28	21	19	—
Capsorubin isomer	7	4	3	3	—
Unidentified	9	4	4	5	6

Comparison of pigment results with published data

Pigment extracts from capsicum cultivars at different stages of maturation and ripening showed chlorophylls *a* and *b* as the only chlorophyll pigments when analysed on cellulose thin layers, contrary to the results of Schanderl & Lynn (1966) who found chlorophyll *a* and *b* and five or more fluorescent chlorophyll-like compounds in Yellow Wax capsicums at different stages of maturation and ripening when pigments were separated on silica gel G thin layers. The present results confirm the conclusions of Bacon (1966) that chlorophyll degradation products isolated by Schanderl and Lynn (1966) were artefacts resulting from pigment separations on silica gel instead of inert cellulose.

The two cultivars College Gold and Golden Californian Wonder show conflicting results in relation to the oxygen transport theory of Cholnoky *et al.* (1956), who suggested that in chlorophyll-containing tissue both the primary (zeaxanthin→antheraxanthin→lutein) and secondary (β-carotene→β-carotene monoepoxide→α-carotene) systems are active, but after the disappearance of chlorophyll, only zeaxanthin and cryptoxanthin take up oxygen and are transformed by it to the epoxides violaxanthin, antheraxanthin and cryptoxanthin-monoepoxide which are subsequently transformed into the red pigments, capsanthin and capsorubin: zeaxanthin accumulates but lutein is absent. This mechanism appears to operate in the College Gold cultivar, but after the disappearance of chlorophyll in the Golden Californian Wonder cultivar, β-carotene epoxides and lutein are produced (Table 4), indicating that both the primary and secondary oxygen transport systems of Cholnoky *et al.* (1956) are operating even in the absence of chlorophyll. Further studies are in progress to elucidate the pigment transformations in this cultivar during ripening.

Laborde (1969) reported the presence in fully ripened red capsicums of a lycopene-like pigment which represented about 50% of the total carotenoids. Analysing the pigments of paprika, chilli powder and fresh Yolo Wonder capsicum cultivars, Laborde found similar lycopene-type pigments and concluded that such results were probably a result of defects of the methods of analysis of previous workers. When pigments of fully ripened red capsicums in the present study were separated on cellulose thin layers developed in solvents C and D, followed by column chromatographic separation on magnesium oxide-super cel where necessary, no lycopene-like pigments were observed or detected spectrally. Pigment extracts of ripe tomatoes separated on cellulose thin layers contained hydrocarbons including lycopene travelling with the solvent, confirming that if lycopene had been present in extracts of red capsicum, it would have travelled also with the solvent.

Further confirmation of the absence of lycopene in extracts of red capsicum cultivars has been made by separation of pigments in extracts of ripe tomatoes on thin layers of magnesium oxide-super cel, in which it was possible to separate the hydrocarbons in the following order: phytofluene + β-carotene,

ζ-carotene, neurosporene, and lycopene. Using the same chromatographic system, no lycopene streak was observed in extracts of any of the four fully ripened red cultivars used in this study. However, when capsicum cultivars are dipped, injected or sprayed with 2-(4-chlorophenylthio) ethyldiethyl ammonium chloride (CPTA), lycopene formation can be induced (Simpson *et al.*, 1974), indicating the possibility of lycopene production in cultivars of different physical, chemical or genetic constitution.

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Erratum

In the paper 'Subjective and objective assessments of the degree of cooking of potatoes heated by different methods' by R. Collison *et al.* (*J. Fd Technol.* 1980, **15,** 1) the ordinates of Fig. 1 should be labelled 'Load (kg × 10.2)' and the ordinates, of Figs. 2 and 5 should be labelled 'Rupture load (kg × 10.2).

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Determination of thermal process schedule for Totapuri mango

NIRANKAR NATH AND S. RANGANNA

Summary

The values for thermal inactivation of pectinesterase (PE) in Totapuri mango syrup homogenate are $F_{208\cdot8}^{18\cdot56} = 1.00$ and $D_{208\cdot8}^{21\cdot4} = 0.456$ at pH 3.6. The F value is equivalent to 2.19 D. In commercial canning a 3 D process is recommended which is adequate to inactivate the PE, the natural microflora consisting of gram-positive and gram-negative nonsporulating rods and cocci, and the test organism *Clostridium pasteurianum* which is able to grow in mango preparations at pH 3.8 and above. *Bacillus coagulans* which causes flat-sour spoilage does not grow in mango preparations. Process times calculated by the graphical method are compared with the values found by formula method using six different procedures. Process requirements under different initial and processing temperatures are given.

Introduction

Mangoes are canned as slices in syrup or as juice, nectar and pulp. In the process of canning, the pH is adjusted to 4.2 or lower. The thermal process for canned fruits evolved on the basis of enzyme inactivation has been shown to be adequate to render the canned product microbiologically safe (Kaplan, Esselen & Fellers, 1949; Dastur, Weckel & von Elbe, 1968; Nanjundaswamy, Saroja & Ranganna, 1973; Nath & Ranganna, 1977a,b,c). Totapuri (Bangalora), which is a regular bearing and high yielding variety of good keeping quality (Indian Council of Agricultural Research, 1967), is being increasingly used for processing in addition to the *Alphonso* variety which is traditionally canned. Nanjundaswamy *et al.* (1973) developed a thermal process for canned Alphonso mango based on the inactivation of peroxidase which was more heat resistant than a strain of yeast isolated from commercial samples of spoiled cans of mango slices in syrup. Tests indicated Totapuri mango to contain pectinesterase

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(PE). The thermal process for canned Totapuri mango slices in syrup determined on the basis of PE inactivation, calculation of process time by the graphical method and different procedures of the formula method, and the microbiological safety of the process determined on the basis of enzyme inactivation are discussed in this paper.

Experimental

Preparation of fruit for studies on thermal inactivation of pectinesterase.

Ripe fruits purchased from the local market were peeled, sliced, and the slices blended. The resulting pulp was quick frozen and stored at 0°F (–18°C) until required (Nath & Ranganna, 1977a).

Thermal inactivation and decimal reduction times of pectinerase

These were determined in pulp and syrup homogenate (TSS 20% and pH 3.6) according to the procedures described earlier (Nath & Ranganna, 1977b,c).

Heat penetration studies

Firm ripe mangoes were washed, peeled, cut into slices and filled (580 g) into 401 × 411 (A 2½) cans. The fruits were covered with 300 g of 40° Brix syrup. In one, the syrup was filled cold and the cans were sealed. Such cans are hereafter, termed as cold filled cans. In the second case, hot syrup was filled into the cans, exhausted for 7 min and sealed. By varying the temperature of the hot covering syrup, cans having initial temperature of 140°F (60°C) and 164°F (73°C) were obtained. Such cans are termed hot-filled cans. The cans were processed in boiling water [207°F (97°C) in Mysore] and at 212°F (100°C) in steam, and cooled in water.

Heat penetration rate into the cans was measured using Ecklund non-projecting, plug-in, needle type thermocouples and a manually operated Leeds and Northrup potentiometer. The temperatures during heating and cooling were recorded every 2 min, and three runs were done for each processing condition.

Plotting of heat penetration data

To calculate the process time by the graphical method, the temperatures corresponding to various times were plotted on rectangular coordinate graph paper [National Canners Association (NCA), 1968].

To calculate by the formula method, heat penetration data were plotted on a semilog paper according to the NCA (1968) procedure. The line through the points were drawn in three different ways: (i) the line of eye-fit, (ii) a straight

line by joining the initial temperature and the final temperature during heating so that it passed within one degree of the final temperature as suggested by Gillespy (1962), and (iii) the line of statistical-fit by applying the analysis of least squares as suggested by Hurwicz & Tischer (1955) in the case of beef.

During processing, there was no heating lag for the bath to achieve 207°F (97°C) and it varied between 0.75 and 1.0 min at 212°F (100°C). Hence, in drawing the line, the heating lag (j_h) was assumed to be 1.0.

The cooling curves were drawn in the same way.

Calculation of process time

Process time was calculated by the graphical (Bigelow *et al.*, 1920) and the formula (Ball, 1923) methods. The process time by the formula method was calculated using the following six procedures:

Procedure A. In this procedure, the formula, $B_B = f_h (\log jI - \log g)$, and the $f_h/U:g$ tables given by Ball & Olson (1957) were used to calculate the process time. Ball assumed the slope of the heating curve (f_h) to be equal to the slope of the cooling curve (f_c) and the lag of the cooling curve (j_c) to be 1.41 in deriving the formula. f_h found from the heating curve drawn by eye-fit was used in this calculation.

Procedure B. This was similar to 'A' except that correction for the difference between f_h and f_c was applied according to the procedure suggested by Ball (1923). f_c found from the cooling curve drawn by eye-fit was used.

Procedure C. This was similar to 'A' except that the g value corresponding to the actual j_c found from $f_h/U:g$ tables of Purohit & Stumbo (1972) was used.

Procedure D. This was similar to 'C' except that the f_h value found by plotting the heat penetration curve according to the procedure suggested by Gillespy (1962) was used in the calculation.

Procedure E. This was similar to 'A' except that f_h found from the heat penetration curve drawn by applying the analysis of least squares was used in the calculations.

Procedure F. This was similar to 'C' except that f_h and j_c found from the heating and the cooling curves respectively drawn by applying the analysis of least squares were used in the calculations.

There was no come-up time when the cans were processed in boiling water. However, when processing was done in steam in the retort, an allowance of 42% of the come-up time was given to calculate the pseudo-initial temperature (Ball & Olson, 1957).

Examination of microbiological safety of the process evolved

(a) *With microflora naturally present.* To isolate the heat resistant micro organism from the natural microflora of the fruit, hot-filled cans of over ripe slices (pH 4.6) were processed for various periods at 207°F (97°C). The processed cans were

incubated at 86 and 98.6°F (30 and 37°C) for 4 weeks and at 122°F (50°C) for 2 weeks. Microbiological examination of the incubated cans was carried out according to the procedure suggested by the National Canners Association, (1968).

To test the ability of the bacteria isolated from bulged cans to survive below pH 4.6, they were subcultured into sterile tubes of mango pulp and the nutrient broth containing mango serum, the pH of which had been adjusted to 3.8, 4.2 and 4.6 prior to autoclaving. The inoculated tubes were incubated and examined.

(b) *Using* B. coagulans *and* Cl. pasteurianum. *B. coagulans* and *Cl. pasteurianum* purchased from American Type Culture Collections were used. The spores of *B. coagulans* were produced using proteose-peptone ager (National Canners Association 1968) and of *Cl. pasteurianum* using liver broth with tomato according to the procedure suggested by Stumbo (1973).

Thermal death time (TDT) was determined by the tube method (National Canners Association 1968) using sterile tomato juice serum adjusted to pH 4.5 and spore concentration of 2 to 3 million per ml. Correction for the heating lag during the come-up time was applied according to the procedure described earlier (Nath & Ranganna, 1977a). The TDT curve was drawn by applying the analysis of least squares (Brownlee, 1960). The heated samples containing spores of *B. coagulans* were subcultured on proteose-peptone agar and of *Cl. pasteurianum* in liver broth containing crushed tomatoes.

Thermal death time in test material

To check whether Totapuri mango supported the growth of *Cl. pasteurianum* or not, the pH of mango pulp and syrup homogenate was adjusted to 3.6, 3.8, 4.0, 4.5, 5.0 and 5.5 and sterilized in screw-capped tubes for 20 min at 240°F (115.6°C). Three samples of each were inoculated with the spores of *Cl. pasteurianum* under anaerobic conditions (Stumbo, 1973), incubated at 82.4 to 86°F (28 to 30°C) for 15 days, and examined periodically. Growth was positive beyond pH 3.8. Hence, TDT of the spores was determined in mango pulp and in drained and filtered syrup from the canned product. The pH of the preparation was adjusted to 3.6 and 4.0, and sterilized before inoculation.

Mango pulp and syrup homogenate did not support the growth of *B. coagulans,* and hence TDT was not determined.

Inoculated pack studies

Hot-filled cans of mango slices were inoculated with the spores of *B. coagulans* or *Cl. pasteurianum* at the rate of 5 million spores per can, exhausted, sealed and processed at 207°F (97°C) for 12, 14 and 16 min. The cans were incubated and examined (National Canners Association, 1968).

Storage studies

The hot-filled cans were processed for 17 and 30 min (the time used commercially) at 207°F (97°C). The cans were stored at room temperature for an extended period, and at 93.2–98.6°F (34–37°C) and 122–131°F (50–55°C) for 30 days.

Cut-out examination of the canned product was made according to the procedure given in *Manual of Analysis of Fruit and Vegetable Products* (Ranganna, 1977). Texture of the fresh and processed mango slices was determined using a recording shear apparatus developed by Voisey and Hansen (1967). The texture is expressed as the maximum force in grams required to shear the piece that fits into the triangular slot of the test plate. An average of ten readings was taken as the texture of the fruit.

Sensory evaluation of the canned product was carried out by a panel of ten members who were familiar with the canned products.

Results and Discussion

Analytical data of the edible portion and the syrup homogenate used in TIT studies are given in Table 1. Acidity, pH, TSS and the PE activity in the edible portion of the fresh fruit varied considerably.

Table 1. Total soluble solids, acidity, pH and pectinesterase activity in Totapuri variety of mango and syrup homogenate used in thermal inactivation studies

Particulars	Edible portion*	Syrup homogenate for TIT studies†
TSS (%)	11.5–18.0	20
Acidity as anhydrous citric acid (%)	0.21–0.88	0.41–0.43
pH	3.15–4.30	3.6
Pectin esterase activity (PE u x 10^4 per ml)	1.16–5.83	2.23–3.17

Prepared by * blending edible portion of mango and † blending pulp as prepared in * with sucrose syrup in the ratio 11.6 : 6

F, D and z values of pectinesterase

The pH of Totapuri mango varies from 3.15 in firm mature fruit to 4.3 in soft ripe fruit. The fruits do not ripen uniformly. At pH 4.3, though the flesh near the peel is firm, it is soft near the kernel and is unsuitable for canning as slices. The fruits having a pH of about 3.6 are firm uniformly and best suited for canning as slices in syrup. Hence, TIT studies were carried out at pH 3.6.

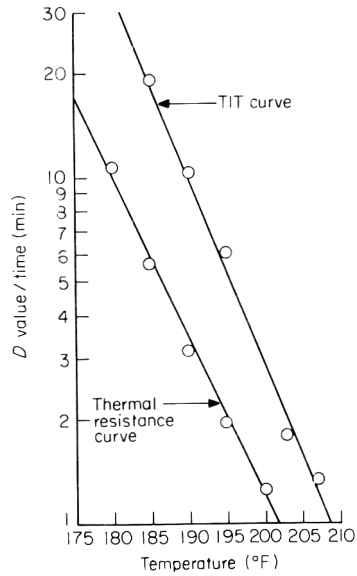

Figure 1. TIT and thermal resistance curves of PE in syrup homogenate of Totapuri mango at pH 3.6. Y- axis represents time in min for the TIT curve and *D* value for the thermal resistance curve.

The uncorrected TIT of PE was $F_{218.7}^{25.34} = 1.0$. The come-up time was 5.14 min (mean value) of which 45.10% had lethal effect. The correction required for the heating lag during the come-up time was 2.82 min.

The TIT curve of PE at pH 3.6 in syrup homogenate is shown in Fig. 1. The *F* value was 1 at 208.8°F (98.2°C) with a *z* value of 18.56 (10.31). The TIT curve, drawn by applying the analysis of least squares, showed a high degree of correlation ($r = -0.9966$).

The *D* value found from the thermal resistance curve (Fig. 1) was 0.456 at 208.8°F (98.2°C) with *z* value of 21.4 (11.89). The thermal resistance curve, like the TIT curve, showed a high degree of correlation ($r = -0.9970$). The decimal reductions (F/D) required to achieve $F_{208.8}^{18.56} = 1.0$ was 2.19. The *z* value from the thermal resistance curve was slightly higher than from the TIT curve (Fig. 1).

Process calculation

By graphical method. Heat transfer into mango slices canned in syrup was by convection. A temperature of 208.8°F (98.2°C) at which the *F* value of PE was 1, was chosen as the base temperature for process calculations.

The heat penetration curve and the corresponding inactivation rate curves for canned mango slices filled hot and processed at 212°F (100°C) are shown in Fig. 2. The graphical interpolation curve to find the process time corresponding to the desired *F* values is shown in Fig. 3. The process times calculated are given in Table 2.

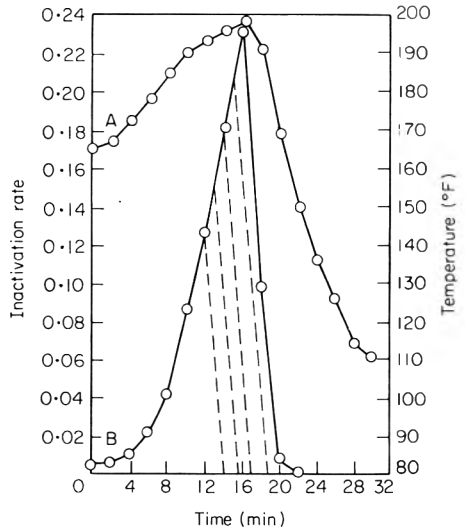

Figure 2. Heat penetration curve (A) for Totapuri mango slices canned in 401 × 411 (A 2½) cans with initial temperature of 164°F (73°C) processed at 212°F (100°C) and the corresponding inactivation rate curve (B).

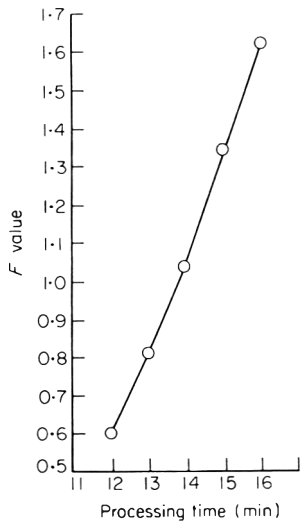

Figure 3. *F* value *vs* process time plot corresponding to Fig. 2.

Table 2. Process time calculated by the graphical method for different F values*

F value for process calculation	Process equivalence	Process time (min)
$F_{208\cdot8}^{18\cdot56} = 1.00$	2.19 D	13.8
$= 1.14$	2.50 D	14.4
$= 1.37$	3.00 D	15.1

*For mango slices filled with hot syrup, exhausted to a centre temperature of 164°F (73°C) and processed at 212°F (100°C) (in steam).

Kaplan *et al* (1949), Nebesky *et al.* (1950) and Nath and Ranganna (1977a,c) reported that in some of the canned products, wherein the sterilization value of the process was equal to the F value of the test enzyme, the same had not been completely inactivated and it would be advisable therefore, to use a slightly higher F value for process calculation. Variations in the process time with an increase in the F value (or decimal reductions) of the process are very small (Table 2). A 3.0 D process instead of a 2.19 D process of PE inactivation for Totapuri mango slices at pH 3.6 is recommended. The process times for the canned product processed under different initial and processing temperatures are given in Table 3.

By formula method. The graphical method of process calculation is an accurate method as no assumptions about the nature of the heat penetration curve are involved. The only possible source of error is in the manual-graphical integration of lethality. However, the value found can be used only when the processing conditions are identical to the conditions used in the heat penetration studies. The formula method overcomes this disadvantage and enables interconversion of data.

Lenz and Lund (1977) have compared newer methods of process calculation with the well established graphical or formula methods. Comparative data of the process time evolved by the graphical and the formula methods for the same material are scarce. Moreover, the data are limited to the low-acid conduction heating foods wherein the process requirements are high.

(a) *Plotting of heat penetration data.* Semilog plots of heating and cooling curves for mango slices filled hot and processed at 207°F (97°C) are shown in Figure 4. Similar curves were drawn for cans processed under other processing conditions. Differences between f_h and f_c values found by visual fit and statistical fit were not much, but the f_h values found by Gillespy's procedure were generally higher (Table 3).

Table 3. Process time calculated by formula method using different procedures and graphical method to achieve $F_{250\cdot8}^{18\cdot56} = 1.37$ (3 *D* process) at pH 3.6 for mango slices canned in 401 × 411 (A 2½) cans

^{P}T (a) (°F)	^{I}T (b) (°F)	Formula method: Procedure*	Process parameters: f_h (min)	j_h	f_c (min)	j_c	Process time† (min)	Graphical method process time (min)
207 (97°C)	80 (27°C)	A	20.10	1.00	20.00		21.57	20.8
		B	20.10	1.00	20.00		21.57	
		C	20.10	1.00	20.00	1.00	22.38	
		D	20.10	1.00	20.00	1.00	22.38	
		E	20.40	0.91	20.59		21.07	
		F	20.49	0.91	20.59	0.97	21.99	
	140 (60°C)	A	22.00	1.21	19.60		18.84	19.8
		B	22.00	1.21	19.60		19.00	
		C	22.00	1.21	19.60	1.00	20.05	
		D	25.20	1.00	19.60	1.00	20.61	
		E	21.27	1.28	19.23		18.90	
		F	21.27	1.28	19.23	1.00	19.97	
	164 (73°C)	A	24.00	1.30	18.40		16.25	16.6
		B	24.00	1.30	18.40		16.75	
		C	24.00	1.30	18.40	1.31	16.15	
		D	30.80	1.00	18.40	1.31	15.55	
		E	24.58	1.30	17.45		16.50	
		F	24.58	1.30	17.45	1.41	16.11	
212 (100°C)	84 (29°C)	A	16.80	1.28	21.80		18.88	19.0
		B	16.80	1.28	21.80		18.56	
		C	16.80	1.28	21.80	1.12	19.35	
		D	20.40	1.00	21.80	1.12	20.37	
		E	17.59	1.19	20.22		19.00	
		F	17.59	1.19	20.22	1.16	19.29	
	164 (73°C)	A	26.00	1.22	19.60		14.59	15.1
		B	26.00	1.22	19.60		15.08	
		C	26.00	1.22	19.60	1.20	14.85	
		D	31.60	1.00	19.60	1.20	14.18	
		E	27.32	1.11	20.65		14.48	
		F	27.32	1.11	20.66	1.17	14.90	

*Procedures A to F described under 'Experimental'. Correlation coefficient (r) for heating (f_h) and cooling (f_c) curves varies from −0.9918 to −0.9993

†Corrected zero time is added when processed at 212°F (100°C) for making the processing time from steam on to steam off to compare with the graphical method.

(a) Processing temperature. (b) Initial temperature.

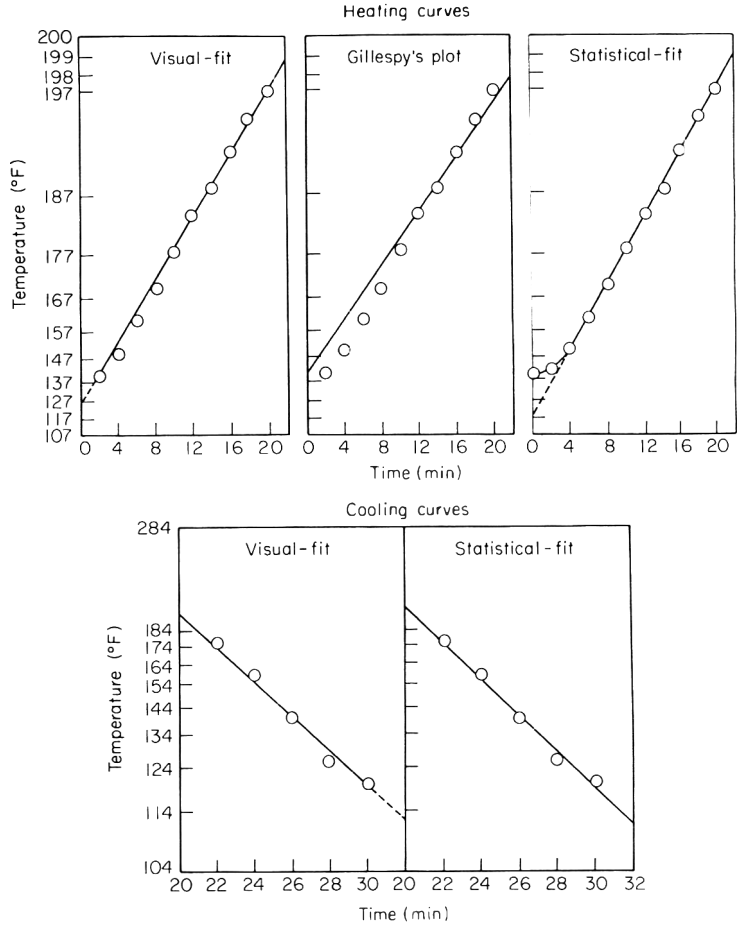

Figure 4. Semilog plot of heating and cooling curves for Totapuri mango slices with initial temperature of 140°F (60°C), processed at 207°F (97°C) and cooled in water at 84°F (29°C)

(b) *Calculations of process time.* The process times calculated by procedures A to F were generally within ± 1 min of those found by the graphical method except in the case of values found by procedure D which were either high or low (Table 3). Procedure B, though laborious, gave values within 0.8 min of the graphical method. Since the difference between the values obtained by the procedures A to F of the formula method except D and by the graphical method is not much, any one of them can be used for calculations.

Microbiological safety of the process evolved

Spoilage in acid foods is, generally, caused by non spore-forming bacteria like lactobacilli or yeasts and moulds. Heat tolerance of these microorganisms has been reported to be lower than that of peroxidase or PE (Mannheim & Ziv,

1962; Dastur *et al.*, 1968). In addition to these, *B. coagulans* and *Cl. pasteurianum* have been occasionally reported to cause spoilage (National Canners Association, 1968). Hence, tests were made to ensure that the process evolved on the basis of enzyme inactivation was microbiologically safe.

(a) *Heat-resistant organisms from the natural microflora.* The spoilage microorganisms isolated from the bulged cans of soft ripe mango slices processed for 30 min consisted of a mixed flora of nonsporulating gram-positive and gram-negative rods and cocci. The pH of the canned product was 4.64. No spoilage occurred when the pH of the canned product was adjusted to 4.2–4.3.

Microorganisms from the bulged cans, when inoculated into sterile mango pulp or serum broth of different pH did not grow at pH 4.2 and below. This preliminary result was further confirmed by the inoculated pack studies. The isolated bacteria were inoculated into the fresh hot-filled cans of ripe mango and processed for 15 min at 207°F (97°C). The pH of the canned product was 3.75. The cans remained normal even after extended incubation. Subculturing studies did not reveal the presence of any bacteria in the processed cans.

(b) Using *B. coagulans* and *Cl. pasteurianum.* As no heat resistant, aciduric spoilage microorganism could be isolated from the natural microflora of mango, possibility of spoilage by *B. coagulans* and *Cl. pasteurianum* was investigated. TDT of these organisms in tomato juice at pH 4.5 were lower than the values reported by the National Canners Association (1968) (Table 4).

In a preliminary study, sterile mango pulp and syrup homogenate adjusted to different levels of pH were inoculated with the spores of the test organisms. They supported the growth of *Cl. pasteurianum* at pH 3.8 and above but not of *B. coagulans.* TDT curves for the former in pulp and in the syrup drained from the canned product are given in Fig. 5.

In the determination of the TDT, the mean come-up time was 2.44 min of which 0.83 min (33.76%) had lethal effect. The correction required was 1.61 min which is higher than the corrections recommended for experimental heating times in steam by Sognefest & Benjamin (1944). The F values of *Cl. pasteurianum* either in pulp or syrup at pH 3.6 and 4.0 (Table 4) were lower than the TIT of PE ($F_{208\cdot8}^{18\cdot56} = 1.0$) in syrup homogenate at pH 3.6. Hence, the process time evolved on the basis of PE inactivation is adequate to prevent likely spoilage caused by *Cl. pasteurianum.*

(c) *Inoculated pack studies.* These studies were carried out to confirm the results obtained by the TDT studies. Canned mango slices (pH 3.65) were inoculated with 5×10^6 spores of *Cl. pasteurianum* or *B. coagulans*, exhausted to a centre temperature of about 160°F (71°C), sealed and processed for 12, 14 and 16 min at 207°F (97°C) and cooled. The cans remained normal after incubation. Subculturing studies revealed that neither the spores of *B. coagulans* nor *Cl. pasteurianum* survived the processing for 12 min as against the calculated process time of 16.6 min.

These results indicated that the process evolved on the basis of enzyme inactivation was microbiolgically safe.

Table 4. Thermal death times of *Bacillus coagulans* and *Clostridium pasteurianum*

Fruit	Preparation	Bacteria	pH	Uncorrected* TDT	Come-up time (min)	Effectiveness (%)†	Corrected TDT
Tomato	Juice	*B. coagulans*	4.5	$F_{246.0}^{21.60} = 1.0$	2.39	39.17	$F_{212}^{14.40} = 5.31$
		Cl. pasteurianum	4.5	$F_{217.5}^{19.60} = 1.0$	2.39	37.83	$F_{212}^{13.60} = 0.33$
Totapuri mango	Pulp	*Cl. pasteurianum*	3.6	$F_{210.5}^{21.70} = 1.0$	2.48	32.61	$F_{212}^{15.51} = 0.26$
			4.0	$F_{215.5}^{20.76} = 1.0$	2.48	31.44	$F_{212}^{14.49} = 0.53$
	Syrup‡	*Cl. pasteurianum*	3.6	$F_{209.5}^{21.72} = 1.0$	2.45	29.82	$F_{212}^{14.31} = 0.16$
			4.0	$F_{214.2}^{19.13} = 1.0$	2.45	31.79	$F_{212}^{13.41} = 0.42$

*TIT uncorrected for heating used for calculating the effectiveness of the come-up time.
†Percentage of the come-up time having lethal effect on the bacteria.
‡Syrup of 20° Brix drained from the canned product.

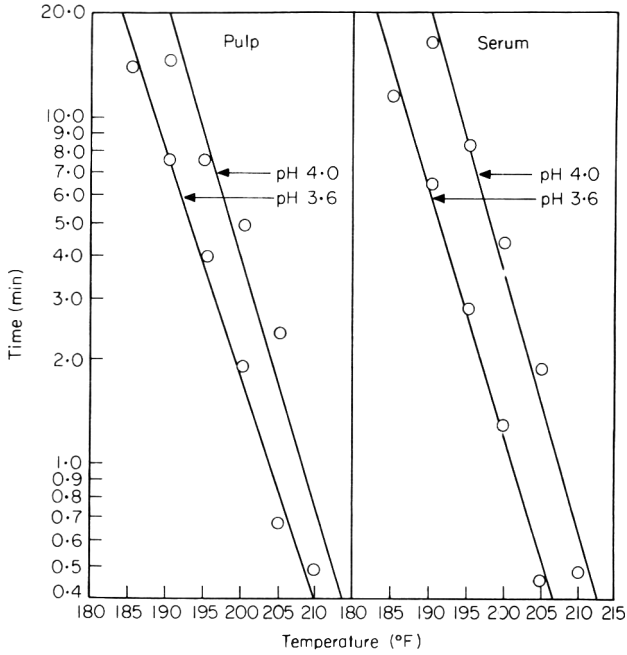

Figure 5. TDT curves of *Cl. pasteurianum* in Totapuri mango preparations.

Quality of the canned product

No residual PE activity was found in the cans processed for the calculated period either immediately after processing or on storage for 6 months at the room temperature. The vacuum was initially 20 in of Hg which reduced to 13 to 15 in during storage (Table 5).

The drained weight ranged from 64.32 to 68.57% and the cut out Brix was 22°. The pH of the canned product was 3.68 and acidity was between 0.43 to 0.45%. Texture of the fresh fruit was 499.4 g, expressed as the shear force. Initial texture readings of hot-filled cans processed for 17 min, and the control cans processed for 30 min (processing time commercially followed) at 207°F (97°C) were 380.7 and 301.6 g respectively. During storage for 6 months, there was further decrease in the texture readings (Table 5).

The canned product processed for 17 min at 207°F (97°C) had retained the natural colour, and the flavour was good. The syrup was clear.

Recommendation for commercial processing

The value for thermal inactivation of PE in syrup homogenate was $F_{208\cdot8}^{18\cdot56} = 1.0$ at pH 3.6 which was equivalent to 2.19 D. Commercially, a 3 D process based on PE inactivation in ripe Totapuri mango slices ensures a microbiologi-

cally safe and organoleptically acceptable product. The process time required to achieve this at different initial and processing temperatures are given in Table 3.

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Engineering factors in the production of concentrated fruit juices

1. Fluid physical properties of orange juices

M. MORESI AND M. SPINOSI

Summary

This study presents the essential physical properties (boiling-point rise, viscosity, density, specific heat) of orange juices, necessary for the optimization of processing units for concentrated orange juices.

When these physical properties were correlated with the sucrose content of juice, expressed as degrees Brix, in the range 10–65° Brix and compared with those of aqueous sucrose solutions, significant differences were observed in respect of viscosity, specific heat and elevation of boiling point.

Introduction

The recent evolution of fruit juice production and its trends for the immediate future have involved improvement and automation of the processes of extraction, clarification and dewatering (design and utilization of plant and machinery) and an increase of flexibility in treating different kinds of fruit.

The water content of fruit juices is usually about 90% by weight and its reduction may be the last step in food processing prior to packaging.

This step reduces packaging, transport and storage costs, whilst the reduced water activity enhances storage stability. Sensory acceptability and convenience for the consumer are improved.

However the concentration of fruit juices is a delicate affair, since many of their constituents are chemically unstable even at moderate temperatures. To obtain good products, pasteurization (to decrease bacterial count and to inactivate pectinesterase activity) and concentration must meet strict standards. Moreover, the quality of concentrated juices is greatly dependent on the pattern of odorous compounds in the fresh juice . These aroma compounds are volatile and can be lost by evaporation.

At present, concentration of fruit juices can be obtained by using the follow-

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ing processes: evaporation with or without aroma recovery by stripping and/or distillation, reverse osmosis or ultrafiltration with or without aroma recovery from the permeate by distillation, and freeze concentration.

The selection of the concentration process is a purely economic problem and, for instance, Thijssen & van Oyen (1977) showed that the costs of dewatering with aroma recovery appear to be lowest for long tube falling film and plate evaporators.

At present, well-established criteria for designing any juice-processing unit do no exist, and equipment is usually purchased together with technological know-how from a small number of manufacturers. Therefore these units are often overdesigned.

An optimization procedure could be set up, requiring the following: (a) characterization of the essential physical properties of fruit juices (*i.e.*, boiling point rise, density, specific heat, viscosity, thermal conductivity, etc.); (b) modelling of concentration process; (c) objective function to choose the process that performs the job optimally at given costs of capital, utilities, labour, etc.

The data required at step (a) are usually not available. Honig (1953) has reported the properties of aqueous sucrose solutions. Desrosier (1970) gave boiling points of typical fruit juice/sugar mixtures at various pressures for soluble solids concentrations ranging from 50 to 76% by weight.

The data are for unknown fruit/sugar mixtures and are of limited use in evaporator design.

Varshney & Barhate (1978) presented boiling point data for pineapple, mango and lemon juices at various concentrations and pressures.

The present study is the first in a series of investigations to characterize the essential physical properties of some fruit juices and to optimize the pasteurization and concentration unit of any fruit juice production process. In this paper, boiling-point elevations, densities, viscosities and specific heats of orange juice at different concentrations are reported.

Materials and methods

(1) Materials

Juice was extracted from mature Italian type ('Ovale') fruits in a manually operated screw press, centrifuged in a continuous centrifuge at 1500 rev/min and then filtered under vacuum on an ordinary cloth filter to remove suspended particles.

The concentration of orange juice was measured by refractometer at 20°C and expressed as degrees Brix (percentage by weight of equivalent sucrose in the solution) as described previously (Ministero Agricultura e Foreste, 1961; Safina, 1971; U.S. Dept. Agr. Prod., 1949). The correction of degree Brix was made by taking into account the acidity of orange juice, according to Stevens & Baier (1939).

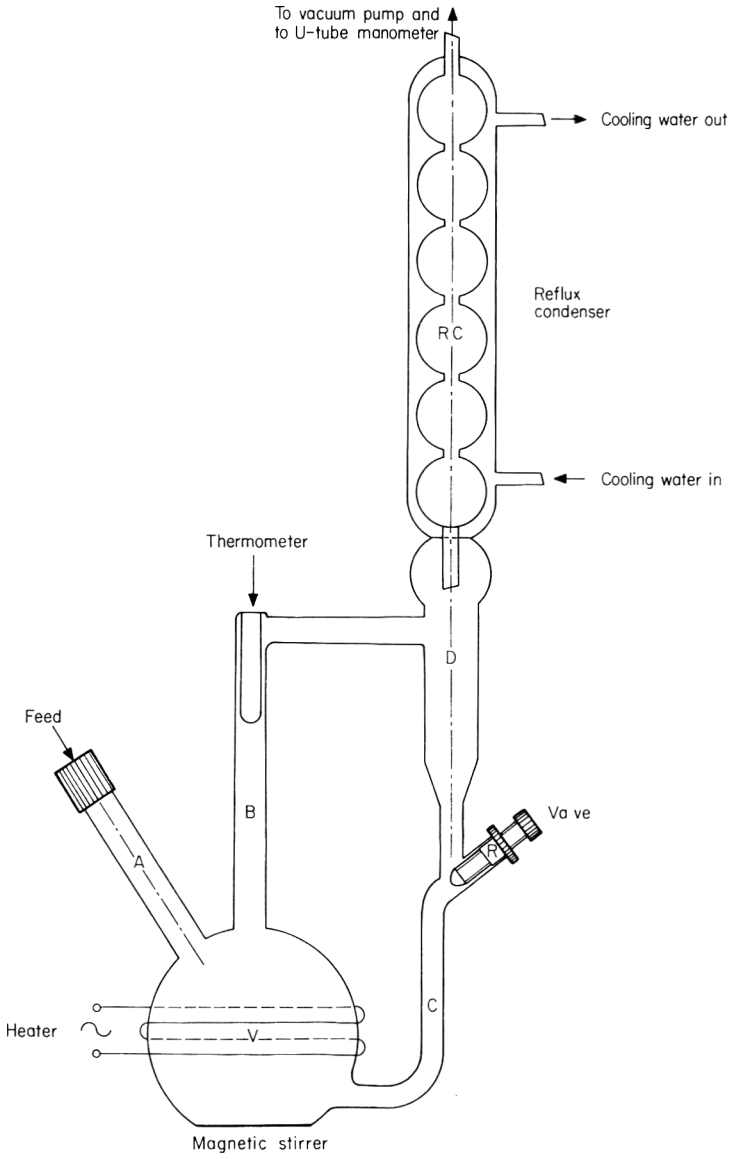

Figure 1. Schematic diagram of experimental boiling point apparatus.

The juice was concentrated under vacuum (about 60 mm Hg abs.) in the range from 9.6 to 65° Brix.

When there was any substantial time gap between two processes, the juice was stored at about 4°C before and after concentration.

(2) *Apparatus and procedure*

2.1 *Measurement of boiling-point elevation.* The apparatus shown in Fig. 1 was used. It consisted of a 6.5 cm flat-bottomed Pyrex flask V. Each sample was

introduced into V by means of a tube A. When the juice was boiling a recirculation flow was established between tubes B and C. The liquid-vapour mixture, liberated from the liquid surface, went up along tube B, thus containing the bulb of a thermometer. Then, a catchall D, installed in the liquid-vapour line, removed entrained liquid particles, which returned to the bulk of the liquid, and allowed the vapours to enter the reflux condenser RC. These vapours were condensed and the condensate flowed down through the same tube C. Valve R allowed control of the recirculation flow rate. This maintained the concentration of juice constant.

The apparatus was connected to a vacuum pump to create a pressure ranging from 60 to 760 mm Hg abs. The pressure was measured by means of a U-tube manometer. The sample was heated by means of a resistance heater wrapped around the external surface of V and mixed by a magnetic stirrer.

The performance of the apparatus was checked using water and aqueous sucrose solutions whose boiling points at various concentrations and pressures are known, and was found to be good.

In each experiment a 120 ml sample of concentrated juice was charged into the boiling vessel and all connections were made. The cooling water flow was started in the reflux condenser, the vacuum pump started to obtain a pressure of about 60 mm Hg abs. and the fluid was mixed and heated slowly. The boiling point of the solution and associated pressure were recorded, the pressure and temperature readings being constant for at least 5 min.

The vacuum was then decreased by about 50 mm Hg and the procedure was repeated until the atmospheric pressure was reached. The heating was then stopped and the vessel cooled down to room temperature. The juice was partially removed and the concentration checked. In a few cases the run was repeated to check the previous results.

Juice of another concentration was then placed in the boiling vessel and the above procedure repeated.

2.2 *Measurement of viscosity*. The viscosity of each solution was determined with a Höppler falling sphere viscometer (DIN 53016; Karl Schneider & Sohn, Wertheim, Germany) at 25, 35 and 50°C in a constant-temperature water bath.

The falling times of calibrated glass and stainless steel spheres between two given lines in water and orange juice were recorded and used to determine the viscosity of each solution.

2.3. *Measurement of density*. The density was measured by filling a calibrated volumetric flask with the orange juice to a marked volume and determining the weight at constant temperature (21°C).

2.4. *Measurement of specific heat*. The specific heat was measured with a 'Thermal Analyzer' Dupont 990 (Delaware, U.S.A.).

The specific heat of a test sample was determined by comparing the thermal lag between sample and reference systems under 'blank' and 'sample' conditions. Specific heat was calculated by measuring the difference in Y-axis displacement (calorimetric differential) between the sample and blank curves at any desired temperature. The cell calibration coefficient was determined by running a water sample for each temperature in the range 10–40°C.

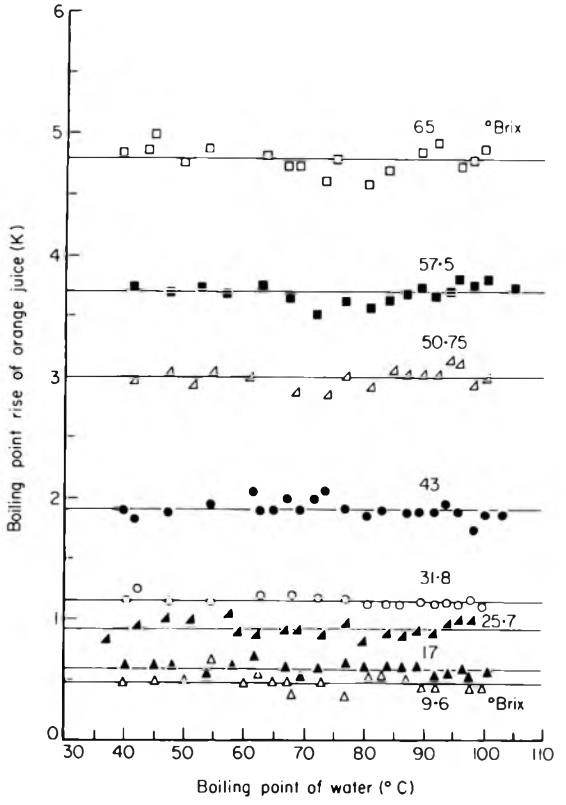

Figure 2. Boiling-point rise, ΔT_b, of orange juice *vs* boiling point of water, T_A.

(3) *Results*

The experimental boiling point elevations, ΔT_b, of concentrated orange juice *vs* boiling points of water at the same pressure are shown in Fig. 2.

The experimental viscosity of each solution, μ, is plotted as a function of temperature in Fig. 3.

Figure 4 shows the experimental density, ρ, at 21°C *vs* concentration of juice, expressed as °Brix.

The experimental values, c_p, at 25°C are plotted against concentration in Fig. 5. In the range 10–40°C the specific heat of each sample was about constant (the maximum standard deviation was 0.126 J/g-°C).

Analysis of results and discussion

1. *Boiling-point elevation*

The boiling points of orange juice, T_S, at various concentrations increase linearly with the boiling point of water, T_A, as stated by Dühring's Rule.

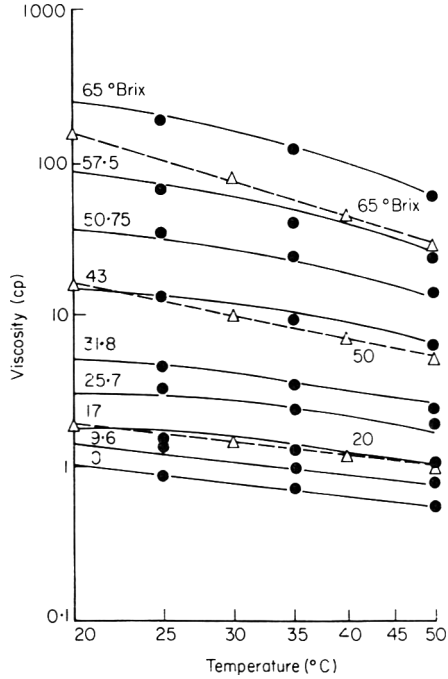

Figure 3. Variation of the viscosity of orange juice, sucrose solution and water with temperature. ●, Orange juice, (this work); △, sucrose solutions (Honig, 1953).

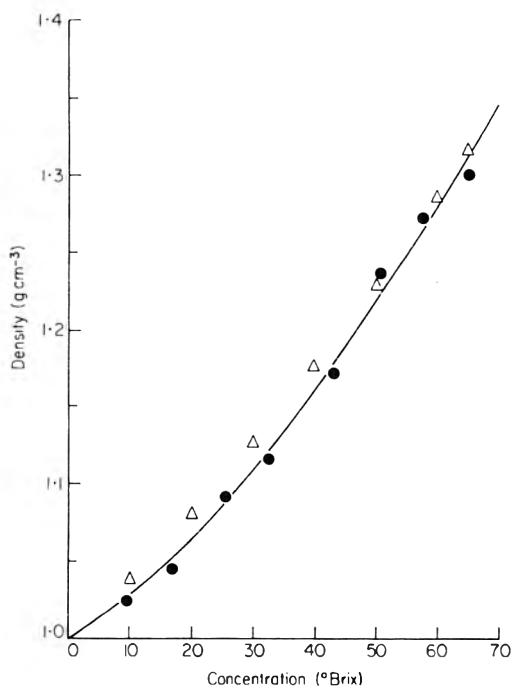

Figure 4. Density of concentrated orange juices and sucrose solutions at 21°C as a function of their concentration. ●, Orange juice (this work); △, sucrose solutions (Honig, 1953).

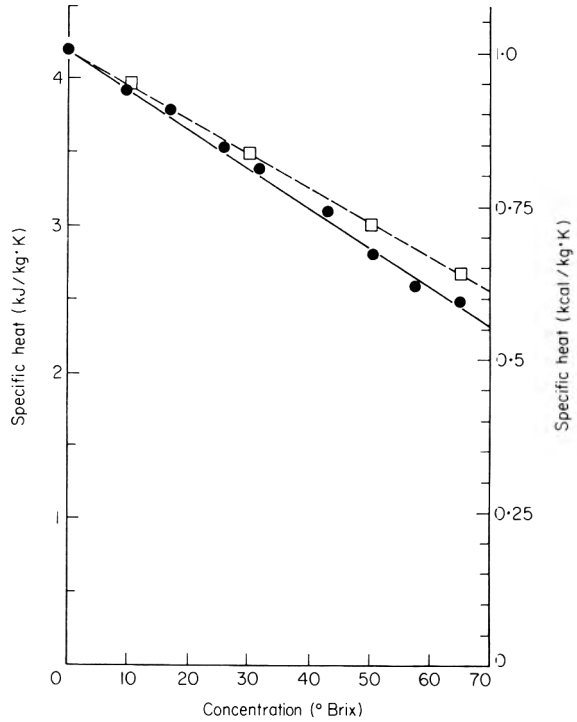

Figure 5. Specific heat of orange juices and sucrose solutions at 25°C as a function of their concentration. ●, Orange juice (this work); □, sucrose solutions (Honig, 1953).

Therefore, at constant concentration we have:

$$T_S = m_0 + m_1 T_A \tag{1}$$

where m_0 and m_1 are constants. These unknown parameters for each orange juice concentration were obtained by using the method of the least squares and are tabulated in Table 1 together with correlation coefficient, r^2, and degrees of freedom, θ.

From Table 1 it may be observed that m_1 is about 1; that is, the resulting plots are straight lines and plots for different concentrations are roughly parallel. This means that the boiling point rise, ΔT_b, at each concentration of juice is independent of T_A and is related only to the sugar content of the juice. From eqn (1), we find:

$$\Delta T_b = T_S - T_A \simeq m_0 \tag{2}$$

Hence, the values of ΔT_b were calculated by subtracting the boiling point of water from the observed boiling point of a given sample for each experimental pressure and plotted as a function of boiling point of water in Fig. 2.

The mean values of ΔT_b for all the experimental runs with their standard

Table 1. Values of constants m_0 and m_1 in equation $T_s = m_1 T_A$ for orange juices' plot of Fig 2, correlation coefficient, r^2, of each regression line and degrees of freedom, φ, as a function of concentration.

Concentration °Brix	m_0 (K)	m_1 —	r^2 —	φ —
9.60	0.5285	0.999	0.999	17
17.00	0.6359	0.999	1.000	18
25.70	0.9110	1.000	1.000	18
31.80	1.3224	0.998	1.000	16
43.00	2.0780	0.998	1.000	21
50.75	2.6130	1.005	1.000	16
57.50	3.5940	1.001	1.000	17
65.00	6.0930	0.987	0.995	16

errors were then calculated and are shown in Table 2. These mean values of ΔT_b *vs* their respective concentrations were finally plotted in Fig. 6.

The boiling point elevation of a liquid A caused by addition of a non-volatile solute B at low molality can be calculated from first principles (Moore, 1972) as

$$\Delta T_b = \frac{R\, T_o^2}{\Delta H_v}\, x_B \tag{3}$$

where R is the gas constant (kJ/kmole- K), T_0 the boiling point of solvent A(K), ΔH_v is its enthalpy of vaporization per mole (kJ/kmole) and x_B the mole fraction of solute. Eqn (3) can be re-written as follows

$$\Delta T_b = \frac{R\, T_o^2}{\Delta H_v}\, \frac{1}{1 + \frac{1-y_B}{y_B} \cdot \frac{M_B}{M_A}} \simeq \frac{R\, T_o^2}{\Delta H_v} \cdot \frac{y_B\, M_A}{(1-y_B) M_B} \tag{4}$$

Table 2. Mean values of boiling-point rise and their standard errors as a function of concentration.

Concentration (°Brix)	ΔT_b (K)	Standard error (K)
9.6	0.474 ±	0.051
17.00	0.584 ±	0.050
25.70	0.919 ±	0.072
31.80	1.160 ±	0.044
43.00	1.912 ±	0.043
50.75	3.003 ±	0.089
57.50	3.704 ±	0.086
65.00	4.804 ±	0.109

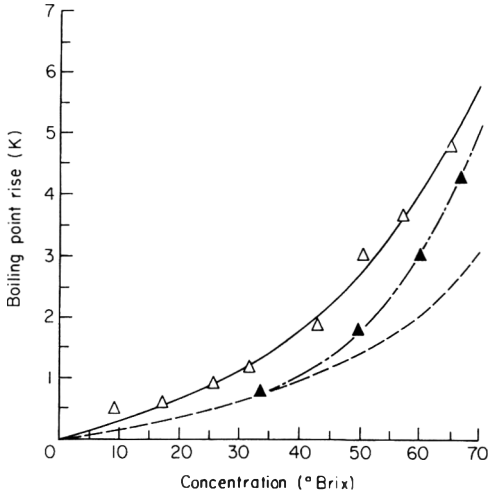

Figure 6. Variation of the boiling-point rise of orange juice and sucrose solution with concentration. △, Orange juice (this work); ▲, Sucrose solutions (Honig, 1953); ———, calculated by eqn (5); ----, calculated by eqn (4).

where M_A and M_B are the molecular weights of solvent and solute, respectively, and y_B the weight fraction of solute. Thus, the estimation of boiling point rise from eqn (4) will require accurate knowledge of the fraction of solutes in the solution, which is difficult in this case because orange juice contains many solutes.

The broken line of Fig. 6 was calculated by using eqn (4) with $T_0 = 373.15$ K and y_B equal to the weight fraction of equivalent sucrose. The error in the estimation of ΔT_b of orange juice is great even at low concentrations and increases as the concentration increases, according to Foust *et al.* (1960).

Therefore, the experimental values of ΔT_b (open symbols) of Fig. 6 were correlated as

$$\Delta T_b = a_0 + a_1 y_B + a_2 y^2_B + a_3 y^3_B \qquad (5)$$

where y_B is the weight fraction of sucrose in the juice, by using a non-linear optimization method to maintain $a_0 = 0$ and therefore $\Delta T_b = 0$ for $y_B = 0$ (pure water). The values of all the above parameters are listed in Table 3.

The continuous line of Fig. 6 shows the agreement between the calculated and experimental boiling-point rises: the mean standard error was less than 8% and the deviation about the regression line was 0.093.

Furthermore, the experimental ΔT_b values of aqueous sucrose solutions (closed symbols) at atmospheric pressure (Honig, 1953) were plotted in Fig. 6 to give the order of magnitude of the error in the estimation of ΔT_b, when these boiling-point rises are used instead of those of orange juices. For instance, the error is 22% at 65° Brix.

Table 3. Regression equations of the physical properties of orange juices.

Physical property	Regression	Unit
Boiling-point rise	$\Delta T_b = 3.2\ y_B - 2.42\ y^2_B + 14\ y^3_B$	K
	$\alpha = 34.668 - 0.2024\ y_B + 0.0162\ y^2_B$	cp
Viscosity	$\beta = -6.1055 + 0.0396 y_B - 2.68 \times 10^{-3} y^2_B$	–
Density	$\rho = 0.9944 + 0.307\ y_B + 0.282\ y^2_B$	g cm^{-3}
Specific heat	$c_p = 4.186 - 2.679\ y_B$	Jg^{-1}(K)$^{-1}$

(2) *Viscosity*

The viscosity of each solution can be expressed as

$$\mu = \alpha T_K^{\beta} \tag{6}$$

where α and β are functions of the sugar content of the juice and T_K is the absolute temperature (K).

A linear regression between $\ln\mu$ and $\ln T_K$ resulted in a set of parameters α and β with regression coefficients ranging from 0.97 to 0.99.

These parameters were correlated with their respective concentrations by using a polynomial form with the method of the least squares. A polynomial of the 3rd degree was found to reconstruct significantly the original values of α and β by means of an *F*-test: their regression coefficients were 0.96 and 0.97, respectively.

A non-linear optimization method was finally used to minimize the standard error between the experimental and calculated values of viscosity.

The continuous lines of Fig. 3 were calculated by using eqn (6) with α and β expressed as listed in Table 3: the mean standard error was less than 8%.

The broken lines of Fig. 3 apply to aqueous sucrose solutions at 20, 50 and 65°Brix and allow a direct comparison between the viscosities of orange juice and sucrose solutions. For instance, at 50°C the viscosity of orange juice at 65°Brix is about twice that of a sucrose solution at the same concentration.

Furthermore, after extraction orange juice contains about 12% of seeds, pieces of peel and pulp, which are usually reduce to 1–5% by means of paddle and screen type finishers and centrifuges before the concentration of juice (Tressler & Joslym, 1961). This residual material further increases the viscosity of industrial orange juices and moreover can modify the rheological behaviour of the fluid.

(3) *Density*

The density of orange juices is a non-linear function of their concentration, as shown in Fig. 4. By the method of the least squares the following was obtained:

$$\rho = b_0 + b_1\ y_B + b_2\ y^2_B \tag{7}$$

with a regression coefficient equal to 0.994. The values of the above parameters are shown in Table 3.

The continuous line of Fig. 4 was calculated by using eqn (7): the mean standard error is 0.65% and the deviation about the empirical regression line is $s^2_1 = 0.74 \times 10^{-4}$ with 8 degrees of freedom.

The density of orange juice (closed symbols) at concentrations below 40° Brix seemed to be smaller than that of sucrose solutions (open symbols) at the same concentration (Honig, 1953) (see Fig. 4).

To establish if this statement had a statistical significance at a given confidence level, the deviation of the densities of sucrose solutions (see Fig. 4) about the empirical regression line – eqn (7) – was calculated, thus obtaining $s^2_2 = 1.38 \times 10^{-4}$ with 8 degrees of freedom. The ratio s^2_2/s^2_1 is $1.85 < F_{0.95}(8,8) = 3.44$.

Therefore, the differences between the two sets of experimental data (closed and open symbols of Fig. 4) are not statistically significant at the 95% confidence level.

(4) *Specific heat*

Figure 5 shows that the experimental specific heat of orange juice (closed symbols) is a linear function of sugar content. The data were correlated by using the method of the least squares as follows:

$$c_P = p + q\, y_B \tag{8}$$

where p and q are constants, the values of which are listed in Table 3. The regression coefficient is 0.996 and the standard error is less than 1.5%.

The literature c_P values of sucrose solutions (Honig, 1953) (open symbols) were also plotted in Fig. 5.

Orange juices have a smaller c_P value with respect to the above solutions, as orange juice is a mixture of water and sugar with small amounts of organic compounds (citric acid, aldehydes, aminoacids, etc.). These compounds, which are not present in sucrose solutions, reduce the value of c_P of juice.

Acknowledgments

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Measurement of the spreadability of margarine and butter using a single pin maturometer

P. W. BOARD, K. AICKEN AND A. KUSKIS

Summary

Single pin maturometer (SPM) readings were taken on samples of margarine and butter having temperatures in the range 0–25°C. The spreadability of the same samples at the same temperatures was also assessed by a panel of twenty adults using an hedonic scoring scale. The SPM readings and scores for spreadability varied markedly with the type of product and its temperature. The temperature corresponding to maximum scores for spreadability for a hard margarine and butter was about 20°C and for a soft butter was about 15°C. A soft margarine received scores of more than 6(= very good) on the 7 point hedonic scale over the temperature range 0–10°C and the data indicated that spreadability may also be 'very good' at temperatures just below 0°C. The SPM reading corresponding to the maximum score for spreadability was about 100 *g* for all samples. The SPM was shown to be suitable for the routine assessment of the spreadability of margarine and butter.

Introduction

Spreadability is one of the important quality attributes of margarine and butter and instruments for measuring spreadability were first developed about 50 years ago (Mulder, 1953). These instruments are of two main types; those in which spreadability is measured in terms of the force required to extrude the sample through one or more orifices and those in which the force required to spread the sample with a knife is measured. In both types of instrument the sample undergoes rapid and gross deformation as it does when being spread onto bread by consumers.

Apart from ensuring that the sample undergoes marked deformation during the measurement of spreadability the currently used instruments vary greatly in

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design and operation and it is usually impossible to relate the results from one to another in basic rheological terms (Mulder, 1953). However, the practical requirements of instruments of this type are that they give results of acceptable reproducibility, that they are sufficiently sensitive to detect differences of practical importance between samples, that the measurements can be related to the results of sensory assessment of spreadability in a meaningful way and that the instruments are convenient to use. The extrusion instrument used by Prentice (1954) and the modified Huebner-Thomson apparatus which employs a knife and was used by Riel (1960) apparently meet these criteria.

Prentice (1954) found that the linear regression of the logarithm of the force at the end of the extrusion stroke against the results of sensory assessments of spreadability by a panel of three for 300 samples of butter, was highly significant, with a correlation coefficient of 0.935. Riel (1960) used a panel of fifteen adults to assess the spreadability of fifty-seven samples of butter and thirty-eight samples of margarine. His plots of sensory score against logarithm of resistances to spreading gave broken straight lines for both types of product. In addition the objective measurements corresponding to the sensory designation 'desirable spreadability' were similar for butter and margarine.

This paper describes an evaluation of the suitability of the single pin maturometer (SPM) (Huntington & Rutledge, 1974) for measuring the spreadability of margarine and butter. The SPM measures the resistance offered by the sample to penetration by a blunt pin; it might therefore be considered to be a third type of instrument for measuring spreadability. As the blunt pin penetrates 19 mm into the sample at a speed of almost 1 cm/sec the measurements are made under the required conditions of rapid and gross deformation of the sample (Prentice, 1954; Riel, 1960; Dixon, 1966). However, unlike conditions in extruders and in the instruments incorporating a knife, the product under test by the SPM may move in any direction away from the advancing face of the blunt pin as the measurement is made.

Since submitting this paper for publication our attention has been drawn to similar studies to ours on butter and margarine (de Man, Dobbs & Sherman, 1979). In that work spreadability was determined by sensory methods and by several physical methods including penetrometer measurements.

Methods

Samples

Commercial samples of hard and soft margarine and of butter were used. A sample of experimental butter having an enhanced level of linoleic acid and a soft texture was also tested. This butter was produced from cream from cows which had been fed a protected supplement based on oil seeds; the supplement gave increased levels of linoleic acid in the milk and body fats of the cows (Scott *et al.*, 1970) and thereby permitted the direct production of the soft butter.

Objective measurement of spreadability

The blunt pin (3.2 mm diam.) was driven vertically by a constant rate, constant diameter cam operating at 10 rpm and having a throw of 2.54 cm. The pin penetrated the horizontal surface of the sample to a depth of 19 mm and the maximum force (g) resisting penetration was measured. Force was measured using a ring spring and linear differential transducer which was connected to a pen recorder having a full chart response speed of 0.7 sec.

Samples were held in glass dishes (55 mm diam. × 30 mm depth) so that measurements could conveniently be made at various temperatures. Care was taken in filling the dishes to avoid incorporating pockets of air. After filling, the samples were held at constant temperatures of 0, 5, 10, 15, 20 and 25°C for 24 hr to ensure that they were at the required test temperature and to allow some recovery of their structure which would have been modified during filling (Mulder, 1953).

Twenty SPM readings were made on the spread in each dish, care being taken to distribute the test points evenly across the surface of the sample. There was no evidence that later readings were affected by earlier readings on the same sample nor was there evidence of wall effects.

Sensory measurements

Spreadability was assessed by a panel of twenty adults who used a 7-point hedonic scale which ranged from 1, 'extremely poor spreadability', to 7, 'ideal spreadability'. Panellists were reminded that the use of this scale implied that samples which they judged to be too hard or brittle, or too soft or oily should be given low ratings. The panellists were members of the laboratory staff and although they were familiar with sensory testing they were not specially trained in assessing spreadability.

The panellists assessed two sets of three samples at a sitting in eight sessions in a partially balanced incomplete blocks design. The samples were presented as spheres of about 10 g and the panellists spread the samples onto fresh white bread using whatever technique they preferred. The samples were individually cooled before serving and orange lights in the taste test booths masked the colour of the spreads. The taste test booths were air conditioned and had a temperature of approximately 22°C. The temperature of the bread, knives and plates was approximately 22°C to reproduce conditions usually encountered in spreading bread in the home.

Special steps were taken to ensure that the temperature of the samples presented to the panel was as close as possible to the temperature of the equivalent samples used for the SPM measurements. The individual samples in 50 ml glass serving dishes were held at the required temperature for 24 hr before testing. A few minutes before each session the dishes were moved to the sensory laboratory in insulated boxes which also contained plastic bags of water at the required temperature. Measurements with thermocouples showed that

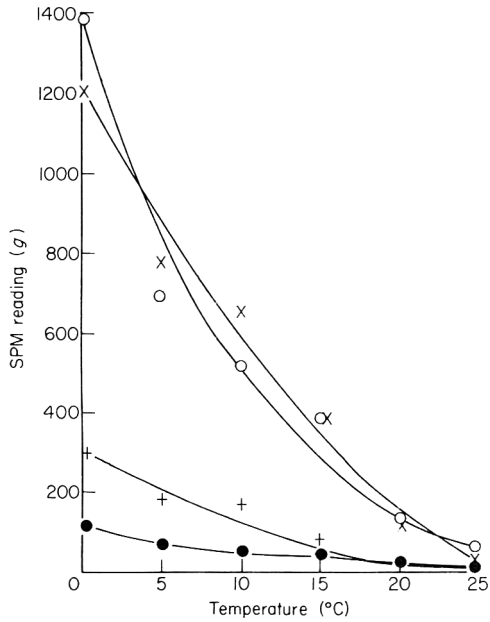

Figure 1. Effect of temperature on the SPM readings for: soft margarine (●——●), hard margarine (○——○), butter (×——×) and soft butter (+——+).

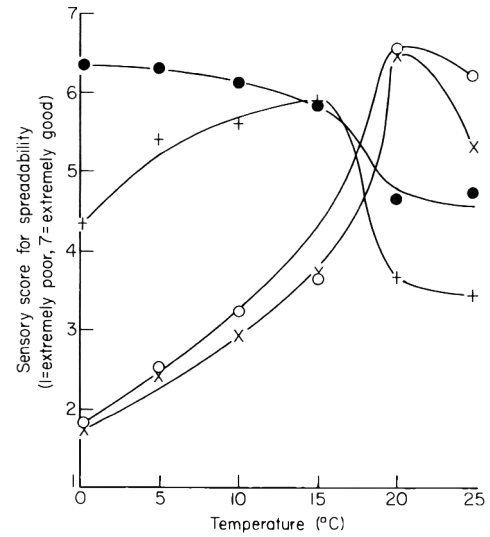

Figure 2. Mean sensory scores for spreadability plotted against temperature for: soft margarine (●——●), hard margarine (○——○), butter (×——×) and soft butter (+——+).

the temperature of the samples changed by less than 0.5°C before the samples were given to the panel. For serving, each dish was fitted into a cavity in a block of polystyrene foam (10 × 10 × 4 cm) and the top of the block was covered with aluminium foil. This system restricted the change of temperature of the samples to less than 2C° in 10 min but most panellists completed their assessments in less than 5 min.

Results and discussion

The results of the SPM measurements on the margarine and butter at temperatures in the range 0–25°C are shown in Fig. 1; each point is the mean of twenty samples. Smooth curves were fitted to the experimental points by eye to make it easier for the reader to follow trends. The data clearly show that the SPM measurements allow the samples to be distinguished in the expected way; the hard margarine and butter were firmer than the soft margarine and soft butter. The s.e. of the mean expressed as a percentave of the reading was in the range 1–2% for the samples of margarine and soft butter at temperatures from 0–15°C. At higher temperatures the SPM readings were low and the percentage s.e. was often larger than 2% but never more than 4%. The percentage s.e. for the SPM readings for butter was less than 1% for all temperatures.

The low percentage s.e. for butter compared with the percentage s.e. for the other products may be associated with the intrinsic structure of the products and their capacity to re-establish their structure after they were transferred to the test dishes. This aspect was not investigated but it seems likely that the s.e. would be less if the SPM measurements were made on the product in its original package and this would probably be the preferred procedure in the routine assessment of spreadability.

Figure 2 shows the raw mean of the sensory scores for spreadability obtained from two sittings of the panel for each product and each temperature. Again, the curves are smooth lines which were fitted to the experimental points by eye to assist the reader to follow trends.

Data for the s.e. of the mean score for spreadability for each sitting indicated that the panellists were more consistent in assessing samples having extremes of spreadability i.e., ideal spreadability or poor spreadability, than samples having an intermediate spreadability.

The maximum score for spreadability for butter and hard margarine was given for samples having a temperature of about 20°C, and for soft butter the maximum occurred at about 15°C. The scores for soft margarine did not show a maximum but spreadability was assessed as 'very good' or better than that, corresponding to sensory scores of 6 or higher, for the temperature range 0–10°C. It appears that the spreadability of soft margarine may be high even at temperatures some degrees below 0°C. These results conform in general with the results obtained by de Man *et al.* (1979) from panellists who assessed the spreadability of several samples of butter and margarine on soda crackers. Our

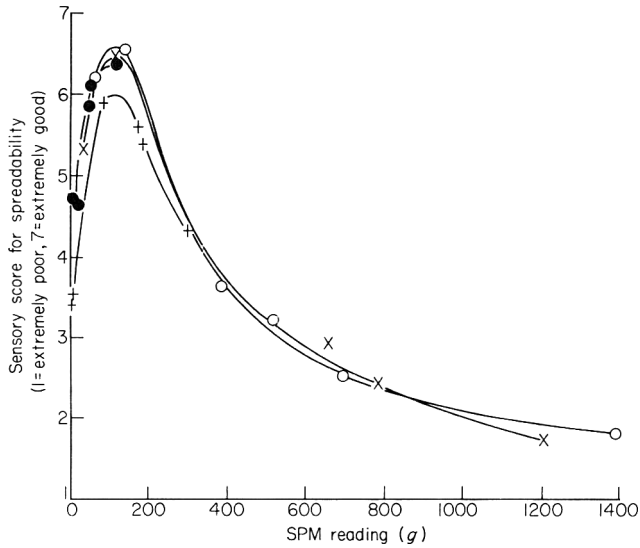

Figure 3. Relationship of sensory score for spreadability and SPM reading for: soft margarine (●——●), hard margarine (○——○), butter (×——×) and soft butter (+——+).

results however differ appreciably from those of Riel (1960) who reported that butter had a 'desirable' spreadability at temperatures in the range about 15–18°C and a sample of margarine had a range of about 11–15°C.

The difference between Riel's results and those of the present study may be related to differences in the properties of the butters and margarines tested, to differences in the properties of the bread used in assessing spreadability or to differences in the scales used for scoring spreadabiltiy; Riel's scale used descriptions of 'hardness' and 'softness' for spreadability while the scale used in this work was hedonic for spreadability.

The data in Figs. 1 and 2 were used to plot the relationship between SPM reading and spreadability as assessed by the panel; the relationships are shown in Fig. 3 and again smooth curves were fitted to the points by eye to assist the reader. The maximum scores for spreadability occurred for all samples at a SPM reading of about 100 g. The SPM reading corresponding to the maximum score for spreadability, and the maximum scores for spreadability were similar for the four products.

The score of 5 was designated 'good spreadability' on the scoring scale so it is reasonable to assume that samples receiving scores of 5 or more would be at least satisfactory in respect to that attribute. The range of SPM readings corresponding to scores of 5 or more were about 20 to 200 *g* and it appears that this is a practical range for manufacturers to aim for in margarine and butter for table use.

The results of this study show that the SPM is suitable for measuring the spreadability of margarine and butter. The instrument gave readings of acceptable reproducibility even on samples transferred to test dishes. It is of course essential to standardize conditions for recovery to obtain reproducible measurements of spreadability and long periods may be required for full recovery (Mulder, 1953). Reproducibility should be improved if the measurements are made on structurally undamaged samples in their original package, as would probably be done in commercial practice. The instrument is sufficiently sensitive to detect textural differences of practical importance, it is convenient to use and the results it gives are usefully correlated with scores for the sensory assessment of spreadability.

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Storage life of chilled Patagonian hake *(Merluccius hubbsi)*

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Summary

The storage life of iced Patagonian hake (*Merluccius hubbsi*) was studied. Seasonal changes were investigated by means of organoleptic assessments (raw and cooked), total volatile bases (TVB) and pH.

During summer-time (December to March) the keeping time, from the edibility point of view, for round hake in ice is not more than 9 to 10 days; in the remaining months the storage life under the same conditions is up to 14 to 15 days.

The difference could be due to the biological condition of hake during and after the spawning time (end of spring–beginning of summer), the shallow and temperate waters of the fishing grounds in summer, and the heavy feeding after spawning.

Comparison trials between gutted and ungutted hake in ice, and between ungutted hake in ice and in chilled sea water (CSW) were also performed.

The duration of *rigor mortis* of whole hake stored in ice, and the feasibility of quality assessment by an electronic device were also studied.

Introduction

The hake fisheries in the South West Atlantic are becoming more important, as can be seen in the Report of the FAO Technical Consultation on the Latin American Hake Industry (FAO, 1978) which was held in Montevideo in October 1977.

The Patagonian hake (*Merluccius hubbsi*) is the most important one in South American waters according to the potential yield and exportation figures of recent years (Boerema, 1978).

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Table 1. Basic information on the experiments performed

Date	Experiment no.	Code exp.	ROA	COA	TVB	TM	pH	Ship		Catch position	Number of fish evaluated
15.12.73	1	UI	yes	–	–	–	–	PS		43° 36′ S 65° 00′W	180
22.02.78	2	UI	yes	–	yes	–	yes	AL	c.a.	42° 00′ S 62° 00′ W	108
07.03.78	3	UI	yes	–	yes	–	yes	AL	c.a.	41° 00′ S 56° 30′ W	90
31.05.78	4	UI	yes	–	yes	yes	yes	AL	c.a.	39° 00′ S 55° 30′ W	208
07.09.78	5	UI	yes	–	yes	–	yes	AL	c.a.	37° 00′ S 54° 00′ W	180
03.09.78	6	UI	yes	–	yes	yes	–	WH		47° 37′ S 63° 10′ W	112
28.09.78	7	UI	yes	–	yes	yes	–	WH		36° 20′ S 55° 10′ W	90
03.10.78	8	U-CSW	yes	–	yes	yes	–	WH		39° 45′ S 59° 55′ W	90
07.11.78	9	UI	–	yes	yes	yes	yes	WH		43° 43′ S 59° 35′ W	112
07.11.78	10	GI	–	yes	yes	yes	yes	WH		43° 43′ S 59° 35′ W	112
07.11.78	11	HG-I	–	yes	yes	yes	yes	WH		43° 43′ S 59° 35′ W	112
11.03.79	12	UI	yes	yes	yes	yes	yes	AL	c.a.	41° 30′ S 59° 00′ W	160

Exp. codes: UI; ungutted in ice; U-CSW, ungutted in chilled sea water; GI, gutted in ice; HGI, headed and gutted in ice.

Although the species in itself is recognized as being as good as the hake species in the North Atlantic (Pedraja, 1978; Ludorff & Meyer, 1973; Anon, 1973), some problems of quality arise due to handling procedures, seasonal changes, etc.

It has been pointed out that unlike the North Atlantic white fish, there is a considerable lack of data on the Patagonian hake, particularly regarding keeping time on ice, cold storage and its seasonal variations.

This work deals mainly with the keeping time of whole Patagonian hake on ice, the form in which it is usually landed by trawlers in Argentina and Uruguay. However, a comparison with gutted iced hake and with the chilled sea water system (CSW) is also made.

Materials and methods

Table 1 summarizes the experiments performed, with reference to the place of catch, season (date), vessel and types of analysis and assessments.

The codes PS and WH correspond to experiments performed on board the research ships PROFESOR SIEDLECKI and WALTHER HERWIG of Poland and the Federal Republic of Germany respectively. The code AL corresponds to catches of the Argentinean commercial trawler ALTALENA (side trawler, 51,44 m) evaluated on land.

Although the experiments on board WH and PS may be of dubious practical application, because of more careful handling, only minor differences with commercial samples treated with reasonably careful handling were found in practice. This result was in accordance with the findings of Huss *et al.* (1974).

All the trials were performed in plastic boxes with sufficient crushed ice and stored in cold chambers at a temperature of *ca* 0°C. During the experiments samples of not less than sixteen fish were analyzed each time, except for run no. 1 where ten fish were used.

On average the organoleptic assessments were performed by a group of four experienced assessors. A pooled sample from one fillet for each fish used in the organoleptic assessment was utilized for the chemical determinations.

The raw organoleptic assessment (ROA) was made according to the scale developed for the Patagonian hake by the FAO-Fishery Development Project in Argentina (da Encarnacao, 1974). This scale ranges from 0 for the best quality to 5 for the worst, and it is shown in detail in Table 2.

The cooked organoleptic assessment (COA) was made on fillets wrapped in aluminium foil and cooked by steaming in a casserole for 10 min. A scale was developed also ranging from 0 (the best quality) to 5 (the worst). This scale is shown in Table 3.

The total volatile bases (TVB) were determined by a modification (Giannini, Davidovich & Lupín, 1979) of the Nordsee direct distillation method (Nordsee GmbH, 1972). Not less than two assays were performed on each pooled sample.

Table 2. Organoleptic score—ungutted hake.

		0	1	2	3	4	5
Skin	Outer slime	Transparent-not coloured		Milky	Opaque	Cloted	Yellowish
	Pigmentation	Bright, iridiscent	Natural	Less natural, not bright, not iridiscent	Faded	Discoloured	Grey
Eyes	Colour	Black pupil, translucent cornea (bright)	(less bright)	Translucent cornea, not bright	Opalescent cornea	Gray Pupil, milky cornea.	Opaque, Discoloured
	Sinking	Completely convex		Less convex	Plane	Slightly concave	Completely concave, sunken
Gills	Colour	Bloody red		Dull red	Pale red	Dirty yellow	White-grayish
	Odour	Fresh (algae, sea)	Neutral	Sweet	Slightly rancid	Slightly disagreeable	Off odours, nauseous
Flesh	Meat	Firm (rigid)	(slightly elastic)	Elastic	Flexible	Soft	Very soft
Quality	Belly	Intact (firm-rigid)	(not rigid)	Distended (firm)	Soft (not firm)	Fragile	Perforated
Peritoneum		Dificult to tear from flesh (bright black)	(black)	Easy to tear from flesh	Teared	Damaged (incomplete)	Burst
Back	Colour of meat next to bone	Bright white	White–not bright	Slightly pale red	Pale red	Red	Grizzly
Bone	Meat Adherence to bone	Very Adherent		Adherent	Slightly adherent	Not adherent	Meat separated from bone

Table 3. Organoleptic score – cooked hake fillet

Factor	0	1	2	3	4	5
Odour	Fresh sweet characteristic	Lightly sweet –not specific	Neutral	Slightly acid	Acid	Nauseous
Flesh colour	Snow white	Pearl white	Dirty white	Slightly yellow	Yellowish	Grey
Fat layer colour	White	Pearl yellow	Pearl brownish	Slightly brown, uniform	Brown	Dirty brown
Texture	Very firm	Firm	Slightly split	Mealy	Soft	Badly split, very soft
Flavour	Characteristic	Characteristic, stronger	Fishy	Rancid	Bitter	Disagreeable
Palatability	Very Palatable	Palatable	Good	Regular	Bad	Unacceptable

The essential features of the procedure used were 10 grams of ground fish, 300 ml of tap-water, 1.5 g of OMg and 8 drops of silicone antifoaming agent were placed in a direct distillation apparatus. Then 180 ml of distillate were collected in a beaker with 50 ml of 2% boric acid solution and mixed indicator (methyl red – bromocresol green). Afterwards the beaker contents were titrated to the end point with 0.1 N H_2SO_4.

The pH was determined directly by means of a glass electrode set in different parts of the minced, pooled sample.

Two kinds of measures of the *rigor mortis* conditions were made; the first by means of hand pressure on the fish body and grading into three types: full *rigor*, partial *rigor* and flexible. The second was by means of an improved version of the penetrometer device used by Messtorff (1954).

The penetrometer is basically a 5 mm diameter steel bar with a hemispherical head, which can travel up to 20 mm, working against a spring with a restitution constant of 4.45 g/mm. The device was pressed perpendicular to the fish skin until a reference plate corresponding to the level of 20 mm displacement of the bar rested on the skin surface and then the travel of the bar was recorded. The graduations can be appreciated down to 0.1 mm. The values of the travel in mm are used here to define the *rigor mortis* condition. The resistence of the muscle to the displacement can be calculated from the following equation:

$$\text{Resistence} = 27.212\ \text{g} + 4.45\ (\text{g/mm}) \times \text{travel (mm)}$$

All the experiments were performed on batches of hake, placed in ice immediately after opening the net. Each experimental point was obtained as the average value for sixteen hake. The Torrymeter average value (TM) was determined over sixteen fish, although the individual values were also recorded. Statistical evaluations have been used wherever appropriate and possible.

Although different assessment scales and chemical methods appear suitable for the study, those selected are among the most commonly used for Patagonian hake evaluation in commercial practice and they also conform to the Argentine's food law regulations.

Results

Seasonal variations

The seasonal variations of Patagonian hake greatly affect the keeping time in ice. In Fig. 1 we can see the ungutted hake ROA variations *vs* days in ice for the so-called winter-time, April to November, and summer-time, December to March.

The classical s-shaped curves obtained were approximated by a straight line in the intermediate zone for statistical purposes. The confidence limits shown are for a 95% probability.

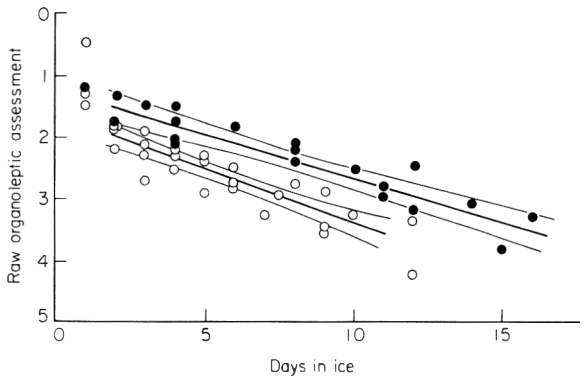

Figure 1. Raw organoleptic assessment of ungutted hake stored in ice. ●, Winter-time; ○, summer-time.

The differences in the average value and in the confidence limits, indicate a strong seasonal influence. This result corroborates the practical knowledge of fishermen and processors in that the summer-caught hake has a shorter keeping time in ice than that caught in the other seasons. The acceptability borderline was established at a score of 3 to 3.5.

A similar difference can be appreciated from the cooked organoleptic assessment (COA) values for experiments nos. 9 and 12.

In Fig. 2 the TVB-value variations for ungutted hake stored in ice for the same periods can be seen. The data were plotted on a semilog axis; in this way the first and the second stages in the variation can be approximated by straight lines.

Again a sharp difference between the summer and winter hake was found.

For the first stage in the TVB variation the plateau hypothesis was verified with the zero slope test according to Himmelblau (1970). As is known, no variation in the ice storage can be recorded by means of the TVB value in this first stage.

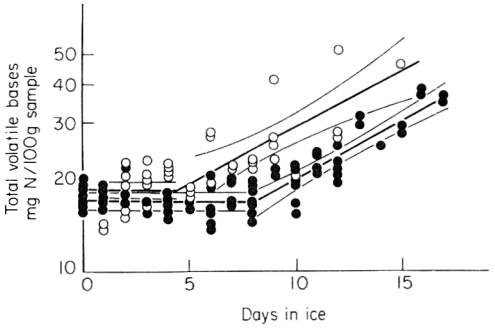

Figure 2. Total volatile bases values of ungutted hake stored in ice. ●, Winter-time; ○, summer-time.

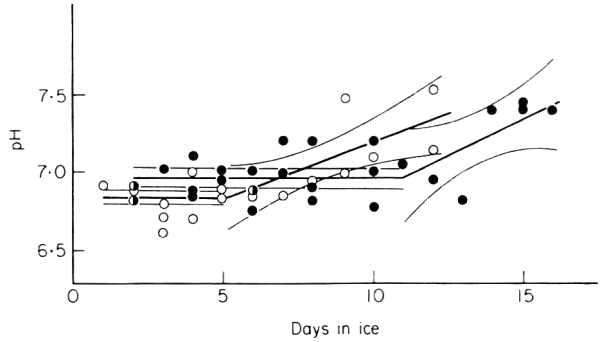

Figure 3. pH values of ungutted hake stored in ice. ●, Winter-time; ○, summer-time.

The second stage shows a rapid increase in the TVB value, but the break point appears later in winter (8th day) than in summer (4th – 5th day).

The second stage slopes have approximately the same value. This means that there is an equal rate of deterioration in this stage, from the TVB point of view, in each season. However the values in the second stage tend to be more scattered in summer-time.

According to the Argentine food regulations, and as it is usually accepted, fish with TVB values above 30 mg N/100 g sample is unsuitable as food. This means that, on average, the ungutted hake can be stored in ice for up to 10 days in summer and up to 14 days in winter.

Finally the variation in the pH values of the flesh is shown in Fig. 3. The pH is not usually accepted as a good parameter for fish quality assessment, due mainly to the scattering of results, although, as was shown by Love & Haq (1970) it is important in relation to texture changes. At the same time, according to the regulations of the Argentine and of other countries, the pH value must not be above 7.5 for fish other than Elasmobranchii.

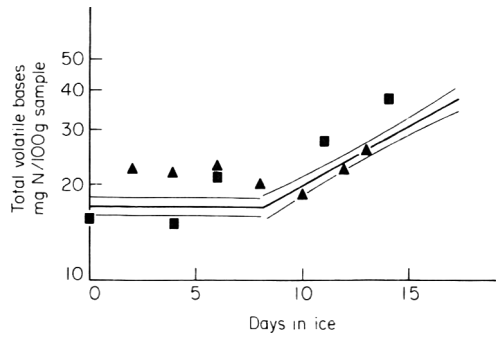

Figure 4. Total volatile bases values of: ▲, gutted winter hake stored in ice; ■, ungutted winter hake stored in CSW. Superimposed, with full lines, are the average values of TVB of ungutted winter hake stored in ice.

The pH variations were also approximated by straight lines for comparison purposes. In winter-time as in summer-time, two stages can be observed. After the pH change in the fish, quality can be assessed by measuring the pH value; in the second stage, an increase in the pH occurs as a result of deteriorative changes in the fish.

The steady pH value reached after *rigor mortis* development, usually called the ultimate pH value, appears to be a litte lower in summer than in winter. This is in accordance with the results of Love (1976) for cod. The steady behaviour of this ultimate pH value till the breaking point is reached was statistically verified according to the zero slope test.

With reference to pH, the hake caught in winter has a longer keeping time in ice than those caught in summer. The 7.5 pH borderline appears roughly equivalent to the borderline determined for the ROA or TVB values.

Handling procedures

Experiment no. 8 was carried out with ungutted hake kept in chilled sea water. The TVB values are shown in Fig. 4 together with the mean values found for hake kept in ice.

As far as TVB values are concerned, the keeping time in CSW is seen to be slightly less than that of storage in ice. A similar result for ungutted whiting was reported by Huss & Asenjo (1976).

The values of the ROA are judged worthless in comparing these storage methods because fish kept in CSW suffers adverse effects as the sea water washes gills, eyes and skin thus modifying the original external characteristics of fish, and so quickly affecting the ROA scores, even if no real deterioration has taken place in the flesh.

At the same time the salt in the sea water reduces the Torrymeter value.

Nevertheless, improvement of the CSW system could in practice result in a reduction of mechanical damage due to poor handling in boxes.

In Fig. 5 the COA variation for gutted and ungutted hake stored in ice during winter-time can be seen. The data corresponds to experiment no. 10, gutted, and experiment no. 11, headed and gutted, and were represented over the straight line approximation for the ungutted hake. The statistical analysis shows, within a 95% confidence limit, that the tested samples were organoleptically almost equal in spite of the handling procedure. This characteristic was pointed out for the Chilean hake (*Merluccius gayi*) and for the Patagonian hake by Huss & Asenjo (1978).

In the same way there are no appreciable differences in the TBV values as is shown in Fig. 4.

It is neccesary to point out, however, that the headed and gutted hake fillets appeared more discoloured in the cutting zone than the gutted or ungutted fillets.

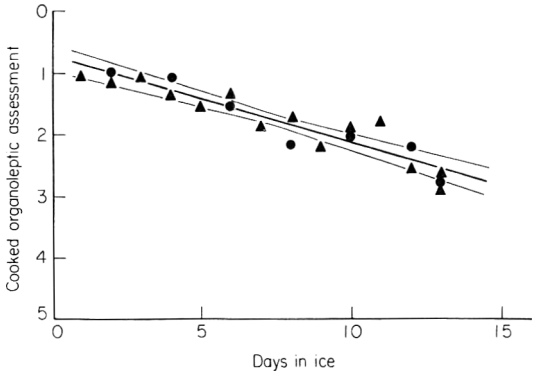

Figure 5. Cooked organoleptic assessment of: ●, ungutted winter hake stored in ice; ▲, gutted winter hake stored in ice and headed and gutted winter hake stored in ice.

Rigor mortis

Although it would be highly convenient to completely process fish on board, in a pre-*rigor* condition the shortness of this condition in hake (2 hr) together with the usually large catches and the limited capacity of the processing machines, make this task impossible to achieve in practice, except in the case of relatively small catches.

At the same time, due to the phenomenon known as 'thaw *rigor*', the failure to adopt correct thawing procedures has occasionally affected the quality of individually quick frozen fillets and, to a lesser degree, that of headed and gutted hake frozen in a pre *rigor* state, giving rise to complaints unrelated to the initial good quality of the stock.

Commercial and processing problems and the low yields of fillets obtained during the *rigor mortis* state make it desirable to delay processing until the *rigor* condition has disappeared.

On the other hand, in the case of trading fresh fish on land, the firmness of fish in *rigor* is taken as a sign of good quality. For processing, however, the same considerations made for on-board processing apply. Some of these problems have been mentioned already by Bramsnaes & Hanson (1965).

In Fig. 7 the *rigor mortis* development according to the penetrometer readings can be seen. The results are roughly in accordance with the findings in Fig 6 and after reaching the maximum level the values tend asymptotically to the *pre rigor* average level.

The penetrometer was also used during experiments 6 to 11 as a means of evaluating textural changes after the *rigor mortis* resolution, but no appreciable variation was recorded. Although no change was observed with the penetrometer reading, a progressive tendency of the fillets to split appeared with the increasing number of days in ice and this tendency showed itself more quickly and was more evident in summer than in winter.

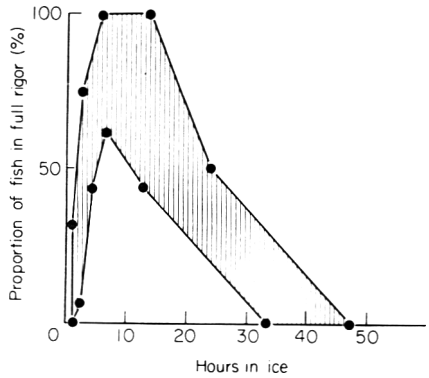

Figure 6. Percentage of ungutted winter hake stored in ice in full *rigor* at various times.

At the same time, with reference to texture, it should be said that during the course of these experiments, neither softening nor liquefaction (milkiness) of the flesh due to action of parasites (*Kudoa* spp. syn. *Chloromyxum* spp.) were observed in the fillets that contained them.

Similar observations were made by Chiodi (1966) after carrying out experiments for 2 years.

Further study is necessary to establish if any softening may be found in hake caught at a particular time of the year or in particular fishing areas.

Quality assessment by electronic means

During experiments 4 and 6 to 12 and during the *rigor mortis* experiments, measurements were made with the GR Torrymeter, always averaging sixteen hake.

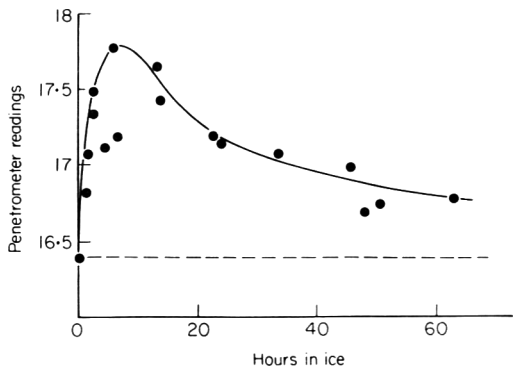

Figure 7. Penetrometer readings of ungutted winter hake stored in ice.

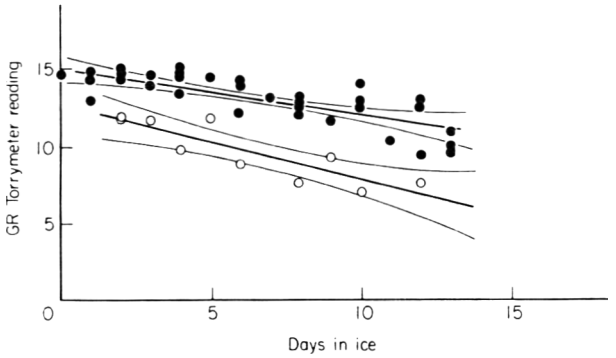

Figure 8. GR Torrymeter readings *vs* days in ice of: ●, ungutted winter hake stored in ice; ○, ungutted summer hake stored in ice.

In Fig. 8 we can see the Torrymeter reading variation for ungutted hake stored in ice during winter and summer.

The data were approximated by straight lines and the confidence limits for 95% probability were shown.

The mathematical expressions are:

Summer TM = 12.55 – 0.46 Time (days); $r = 0.85$
Winter TM = 14.94 – 0.29 Time (days); $r = 0.76$

The aggreement between the GR Torrymeter readings and the ROA in Fig. 9 and the COA in Fig. 10 can be seen. The results in both cases were approximated by means of straight lines and a confidence limit of 95% was used.

The mathematical expressions of the least squares regression straight lines are:

TM = 18.31 – 3.38 ROA
TM = 17.95 – 3.13 COA

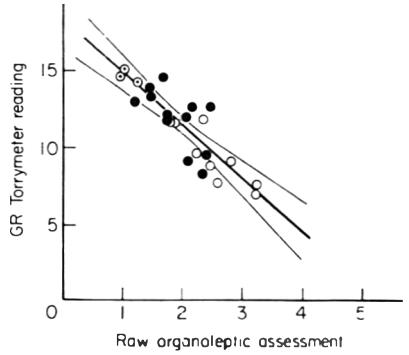

Figure 9. GR Torrymeter readings *vs* raw organoleptic assessment of : ●, ungutted winter hake stored in ice; ○, ungutted summer hake stored in ice; ⊙, ungutted winter hake stored in ice, in *rigor*.

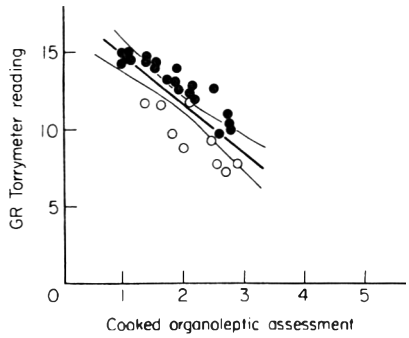

Figure 10. GR Torrymeter readings *vs* cooked organoleptic assessment of: ●, ungutted winter hake stored in ice; ○, ungutted summer hake stored in ice.

and the correlation coefficients were 0.86 and 0.78 respectively.

The straight lines are roughly equivalent, agreeing with the result obtained by Jason & Lees (1971), forced although different organoleptic assessment scales were used.

The scattering of results seems to be unavoidable in practice, not only because of the seasonal changes or the use of separate samples to make the correlation, but also because of the differences in organoleptic judgements of the assessors.

Discussion and conclusions

Many of the results obtained are in agreement with the existing knowledge of the characteristics of other species of white fish. As is generally accepted, the organoleptic assessment also appears to be the most appropriate way to judge Patagonian hake stored in ice. The TVB and pH values do not show changes during the first days of ice storage, but the TVB value appears to be useful in order to establish the limit of acceptability.

Nevertheless, the organoleptic assessments, as well as the TVB, Torrymeter and pH values, clearly show the seasonal influence.

On average, the Patagonian hake spoils faster in summer than in winter. From Figs 1, 2 and 3 it is possible to establish a keeping time of 9 to 10 days in summer and one of 14 to 15 days in winter.

The overall keeping time of ungutted hake in ice during winter time can be compared with that normally accepted for iced gutted cod, averaging 15 days, according to Waterman (1968) and Meyer, Antonacopoulos & Flechtenmacher (1969).

The slight effect of gutting on the keeping time of Patagonian hake, evident in Figs 4 and 5, was also pointed out by Huss & Asenjo (1978). The reason for this could be the high percentage of empty stomachs observed during the biological studies on Patagonian hake in winter (Angelescu & Cousseau, 1969).

On the other hand the keeping time in ice during summer is more in accordance with the figure of Burt (1974) for the Cape hake, the values of Huss & Asenjo (1978) for the Patagonian and the Chilean hakes, and the value given by Dassow & Beardsley (1974) for Pacific hake (*Merluccius productus*).

The large difference in averages between the Patagonian hake caught in winter and those caught in summer could be explained by one or more of the following reasons:

(a) The biological condition. During the summer a large proportion of hake is associated with an immediate post spawning condition. From a chemical point of view this means that the fat content in the flesh is at a minimum and the water content reaches its maximum (Chiodi, 1966).

Love (1960) has shown that the maximum seasonal water content is a good indicator as to when cod (*Gadus morhua*) is in its worst condition. When the water content is at its maximum, cod deteriorates more quickly. In the same way, the worst condition of Patagonian hake appears to be in the summer-time.

Additionally, as can be seen in Fig. 3, a final, rather low pH value appears, and this could also be associated with textural losses in fillets (Love, 1976).

(b) Water temperature. During winter time hake moves northward and concentrates in the area between 35° and 40° S at depths of 100 to 500 m. In summer time they concentrate in shallower waters, between 50 and 150 m, in the area south of 41° S (Boerema, 1978).

In winter-time the temperature of the water in which hake is caught is around 4–7°C (Angelescu & Cousseau, 1969), while in summer-time the temperature reaches 11°C or more if near the coast (Angelescu & Gneri, 1966).

A similar adverse effect of water temperature on the quality of Newfoundland cod was pointed out by Idler *et al.* (1965), the temperature values and differences being similar to those observed for Patagonian hake.

(c) The extent of feeding. It is possible to establish that there is a maximum level of empty stomachs during winter and a 'heavily-feeding' condition during summer (Cousseau, 1977).

The stomachs of heavily fed hake tends to burst easily, not only in the net, but also during the handling operations following catch.

The faecal contamination produced, along with the highly active enzyme systems spread on the fish, tend to make it deteriorate more quickly. As was pointed out by Castell (1971) this effect supplements the other adverse effects observed after spawning.

All these effects, alone or combined, are mainly of importance during summer, but it should be borne in mind that, ocassionally, they can affect winter catches. Regarding this, the short keeping time in ice found for Patagonian hake in winter by Huss (1971) could be explained on the basis of the advanced sexual maturity observed in the fish used in those experiments.

Sometimes the processors and buyers relate the short keeping time in summer to the rise of the ambient temperature. Although this is an over simplifica-

tion, it is necessary to keep in mind that a delay in icing will adversely affect the quality as was observed for Cape hake by Burt *et al.* (1974). Sometimes in commercial practice, the combination of inadequate handling and the worst environmental and/or physiological conditions can cause a catch to become completely spoiled before landing.

With reference to the comparative experiments of ice boxing *vs* CSW and gutted *vs* ungutted hake, it should be pointed out that the values are only indicative of the behaviour during winter. Nevertheless the results obtained are in accord with those of Huss & Asenjo (1977) for Chilean hake.

The behaviour of Patagonian hake during *rigor mortis* appears to correspond to the early findings of Messtorff (1954) and Cutting (1939) for white fish in the North Sea and North Atlantic.

The Torrymeter readings together with an organoleptic assessment appear to be useful. In spite of the scattered data they provide a means of helping to speedily assess quality in dubious situations such as when fish in poor physiological condition macroscopically appears sound.

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A modern dry-salting process for Wiltshire bacon

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Summary

Bacon made by a 5-day process using brine injection followed by dry-salting has been compared with that made by a longer conventional Wiltshire process. The eating quality and appearance of the two bacons were similar. The slightly poorer storage stability of dry-salted back in vacuum packs was attributed to a low salt concentration which could be corrected by increased brine injection in this region. Dry-salting slightly improved the storage stability of collar in vacuum packs because initial bacterial counts were lower than in the immersion-cured. Comparison of dry-salted bacons made with and without nitrate in the injection brine showed that nitrate did not affect nitrite level during vacuum-packed storage.

Introduction

Processing meat by rubbing salt into its surface is the oldest known form of curing and, until the 1930s, was the recognized way of making Wiltshire bacon in the U.K. Pig sides were covered completely with a mixture of dry salt and saltpetre (potassium nitrate) and cured slowly as bacteria reduced the nitrate to nitrite. This dry process was eventually replaced by an immersion process in which pig sides were injected by hand with an aqueous solution of salt and nitrate and submerged in large tanks of similar brine (also containing nitrite formed from nitrate), for 4 to 5 days before being drained and matured for 1 to 2 weeks. Nitrite is now added directly to curing brines and hand injection has been replaced almost entirely by multineedle injection with machines capable of distributing brines more efficiently throughout bacon sides. Consequently, curing times have been reduced to 7–10 days.

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In recent years the desire for even shorter curing times and greater control over levels of curing salts in bacon has renewed interest in dry-salting as a possible way of eliminating the wet immersion stage. All the nitrite and nitrate (if added) and most of the salt could be injected directly into the sides and the rest of the salt could be applied to the outside surfaces. Continuous machines which automatically coat sides with the required amount of salt are already being used in the U.K. and Denmark in conjunction with shorter immersion times. If dry-salting was used to eliminate the immersion stage, Wiltshire bacon manufacture could become a line process from which sides would go straight into maturation.

We have used a dry-salting process to make bacon and compared its quality and stability with bacon cured by a longer traditional Wiltshire immersion process. Since previous studies (Taylor & Shaw, 1975) showed that bacon could be immersion-cured with brines which contained no added nitrate, we also examined the effect of similar omission of nitrate from the injection brine used in a dry salting process.

Experimental

Two experiments were carried out: in comparison A, dry salted bacon was compared with bacon made by traditional Wiltshire immersion curing; in comparison B, dry salted bacons made with and without nitrate were compared.

Bacon manufacture

In each experiment bacon was made form seven Grade 'A' pigs taken from a normal factory production line. The compositions of the curing brines are shown in Table 1. In comparison A, both methods of curing were designed to produce bacon sides with back lean containing 4–5% salt, 60–100 ppm nitrite and 200–300 ppm nitrate. In comparison B, the dry-salting was designed to give similar concentrations of salt and nitrite and, where included, near maximum permitted level of nitrate in the bacon. In each comparison the left side of a pig received one treatment and the right the other.

All sides were injected by multineedle machine (Swissvac CUR-O-MAT) to a weight gain of approx. 10% on trimmed weight. Immersion-cured sides were then immersed for 3 days in freshly prepared brines and matured at 5°C for a further 7 days before sampling. Sides for dry-salting were taken immediately after injection and approx. 0.8 kg dry salt rubbed over their surfaces by hand. They were then hung by the Achilles tendon in a curing cellar at 5°C and 85% r.h. for 5 days before sampling.

Table 1. Composition of curing brines

Comparison	Treatment	*Injection brine*			*Immersion brine*		
		Salt (%w/v)	*$NaNO_2$* (ppm)	$NaNO_3$ (ppm)	Salt (%w/v)	$NaNO_2$ (ppm)	$NaNO_3$ (ppm)
A	Dry salted with nitrate	16	1500	1600	—	—	—
	Immersion cured with nitrate	16	700	900	26	1000	1600
B	Dry salted with nitrate	16	1500	4000	—	—	—
	Dry salted without nitrate	16	1500	—	—	—	—

Slicing, packing and storage

Portions of collar bacon were removed, sliced, packed and sampled as described by Taylor, Shaw & Jolley (1976). The packs were stored for up to 20 days at 5°C and 15 days at 15°C. Portions of mid-back from each side were sliced to give three packs of four slices per side. These provided samples initially, after 35 days at 5°C and after 19 days at 15°C.

Microbiological examination

In comparison A, all sides were examined at the end of the curing process. Five 10 cm^2 areas were swabbed (wet and dry), three from the rind and two from the inside surface (pleura) and swabs were bulked in 10 ml 0.1% peptone + 4% NaCl diluent to give a 50 cm^2 composite sample for each side. Duplicate drops (0.017 ml) of suitable decimal dilutions were transferred to the surface of plates of Plate Count Agar (PCA, Oxoid) + 4% NaCl by means of calibrated dropping pipettes (Astell Cat. No. 851 and 852). The drops were spread over a quarter of the plate area and the total viable count obtained after incubation for 5 days at 25°C.

The lean of vacuum-packed samples of collar bacon and the eye muscle of back bacon were examined using the methods described by Taylor *et al.* (1976).

Odour

When vacuum packs were opened the odour of the bacon was assessed by a panel of four experts who noted the presence of off-odours and judged whether these would cause the bacon to be accepted or rejected by a consumer.

Chemical analysis

Within 1 to 2 hr of opening the packs, chemical analysis commenced on samples taken from the minced bulk used for microbiological examination. One gram was homogenized with 10 ml distilled water and pH measured on a Radiometer PHM63 Digital pH Meter. Moisture content was determined and samples were extracted, deproteinized, and analysed for nitrate, nitrite and chloride as described previously (Taylor *et al.* 1976).

Organoleptic assessment

In comparison A, portions of back bacon were taken from two pairs of freshly cured sides and sliced to give forty slices from each. Twenty slices from each side were submitted to a ten-member taste panel and the remaining twenty were vacuum packed and held at −20°C for duplicate assessment 1–2 weeks later. In comparison B, similar assessments were made on three pairs of sides. Since immersion curing and dry-salting required different curing times, sides from different cures were assessed separately.

In both comparisons the raw slices were assessed for colour of fat and lean, and assessed for flavour of cooked fat and lean as described previously (Taylor & Shaw, 1975). The panel also assessed saltiness on a 9-point scale: 'extremely under salty' (−4) through 'ideal' (0) to 'extremely over salty' (+4).

Results

Chemical analysis

Table 2 shows pH values and concentrations of nitrite, nitrate and salt in collar and back bacon at the beginning of storage. Changes in the concentration of nitrite in collar bacon during storage at 5 and 15°C are shown in Fig. 1(a) for comparison A, and in Fig. 1(b) for comparison B.

In comparison A, concentration of nitrite fell faster in dry-salted collar bacon during storage than in immersion-cured. Although nitrite was initially higher in the dry-salted collar bacon, at the end of storage at both temperatures it was lower than in immersion-cured. The difference was more marked with back bacon: after 19 days at 15°C nitrite in dry-salted had dropped from 74 ppm to 10 ppm, but only from 106 ppm to 101 in immersion-cured; after 35 days at 5°C nitrite concentrations were 29 ppm in dry-salted and 129 ppm in immersion-cured. Nitrate was depleted more rapidly in immersion-cured bacon than in dry-salted. After 9 days storage at 5°C, 54% of the initial nitrate had disappeared from immersion-cured collar against only 19% from dry-salted; at 15°C, the corresponding figures were 64% against 35%.

In comparison B, where dry-salted bacons were compared, the inclusion of nitrate in the injection brine had no apparent effect on the pattern of nitrite

Table 2. Analysis of bacon at beginning of storage

Comparison	Treatment	Bacon	pH	$NaNO_2$ (ppm)	$NaNO_3$ (ppm)	NaCl (%w/v)	NaCl (% on water)
A	Dry salted with nitrate	Collar	6.32	125	184	4.9	7.9
		Back (lean)	5.90	74	155	3.4	4.7
	Immersion cured with nitrate	Collar	6.40	99	248	4.8	7.0
		Back (lean)	5.90	106	327	5.1	7.0
B	Dry salted nitrate	Collar	6.15	165	526	5.0	7.2
		Back (lean)	5.70	89	374	3.6	4.7
	Dry salted without nitrate	Collar	6.10	123	32	4.6	6.5
		Back (lean)	5.75	92	27	4.0	5.5

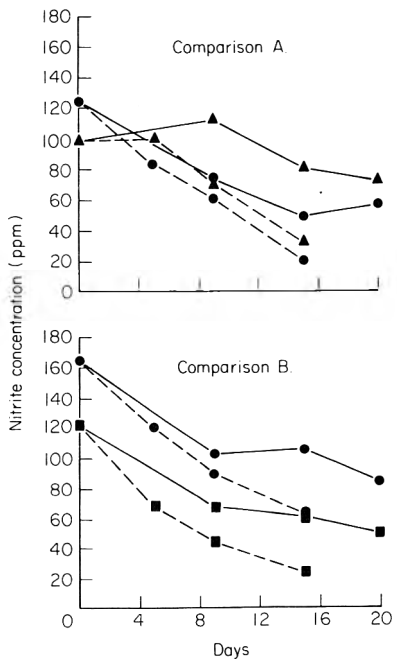

Figure 1. Changes during storage at 5 and 15°C in the concentration of nitrite in the lean of collar bacon. Comparison A: ●———●, dry-salted at 5°C and ●----●, 15°C; ▲———▲, immersion-cured at 5°C and ▲----▲, at 15°C. Comparison B: ●———●, dry-salted with nitrate at 5°C and ●----●, at 15°C; ■———■, dry-salted without nitrate at 5°C and ■----■, at 15°C.

Table 3. Bacterial numbers on the lean of bacon during storage at 5° and 15°C

Comparison	Bacon	Days stored	$\log_{10}$ viable count/g				$\log_{10}$ count of lactic acid bacteria/g			
			5°C		15°C		5°C		15°C	
			Cure 1	Cure 2	Cure 1	Cure 2	Cure 1	Cure 2	Cure 1	Cure 2
A. Dry salted with nitrate (cure 1) and immersion cured with nitrate (cure 2)	Collar	0	4.2	5.3	4.2	5.3	2.4	1.7	2.4	1.7
		5	—	—	5.4	6.7	—	—	4.3	5.7
		9	4.3	6.7	6.5	6.8	2.0	5.2	5.7	5.8
		15	5.3	6.9	7.3	7.0	4.5	5.6	6.5	6.2
		20	6.5	6.9	—	—	5.9	6.6	—	—
	Back	0	3.3	5.3	3.3	5.3	1.7	2.7	1.7	2.7
		19	—	—	7.7	5.8	—	—	6.7	5.5
		35	7.0	6.2	—	—	6.4	5.2	—	—
B. Dry salted with nitrate (cure 1) and dry salted without nitrate (cure 2)	Collar	0	5.5	6.2	5.5	6.2	2.0	1.7	2.0	1.7
		5	—	—	6.7	6.1	—	—	4.7	4.4
		9	5.2	6.1	6.6	6.6	1.9	2.6	5.8	5.1
		15	5.3	5.5	7.2	6.9	4.1	3.8	6.6	6.0
		20	5.6	5.8	—	—	5.2	5.4	—	—
	Back	0	5.5	5.0	5.5	5.0	1.7	1.7	1.7	1.7
		19	—	—	7.0	6.7	—	—	6.9	6.3
		35	6.3	5.1	—	—	6.1	5.0	—	—

disappearance in either collar or back. Bacon made with nitrate had a higher initial concentration of nitrite than that made without nitrate and the difference was maintained throughout storage at both temperatures.

Microbiology

In comparison A the total viable counts at the end of the curing process were significantly lower ($P<0.01$) on the dry-salted sides than on the immersion-cured. Counts on the dry-salted sides were in the range 4.1–4.5 $\log_{10}$no/cm^2) with a mean of 4.3, whereas the range was 4.7–6.3 with a mean of 5.4 on the immersion-cured sides.

Total viable counts and numbers of lactic acid bacteria on the bacon during vacuum-packed storage are shown in Table 3. On collar bacon these were usually lower with dry-salting. Dry-salted back bacon had lower initial counts but considerably higher counts than immersion-cured after prolonged storage. Curing dry-salted bacon without nitrate did not affect its microbiological condition during vacuum-packed storage.

Table 4. Numbers of packs rejected on basis of odour on opening after storage at 15°C. Seven packs from each cure were examined at each observation time.

Comparison	Treatment	Collar			Back
		5 days	9 days	15 days	19 days
A	Dry salted with nitrate	0	0	0	1
	Immersion cured with nitrate	0	1	2	0
B	Dry salted with nitrate	0	0	2	0
	Dry salted without nitrate	0	0	3	2

Odour

Table 4 shows the number of packs rejected at each sampling time. None were rejected in any of the bacon stored at 5°C. At 15°C, in comparison A no packs of dry-salted collar bacon were rejected and no off-odours were reported, whilst off-odours were generally more noticeable in the comparable immersion-cured bacon after 9 day's storage. Dry-salted back bacon at 15°C was marginally less stable then immersion cured back.

In comparison B, omitting nitrate from dry-salted bacon marginally increased the incidence of off-odours at the end of storage in both collar and back.

Organoleptic assessment

The mean taste panel scores for the experimental back bacons are shown in Table 5. Analysis of variance was performed separately on both comparisons.

Table 5. Raw colour, saltiness and cooked flavour acceptability scores in back bacon. Saltiness is scored on a 9-point scale ranging from 'extremely salty' (+4) through 'ideal' (0) to 'extremely under salty' (−4). All other scoring is on an 8-point scale ranging from 'like extremely' (+7) to 'dislike extremely' (−7). (Means ± standard deviations)

Comparison	Raw colour		Cooked flavour acceptability		
	Fat	Lean	Saltiness	Lean	Fat
A. Dry salted with nitrate	1.8(±2.4)	1.3(±3.1)	−0.6(±1.2)	1.2(±2.8)	1.5(±2.9)
Immersion cured with nitrate	2.1(±2.7)	0.6(±3.0)	−0.2(±1.0)	2.7(±2.3)	1.8(±1.9)
B. Dry salted with nitrate	2.5(±2.1)	2.1(±2.1)	0.1(±1.2)	2.6(±2.6)	3.1(±2.4)
Dry salted without nitrate	2.9(±1.9)	2.7(±1.8)	0.4(±1.4)	3.0(±1.8)	2.5(±2.2)

In comparison A, the dry-salted bacon was not scored as highly as the immersion-cured for flavour of lean, but the difference was not significant. In comparison B, inclusion of nitrate in the injection brine had no apparent effect on any of the quality characteristics.

Discussion

These experiments showed some differences between dry-salted bacon and bacon made by conventional immersion curing. The methods were designed to give uniform distribution of curing salts throughout sides, but in the dry-salted bacon their concentrations were lower in back than in collar. The immersion stage obviously contributes more to concentrations of curing salts in back bacon than in collar and a commercial dry salting process should compensate for this by injecting more brine along the back. Dry-salted sides also had lower total viable counts which was almost certainly due to the shorter curing time (5 days for dry-salting, 10 days for immersion) and this imparted a slightly better storage stability to the vacuum-packed collar bacon. This benefit was not obtained with vacuum-packed back bacon because it was outweighed by more rapid bacterial growth at the lower curing salt concentrations.

The most interesting observation was that the pattern of nitrite loss in dry-salted bacon was quite different from that in immersion-cured. Nitrite fell steadily in the dry-salted collar and back whether or not nitrate was present, whereas, in immersion-cured, nitrate was depleted to maintain the level of nitrite, especially during the initial period of storage. Jolley (1979) has demonstrated the importance of the bacterial flora on immersion-cured sides to the conversion of nitrate to nitrite in vacuum packs, and the difference in patterns of nitrite loss may be the result of fewer nitrate reducing bacteria developing on dry-salted bacon during curing. There was no evidence from this study that loss of nitrite during storage is likely to cause spoilage problems in dry-salted collar bacon, and Taylor & Shaw (1975) have shown that it has no effect on the stability of back bacon of normal pH. Although off-odours were a little more common in bacon made without nitrate (comparison B) there was no corresponding difference in bacterial counts and we can see no strong reason for including nitrate in curing brines used in a dry-salting process.

The differences discussed are no obstacle to the use of dry-salting. These experiments show that bacon which is similar in appearance and eating quality to that produced by an immersion process can be produced in less time, and larger scale factory trials have shown that yields are also similar. Dry-salting offers obvious commercial advantages. Immersion tanks and brines are not required in new factories, and the space they occupy in existing factories can be used to extend maturation areas and increase production. Putting sides into immersion and withdrawing them for maturation is labour intensive and introduces factors such as brine/bacon ratio and tightness of packing which affect the

uptake of curing salts, leading to variability in the product. Reduction in the permissible levels of curing salts in bacon has placed a greater emphasis on precise and uniform distribution of brine and the immersion process inevitably produces gradients in the concentration of curing salts so that excessively high levels of nitrite can occur in the outer layers of bacon sides (Patterson *et al.*, 1976). Dry-salting in conjunction with efficient brine injection can more readily control the levels of curing salts added to bacon and give a more consistent product.

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Changes in the free -NH_2, free -CO_2H and titratable acidity of meat proteins

P. B. MADOVI

Summary

The 2, 4, 6-trinitrobenzene sulphonic acid (TNBS) spectrophotometric assay and formol titration were used to measure changes in free -NH_2 and free -CO_2H respectively, in meat proteins dissolved in 3% sodium dodecyl sulphate (SDS). Changes in the titratable acidity of the meats was also determined. The free -NH_2 groups were found to decrease markedly with cooking while -CO_2H remained relatively constant. Intermediate moisture beef (*Longissimus dorsi*) processed and stored at 38°C showed the free groups increasing for up to 8 weeks' storage due to proteolysis, followed later by a sharp fall due to cross-linking. But titratable acidity of the IM beef samples continued to rise with storage.

Introduction

During processing or storage of meat and meat products physico-chemical changes occur. These changes affect the level and balance of free amino groups, free carboxylic groups and other reactive sites of the proteins. Hamm & Detherage (1960) found that free carboxylic groups in the meat decreased as the temperature was raised to 70°C. This they claim, was due to the concomitant loss in the water-holding capacity of the meat. However, at higher temperatures Maillard type browning reactions usually occur due to sugar-protein interactions. Under such conditions a fall in the amount of free amino groups (Hodge, 1953) in the meat and lysine availability (Bender, 1966, 1972) would result. The non-enzymic browning (NEB) reactions would also cause the acidity of the proteins to increase (Gould & Frantz, 1945; Grimbleby, 1954).

To monitor such losses in free -NH_2 detrimental to protein quality, the TNBS

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reagent introduced by Satake *et al.* (1960) may be applied (Mokrash, 1967). This reagent couples with the free α-amino groups at pH 8 to give products with a high extinction coefficient at 340 nm in a spectrophotometric assay.

For α-carboxylic groups and titratable acidity (TA) determination, the formol titration was used. Kass & Palmer (1942) used this technique to detect changes in free $-CO_2H$ in heated milk proteins. Gould & Frantz (1945) and Grimbleby (1954) used it to determine changes in titratable acidity of heated milk proteins. It is a rapid technique based on the fast reactions of formaldehyde with amino groups leaving behind the acid groups free to be titrated.

In the present studies modifications of the TNBS and the formol titration assays were used in an attempt to, simultaneously, measure the changes in free $-NH_2$, and free $-CO_2H$ and TA respectively in meats and meat products during cooking, processing and storage.

Materials and methods

Preparation of samples

Ground or minced meat samples were dispersed in 3% SDS (1 g% w/v), homogenized and allowed to soak for 30 min. They were placed on a boiling water bath for a further 30 min. Finally, they were centrifuged whilst still hot at 5,000 ***g*** for 30 min. The resultant supernatant was decanted and used in the analyses.

Leucine standard solutions were prepared and used to prepare standard calibration curves. This was carried out only once using a 1.5 m*M* solution for the TNBS assay and 4.0 m*M* solution for the formol titration.

Reagents

(a) TNBS assay. pH 8.2 phosphate buffer: prepared by adding 43 ml of 3.32% (w/v) solution of $NaH_2PO_4 . 2H_2O$ to one litre of a 3.78% (w/v) solution of $Na_2HPO_4 . 2H_2O$.

TNBS solution: prepared to 0.10% (w/v) by dissolving 100 mg TNBS from a grade equivalent to Sigma Chemical Co. Ltd. No. 5878 in 100 ml distilled water in a volumetric flask, covered with aluminium foil to exclude all light. This solution was prepared daily and kept at 4°C until used.

A 0.1 N hydrochloric acid solution and 3% w/v SDS solution were also prepared in the usual way.

(b) Formol titration. 0.02 N NaOH: prepared from a stock solution of 0.1 N sodium hydroxide made from a commercial ampoule. The distilled water used must be boiled for at least 20 min. and the fresh solution must be standardized against a fresh solution of 0.02 N potassium hydrogen phthalate.

Formaldehyde: prepared by adjusting a 37–40% w/v formalin solution A.R. to pH 9 with 0.1 N sodium hydroxide solution. This solution was freshly prepared each time when required.

(a) TNBS assay.

Instrumentation

For the TNBS assay an ordinary u.v. spectrophotometer was used. The formol titration was carried out using a Radiometer Automatic Titrator type TTT 60 coupled to an autoburette ABU 12, a pH meter PHM 62, titration assembly TTA 3 and a servograph REC 61 with Titrigraph module REA 160 (Radiometer, Copenhagen, Denmark). The autoburette contained the 0.02 N sodium hydroxide solution used and the titration assembly the glass electrode.

Method

(a) TNBS method

This involved two assays; amino nitrogen assay and Micro-Kjeldahl assay for nitrogen estimation.

Duplicate aliquots (0.25 ml) of a test and leucine standard solutions was added to test tubes containing 2.0 ml of pH 8.2 phosphate buffer. A blank of 0.25 ml 3% SDS was also prepared. TNBS solution (2 ml) was added to each tube, the contents mixed and the tubes incubated in a covered water bath (to exclude all light) at 50°C for 60 min. After incubation the reaction was stopped by the addition of 0.1 N HC1 (4.0 ml) solution to each tube. The tubes were then allowed to cool for 30 min. The absorbance of the solutions was finally read at 340 nm against the blank. Since the free ($-NH_2$) was linearly related to the colour intensity of the TNBS reaction (Adler-Nissen, 1978) a leucine standard calibration curve was used in the calculations. Nitrogen estimation was carried out using the Micro-Kjeldahl technique for both the meat solutions and the entire meat samples.

(b) Formol titration

The titration technique involved two stages; titratable acidity and formol titration. Duplicate samples (20 ml) were pipetted into the titration vessel of the Radiometer automatic titrator and titrated with 0.02 N sodium hydroxide solution to a pre-selected end point of pH 9.0 ± 0.01. The amount of sodium hydroxide solution required to reach this pH was the titratable acidity of the sample.

To the 20 ml of sample treated as above to pH 9.0 ± 0.01 4 ml of formal-

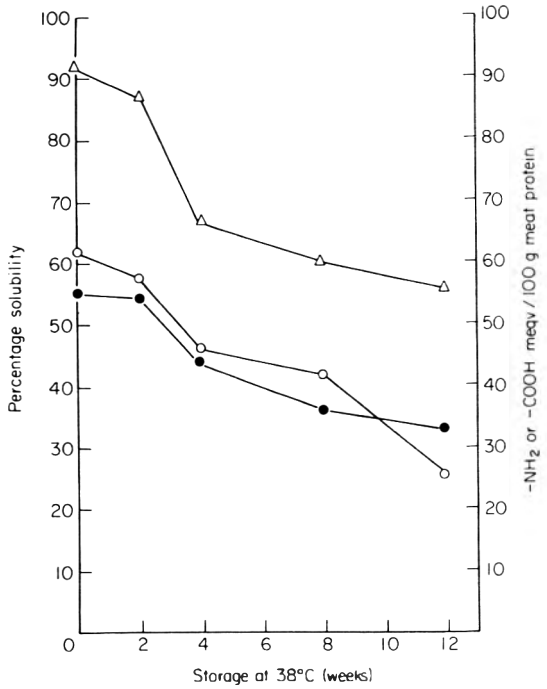

Figure 1. Solubility of meat protein nitrogen in 3% SDS (△———△), changes in free amino (●———●) and free carboxylic groups (○———○) (uncorrected for decrease in total soluble nitrogen) during storage of IM beef at 38°C. Solubility defined as (soluble N × 100)/total N.

dehyde (37–40% w/v) adjusted also to the final pH (pH 9.0) were added and allowed to mix. This gives a final formaldehyde concentration to within the range 6–9% w/v as recommended by Levy (1934). The resultant acidity (i.e. formed on adding formaldehyde) was then titrated back to pH 9.0±0.01 (the end point) to give the formol titre. The latter was used in the leucine standard calibration curve to determine free ($-CO_2H$).

Results and observations

Solubility in 3% SDS

Sodium dodecyl sulphate (SDS) in combination with β-mercaptoethanol, is known to dissolve relatively insoluble proteins such as those in IM meats. But in the present studies SDS seemed to dissolve these meats quite well without the β-mercaptoethanol which could not be incorporated in the solvent since it interferred in the formol titration assay.

The decreasing trend in the IM beef percentage solubility with storage was similar to that observed for the loss in free $-NH_2$ and free $-CO_2H$ uncorrected for soluble nitrogen (Fig. 1). Generally, fresh muscle tissue seemed to be more soluble than cooked or processed (Table 1).

Table 1. Solubility, titratable acidity, free amino and free carboxylic groups of meats* and meat products

Sample		Percentage solubility† in 3% SDS	TA‡ (ml 0.02N NaOH)	Free -NH_2 (meqv/100mg soluble N)	Free -CO_2H (meqv/100mg soluble N)
Beef (*L. dorsi*)	Raw	92.5	1.02	24.63	13.21
	Cooked§	85.5	1.22	12.59	13.35
Pork (*L. dorsi*)	Raw	92.5	1.42	30.13	13.64
	Cooked	84.0	1.32	18.57	13.98
Chicken (breast)	Raw	99.4	2.19	21.14	13.93
	Cooked	98.2	1.41	17.61	13.99
Bovine liver	Raw	89.9	1.18	19.38	19.56
	Cooked	99.1	1.22	18.99	15.13
Cod (fish)	Raw	100.7	0.51	17.38	15.03
	Cooked	100.3	0.37	7.79	15.26
Intermediate moisture beef		91.6	1.24	14.05	12.39
Corned beef (Argentinian)		62.0	0.76	19.71	11.07
Ham		54.3	0.89	27.43	15.36
Luncheon meat		75.7	0.53	18.86	6.07
Tesco fresh beef/pork sausage		95.0	0.60	5.92	1.02
Bovine lung		32.8	0.77	32.65	21.17
Bovine tripe		46.7	0.13	13.14	6.43

* Meat defined here as animal tissue fit for use as food.
† Solubility defined as soluble N/Total N × 100.
‡ Titratable acidity for 20ml sample solution (1% w/v) in 3% SDS.
§ Cooked meat defined as raw meat left in boiling water for 30 min.

Free amino group estimation

Although raw meats generally showed the highest levels of free amino groups these fell quite markedly on cooking the meat (Table 1). IM beef *(L. dorsi)* and meat broth stored at 38°C showed the free groups, as a percentage of total soluble nitrogen, to increase to a maximum at 8 weeks' storage followed by a marked decrease (Fig. 2). The increase was possibly due to proteolysis and the fall to cross-linking.

Free carboxylic group estimation

The free carboxylic groups of the meats, as a percentage of total soluble nitrogen, remained relatively constant when the meat was cooked. Processed meats on the other hand showed low levels of free carboxylic groups (Table 1).

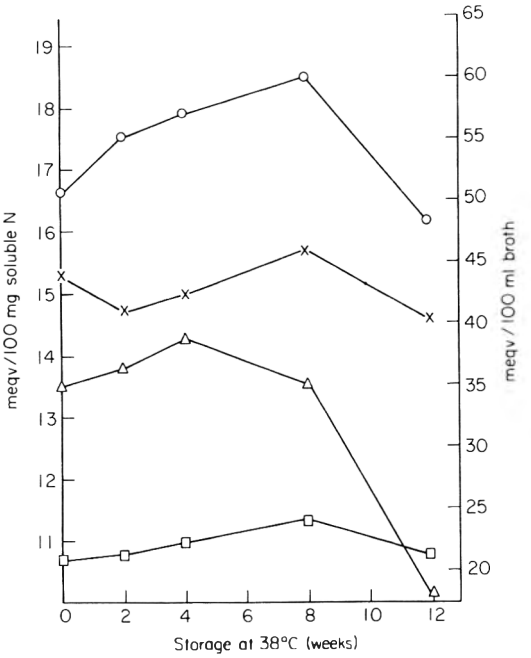

Figure 2. Changes in free amino groups and free carboxylic groups in IM beef and broth during storage at 38°C. o——o Meat broth free $-NH_2$; ×——× IM beef free $-NH_2$; △——△ IM beef free $-CO_2H$; □——□ Meat broth free $-CO_2H$.

IM beef samples showed an increase in free carboxylic groups in the first 4 weeks followed by a fall (Fig. 2). The same trend was observed for the meat broth but in this case the decrease came after 8 weeks' storage.

Titratable acidity

The results obtained show that the acidity was generally low in processed meats (Table 1) but in IM beef and broth samples it increased with storage time (Fig. 3) at 38°C. The rate of increase in acidity was greater after four weeks storage. On the whole, changes were larger initially for the meat broth samples but this pattern was reversed after 8 weeks (Fig. 3).

Discussion

The meats and meat products studied generally showed a greater level of free amino groups than free carboxylic groups (Table 1 and Fig. 2). This perhaps, is because the TNBS reaction essentially estimates free α-NH_2 and ε-NH_2 of lysine (Adler-Nissen, 1978) while the formol titration measures only free α -CO_2H. The latter groups seemed to be fairly stable to cooking while free -NH_2 suffered considerable destruction (Table 1).

Hamm & Detherage (1960) found that the amount of acidic groups in meat

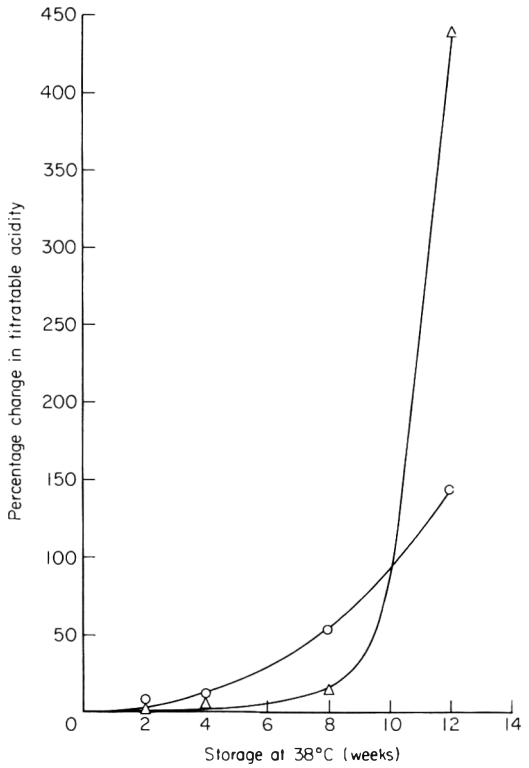

Figure 3. Changes in IM beef (○———○) and broth (△———△) titratable acidity during storage at 38°C.

proteins fell as the temperature was raised to 70°C. These workers attributed this fall to the concomitant moisture loss that occured. Our findings however, dispute this point since cooked meats (Table 1) showed no significant loss in free carboxylic groups. Instead, there was a considerable fall in the level of free amino groups of the meats on cooking. This possibly, was due to aldose-protein or similar interactions with the free amino groups.

For the IM beef and meat broth samples stored at 38°C, the changes observed seemed to agree with the findings of Obanu, Ledward & Lawrie (1975a,b) and Obanu (1976a,b). These workers observed that there were two contrasting reactions in stored IM beef; proteolysis and cross-linking; causing product quality loss (e.g. colour and solubility, Fig. 1). From Fig. 2 it is evident that proteolysis is dominant in the first 8 weeks' storage causing the increase in free amino and free carboxylic groups observed. After this period cross-linking almost certainly predominates over proteolysis leading to a fall in the level of the free groups (Fig. 2) and a rapid increase in titratable acidity (Fig. 3).

Elimination of free amino groups in such reactions causes the increase in titratable acidity (Gould & Frantz, 1945; Grimbleby, 1954) observed in some cooked meats (Table 1) and in browned IM products (Fig. 3). Cooked pork with a high content of free amino groups (Table 1) and reducing sugars (Lawrie,

1979; Sharp, 1957; 1958) than cooked beef was found to suffer more from NEB. This difference in susceptibility to browning between pork and beef perhaps shows the importance of NEB reactions in the destruction of free -NH_2 in meat proteins. Mechanisms responsible for loss of free amino groups through Maillard and similar reactions have been reviewed (Hodge, 1953; Burton & McWeeney, 1963; Reynolds, 1963; Hurst, 1972).

Determination of the level of free amino groups, free carboxylic groups and titratable acidity in meats and meat products is important because these factors may influence the colour, texture, tenderness, flavour and nutritional quality of the products during processing or storage. Their importance in this regard, was underlined by the changes observed for IM beef when browning started after 8 weeks' storage (Fig. 2), and, merits further investigation.

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Rheological properties of spinning dopes and spun fibres produced from plasma – alginate mixtures

A. P. IMESON, J. R. MITCHELL AND D. A. LEDWARD

Summary

The tensile and shear strengths of fibres produced by extruding dopes of 2.0% sodium alginate and 6.0% blood plasma into a coagulating bath of calcium chloride (5% w/v) at pH 4.0, varied according to the guluronic acid block content and molecular weight (viscosity) of the alginates. The shear resistance of the fibres was not dependent on guluronic acid block content or alginate viscosity. However, when calculated per gram of dry matter, fibres containing alginates of high guluronic acid block contents had significantly greater resistance to shear than fibres spun from alginates of low guluronic acid block content although there was still no significant dependence on alginate viscosity or degree of polymerization.

The tensile strength of fibres produced from high guluronic acid block alginates was not related to the viscosity of the sample. However, in fibres containing low guluronic acid block contents the strength increased as the degree of polymerization increased. These relationships were equally valid whether calculated on a wet or dry basis. In addition there was an inverse correlation between percentage elongation at maximum tensile stress and the viscosity of the spinning dopes.

Possible explanations for these observations are discussed.

Introduction

Products which imitate meat in appearance, texture and flavour may be prepared by extruding concentrated alkaline protein extracts into acid salt coagulating baths (Boyer, 1954). Recently it has been shown that the inclusion of sodium alginate into a solution of blood plasma produces a dope which has a stable viscosity suitable for spinning. Thus the need for prior concentration of

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the protein or subsequent treatment with alkali is unnecessary (Imeson, Ledward & Mitchell, 1979). Also, addition of charged polysaccharides, such as carrageenan and carboxylmethyl cellulose, to protein dopes enables the mixtures to be spun more easily (Huang & Rha, 1977).

Fibrous or crispy meat analogues may be spun from alginate-protein mixtures by adjusting the amount of air in the spinning dope and by stretching the fibres in the coagulating bath (Université Laval, 1977). Furthermore fibres with different shear strengths and protein contents are obtained from mixtures extruded into coagulating baths containing different concentrations of acetic acid and/or calcium chloride (Imeson *et al.*, 1979).

This study was made using different alginates in the spinning dope and hence extend further the range of fibre characteristics that may be obtained.

Different species of alginate contain varying proportions of poly (α-L-guluronic acid), poly(β-D-mannuronic acid) and segments where the two sugars alternate. The solution and gelation properties of alginate in the presence of divalent ions depend on the polymer composition (Smidsrod & Haug, 1972). The homopolymeric guluronic acid regions (G blocks) are mainly involved in the interaction between calcium ions and alginate (Grant *et al.*, 1973). Consequently high G block calcium alginate gels tend to be hard and brittle, whereas low G block gels tend to be weak and elastic (Penman & Sanderson, 1972).

In this work the rheological behaviour of solutions of blood plasma and sodium alginate was investigated. The types of alginate appropriate for preparing spinning dopes of suitable handling properties were identified from samples of low, medium and high viscosity alginates containing high or low G blocks.

In addition fibres were spun from these protein-polysaccharide mixtures to determine the effects of alginate viscosity and G block content on the shear and tensile properties of fibre bundles.

Materials and methods

Alginates

The characteristics of seven samples of sodium alginate kindly supplied by Alginate Industries Ltd. are shown in Table 1.

Solution viscosities were determined for mixtures of sodium alginate (1%) and Calgon (0.25%) in distilled water at 25°C using a Deer rheometer fitted with a 4° cone and plate assembly at a shear rate of 49 sec^{-1}. Moisture was determined by heating to constant weight at 105°C.

Blood plasma

Pigs' blood was obtained immediately post-slaughter at a local abattoir and, to prevent coagulation, was mixed with 10% v/v sodium citrate solution (10% w/v). The plasma was separated by centrifugation at 2500 ***g*** for 15 min. It had a

Table 1. Properties of tested alginates

Sample	Moisture content (%)	Deer viscosity (centipoise) (Shear rate 49 sec^{-1}, 25°C)	Approximate guluronic acid* block content (%)
A	11.3	58	60
B	10.2	100	55
C	11.1	158	60
D	12.5	49	30
E	13.0	106	25
F	12.9	313	25
G	14.6	108	25

*Supplied by Alginate Industries Ltd.

pH of 7.2 and protein and ash contents of 6.32% and 1.10% respectively. Calcium content of the ash was 1.2%. The plasma was blast frozen and stored at −20°C until required.

Preparation of spinning dope

The thawed plasma was diluted with a small volume of water to give a 6.0% protein solution. Sodium alginate was dissolved in the plasma giving a protein to polysaccharide ratio of 3 to 1. The solutions were de-aerated by centrifugation at 1000 *g* for 5 min. The dope had a pH in the range 6.5–6.9 for solutions containing high G block alginates and pH values of 7.4–7.5 for dopes containing low G block alginates.

Rheological characteristics of the spinning dopes

Flow curves of each of the spinning dopes were measured with a Deer Rheometer using a concentric cylinder at 25°C. Shear rate was measured both for increasing applied shear stress and for decreasing shear stress.

Fibre spinning

Tows were prepared by extruding the dope through a spinneret (40 holes, 8×10^{-5} m diam. each) at an extrusion rate of 0.19 m min^{-1} and a take-up rate of 7.2 m min^{-1} into a coagulating bath of calcium chloride (5% w/v) adjusted to pH 4.0 with acetic acid. This pH was chosen as it is the value at which blood plasma and sodium alginate precipitate as a protein-polysaccharide complex (Imeson *et al.*, 1978) and is approximately midway between the pK values of polyguluronic and polymannuronic acids (4.2 and 3.7) and thus, if differences are to be seen between the fibres they should be apparent at this pH. Constant extrusion and

take-up rates were maintained during spinning. The coagulating bath was kept at pH 4.0 by small additions of acetic acid.

Fibre bundles extruded in exactly 2 min were used for tensile measurements. Tows extruded in exactly 12 min were used for measurement of shear strength.

Shear strength and tensile strength of tow

Shear strength values were obtained by the Instron Food Testing Instrument (Table Model 1140) fitted with a Warner-Bratzler blade using a crosshead speed of 50 mm min^{-1}. Mean values were obtained from eight measurements taken from each tow.

Variations in dope viscosity resulted in different tow sizes being produced in the time intervals and previous work has shown that shear resistance varies with the dimensions of the sample (Pool & Klose, 1969). Results from plasma-alginate tows indicate that the shear strength is proportional to the area raised to a power of 0.59 (or diameter to the power 1.18) (Imeson, unpublished results) which closely agress with a previous value obtained from cooked turkey samples (Poole & Klose, 1969). Since the tows had a constant length of 170 mm their cross-sectional areas could be calculated from their tow weights. Thus a comparison of shear strengths per unit of tow area was made after dividing the shear reading by the tow area to the power 0.59.

Tensile measurements were made with an Instron fitted with serrated jaws using a crosshead speed of 100 mm min^{-1}. In the few cases in which the sample slipped or broke at the jaws, the readings were discarded. Tensile strength readings were divided by the tow weight to allow for differences in tow area.

Moisture content was determined by heating the samples to constant weight at 105°C.

Results

All of the spinning dopes could be handled very easily, especially those prepared from medium viscosity alginates.

No significant differences were observed between the shear rate values obtained on the spinning dopes for both increasing and decreasing applied shear stress. Figure 1 shows the pseudoplastic flow curves for each of the dopes. Samples containing high viscosity alginate showed the greatest changes in apparent viscosity as the shear rate increased, but changes were also found in the low viscosity samples. For example, the apparent viscosity of mixture F rapidly decreased from 135 to 34 P as the shear rate increased from 3 to 100 sec^{-1}, whereas, over the same range of shear rates, mixture D decreased from 12.6 to 7.5 P.

Shear resistance measurements for the spun fibres are shown in Table 2. There is no significant difference in shear force values obtained for tows containing low or high alginate of different viscosities. Nevertheless, when the

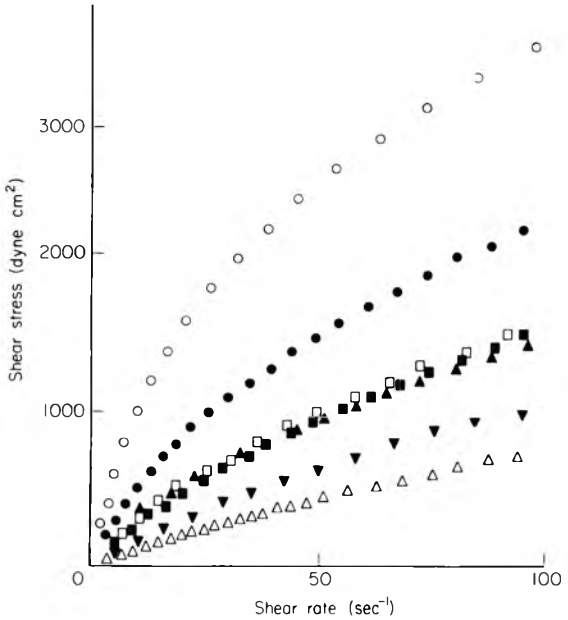

Figure 1. Flow curves of the spinning dopes measured with a Deer Rheometer of concentric cylinder geometry at 25°C. The protein-polysaccharide ratio in the dopes was 3:1 and the data refers to polysaccharide sample A(▼), B(□), C(●), D(△), E(▲), F(○), G(■), of Table 1 respectively.

data is expressed per gram of dry matter, variation between samples is apparent. Calculations show that fibres produced using high G block alginate are significantly different ($P<0.001$) from those spun from mixtures containing low G block alginate. However, there is no significant difference in shear strength when the alginate viscosity or degree of polymerization is increased.

The tensile strength of the fibre bundles produced from high G block alginates did not appear to be related to the viscosity of the sample (Table 2). However, in the fibres containing small amounts of G block the strength increased as the degree of polymerization increased. In addition, there is an inverse correlation between percent elongation at maximum tensile stress and the viscosity of the spinning dope ($r = -0.93$; $P<0.01$).

The data also shows that the high G fibres are able to retain more moisture than the low G fibres.

Discussion

It is readily apparent from the results shown in Table 2 that fibres of vastly different rheological properties can be generated by spinning proteins with alginates of differing guluronic acid contents into 5% calcium chloride baths. It has previously been shown that variations in calcium content and pH of the coagulating bath will lead to the formation of fibres of differing rheological

Table 2. Rheological properties of the spinning dopes and spun fibres prepared from plasma-alginate mixtures

Sample	Dope viscosity (Poise : shear rate 49 dec^{-1})	Fibre moisture content (%)	Shear strength*		Tensile strength†		Percentage elongation at max. tensile load‡
			$N.cm^{-2}$	$N.cm^{-2}$ dry matter	$N.cm^{-2}$	$N.cm^{-2}$ dry matter	
A	12.5	92.5	42.3±4.0	566±54	28.3±3.3	380±44	106±15
B	20.1	92.5	50.2±2.3	668±31	30.2±3.3	404±44	89±9
C	29.9	92.1	49.2±4.3	620±54	30.8±2.7	390±34	75±13
D	8.5	88.3	41.1±4.6	350±59	32.7±2.8	279±23	111±10
E	18.6	88.6	42.6±6.0	374±53	45.1±3.2	397±28	110±10
F	49.2	85.9	51.2±5.2	363±37	62.7±6.0	444±43	55±5
G	19.0	89.2	38.3±6.0	355±56	38.7±7.8	358±72	111±11

*values are mean ± standard deviation of 8 measurements from each of 2 tows
†values are mean ± standard deviation of 4 measurements from each of 6 tows
‡percentage elongation = $\frac{\text{(length at maximum force-original length)} \times 100}{\text{original length}}$

properties (Imeson, Mitchell & Ledward, 1979). Thus these alginate-protein mixtures do appear to have potential for generating a range of textured food products including meat analogues.

Voisey (1976) has analysed the stresses involved in the Warner-Bratzler test for meat and concluded that the fibres are subjected primarily to a tensile stress in the direction of the fibre axis. If this is the case then a correlation between the tensile and shear force measurements would be expected, as indeed has been reported for meat (Bouton & Harris, 1972). For our data there is no significant correlation between the tensile and shear force measurements irrespective of whether these are compared on the dry matter or wet weight basis. This suggests that in our case the tensile and shear strength measurements involve different types of stresses. Since only tensile stresses can occur in the tensile strength measurements it would appear that for the shear test using the Warner-Bratzler procedure, shear stresses are to some extent involved in the mechanical failure of these fibres.

We have previously suggested that calcium alginate protein fibres at pH 4 consist of a calcium alginate gel with protein trapped within the matrix of the gel but not interacting with the polysaccharide to any great extent (Imeson *et al.*, 1979). If this is the case then the properties of the fibres should resemble those of a calcium alginate gel. The lower moisture content of the fibres obtained from the low guluronic alginates support this view since Smidsrod & Haug (1972) found that the reduction in volume of an alginate solution on gel formation by dialysis against excess $CaCl_2$ was maximal for an alginate with a mannuronic acid content of 30%, i.e. the alginate concentration in the gel would be greatest for an alginate of this concentration.

Both the rheological test methods employed measure the force required to rupture the fibres. Although the rheological properties of alginate gels have been quite extensively studied most investigations have been concerned with their behaviour at small deformations prior to rupture (Smidsrod & Haug, 1972; Segeren *et al.*, 1974; Mitchell & Blanshard, 1976) and only a limited amount of work has been carried out on the rupture strength of the gels (McDowell, 1975; Mitchell, 1979). The conclusions from the latter studies were that at high calcium concentrations the rupture strength of the gel increased with increasing guluronic acid content and molecular weight of the alginate. The shear values show the expected increase in strength with guluronic acid content but no such difference is apparent in the tensile measurements.

It would be expected that the shear and tensile strengths and also probably the percentage elongation would increase with dope or alginate viscosity i.e. with the molecular weight. Only in the case of the tensile strength of the low guluronic acid alginates is there evidence for an increase in strength with molecular weight and there is a negative rather than a positive correlation between percentage elongation and viscosity. This casts some doubt on the idea that these fibres are essentially homogeneous, isotropic alginate gels. There are a number of factors that might be responsible for these rather unexpected results.

These include: (a) the presence of the protein, (b) the non-isotropic nature of the fibres and (c) the level of calcium.

On the limited data available it is not possible to be definitive as to which (if any) of these factors are important. In our previous investigation we showed that the shear strength of the fibres was independent of calcium concentration in the bath at levels greater than 3.0%. Although the calcium requirement may depend to some extent on the guluronic acid content of the alginate and its molecular weight it seems unlikely that the 5.0% bath was insufficiently concentrated to satisfy the requirements of all the alginate samples employed.

A more probable explanation is that the degree of orientation of the alginate chains in the fibres will depend on the viscosity of the alginate. The orientation will be greater for the low molecular weight alginates because the intermolecular entanglements preventing the natural flow orientation of the polymer will be much less than in the high molecular weight samples. Fibres containing polymers orientated parallel to the axis of the fibre will be stronger in tension than fibres containing randomly orientated polymers. This effect may nullify the molecular weight dependencies observed for an isotropic gel. In addition it seems plausible that orientation will permit a longer elongation prior to break.

The pH of the coagulating bath (4.0) is close to the pH at which the interaction between blood plasma and sodium alginate, as evidenced by precipitation of protein with alginate, is maximal (Imeson *et al.*, 1978). It does therefore seem possible that the texture of the fibre may be influenced by the presence of protein. The interaction between the protein and alginate is primarily electrostatic in nature and since the pK values of polymannuronic acid and polyguluronic acid are 3.7 and 4.2 respectively (Haug, 1961) the charge on the two different alginate types at pH 4.0 and hence the extent to which they interact with the protein will be different. This could also be a contributory factor influencing the texture of these fibres and may partly explain the variation between the properties of the fibres formed with high and low guluronic acid alginates at pH 4.0.

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Desorption characteristics of hot-soaked parboiled paddy

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Summary

The desorption of water from a thin layer of hot-soaked parboiled paddy grains was studied under constant drying conditions within a temperature range 40–70°C and at a constant relative humidity of 60%. The data of one variety of paddy were correlated with the help of the semi-empirical diffusion equation which was confirmed with the soaking data of a large number of paddy varieties by the authors. The results indicated that activation energy of the diffusional process (7654 cal/mole for moisture absorption and 7600 cal/mole for the desorption process) is independent of the direction of changes in the moisture level.

Introduction

The authors have shown in earlier studies (Bandyopadhyay & Roy, 1976, 1978) that absorption of water by paddy grains during parboiling at elevated temperatures in a batch soaking operation can be described by a semi-empirical diffusion equation. The validity of the equation was proved under some limiting conditions with the soaking data of a large number of paddy varieties (Bandyopadhyay & Roy, 1978). It was felt that investigations should be further carried out to obtain data on moisture in soaked paddy grains under opposite conditions (grains fully exposed to air at a constant temperature and humidity) and to elucidate the process of drying of parboiled paddy. The authors believed that the same diffusion equation might be applicable in case of desorption process also and for this reason an experimental programme was designed with the object of collecting data on moisture desorption from hot-soaked parboiled paddy grain and correlating the different variables of the process. Such correla-

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tion might be useful in the design and evaluation of commercial drying equipment for simple hot-soaked parboiled paddy.

The semi-empirical diffusion equation tested by the authors (Bandyopadhyay & Roy, 1976) is

$$\bar{x} - x_0 = (2/\sqrt{\pi})(x_s - x_0)\ (S/V)\ \sqrt{[D_0 \exp(-E/RT)\theta]} \quad (1)$$

or

$$\bar{x} - x_0 = k_m \sqrt{\theta} \quad (2)$$

where

x_0 = initial, uniform moisture content (g/g dry basis)
$\bar{x}$ = average moisture content for a given aborption period (g/g dry basis),
x_s = effective moisture content at the bounding surface at times greater than zero (g/g dry basis),
S = exposed surface area of a solid (paddy grain) (cm^2),
V = volume of a solid (paddy grain) (cm^3),
D_0 = diffusion constant (in Arrhenius equation) (cm^2/sec),
E = activation energy (cal/mole),
T = absolute temperature (°K),
R = gas constant (cal/mole °K)
θ = absorption time (sec),

and

$$k_m = (2\sqrt{\pi})(x_s - x_0)\ (S/V)\ \sqrt{[D_0 \exp(-E/RT)]}\ \delta$$

or

$$k_m = K \sqrt{[\exp(-E/RT)]} \quad (3)$$

where

$$K = (2/\sqrt{\pi})(x_s - x_0)\ (S/V)\ \sqrt{D_0}$$

In case of desorption of water, the terms $(\bar{x} - x_0)$ and $(x_s - x_0)$ will change to $(x_0 - \bar{x})$ and $(x_0 - x_s)$ respectively.

Materials and methods

For preliminary work, one particular variety of paddy, (e.g. Jaya) was selected from the varieties studied earlier and soaked according to the method already described (Bandyopadhyay & Roy, 1976). The time and temperature of soaking for the variety were 7 hr and 65°C and moisture content of the soaked grains was around 0.5 g/g dry basis. These conditions were found to be the optimum for obtaining a considerable 'degree of parboiling' by the hot-soaking method (Bandyopadhyay & Roy, 1977). The study on desorption was made with a layer of hot-soaked parboiled paddy of one grain depth at a constant temperature and

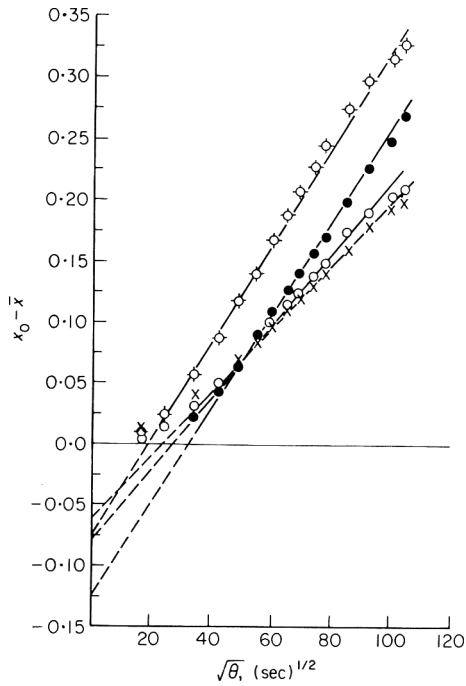

Figure 1. Linear relationship between the residual moisture in the grain and the square root of the desorption period for Jaya variety. ×, 40°C; ○, 50°C; ●; 60°C; ⊹ 70°C.

humidity in a conventional thermogravimetric set-up. The air of desired humidity was obtained by bubbling air through distilled water at a particular temperature in order to saturate it at that temperature and thereafter heating it electrically, to the desired temperature for drying. The air was then allowed to flow through the drying chamber at a velocity sufficient to create an approximately uniform condition for drying in the chamber. The drying temperature was varied from 40 to 70°C and time of desorption was varied for up to 2 hr. The relative humidity was kept constant at 60%.

Results and discussion

The residual moisture in the grains during desorption was calculated from the moisture content of the soaked grains and the instantaneous moisture remained in the grains and plotted against the square root of the time of desorption. The plot of the variety Jaya, presented in Fig. 1, shows the linearity similar to that given by the results of the absorption study (Bandyopadhyay & Roy, 1976). It suggests that the diffusion equation (2) is applicable in the case of moisture desorption also. The initial data up to 20 min or so were not included for analysis on the assumption that there was a time lag for the grains to attain the

Table 1. Slopes and intercepts of linear regression lines

Temperature (°)	$k_m \times 10^3$ g/g (sec)$^{\frac{1}{2}}$	Δx_i g/g
40	2.594	−0.06
50	2.896	−0.076
60	3.895	−0.1276
70	4.003	−0.077

Paddy variety = Jaya.
Initial moisture content of raw paddy = 0.149 g/g dry basis.
Average moisture content of soaked paddy = 0.508 g/g dry basis.

temperature of the drying chamber just after introduction. On extrapolation the lines do not converge to zero value of $x_0 - \bar{x}$ at zero time but leave intercepts whose values become negative, unlike those obtained from the result of absorption study. This disparity is not clear from the experimental results. The slopes k_m and intercepts $-\Delta x_i$ were calculated statistically, and presented in Table 1.

To find if an Arrhenius type relationship exists, according to eqn (3), $\log k_m$ was plotted against the reciprocal of the absolute temperture (Fig. 2). Two features were noted: Firstly, the Arrhenius line, instead of showing a break as observed in the result of absorption study (Bandyopadhyay & Roy, 1976, 1978) showed linearity for the whole temperature range, and secondly, the value of activation energy, 7600 cal/mole, is almost identical with that obtained in the lower temperture region of soaking for the Jaya variety – 7654 cal/mole (Bandyopadhyay & Roy, 1976). The result evidently indicates that the activation energy of the diffusional process – both absorption and desorption of

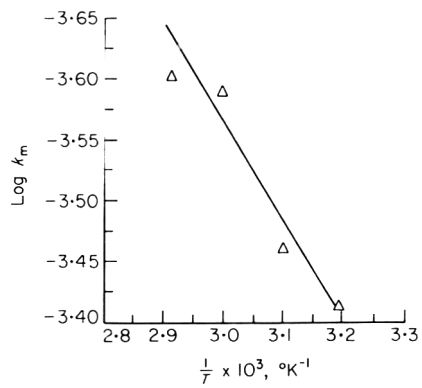

Figure 2. Log k_m as a function of reciprocal of the absolute temperature for Jaya variety.

moisture within the grain – is independent of the direction of migration of moisture. Similar phenomena were observed by Becker on soaking and drying of one particular variety of wheat (Becker, 1959, 1960). The present investigation further confirms the hypothesis propounded by the authors (Bandyopadhyay & Roy, 1976, 1978) that at temperatures below gelatinization temperature of rice starch, simple diffusion of water is predominent during soaking of paddy grains. The sharp change in the value of activation energy due to gelatinization process did not occur during diffusive transport of moisture under constant drying conditions.

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The determination of fluorine in coffee and tea using a microprocessor coupled with a fluoride ion-selective electrode

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Summary

The fluoride content of tea and coffee as normally brewed, and after Schöniger oxygen flask combustion, has been determined with a fluoride ion-selective electrode coupled to a microprocessor analyser in two of its operational modes. Up to forty samples per hour can be assayed in the CONCN mode and the results compare favourably with the known addition (KA) back-up mode.

Introduction

The fluorine content of various plants is important in relation to caries prevention studies (Tamacus, Ramsay & Hardwich, 1974) and the toxicity associated with environmental pollution of sugar cane (Louw & Richards, 1972) and forage (Lovelace, Miller & Welkie, 1968) crops near aluminium smelter and phosphate manufacturing plants. The actual fluorine content of plants rarely exceeds 10 ppm dry weight but certain plants, notably ornamental camellias (Venkateswarlu, Armstrong & Singer, 1965) and teas (Zimmerman, Hitchcock & Gwirtsman, 1957) are natural accumulators of fluorine and may contain 790–3060 and 72–300 ppm dry weight of fluorine respectively. *D. toxicarium* also concentrates the element from a low fluoride soil environment (1–6 ppm) unlike eight other families of plants growing in the same vicinity (Vickery and Vickery, 1972).

This paper describes the application of a fluoride ion-selective electrode coupled with a microprocessor analyser for the rapid assay of fluorine in five brands of teas and three coffees.

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Materials and methods

Preparation of tea and coffee samples

Each tea sample (~5 g) was placed in a teapot (~700 cm^3 capacity), boiling, deionised water was added to the brim and the whole stirred for 20 sec. After the requisite infusion (brewing) period of 2, 3 or 5 min, the contents were rapidly strained into a large beaker, cooled and made up to 1 dm^3. Five separate aliquots (25 cm^3) were mixed 1:1 (v/v) with TISAB (Total Ionic Strength Adjustment Buffer) for the analyses.

Tea bags were weighed and similarly infused and finally the paper only dried and weighed after discarding the tea leaves. The instant coffee sample (~4 g) was stirred into boiled water (~500 cm^3), cooled and made up to 1 dm^3. Again five separate aliquots were diluted 1:1 (v/v) with TISAB prior to fluoride analysis.

Schöniger oxygen flask combustion

This remarkably simple technique for the decomposition of many organic substances involves their combustion on a platinum gauze with oxygen in a sealed container (Schöniger, 1955). The reaction products are absorbed in an appropriate solution before the reaction vessel is opened for analysis of the contents.

Six samples of each brand of coffee or tea (~25 mg) were combusted in a closed flask pre-flushed with oxygen and containing TISAB (50 cm^3). The contents were periodically shaken for 30 min and finally diluted 1:1 (v/v) with deionised water.

Standardization and measurement procedures

Standard fluoride solutions were made from AR stock 10^{-1}M potassium fluoride by serial dilution with deionised water and treated (1:1 v/v) with TISAB comprising sodium chloride (1M), acetic acid (0.25M), sodium acetate (0.75M) and decomplexing sodium citrate agent (10^{-3}M).

An Orion fluoride ion-selective electrode model 94–07 was used for all emf measurements at 25°±0.1°C with an Orion Ionalyser/901 meter (Moody & Thomas, 1979a). The Orion 90–20–00 double junction reference electrode contained ammonium nitrate (4M) in the outer chamber.

The programs of the microprocessor based Orion Ionalyser/901 meter are based on a set of input data, that is, emf, a standard concentration and a slope (S) and are stored in read-only memory. The parameters required to solve the associated equations are fed to the microprocessor by three push-buttons and three thumb-wheel switches and the results read directly from the LED display (Moody & Thomas, 1979a). The instrument was used in two of its eleven modes using the same type of sample (Tables 1 and 2).

Table 1. Typical procedure for fluoride assay in the CONCN MODE of the Orion Ionalyser/901 meter

Operation	LED display	Comments
(A.) Place electrodes in standard 5×10^{-3}M F^-/TISAB Set STD VALUE to 100.000 Set MODE to CONCN Set SLOPE to −55.70 Push CLEAR/READ MV button	−26.4	Value is electrode potential in absolute mV of the standard fluoride
(B.) Push SET CONCN button	100.	Potential of −26.4 mV of standard 5mM F^- is stored in memory and meter is now ready for repeated sample measurements (See C) The 100. LED value relates to the F^-/TISAB standard and the SET CONCN button represents the standard value exactly as entered in A
(C.) Remove electrodes, wash with deionised water, blot and immerse in the tea/ TISAB analate (25 cm^3)	.225	LED relates to sample by eqn (2). i.e. $\frac{.225 \times 5 \times 10^{-3}}{100.000} = 1.125 \times 10^{-5}$M
(D.) Push CLEAR/READ MV button		116.0 This value would classically be related to [sample] using an emf *vs* [F^-] calibration which in this connection is about 10^{-5}M F^- Normally, of course, operation D is omitted but is shown here as a check on the microprocessor value.

Table 2. Typical procedure for fluoride assay in KA/10 Mode of the Orion Ionalyser/901 meter

Operation	LED display	Comments
(A.) Place electrodes in stirred analate from Table 1. (V_0 = 25 cm³).		This potential = E_1.
		The sample $[F^-] \sim 10^{-5}$M is deduced from the CONCN mode and, of course, from the calibration plot to find S. Thus KA/10 mode chosen requires a fluoride/TISAB spike of $10 \times C_0$, i.e. $C_s = 10^{-4}$ M and V_s must be $V_0/10$, i.e., 2.5 cm³.
Set STD VALUE to 1.000		
Set MODE to KA/10		
Set SLOPE to −55.70		
Push CLEAR/READ MV button	116.0	
		The STD VALUE relates to the standard spike, i.e., 10^{-4}M.
(B.) Push SET CONCN button	1.00	E_1 now stored and number set on STD VALUE is displayed. Microprocessor then attempts a calculation but until the spiking is actually made (see C) the calculated values are quite erratic as shown
	1.42	
	1.65	
	1.65	
	−3.74	
	.	
	.	
	.	
	.	
	.	
(C.) Spike with 8.9×10^{-5}M F^-/TISAB (2.5 cm³)	.961	Some of the many calculated values displayed during spiking stage. The reading is updated every 0.5s and rapidly stabilised (~10s) after spiking terminates. The final LED desplay relates to sample by
	.718	
	.	
	.	
	.	
	.	
	.	
	.	
	.128	$C_0 = \frac{0.128 \times 8.9 \times 10^{-5}}{1.000}$ $= 1.14 \times 10^{-5}$M
(D.) Push CLEAR/READ MV button	104.4	This is E_2 and AE = 11.6 mV. Substituting in eqn (3) gives $C_0 = 1.14 \times 10^{-5}$M. This calculation is really unecessary but again offers a check on the microprocessor value.

Use of the microprocessor-based meter considerably simplified concentration determinations which are otherwise often determined from calibration plots of emf *vs* log concentration of standards or by the known addition technique which involves the tedious use of an exponential equation.

Standard calibration (CONCN) mode

The program for direct determinations is based on:

$$E_1 = \text{Constant} - S \log[\text{F}] \quad (1)$$

where E_1 is the emf solicited by the non-spiked solution of unknown concentration C_0 and S the slope factor, 2.303RT/F, determined daily from electrode calibrations with a series of fluoride/TISAB standards. This slope factor which was pre-set by thumb-nail switches remained remarkably stable (± 0.2 mV decade^{-1} or better) during any one day.

The fluoride-reference electrode pair was first immersed in a magnetically stirred standard fluoride/TISAB (5×10^{-3}M) and the operational sequences listed in Table 1 followed for any analate (see C). The performance of the electrochemical cell was periodically checked with the 5×10^{-3}M standard using the CLEAR/READ MV button.

Sample concentrations relate to the LED (Light-emitting diode) display by:

$$[\text{Fluoride Analate}] = \frac{(\text{LED display}) \times [\text{Standard fluoride}]}{\text{STD VALUE}} \quad (2)$$

where LED display is the number calculated on the basis of the particular program chosen; standard fluoride is the concentration (units in ppm, meq or mol dm^{-3}) of the standard (here 5×10^{-3}M) and STD VALUE is the preselected number (for convenience chosen as 100.000, for example). Both the standard fluoride and STD VALUE numbers are fed (like the MODE) to the 901 meter by simple thumbwheel action before any analysis run.

Known addition (KA) mode

This spiking technique is based on only two emf measurements using the actual sample from the CONCN run, the first value, E_1, being for a known volume (V_0) but unknown concentration (C_0). After spiking with a more concentrated fluoride standard (C_s), of volume, V_s, the final emf, E_2, is recorded, when:

$$C_0 = \frac{C_s}{10^{(E_2 - E_1)/S}\left(1 + \frac{V_0}{V_s}\right) - \frac{V_0}{V_s}} \quad (3)$$

The 901 microprocesser preprogrammed with eqn (3) corrects for the volume change and again the fluoride, C_0, is easily found from eqn (2) (Table 2).

Results and discussion

The Schöniger oxygen flask technique (Schöniger, 1955) probably offers the most efficient preliminary treatment developed for fluorine assays of vegetable matter to date (Levaggi, Oyung & Feldstein, 1971). A complete assay is feasible within 30 min compared with at least 4 hr for a sodium hydroxide fusion (Baker, 1972) and about 2 hr for a sodium hydroxide-zinc oxide fusion (Louw & Richards, 1972). Moreover, the quantity of sample, reagents and especially general laboratory ware is drastically reduced. Accordingly, the technique has been employed in this work for total fluorine.

The analysis for total fluorine and inorganic fluoride ions in teas and instant coffees using two operational modes of the Orion microprocesser model 901 is shown in Table 3. Evidently, tea is much richer in fluoride than coffee; cocoa is also relatively poor in this element (Kakabadse *et al.*, 1971).

Most dry teas contain 10 to 300 ppm fluoride on the basis of various infusion techniques but the fluoride found in the young and older leaves of the same camellia plant varies widely (Zimmerman *et al.*, 1957). Singer (1967) demonstrated that the extracted fluoride in their infusions was probably ionic rather than bound. The fluoride electrode only responds to free, that is, ionic fluoride, but the infusion values (Table 3) need not reflect the total ion, F^-, species owing to the presence of aluminium and iron in teas and the use of TISAB for analysis.

However, monofluoroacetate, fluorocitrate, ω-fluorooleate and ω-fluoropalmitate (Vickery & Vickery, 1972; Lovelace *et al.*, 1968; Ward, Hall & Peters, 1964) have been detected in plants and at concentrations depending on specific plant organs. Vickery & Vickery (1972) detected monofluoroacetate in the leaves of *D. toxicarium* whereas Ward *et al.*, (1964) detected neither organofluorine nor inorganic fluorine in the same tissue of that plant. Organofluorine is also concluded to be absent from tea (Zimmerman *et al.*, 1957; Peters & Shorthouse, 1964; Kakabadse *et al.*, 1971) which conflicts with the results of Schöniger flask combustions (Table 3) and the assay of tea leaves, which rose about threefold after ashing at 800°C (Stuart, 1970). However, Peters & Shorthouse (1972) subsequently detected fluorocitrate in commercial tea using the more sensitive GLC (gas liquid chromatography) technique.

The main purpose of this work was to assess the utility of the microprocessor for the rapid potentiometric assay of fluoride present in beverages as commonly brewed. However, some further runs were conducted by repeated second, third, fourth and fifth infusions with 700 cm^3 of boiling deionised water each for 2 min on the tea leaves strained from the primary 2 min infusion with the Glengettie tea product (Table 3). The extra fluoride extracted (using the CONCN mode) was 19.8% of the total after these two further infusions compared with 14.4% after just the one infusion (Table 3). Corresponding values using a TISAB with 0.25 M citrate were 21.9 and 16.7% respectively. No sensible fluoride could be detected in the fourth or fifth infusate using either TISAB reagent.

Only 12–16% of the total fluoride in the five brands of teas, and even less in

Table 3. Mean fluoride contents (ppm) of beverages determined by infusion and Schöniger flask combustion techniques

Beverage	Total fluoride (Schöniger)		Time (min)	Soluble inorganic fluoride (infusion)			
	CONCN MODE	KA/10 MODE		CONCN MODE		KA/10 MODE	
P.G. Tips Tea	1179	1239	2	194.3	(2.1)	196.0	(1.7)
			3	196.8	(0.9)	197.9	(1.0)
	(187.8)*	(226.8)	5	195.3	(1.4)	199.5	(3.5)
P.G. Tips	1143	1236	2	175.6	(4.3)	180.8	(4.9)
	(186)	(176)	3	173.9	(5.9)	176.4	(6.2)
(teabags)			5	183.3	(11.2)	186.3	(11.8)
Glengettie tea			2	217.8	(3.0)	221.2	(3.0)
	1499	1519	3	245.8	(19.4)	247.1	(20.2)
	(186.2)	(187.4)	5	207.4	(2.8)	212.5	(1.6)
Darjeeling and China			2	141.1	(4.2)	142.5	(3.5)
tea	1144	1176	3	159.4	(1.1)	163.3	(1.3)
	(115.6)	(102.8)	5	175.5	(2.6)	178.9	(3.9)
Lapsang Souchong tea			2	138.5	(4.1)	141.1	(5.0)
	1096	1121	3	142.4	(9.4)	145.5	(9.6)
	(90.2)	(95.7)	5	140.0	(5.2)	144.6	(5.4)
Co-op instant coffee	309.3	310.7	—	39.9		39.8	
	(34.1)	(35.3)		(1.7)		(2.1)	
Maxwell House coffee	273.1	278.0	—	30.5		30.5	
	(12.4)	(13.1)		(7.2)		(7.2)	
Nescafé coffee	317.2	319.3	—	31.8		32.5	
	(37.8)	(35.2)		(4.1)		(3.9)	

*Standard deviations in parenthesis

the coffees, is detected potentiometrically in the one-off infusates. Any soluble organofluorine compounds extracted by infusion will of course remain undetected but realistic levels of the toxic monofluoroacetate and fluorocitrate compounds can be discounted. The absence of organic fluorine in a tea containing 150 ppm fluorine prompted Peters & Shorthouse (1964) to comment 'this is of course consistent with the fact that many persons drink large amounts of tea daily without harm'. This statement is still valid despite the detection of about 30 ppm of fluorocitrate in tea by GLC and Peters & Shorthouse (1972) concluded that 'an average person drinking eight cups of tea daily would only be taking 3.4 $\mu g\ kg^{-1}$ which is far from a toxic dose taken orally'. Further investigations are being made to identify this non-infusion fluoride fraction in teas and coffees.

Table 3 lists the fluoride extracted from teas and coffees as a function of time. Singer, Armstrong & Vatassery (1967) found the maximum fluoride to be extracted from Lipton tea bags after 6 min of brewing. Duckworth & Duckworth (1978) found fluoride to be rapidly released into the infusion, a plateau being reached for most tea brands in 4 to 8 min. Ulvestad (1973) measured the extraction of fluoride from twenty-one different brands of tea after 1, 2 and 3 min infusion periods, and except in four instances, the quantities increased during these times. A similar trend is evident in the present work, the inorganic fluorine values for brewed teas corresponding to $\sim$ 1–2 ppm (Table 3).

It is interesting that fluoride levels in other tea brews also range from 1–2 ppm (Ulvestad, 1973; Zimmerman *et al.*, 1957) which is essentially that recommended for fluoridation of potable water supplies. Fluoride in beverages, especially tea, provides an important source of dental plaque fluoride (Tamacus, *et al.*, 1974) and the ability of plaque to take up and store fluoride would then be beneficial and may maintain an almost continuous availability of fluoride ions (Levine, 1976). Dietary fluorine provided by camellia or tea leaves was cariostatic in the case of Wistar rats, and Gershon-Cohen & McLendon (1957) posed the question 'why are healthy (human) teeth not more prevalent in tea drinking countries?'. The fluoride complexation reactions in tea, e.g. $\beta_1\ AlF^{2+} = 10^{6\cdot13}$, could be a contributory factor since aluminium and iron in one commercial tea averaged 2 mg g^{-1} and 2.8 mg g^{-1} respectively (Vickery & Vickery, 1976). Such complexes would not seriously interfere with the potentiometric assay (Tables 1 and 2) owing to the decomplexation function of TISAB. However, the fluorocomplexes which exist in the tea as actually consumed would detract from the cariostatic benefit normally conferred by the 'free' fluoride ion provided by, say, sodium fluoride mouth rinses (Moody & Thomas, 1979b).

The microprocessor ionalyzer/901 meter greatly facilitates the use of ion-selective electrodes (Moody & Thomas, 1979a), the CONCN mode being particularly useful and forty samples per hour can be easily processed. Results with the back-up KA mode are comparable but of course involve an extra time consuming spiking stage.

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Technical note: On the equivalence of isotherm equations

R. BOQUET,*‡ J. CHIRIFE† AND H. A. IGLESIAS†

Introduction

The mathematical description of the water sorption isotherms of foods has been the subject of various studies in recent years (Chirife & Iglesias, 1978; Boquet, Chirife & Iglesias, 1978, 1979).

Recently, van den Berg & Bruin (1978) presented an excellent review on the theoretical aspects of a_w estimation in food systems. As part of that study, the authors went through the literature and found more than seventy-five isotherm equations which were grouped according to their origin. Van den Berg & Bruin (1978) and Chirife & Iglesias (1978) noted that, upon rearrangement, some isotherm equations were found to be identical for fitting purposes.

It is the purpose of the present work to report on the mathematical equivalence found between 'apparently' different isotherm equations. As far as we know most of these reported equivalences have not been noted in the literature. This analysis was performed on the basis of the useful list of more than seventy-five equations compiled by van den Berg & Bruin (1978).

Results and discussion

The following notation will be used throughout this work:

$a_w = p/p_0$ = water activity
M = equilibrium moisture content, dry basis
M' = equilibrium moisture content, wet (total) basis
T = temperature
M_m = monolayer moisture content, dry basis

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All equations analyzed were explicitly written in one of two forms, $M = f(\underset{\sim}{K}, a_w)$ or $a_w = g(M, \underset{\sim}{K})$, where $\underset{\sim}{K}$ is a parameter vector. Only equations with $\underset{\sim}{K}$ components less than 4 were considered in this study

(1) *Equivalence of Hailwood & Horrobin (1946), Anderson (1946), Anderson & Hall (1948), Anderson (1946, variant) and Gascoyne & Pethig (1977) equations*

Hailwood & Horrobin's (1946) equation may be written

$$\frac{1}{M} = \frac{\alpha}{a_w} + \beta + \gamma a_w \tag{1}$$

The other equations may be rearranged as follows:
Andersen (1946),

$$\frac{1}{M} = \frac{1}{CKM_m}\frac{1}{a_w} + \frac{(C-2)}{CM_m} + \frac{K(1-C)}{CM_m}a_w \tag{2}$$

Anderson & Hall (1948),

$$\frac{1}{M} = \frac{1}{CM_m}\frac{1}{a_w} + \frac{(C-2A)}{CM_m} + \frac{A^2 - AC}{CM_m}a_w \tag{3}$$

Anderson (1946, variant),

$$\frac{1}{M} = \frac{1}{CM_m}\frac{1}{a_w} + \frac{C-A-1}{CM_m} + \frac{A(1-C)}{CM_m}a_w \tag{4}$$

Gascoyne & Pethig (1977),

$$\frac{1}{M} = \frac{1}{CKM_m}\frac{1}{a_w} + \frac{(C-2K)}{CKM_m} + \frac{K(K-C)}{CKM_m}a_w \tag{5}$$

(2) *Equivalence of Bradley (1936), Hoover & Mellon (1950), Chung & Pfost (1967) and simplified Chen's (Chen & Clayton, 1971) equations*

Bradley's (1936) equation may be written

$$\ln a_w = AB^M \tag{6}$$

The other equations may be rearranged as follows:
Hoover & Mellon (1950),

$$\ln a_w = \frac{1}{K}\left(\frac{1}{e^{-M_m}}\right)M \tag{7}$$

The equivalence of Chen's simplified equation (Chen & Clayton, 1971) and Chung & Pfost (1967) with Bradley's (1936) one, had been already shown by Chirife and Iglesias (1978).

(3) *Equivalence of Smith's (1946), Peirce's (1929) and Peirce's with correction term (1929), equations*

Smith's (1946) equation may be written

$$M = \alpha + \beta \ln (1 - a_w) \tag{8}$$

Peirce's (1929) and Peirce's with correction term (1929) may be rearranged and written as follows:

$$M = M_m - \frac{1}{K} \ln (1 - a_w) \tag{9}$$

$$M = \frac{1}{K_2} \left[\ln (1 - K_1 M_m) + K_2 M_m \right] - \frac{1}{K_2} \ln (1 - a_w) \tag{10}$$

(4) *Equivalence of Chen's (1971) and De Boer & Zwikker (1929) equations*

Chen's (1971) may be written,

$$\ln a_w = \alpha + \beta \exp (\gamma M) \tag{11}$$

De Boer & Zwikker's (1929) equation may be rearranged as

$$\ln a_w = \ln K_3 + K_2 \exp \left\{ \frac{\ln K_1}{M_m} M \right\} \tag{12}$$

(5) *Equivalence of Dole's (1948), Tester (1946) and De Boer's (1953) equations*

Tester's (1946) equation may be written

$$M = \frac{K a_w}{1 - a_w} \tag{15}$$

Dole's (1948),

$$M = \frac{K a_w}{1 - a_w} \tag{16}$$

and De Boer's (1953),

$$M = M_m \frac{a_w}{1 - a_w} \tag{17}$$

(6) *Equivalence of McGavack Jr & Patrick's (1920) and Freundlich's (1926) equations*

McGavack Jr & Patrick's (1920) equation is,

$$M = \delta^{1/n} K (a_w)^{1/n} \tag{19}$$

Freundlich (1926) is,

$$M = C\, a_w^{1/n} \tag{20}$$

(7) *Equivalence of White & Erying's (1947) and Fuggasi & Ostapchenco (1959) equations*

White & Eyring (1947) equations may be written as,

$$M = \frac{1}{\frac{1}{M_m} - \frac{K}{M_m} a_w}$$

Fuggassi & Ostapchenco's (1959) may be rearranged as

$$M = \frac{1}{\frac{K_3}{K_1} + \frac{K_2}{K_1} - \frac{K_2}{K} a_w}$$

The different parameters originally proposed in some of the various equations may have had different meanings providing physico-chemical information on the sorption process on the assumption of a proposed model. However, for fitting purposes the equations are identical and knowledge of a parameter vector $\underset{\sim}{K}_l$ in a l − form unambiguously determines the parameter vector $\underset{\sim}{K}_i$ in any other i − form.

Acknowledgments

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Technical note: Quality retention of unblanched frozen vegetables by vacuum packing.

II. Asparagus, parsley and celery

E. STEINBUCH

It has been known for a long time that vegetables for freezing have to be blanched sufficiently, in order to obtain an acceptable shelf-life by the proper inactivation of deteriorative enzymes. Several workers have shown that there is a relation between the level of peroxidase and other enzymes and deterioration during storage (Baardseth, 1978). It has been suggested earlier, that the quality of unblanched frozen vegetables might depend on the activity of oxygen-depending enzymes (Aylward & Haisman, 1969), and consequently the elimination of oxygen by vacuum packing might be advantageous. The system of vacuum packing can prolong the shelf life of unblanched frozen mushroom from 2 weeks to 3 months (Steinbuch, 1979). This can be considered as an evidence of the importance of oxygen in frozen plant tissues. However, the evacuation of packages as an alternative for frozen spinach indicate rather negative results (Birnbaum *et al.*, 1979), possibly due to other enzyme systems being operative.

In continuation to the work on mushrooms, experiments have been carried out with the vacuum packing of some unblanched vegetables. In Table 1 the results are summarized, in regard to the observed shelf-life of normally packed or vacuum-packed unblanched asparagus, parsley and celery.

The data of the Table indicate the favourable effect of vacuum packaging on quality retention of unblanched vegetables, resulting in a longer shelf life, depending on the product concerned. Enzymes in the peel of asparagus probably effect the quality retention of the unblanched frozen product. Vacuum-packing of both peeled and un-peeled asparagus can slightly inhibit the development of off-flavours.

The unblanched leaves of parsley appear to possess better frozen storage properties than those of celery. Vacuum packing can contribute to a prolonged maintenance of the original flavour of the leaves of these herbs. Both flavour and colour of sliced celeriac is preserved by vacuum packing for 1 month.

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Table 1. The effect of vacuum packing on the shelf-life of unblanched frozen vegetables

Pretreatment	Asparagus		Parsley	Celery leaves	Celeriac tuber
	Peeled	Non-peeled			
Normally packed	3 months	1 week	2 weeks	1 week	< 1 week
Vacuum-packed	4 months	2 weeks	3 months	1 month	1 month

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J. Fd Technol. (1980) **15**, 353–355

Technical note: The effect of heat shocks on quality retention of green beans during frozen storage

E. STEINBUCH

In continuation to the experiments on vacuum packing of unblanched vegetables for freezing, attention has been paid to the technological possibilities of this treatment for green beans. The application of evacuation as an alternative to blanching gave disappointing results for spinach (Birnbaum *et al.*, 1979). The vacuum packing of other unblanched vegetables, depending on the type of product concerned, can prolong to some extent tenability during frozen storage (Steinbuch, 1979, 1980). Quality retention of unblanched frozen green beans can be prolonged from approximately 2 to 10 weeks (Table 1), but this also appears to depend on the variety of the raw material.

However, the application of vacuum treatments unfortunately does not contribute to stabilization of chlorophyll, for colour changes are comparable with those of the non-treated product (Table 1). Based on these observations, attention has been paid to the application of very short heat shocks, in order to inactivate chlorophyll converting enzymes in the surface of green beans, without damaging the structure of the tissue. The results of the experiment are summarized in the table.

An ultra-short heat treatment, by soaking the green beans for 10 sec in a plentiful amount of boiling water, followed by rapid cooling, can decrease colour deterioration, resulting in an appearance of the end product, visually evaluated as between the unblanched and normally blanched beans. However, the fact has to be emphasized, that the colour of the heat-shocked beans resembles remarkably that of the fresh prepared product. The heat shock process prolonged unexpectedly the quality retention of frozen green beans, especially when this treatment was combined with a preceeding evacuation treatment and subsequent vacuum packing.

The quality characteristics of frozen green beans, being exposed to the above mentioned combination of treatments, resemble those of the freshly cooked produce, due to the maintenance of the crisp firm texture and the retention of the natural flavour and colour.

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Table 1. The effect of vacuum packing, heat shock (10 sec) and evacuation on the quality of unblanched green beans

Processing procedure	Quality evaluation								
	After 2 weeks			After 10 weeks			After 6 months		
	Colour	Flavour	Texture	Colour	Flavour	Texture	Colour	Flavour	Texture
Control, normally blanched	Grass green	Flat	Soft	Grass green	Flat	Soft	Grass green	Flat	Soft
Unblanched	Gray Olive	deviating	Good	Greyish	Rancid	Good	Greyish	Very rancid	Good
Unblanched vacuum packed	Olive-like	Good	Good	Olive-like	Deviating	Good	Olive-like	Rancid	Good
Heat shocked	Olive-green	Good	Good	Olive-green	Good	Good	Olive-green	Deviating	Good
Heat shocked vacuum packed	Olive-green	Good	Good	Olive-green	Good	Good	Olive-green	Deviating	Good
Evacuated heat shocked vacuum packed	Olive-green	Good	Good	Olive-green	Good	Good	Olive-green	Good	Good

Moreover, the results of these experiments indicate the oxygen-dependence of the activity of enzymes, which are harmful to the quality of unblanched frozen vegetables.

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Book reviews

Developments in Sweeteners. 1. Ed. C. A. M. Hough, K. J. Parker and A. J. Vlitos.
London: Applied Science Publishers, 1979. Pp. xii + 192. ISBN 0 85334 820 0. £15.00.

This book is another contribution from the 'Development Series' which sets out to bring sweetness and sweeteners to both public and industrial attention. It emphasizes the necessity to find a new and safe high intensity sweetener and again reminds us of the withdrawal of cyclamate from permitted lists of additives and the precarious position of saccharin. The book consists of seven chapters covering a spectrum ranging from a review of the most common sweetener sucrose through to the more novel protein sweeteners and concludes with a chapter on structure-activity relationships as applied to the sweetness response.

Chapter One contains some interesting but fairly elementary information on the history, production, consumption and nutritional aspects of sucrose. Chapter Two, well presented and with a useful introduction to nomenclature, sets out to show the growing importance of glucose and fructose syrups as sweeteners. Particular attention is paid to recent developments in syrup production and their ever increasing role as food components. Chapters Three, Four and Five review the carbohydrate polyhydric alcohols, protein and dipeptide sweeteners respectively. All of these are well established areas of sweetener research. Chapter Three deals with mannitol, maltitol, sorbitol and xylitol, not so much as high intensity sweeteners but as sweetening agents with other features such as low cariogenicity and low calorific values, two properties much sought after in the ideal sweetener. There has been intensive work carried out in the last decade on the structure and properties, structural modification and potential commercial applications of novel protein sweeteners such as thaumatin and monellin and Chapter Four provides a comprehensive review of this work and of their history. The synthesis and properties of aspartame, the dipeptide sweetener, are reviewed in Chapter Five by Mazur and Ripper with an optimistic outlook for its future as a commercial sweetener.

Dr. Crosby has made a particularly notable contribution to this text on the less common sweeteners. He is well known for his excellent work on dihydrochalcone sweeteners and has included these in the section on synthetic compounds reviewed as possible alternatives to sucrose. He has also discussed some naturally occuring substances such as glycyrrhizin and phyllodulcin.

The concluding Chapter to this book is devoted to the theory of sweetness and discusses the stereochemical features of carbohydrates and their derivatives which contribute to their functional properties. The authors also discuss the temporal aspects of taste which until recently have been given little attention in the literature. They also propose an interesting hypothesis in the chemoreception of sugars, a so called 'orderly queue' mechanism.

To sum up, the book is a valuable source of information and is written in an easy-to-read form. The text illustrates recent developments and theories in sweetener research and it will prove a useful reference volume for scientists working in the field.

S. Z. Dziedzic

Cooling, Freezing, Storage and Transport. Biological and Technical Aspects.
Paris: Institut International de Froid. 1978. Pp. 454. FF 80.

This volume contains the text and discussion of a total of fifty papers presented at Budapest on the occasion of the meeting of the Commissions on Food Science and Technology on Refrigerated Storage and on Refrigerated Land Transport of the International Institute of Refrigeration. The wide range of subjects is divided into eight sections, namely chilled storage of fruit (five papers), evaluating the quality of chilled and frozen foods (ten papers), precooked foods (seven papers), freezing and thawing techniques (four papers), display cases for frozen foods (three papers), cold storage operation (five papers), energy conservation in refrigerated storage (seven papers) and refrigerated transport, choice of equipment, methods of testing, temperature control (nine papers).

With the accent on food technology only a few headings can be mentioned. However, the reader should in no way feel discouraged to explore the content of other sections.

Experiments reported from Rumania deal with the storage of apples and apricots. French workers have explored the storage of apple slices and of peaches prior to industrial use and reports from Cuba investigate the storage of pineapples and bananas. Another group of papers discusses problems of quality evaluation of frozen foods, the need for time-temperature monitoring and a contribution from Hungary reports on the performance of the distribution chain in that country. The quality of frozen fish is explored in a number of papers. Yet another group of reports deals with problems of institutional catering.

Summarizing the contents of this book one may say that nowadays no one would dare to market a food product that has not been thoroughly investigated

and tested, including energy consumption during manufacture, storage and transportation and retailing. Although the nature of such investigations may be similar and results may confirm recurring principles, it is always comforting to find predictions confirmed by facts, such as contained in the papers collected in this book thanks to the activities of the various commissions of the Institute of Refrigeration.

F. Levy

Xylitol. Ed. by J. N. Counsell
London: Applied Science Publishers, 1978. Pp. xiv + 191. £12.00.

This book is the record of a symposium organized by Roche Products Limited in London with the object of explaining the properties of a novel food material which was becoming available as a result of manufacture from birch wood in Finland. Xylitol is a sugar alcohol but is based on the pentose unit instead of the hexose units of the sugars and starches which form the main carbohydrate food materials of the plant kingdom. It is soluble and has a sweet taste; consequently its potential use is as a sugar.

The earlier papers are concerned with the manufacture and properties of xylitol and its use as a replacement of sucrose in confectionery manufacture. The interesting point emerges that few, if any, microorganisms are capable of utilizing this substance, and it is not surprising that a long paper follows on human tolerance to xylitol. It is claimed there are no signs of diarrhoea in children from a single dose of a third of an ounce (10 grams)! A further consequence of the inability of bacteria to ferment xylitol is that it does not promote acid formation on the tooth surfaces and the latter sections of the book and many of the participants at the symposium are primarily concerned with the current theory of the causes of dental caries. Attention is drawn to the potential benefits of replacing 'cariogenic sucrose' by sugar substitutes such as xylitol which have no cariogenic properties. Indeed, apart from its interesting property of absorbing heat when dissolved which results in a cooling effect in the mouth, the only reason for advocating the use of this unnatural substitute for sucrose is its non-cariogenicity. To be fair, it should be mentioned that the opening contributor claims xylitol is currently a component of our diet on the basis of the richest known source, yellow plums, where nearly 1% of the dry matter is xylitol.

The dental properties are, however, of interest and it is there that one feels more pages could have been devoted to the papers and fewer to the discussions which inevitably make disjointed and inconclusive reading. Particularly does this arise because Professor Scheinen himself was reporting his studies at the University of Turku where he compared the dental experience of student volunteers consuming ordinary diets in which the sweetening agent was either

sucrose, fructose or xylitol. Superficially it appears that sucrose is most cariogenic, fructose less so and xylitol non-cariogenic. One of his trials with chewing gum had been interpreted to show that xylitol can produce an anti-cariogenic effect, but on this point the answer to a direct question can best be described as evasive.

However, a closer examination of this evidence, using the greater detail of the original papers, reveals that the evidence for any significant difference between the caries of the sucrose and xylitol groups is quite unconvincing. For example, the increase in caries of the control group, i.e. those eating an ordinary sucrose containing diet, was quite abnormally high while that of the xylitol group was similar to that of the ordinary population who eat an ordinary sucrose containing diet. Even so the sucrose group had less caries than the xylitol group at the end of the trial!

The reason for this book on xylitol is the topical interest in finding a substitute for sucrose, the natural sugar which shares with radio and TV a clear statistical association with the ills of civilisation. Much detail about xylitol is presented, although some will wonder how a material which can cause diarrhoea in amounts well below normal consumption levels of the food it could replace can be advocated on health grounds. Then the dental experts take over bringing out the underlying assumption of the guilt of sucrose, without which there would be no case for such substitutes, and which is so firmly based on the production of acid at the tooth surface.

Why then do the Turku studies provide yet another example of the consistent failure of human trials to provide clear confirmation of this eminently plausible hypothesis that caries does in practice result from the intensity of the acid attack on the tooth surface?

Much is being discovered by modern research but the nutrition and health field is a difficult area where first indications are often altered substantially by further investigation. The food industry has a responsibility to its public, many of whom are being confused and worried by the current plethora of conflicting advice. It should avoid promoting novel materials in place of our traditional foodstuffs until the substitute has been established, beyond all reasonable doubt, to have real advantages and to be innocent of other hazards.

Xylitol did not pass either part of this test, even before the toxicologists discovered an indication of carcinogenicity in laboratory animals.

B. L. Hancock

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CONTENTS

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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	μm = 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	= 4·5461 l
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'.

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